APPLICATION OF NATURAL DYES IN TEXTILE INDUSTRY AND THE TREATMENT OF DYE SOLUTIONS USING ELECTROLYTIC TECHNIQUES

A Thesis Submitted for the Degree of Doctor of Philosophy in the School of Engineering and design at Brunel University

By

KARIMA MASSAUD ABOUAMER

Institute for the Environment
Brunel University, London
United Kingdom

November 2007

DEDICATION

This thesis is dedicated to the memory and soul of my father

ACKNOWLEDGEMENTS

I would like to express my best gratitude and respect to my supervisors Dr A.J. Chaudhary and Dr J. Parrick for their guidance, patience and encouragement throughout my research programme.

I also would like to thank my ex-supervisors Dr S. Mullins, Professor S. Grimes and Professor J. Donaldson, for their advice and guidance throughout the period of research work.

My special thanks to Al-Fateh University and Libyan government for the financial support and full sponsorship to carry out this research.

I am deeply grateful to F. Harib, Dr A. Mayouf, N. Zia, M. Iqbal and A. Karwan, for their great help and assistance in the preparation of this thesis.

In addition I would like to thank Dr K. Almansuri, A. Alharabi, Dr M. Al-Hassan, Dr L. Mehta, Mr H. Dee, N. Sarkis for their help and support throughout the course of this work.

Thanks to all my friends specially K. Al-sharif, S. Mustafa, S. Alsherbini, K. Hamel, M. Marwan, S. Alajili, M. Haqiq, M. Almeslati, A. Al-Shirawi, E. Aquil, A. Abu hajar, F. Alghezawi, M. Naili, N. Kafo and W. Zaidi for their encouragement and continued interest throughout the period of research work.

I am deeply indebted to my friends Neelam and Mubasher for their hospitality, warm welcome and caring.

I am indebted to my mother, my sisters Nadia, Ahlam, Awatef, my brother Hosam, my brothers in-laws Adel and Abu Ajila, my nieces and nephews for their constant encouragement, concern, and strong support and endless love throughout the most difficult times during my stay in the United Kingdom.

ABSTRACT

Anodic oxidation of a commercial dye, methylene blue (MB), from aqueous solutions using an electrochemical cell is reported. Data are provided on the effects of eight different types of supporting electrolytes, concentration of electrolytes, initial dye concentration, current and electrolytic time on the percentage removal of methylene blue. Anodic oxidation was found to be effective in achieving the removal of methylene blue from aqueous solutions.

The optimised electrolytic conditions, for the removal of methylene blue (MB), were applied to the removal of azure A (AA), azure B (AB), azure C (AC), toluidine blue O (TBO), new methylene blue (NMB), dimethyl methylene blue (DMMB), thionine (TH), methylene green (MG), methyl violet (MV), Nile blue (NB), neutral red (NR), acridine orange (AO) and resorufin (RS) from aqueous solutions containing sodium chloride. Results indicated that between 84 to 100% of each dye of phenothiazines was removed during 60 minutes of electrolysis. The percentage removals for the phenothiazine dyes followed the following decreasing order: (MG ≅ MV) > (DMMB ≅ AA) > (AB ≅ AC ≅ NMB) > TBO > TH. However, the azine, acridine and oxazine dyes showed between 98 to 99% colour removal and the following decreasing order: NB ≅ NR > AO ≅ RS. Strongly electron withdrawing substituents such as nitro group or carbonyl group increases the degradation of the phenothiazine chromophore, whereas the electron donating groups such as amino and alkyl amino groups decrease the degradation.

Anodic oxidation studies were extended to the destruction of eight permitted food colours, with azo and triarylmethane chromophore, from aqueous solution containing either sodium chloride or sodium sulphate as a supporting electrolyte. Again, sodium chloride was found to be the best supporting electrolyte and between 97 to 100% colour removal was achieved after 60 minutes of electrolysis. The percentage removal for the single azo based colourants followed the following increasing order: carmoisine > sunset yellow FCF > amaranth > ponceau 4R > tartrazine. However, the binary and ternary mixtures of food colour showed the following increasing order: blue > green > yellow food colours.

The extractions and applications of 54 different types of natural dyes (53 from plants and one from animal origin) are evaluated using simple techniques. The extracted natural dyes were applied in dyeing three types of textile fabrics *viz*: a) paj silk, b) brushed cotton twill and c) crystallized shimmering satin. The effects of two eco-friendly mordants (alum and iron) on the dyeing process were compared with the dyeing process without mordants. The colour fastness to wash and light (both natural and artificial sun light) of these natural dyes were also assessed. The results showed that out of the 54 dyestuffs studied, 32 plants are potentially able to produce marketable natural dyes. These dyes produced good colour and met minimal performance standards for colour fastness to light and washing. The addition of mordants generally increased the fastness properties. Silk gave the best performance of dyeing uptake and stability. Cotton gave the poorest fastness properties. The overall results showed that, considering molecular associations, the fastness properties were of the order: anthraquinones and tannins > indigoid > flavones > flavonols > flavanols > carotenoids > anthocyanins.

Anodic oxidation studies were extended to the destruction of ten natural dyes from aqueous solutions containing either sodium chloride or sodium sulphate as a supporting electrolyte. Anodic oxidation was effective in achieving the removal of green tea (35%), spinach (69%), Langdale yellow and turmeric (95%), carmine, saffron, henna (97%), beetroot, karkade and sumac (98%). However, TOC measurements and the UV analyses indicated that some organic intermediate compounds were formed in the presence of sodium chloride.

CONTENTS

GLOSSARY OF ABBREVIATIONS

A	Animal
AATCC	American Association of Textile Chemists and Colorists
ADI	Acceptable Daily Intake
Alum	Aluminum Ammonium Sulphate
AlMCM-41	Mesoporous Molecular Sieves
AO	Acridine Orange
AOP	Advanced Oxidation Process
AA	Azure A
AB	Azure B
AC	Azure C
A.U.F.S	Absorbance Units Full Scale

BPEO	Best Practicable Environmental Option
BDH	The British Drug House Ltd
BOC	Bell Operating Company
BS EN ISO 105 A03	British Standards for Staining
BS EN ISO 105	British Standards for Colour Change
BS EN ISO 105 B02	British Standards for Colour Fastness to Light
BS EN ISO 105	British Standards for Colour Fastness to Washing C01 to C05 (soap), C06 (phosphate detergent) C08 (non phosphate detergent) C09/UK-TO
BS EN ISO 105 D01	British Standards for Colour Fastness to Dry Cleaning
BS EN ISO 105 E01	British Standards for Colour Fastness to Water
BS EN ISO 105 E04	British Standards for Colour Fastness to Perspiration
BS EN ISO 105 X12	British Standards for Colour Fastness to Rubbing
BS EN ISO 105 E07	British Standards for Colour Fastness to Water Spotting
BS EN ISO E03	British Standards for Colour Fastness to Chlorinated Water

BS EN ISO G01 and G02	British Standards for Colour Fastness to Nitrogen Oxides/Burnt Gas Fumes
BSI	British Standards Institute
BS EN ISO 12947	Abrasion Resistance (Martindale Method)
BS EN ISO 12945	Pilling Resistance
BS EN ISO 13934-1	Tensile Properties (Strip Method)
BS EN ISO 13936-1	Seam Slippage Resistance
BS EN ISO 13935-1 & 2	Seam Tensile Properties
BS EN ISO 13937-3	Tear Properties of Fabrics (Wing-Shaped)
ASTM D4533	Trapezoid Tearing Strength

C	Catechin
C18	Silica Based Packing
CAC	Codex Alimentarius Committee
CAS	Chemical Abstracts Service
CDS	Compact Disc Storage
CE	Capillary Electrophoresis
CI	Colour Index
Cl_2/ H_2O	Chlorine Water
CRE	Constant Rate of Specimen Extension
CV	Cyclic Voltammetry

DIN EN ISO 105 X12	Dutch Standards for Colour Fastness to Rubbing
DMMB	Dimethyl Methylene Blue
DNA	Deoxyribonucleic acid
DSA	Dimensionally Stable Anode
DW	Diacetate, Wool Multifibre Strip for Cross Staining Test

EC	Epicatechin
EGC	Epigallocatechin
ECG	Epicatechin Gallate

EEC	European Economic Community
EGCG	Epigallocatechin Gallate
	Permitted and Approved Food Colours by European Community
EDAX	Energy Dispersive Analysis by X-ray
ETAD	Ecological and Toxicological Association of the Dyestuffs
EA	Environment Agency for England and Wales
EC	European Community
EU	European Union
EPR	Electron Paramagnetic Resonance Spectroscopy
F	Flammable
FAO	Food and Agricultural Organisation
FDA	Food and Drug Administration
FD&C	Food Drug and Cosmetics
GC	Gas Chromatography
GCG	Gallocatechin Gallate
HACSG	Hyper Active Children Support Group
HPLC	High Performance Liquid Chromatography
HRP	Horseradish Peroxidase
I	Irritant
IARC	International Agency for Research on Carcinogens
INS	International Numbering System
IR	Infrared Spectroscopy
ISO	International Standard Organisation
IUPAC	International Union of Pure and Applied Chemistry Nomenclature
KTC	International Private Food Company
KDP	Potassium Dihydrogen Phosphate

LC	Liquid Chromatography
Leuco	is a dye whose molecules can acquire two forms, one of which is colourless
LD_{50}	(Lethal Dose 50) is the dose of a chemical which kills 50% of a sample population
LED	Light Emitting Diodes
LiP	Lignin Peroxidase
M	Mineral
Max (nm)	Maximum Absorption
MB	Methylene Blue
MG	Methylene Green
MS	Mass Spectrum
MV	Methylene Violet
MCM-41	Mesoporous Molecular Sieves
NMB	New Methylene Blue
NB	Nile Blue
NF EN ISO 105 X 12	French Standards for Colour Fastness to Rubbing
NIC's	Newly Industrial Countries
NMR	Nuclear Magnetic Resonance
NR	Neutral Red
O	Oxidising Agent
ODS-2	Spherisorb Octadecylsilane (for Phase Separation) in HPLC
P	Plant
P	Probable Carcinogen
PAC	Polyaluminium Chloride
PDA	Photodiode Array Detector
PDT	Photodynamic Therapy

ppm	parts per million
PPT	Precision Processes Textiles
PVC	Poly Vinyl Chloride
Re	Resorufin
R & S	System of Nomenclature of Stereocenter, (Latin: Rectus = right & Sinister = left)
RT	Retention Time
S	Synthesized
SDC	Society of Dyers and Colourists
SEPA	Scottish Environment Protection Agency
SSF	Solid State Fermentation
T	Toxic
TBO	Toluidine Blue O
TH	Thionine
TLC	Thin Layer Chromatography
TOC	Total Organic Carbon
U	Unknown
UV/VIS	Ultra Violet-Visible Spectroscopy
WHO	World Health Organisation
XRD	X-Ray Powder Diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE PRESENT WORK

Synthetic dyestuffs are extensively used in textile, paper, printing industries and dye house due to their ease of production, fastness and variety of colours [1, 2]. Textile industries consume large volumes of water and chemicals for wet processing of textiles. The chemical reagents used are very diverse in composition, ranging from inorganic compounds to polymers and organic products [2, 3]. The presence of very low concentrations of dyes in effluent is highly visible and undesirable. More than 100,000 commercially available dyes are known and approximately one million tons of these dyes are produced annually worldwide [4]. It has been estimated that more than 10% of the total dyestuff used in dyeing processes is released into the environment [2]. Due to their chemical structure, dyes are resistant to fading on exposure to light, water and many chemicals. Many dyes are difficult to decolourize due to their complex structure and synthetic origin. There are many structural varieties, such as, acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes. Decolouration of textile dye effluent does not occur when treated aerobically by municipal sewage systems [3]. Due to large-scale production and extensive application, synthetic dyes can cause considerable environmental pollution and are serious health-risk factors.

The main aims of the Ecological and Toxicological Association of the Dyestuffs (ETAD), are to establish and minimize environmental damage, protect users and consumers and to co-operate fully with government and public concerns over the toxicological impact of their products [5, 6]. Over 90% of some 4000 dyes tested in an ETAD survey had LD_{50} values greater than 2×10^3 mg/kg. The highest rates of toxicity were found amongst basic and diazo direct dyes [3]. In Great Britain, such matters are regulated by the Environment Agency (EA) for England and Wales, and the Scottish Environment Protection Agency (SEPA) [3]. Government legislation is becoming more and more stringent, especially in the more developed countries, regarding the removal of dyes from industrial effluents. Environmental policy in UK, since September 1997, has stated that zero synthetic chemicals should be released into the marine environment. Enforcement of this law will continue to ensure that textile industries treat their dye-containing effluent to the required standard. European Community (EC) regulations are also becoming more stringent [3].

There are many structural varieties of dyes that fall into either the cationic, nonionic or anionic type. Anionic dyes are the direct, acid and reactive dye [3]. Brightly coloured, water-soluble reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment systems unaffected [3]. Municipal aerobic treatment systems, dependent on biological activity, were found to be inefficient in the removal of these dyes [2]. Nonionic dyes refer to disperse dyes because they do not ionize in an aqueous medium. Concern arises, as many dyes are made from known carcinogens such as benzidine and other aromatic compounds [7]. Nam and Renganathan demonstrated that azo- and nitro-compounds are reduced in the mammalian intestinal environment, resulting in the formation of toxic amines [8]. Anthraquinone-based dyes are most resistant to degradation due to their fused aromatic ring structure. The ability of some disperse dyes to bioaccumulate has also been demonstrated [3].

1.2 NATURAL AND SYNTHETIC DYES (HISTORICAL)

Synthetic Dyes: The first recorded synthetic dye was picric acid, which produced in the 1770's from the interaction of indigo and nitric acid. The discovery of benzene by Faraday in 1824, and its discovery as a constituent of coal tar by Leigh in 1842, had passed largely unnoticed. It was really the work of A.W. Hofmann, from 1845 onwards, that focused the attention of organic chemists on benzene and other such aromatic compounds obtained from coal tar. He had been able to isolate appreciable quantities of benzene and other interesting aromatic compounds from coal tar by fractional distillation and, with the help of a team of able and enthusiastic young chemists, he was able to explore the chemistry of these compounds. It was W.H. Perkins, a British Chemist, whilst working with Hofmann, who discovered Mauveine, in 1856 at the age of 18, and thereby started the 'dyestuff revolution'. However, he was not intentionally working towards preparing synthetic dyestuffs but towards quinine, the anti-malarial drug [9]. The industry quickly developed, mainly in Germany, Switzerland and the UK. Since then the significant dyes discovered were: azo dyes in 1858 by Griess, alizarin red, 1868, by Graebe and Lieberman; indigo in 1870 by von Baeyer; anthraquinone vat dyes in 1901 by Bohn; disperse dyes for cellulose in 1922; fibre reactive dyes by ICI in 1956 [9].

There are very many synthetic dyes available now. Their tinctorial strength, concentration, colour range and colour fastness, particularly to light and detergents, make them superior to natural dyes for nearly all uses. They are relatively cheap and have other advantages, eg, mordants may not be necessary, they can colour synthetic fibres. Manufacturers and processors using dyes have to deal with potential health, effluent disposal and other environmental requirements, usually to statutory limits.

Natural Dyes: They can be defined as those **colourants** (dyes and pigments) obtained from animal or vegetable matter (and minerals), without processing. When used as textile dyes, they are mainly mordant dyes although some belong to other groups (vat, solvent, pigment, direct and acid). Most of the historically important colourants are members of the anthraquinone, naphthoquinone, indigoid and carotenoid groups. There are no natural dyes of the sulphur, disperse, azoic or ingrain types.

1.3 THE PHYSICAL AND CHEMICAL BASIS OF COLOUR

1.3.1 Sight and Colour

Communication between an object and an eye is physical, for a ray of light, a stream of photons carry the message. However, molecules are often the agents of colour in an object and also act as sensors that respond to light once it has entered our eyes. Many natural colours depend on the presence of particular molecules, and the natural colourants discussed in chapters five and six are present in petals and leaves, and are responsible for the colours of flowers, fruits and vegetables. When we look upon a rose with the information described in chapters five and six, it is possible to suggest the molecules that contribute to its shades and hues. We will discover what changes give rise to the colours of a leaf in the autumn, and we will comprehend the ebb and flow of its colour. We will also understand the events that take place in our eyes when we perceive these colours. We will see that, in vision, molecule speaks to molecule, and that the activated molecule in the eye triggers a signal that, in the deep unknown of the head, is interpreted as a colour [10].

It has been said that the presence of colour requires three things: a source of illumination, an object to interact with the light which comes from this source and a human eye to

observe the effect which results. In the absence of any one of these, it may be argued that colour does not exist. A treatment of the basic principles underlying the origin of colour thus requires a consideration of each of these three aspects, which brings together concepts arising from three natural science disciplines, chemistry, physics and biology [11].

1.3.2 Visible Light

Visible light refers to the region of the electromagnetic spectrum to which our eyes are sensitive and corresponds to radiation within the very narrow wavelength range 360-780 nm. Since the sensitivity of the eye to radiation is very low at each of these extremes, in practice the visual spectrum is commonly taken as 380 to 720 nm. Beyond the extremes of this range are the ultraviolet (UV) region of the spectrum (below 360 nm) and the infrared (IR) region (above 780 nm).

The incandescence of the surface layers of the sun results in the mixture of wavelengths that we are accustomed to interpret as ' white' light. If any colour is removed from white light, then the light takes on a hue. Filtering out orange light, for instance, results in the blue-green (cyan) light; filtering out cyan results in orange light. The colour resulting from the removal of a colour from white light is the latter's complementary colour (Table1.1).

Table 1.1: Complementary colour relationships

Wavelength range (nm)	Colour	Complementary colour
400—435	Violet	Greenish-yellow
435—480	Blue	Yellow
480—490	Greenish-blue	Orange
490—500	Bluish-green	Red
500—560	Green	Purple
560—580	Yellowish-green	Violet
580—595	Yellow	Blue
595—605	Orange	Greenish-blue
605—750	Red	Bluish-green

The visible spectrum contains regions recognized by the human visual system in terms of colour, and the approximate wavelength ranges corresponding to the colours are shown in Table 1.1. When light of a given colour is absorbed, the complementary colour (or

remaining part of the incident light) is transmitted or reflected; thus a dye or pigment absorbing light within the blue range is seen in daylight as yellow [10, 11].

A traditional way of demonstrating the relation between colours is in terms of an artist's colour wheel, on which complementary colours are opposite each other along a diameter [10]. Additive colour mixing is illustrated in the colour star (Figure 1.1). The primary colours are red, blue and green. Secondary colours yellow, blue-green (cyan) and magenta are a mixture of the primaries as are the tertiary colours like orange, amber and violet. The colour star is a visual expression of additive colour mixing [12].

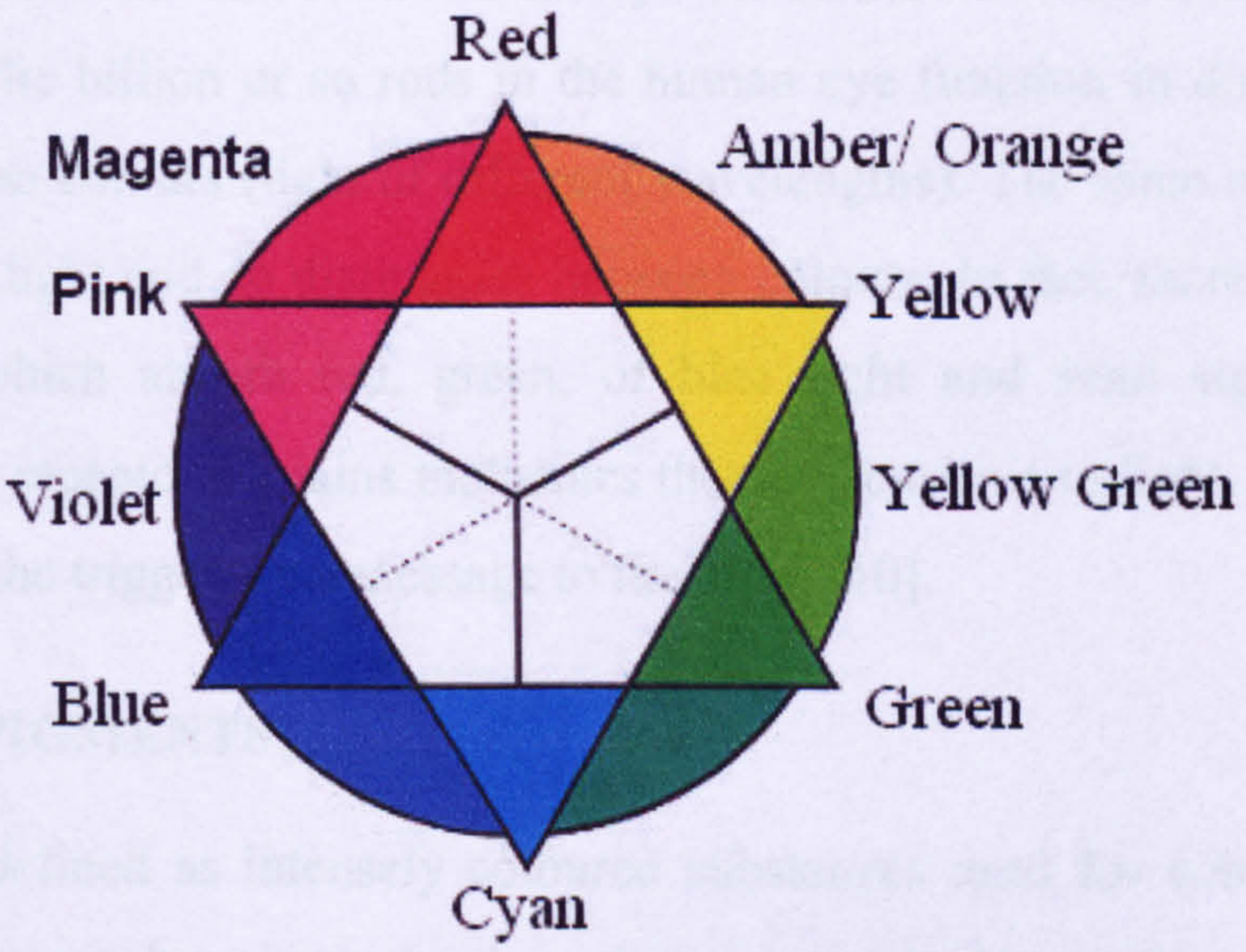


Figure 1.1: The basic colour wheel (the twelve-hue colour wheel) [12]

Substances absorb characteristic wavelengths of light when the incoming radiation excites electrons into different locations within the molecule. The difference in energy between the new and initial locations determines what wavelengths are absorbed. If only a little energy is needed to relocate the electrons, then the substance can absorb red light, for photons of red light have a relatively low energy. If the incident light is white, then the light reflected by such substances is perceived as green. If a lot of energy is needed to change the arrangement of the electrons, then the substance absorbs only high-energy, short-

wavelength light. If the substance absorbs blue-indigo light (which is short-wavelength light), then the light it reflects is perceived as orange.

The colour green is interesting in this regard. On the colour wheel, it lies opposite both red and violet, where the two ends of the visible spectrum meet. Hence green can arise when low-energy, long-wavelength red light is removed from white light, or when high-energy, short-wavelength violet light is removed, or when both are removed [10].

1.3.3 Vision

Although the receptors in the eye are sensitive to a physical stimulation-light of various wavelengths- once light has struck, all the detection, processing, and transmission of the neural signal is chemical. The retina of the eye consists of two kinds of receptors, called rods and cones. The billion or so rods in the human eye function in dim light but do not distinguish between colours (light of different wavelengths). The three million or so cones function in bright light and do distinguish between colours. In fact, there are three kinds of cones, each of which absorb red, green, or blue light and send signals to the brain accordingly. Each receptor contains molecules that are sensitive to light, and their response to illumination is the trigger for a message to the brain [10].

1.4 DYES AND PIGMENTS

Dyes have been defined as intensely coloured substances used for colouration. They are retained in substances by physical adsorption, mechanical retention, the formation of covalent chemical bonds or of complexes with salts or metals, or by solution. Dyes lose their crystal structures during application by dissolution or vapourisation.

Pigments retain their crystalline or particulate structure throughout their application. However, in the literature and common usage, the terms dye and pigment tend to be used rather loosely and interchanged but dye is often used for textile and food colourants, and pigment for inks, paints and cosmetics. Dyes and pigments [9] are distinguished on the basis of their solubility characteristics: essentially, dyes are water-soluble, pigments are insoluble. A water-soluble dye can be converted to a pigment by making it into a lake, which combines the colour with a basic radical such as aluminium or calcium to make a salt

on a substrate of alumina. The substrate is insoluble and thus provides an insoluble form of the dye, i.e., a pigment. The term **colourants** is frequently used to encompass both types of colouring materials. Colour may be introduced into manufactured articles, for example textiles and plastics or into a range of other application media, for example paints and printing inks, for a variety of reasons but most commonly the purpose is to enhance the appearance and attractiveness of a product and improve its market appeal [11].

1.5 CLASSIFICATION OF DYES

Dyes are classified in two ways: by chemical composition, principally used by manufacturers, and by application class or end-use, principally by dyers. There is a common ground between the two methods of application. Certain groups of dyes with their specific chemical character and the methods of dyeing are dependent on each other. Each dye is described under the internationally accepted Colour Index (CI) classification system [13], published by the Society of Dyers and Colourists (SDC), United Kingdom, in cooperation with the American Association of Textile Chemists and Colorists (AATC), provides a detailed classification of commercial dyes and pigments by CI generic name, based on its application characteristics, and CI Constitution Number based on its chemical structure.

1.5.1 Classification of Synthetic Dyes

1.5.1.1 Classification According to Structure

This classification of dyes based on the chemical structure or on the basis of the chromophoric system. This system of classification has many advantages [14]. It readily identifies dyes as belonging to a group which has specific characteristic properties, and it is the classification used most widely by both the dye chemists and the dye manufacturers [15].

1.5.1.2 Classification According to Application

The classes of dyes defined by the application [16] or end-use, and hence the terms most applicable to textile dyeing are:

Acid dyes - these are sodium salts usually of sulphonic acid, but in a few cases of carboxylic acids. They are water soluble anionic dyes that are applied to fibres such as silk, wool, nylon and modified acrylic fibres from neutral to acid dyebaths. Attachment to the fibre is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fibre. Acid dyes are not substantive to cellulosic fibres (e.g. acid yellow 6 (sunset yellow FCF), acid red 14 (carmoisine)).

Basic dyes - water-soluble cationic dyes, they are usually hydrochlorides or salts of organic bases. They are applied to wool, silk, cotton and modified acrylic fibres. They bond to the fabric by salt linkage. Basic dyes are also used in the colouration of paper, printing inks and cosmetics. They give high tinctorial strength but low fastness to light (e.g. phenothiazines, acridines and phenoxazines) [17].

Direct (Substantive) dyes - water-soluble anionic dyes, as their name implies, require no mordant and possess a distinct tendency to leave solution and attach themselves to fabrics. Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains. Congo red is a direct dye for cotton [17].

Mordant dyes - as the name suggests these dyes require a mordant. The mordant forms a coordination complex between the fibre and dye. Metallic salt or lake formed directly on the fibre by the use of aluminium, chromium or iron salts that cause precipitation *in situ*. This improves the fastness of the dye on the fibre such as wash, light and perspiration fastness. The choice of mordant is very important as different mordants can change the final colour significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. One of the oldest dyes of this type is alizarin from madder.

Vat dyes - water-insoluble dyes applied mainly to cellulosic fibres as soluble leuco (ie, colourless) salts after reduction in alkaline bath (e.g. Indigo) [16].

Reactive dyes - they are the newest class of textile dyes, first introduced commercially in 1956 and were used to dye cellulosic fibres, wool and nylon. They attach to the fibre (usually cotton, wool or nylon) by forming a covalent bond. Reactive dyes are known for their bright colours and very good to excellent light fastness and washfastness [16].

Disperse dyes – water-insoluble, nonionic dyes used for dyeing hydrophobic fibres from aqueous dispersion. Originally developed for the dyeing of cellulose acetate, they can also be used to dye nylon, triacetate, polyester and acrylic fibres. Disperse dyes are also used for sublimation printing of synthetic fibres, and are used in crayons and inks [17].

Azo dyes - form the largest single class; they account for one-third of all dyes produced. They are made by coupling a diazotised aromatic amine with a phenol, or amine. It is the largest group of dyes, with –N=N- as a chromophore, in an aromatic system. Depending upon the number of azo-groups present they are called as monoazo, disazo, trisazo, tetrakisazo and polyazo dyes. All types of azo-dyes amount to over one thousand, commercially most important class of synthetic colouring compound. It has wide variety of application [11]. Tartrazine, carmoisine, sunset yellow FCF are examples of azo dyes.

Anthraquinone dyes - anthraquinone is the basic unit of this class of dyes. It is faint yellow in colour, which is sufficient to use as a dye but it cannot be classified as a dye. Introduction of hydroxyl and amino groups in anthraquinone leads to production of a wide range of colour. Dyes containing anthraquinone unit belong to mordant, disperse and vat dyes. Its quinonoid system acts as a chromophore. Anthraquinone dyes have excellent fastness properties [10], (e.g. carminic acid).

Ingrain dyes - Ingrain dyes are dyes synthesised directly in the fabric. Often the reactants are water-soluble, but the actual dye has less water solubility and in addition binds to the fabric via auxochrome groups. Azo dyes can be applied by ingrain dyeing method with a diazonium coupling reaction [15]. This method is often used in the production of compounds through a type of stencil. This is known as screen printing.

Sulphur dyes - they are macromolecular compounds characterised by di-and polysulphide bonds (-S_n-) between aromatic residues [18]. They furnish dull shades with good fastness to light, washing, and acids but susceptible to chlorine and light. Sulphur dye is often used commercially to produce a good black on cellulosic fabrics and deep shades on cotton.

Solvent dyes - dissolved into the substrate (eg, varnish, waxes, inks, oils).

Metal-complex dyes - are combinations of a dyestuff and a metal, usually chrome. They are developed from the older mordant dyes and are highly light and wash-fast, used primarily on wool (e.g. Red 7- Fast Chrome Red 2B).

Food dyes - one other class which describes the role dyes have rather than their mode of use is food dyes. This is a special class of dyes of very high purity. They include direct, mordant and vat dyes. Their use is strictly controlled by legislation. Many are azo dyes but anthraquinone and triphenylmethane compounds are used for colours such as green and blue. Some naturally occurring dyes are also used [19]. Finally, food and cosmetic dyes must, in addition to the usual properties, be non-toxic.

A number of other classes have also been established and these include: Oxidation bases (mainly hair and fur), leather dyes [19].

1.6 CHEMISTRY OF DYES

Since the discovery of the first synthetic dyes in the mid-19th century, chemists have been intrigued by the relationship between the colour of a dye and its molecular structure. Since these early days, the subject has been of special academic interest to those fascinated by the origin of colour in organic molecules. In addition, an understanding of colour and constitution relationships has always been of critical importance in the design of new dyes. In the very early days of synthetic colour chemistry little was known about the structures of organic molecules.

Perhaps the most notable early contribution to the science of colour and constitution was due to Witt who, in 1876, proposed that dyes contain two types of group, which are responsible for their colour. The first of these is referred to as the *chromophore*, which is defined as a group of atoms principally responsible for the colour of the dye. Secondly, there are the *auxochromes*, which he suggested were 'salt-forming' groups of atoms whose role, rather more loosely defined, was to provide an essential 'enhancement' of the colour. This terminology is still used to a certain extent today to provide a simple explanation of colour, although Witt's original suggestion that auxochromes were also essential for dyeing properties was quickly recognized as having less validity. A further notable contribution was made by Hewitt and Mitchell who first proposed in 1907 that conjugation is essential for the colour of a dye molecule. In 1928, this concept was incorporated by Dilthey and Witzinger in their refinement of Witt's theory of **chromophores** and **auxochromes**. They recognized that the chromophore is commonly an electron-withdrawing group, that auxochromes are usually electron-releasing groups and that they are linked to one another through a conjugated system. In essence, the concept of the donor—acceptor chromogen was born. Furthermore, it was observed that a **bathochromic shift** of the colour, *i.e.* a shift of the absorption band to longer wavelength, might be obtained by increasing the electron-withdrawing power of the chromophore, by increasing the electron-releasing power of the **auxochromes** and by extending the length of the conjugation [11, 16].

The chromophore and auxochrome theory, which was first proposed more than 100 years ago, still retains some merit today as a simple method for explaining the origin of colour in dye molecules although it lacks rigorous theoretical justification. The most important chromophores, as defined in this way, are the azo (—N=N—), carbonyl (C=O), methine (—CH=) and nitro (NO_2) groups. Commonly encountered auxochromes, groups that normally increase the intensity of the colour and shift the absorption to longer wavelengths of light, include hydroxyl (OH) and amino (NR_2) groups. The concept may be applied to most chemical classes of dye, including azo, carbonyl, methine and nitro dyes, but for some classes, which are not of the donor—acceptor type, for example the phthalocyanines, it is less appropriate.

1.7 APPLICATION OF DYES

Synthetic dyes are extensively used in many fields of up-to-date technology, e.g., in various branches of the textile industry [1], of the leather tanning industry [20] in pulp industry [21], in food technology [19], in agricultural research [2], in light harvesting arrays [22], in photoelectrochemical cells [23], and in hair colourings [19]. Moreover, synthetic dyes have been employed for the control of the efficacy of sewage [24] and wastewater treatment [3], for the determination of specific surface area of activated sludge [24] and for tracing ground water [2].

The use of natural dyes in the UK and the rest of the Western economies have been replaced commercially by synthetic dyes, based mainly on aniline and using petroleum or coal tar as the raw stock. The range of synthetic dyes available is large and the dyestuff business is worth approximately £2.5 billion per year world wide [19].

1.7.1 Non-textile Application of Dyes

The application of functional dyes and pigments include a wide range of electronic applications [11, 14, 18, 22, 23] including liquid crystal displays, microfilters, solar cells, lasers and optical data storage, some of the developed reprographic techniques, such as electrophotography and ink-jet printing and a range of biomedical uses. Figure 1.2 shows some of dyes and pigments applications in high-technology.

1.7.2 Biological and Medical Applications of Dyes

1.7.2.1 Photodynamic Therapy (PDT)

Arguably the most significant recent medical development which involves the use of dyes is photodynamic therapy (PDT). PDT is a treatment for cancer that uses a combination of laser light, a photosensitising compound (the dye), and molecular oxygen. In this treatment, the photosensitiser is given intravenously to the patient and some time is allowed (3-96 h) so that it equilibrates within the body. During this time the photosensitiser penetrates into the tumour cells. Irradiation of the cells with laser light may then initiate their destruction, thus providing a potential means for destroying the tumour. The method is rapidly gaining acceptance as a treatment for certain forms of cancer, which shows significantly fewer side-

effects than conventional treatments. A variety of modified porphyrins have been investigated for this purpose and particular promise has also been shown by a number of phthalocyanine derivatives [11]. Recently, the use of phenothiazinium dyes such as methylene blue and its derivatives in the photodynamic therapy of cancer and its related antimicrobial protocols, e.g. blood product decontamination, has been studied by Wainwright et al. [25].

1.7.2.2 Staining and Fluorescent Staining

Some colour compounds are being used in biochemistry, biology and medicine for visual (qualitative) or for quantitative identification of morphological (e.g. histological) structures. These methods are based on the application of colourants as an analytical tool for the identification of chemical structures and reactions [18]. Among the most widely used fluorochromes in biomedical applications are fluorescein, rhodamines and acridines derivatives [11].

1.7.3 Dyes as Titration Indicators in Analytical Chemistry

Dyes are used as indicators in titrimetric analysis of all types. All indicators are donor acceptor systems in which the particles donated or accepted may be electrons (in redox titrations), protons (in acid-base titrations), or metal ions (complexometric titrations). Instrumental analytical techniques such as potentiometry, polography and conductometry have been developed and replaced the conventional colour indicators [18]. Phenazine, oxazine and thiazines are employed in redox titrations [18]. Azo and triaryl methane used as indicators [18].

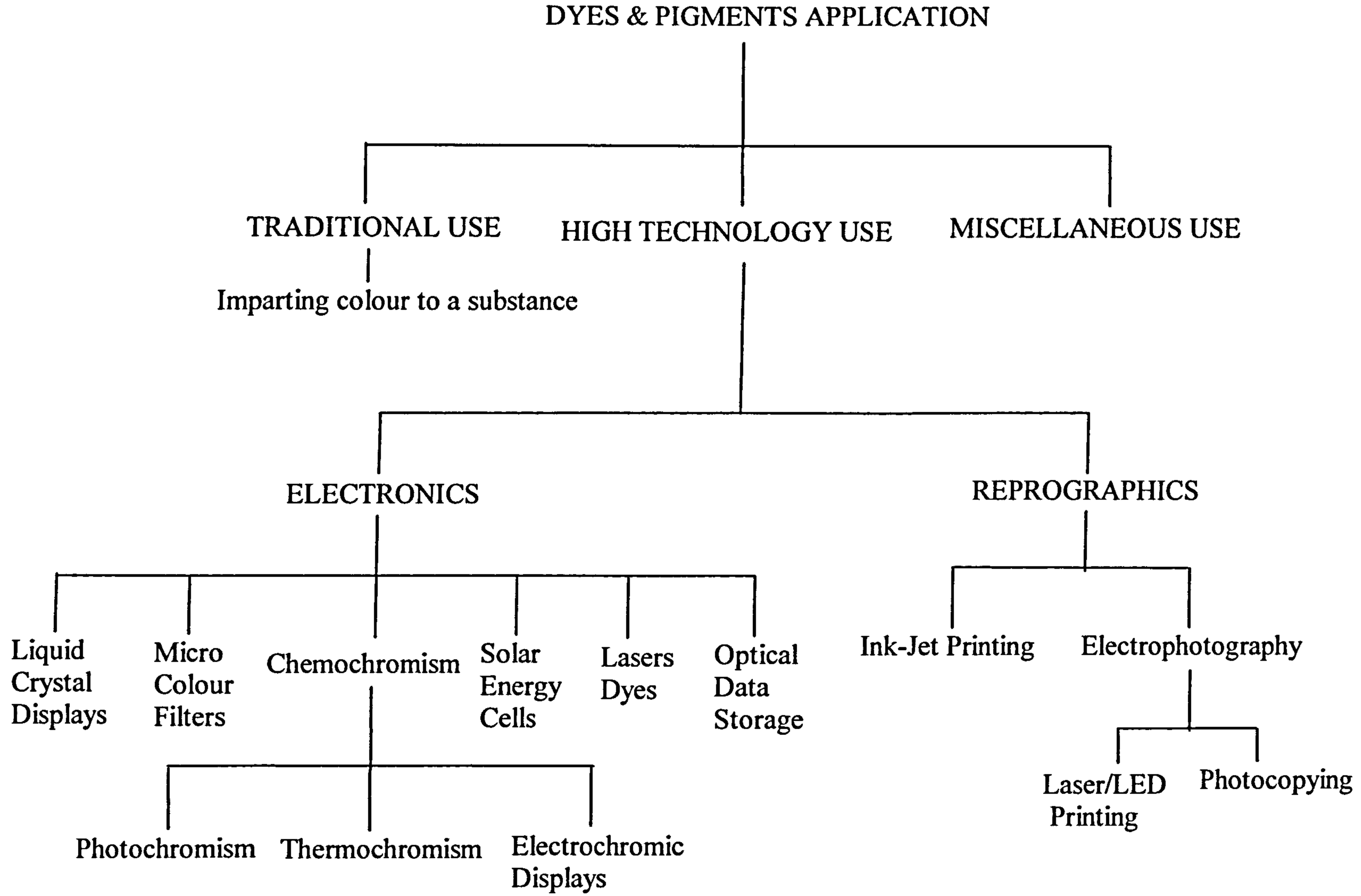


Figure 1.2: Uses of dyes and pigments [23]

1.8 ECOLOGY AND TOXICOLOGY OF COLOURANTS:

1.8.1 Environmental Assessment of Dyes

The major environmental problem of colourants therefore is the removal of dyes from effluents. Untreated effluents from dyestuff production and dyeing mills may be highly coloured and thus be particularly objectionable if discharged to open waters. Their dye concentration may be well below 1ppm, i.e. lower than many other chemicals found in wastewaters, but the dye colour will be visible even at such low concentrations [18].

1.8.2 Hazards of Dyes

Health, safety, and environmental issues have become increasingly important in recent years, especially in manufacturing industries such as the colourant industry. Organic colourants have been used by mankind for thousands of years. Until the late 19^{th} century these colourants were obtained from nature [11]. It was not until after Perkin's discovery of the first synthetic dye, Mauveine, in 1856 that organic colourants and their precursors, the dye intermediates, began to be manufactured on a large scale. This meant that workers in dyestuffs plants became exposed on a large scale to both the colourants themselves and the chemical intermediates used to manufacture them. Over many years it gradually became apparent that workers who produced dyes based upon 2-naphthylamine and benzidine [11] developed a high incident of bladder cancer, and it was later established that both these chemicals are potent bladder carcinogens [7]. Once this information was known, all responsible colour manufacturers took action to cease the production of these proven human carcinogens and their applications in dye manufacturing processes [18, 23].

Any synthetic dye is usually screened at some stage for its safety to human and animal health. This has resulted in the withdrawal of several dyes as their hazards become recognised, for example, the benzidine dyes, which can cause bowl cancer. Chrome colours cannot be used on articles for use by children or on things that come into contact with food. Carbon black, the most widely used printing ink pigments, is thought to be a potential carcinogen. Natural dyes used in food are screened for safety but the information is not known for most of the natural dyes used in craft dyeing, and with

potentially wider use. There is a tendency to assume that natural products are safer and better than synthetic products because they are natural [19].

1.8.3 Environmental Damage

Unsafe disposal of hazardous wastes can affect soil, water or the atmosphere. The route it takes from the site of disposal and effect it has depends not only on the physical, chemical and biological properties of the wastes but also on the characteristics of the disposal site and the underlying geology. Toxic substances contained in hazardous wastes not only affect life processes in the flora and fauna, but also damage and destroy natural resources. Such contamination may pose a serious threat to the diversity of vegetation and animal life [26].

1.8.4 Health Effects

The improper disposal of hazardous waste has serious health implications. Toxic substances can enter the body by inhalation, ingestion and absorption through direct skin contact. Hazardous wastes can be pathogenic, mutagenic, cytotoxic, and carcinogenic to humans, and/ or affect foetal and neonatal growth and development. The potential danger posed by a chemical after it enters the environment is mainly a function of its toxicity and the extent of human exposure. Exposure may be by direct contact or through the food chain.

The health effects may be acute reactions such as headaches, nausea, and eye or skin irritations. There may be long-term damage such as exposure to carcinogens. Long-term damage is the most difficult to asses. The extent of long-term damage depends on various factors such as different ecological and weather conditions in Newly Industrial Countries (NIC's) and nutritional aspects cultural differences and socio-economic conditions. These factors may also influence the probability and effects of the exposure [26].

1.9 AVAILABLE TECHNIQUES FOR THE DEGRADATION OF DYES

Table 1.2 gives a compilation of the most widely used methods and the newer achievements in the technologies developed for the removal of synthetic dyes from water

and wastewater, classification and short description of the methods, critical evaluation of the technological processes and the comparison of their advantages and disadvantages, with emphasis on the methods used for the dyes investigated in this research study.

These methods have been discussed under three categories: chemical, physical and biological. Currently the main methods of textile dye treatment are by physical and chemical means with research concentrating on cheaper effective alternatives. Complete mineralization to CO_2, H_2O, NO_3^-, SO_2^{4-}, Cl^- etc. is the ideal goal, and can only be achieved after long periods of treatment and by a combination of these methods.

1.9.1 Physical Treatments

1.9.1.1 Adsorption

Adsorption techniques have gained favour recently due to their efficiency in the removal of pollutants too stable for conventional methods. Adsorption produces a high quality product and, in some cases, the process is economically feasible. Decolourisation by this process is a result of two mechanisms: adsorption and ion exchange [3], and is influenced by many physio-chemical factors, such as, dye/ sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time [2].

1.9.1.2 Activated Carbon

This is the most commonly used method of dye removal by adsorption [4] and is very effective for adsorbing cationic, mordant, and acid dyes and to a slightly lesser extent, dispersed, direct, vat, pigment and reactive dyes [3]. Performance is dependent on the type of carbon used and the characteristics of the wastewater Activated carbon is expensive and the loaded carbon has to be reactivated which usually results in 10-15% loss of the sorbent and also there is a noticeable reduction in the adsorption capacity [3]. The regeneration of activated carbon using solutions produces a small additional effluent which needs to be treated before final disposal. The efficiency of the reactivated carbon for dye removal becomes unpredictable and massive doses of carbon are needed for wastewater treatment [27].

Table 1.2: Principal existing and emerging processes for dyes removal from industrial effluents [3, 4]

Methods	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation/Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favourable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes, concentrated sludge production
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for all dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Fenton's reagent	Effective decolourization of both soluble and insoluble dyes	Sludge generation
	Photochemical	No sludge production	Formation of by-products
	Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
	Electrochemical destruction	Breakdown compounds (CO_2, H_2O) are non-hazardous	High cost of electricity
	NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
	Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
	Selective bioadsorbents	Economically attractive, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

1.9.1.3 Fly ash and Coal (mixture)

Fly ash is a waste material originating in great amounts in combustion processes. Although it may contain some hazardous substances, such as heavy metals, it is widely utilized in industry for the removal of Omega Chrom Red ME from effluents in many countries [4]. However, bagasse fly ash generated in the sugar industry does not contain large amounts of toxic metals and has been widely used for adsorption of dyes.

1.9.1.4 Silica gel

An effective material for removing basic dyes [4], however, some side reactions, such as air binding and air fouling with particulate matter, prevents it being used commercially. Table 1.3 shows some inorganic support materials studied for dye(s) removal from aqueous solutions.

Table 1.3: Some inorganic supports materials studied for dye(s) removal from aqueous solutions

Adsorbent(s)	Dye(s)	References
Fibrous clay	Methylene blue	[28]
Mesoporous AlMCM-41	Methylene blue, thionine	[29]
Mesoporous MCM-41	Methylene green	[30]
Perlite	Methylene blue	[31]
Fe (III)/Cr (III) hydroxide industrial solid waste	Methylene blue	[32]
Bone charcoal	Compact disc storage (CDS) and organic dyes	[33]
Fuller's earth	Methylene blue	[34]
Glass powder	Carminic acid	[35]
Kaolinite	Methylene blue	[36]
Activated clay	Brilliant blue FCF	[37]
Petroleum coke	Methylene blue	[21]
Lime, alum, polyaluminium chloride	Methylene blue	[38]
Amberlite	Methylene blue, azure A, azure B, toluidine blue	[39]
Silica gel	Nile blue	[40]

MCM-41: molecular sieves of cetyltrimethylammonium bromide

1.9.1.5 Peat

Peat is a porous and rather complex soil material with organic matter in various stages of decomposition [4]. The cellular structure of peat makes it an ideal choice as an adsorbent. It

has the ability to adsorb polar organic compounds from dye-containing effluents. Peat may be seen as a viable adsorbent in countries such as Ireland and UK, where it is widely available. Peat requires no activation, unlike activated carbon, and also costs much less [3]. Due to activated carbon's powdered nature, it has a much larger surface area, and hence has a better capacity for adsorption. Spent peat may be burned and utilised for steam raising, or, potentially, as substrate in solid state fermentation (SSF), for protein enrichment.

1.9.1.6 Agricultural Wastes

Some low cost botanical materials had directly been used as sorbents for dye adsorption from wastewater, which included peanut hull [41], Neem (*Azadirachta indica*) leaf [42], apple pomace, wheat straw, corn cob, barley husk [43], Guava leaves [44], palm fruit bunch [45], plum kernels [4] and aquatic plants [27]. The use of these substrates for dye removal is advantageous mainly due to their widespread availability and cheapness. They are economically attractive for dye removal, compared to activated charcoal, with many comparing well in certain situations [4, 43] at least in laboratory. These materials are so cheap that regeneration is not necessary and the potential exists for dye-adsorbed materials to be used as substrates in solid state fermentation (SSF) for protein enrichment. Table 1.4 shows some low cost materials studied for dye(s) removal from aqueous solutions.

Table 1.4: Some low cost materials studied for dye(s) removal from aqueous solutions

Adsorbent(s)	Dye(s)	References
Neem (*Azadirachta indica*) leaf powder	Methylene Blue	[42]
Peanut hull	Methylene blue, neutral red, amaranth, sunset yellow	[41]
Rice husk	Methylene blue	[46, 51]
Indian Rosewood sawdust	Methylene blue	[43]
Silk cotton hull, coconut tree sawdust, sago waste, maize cob	Methylene blue	[47]
Date pits	Methylene blue	[48]
Activated carbon from newspaper waste	Methylene blue	[49]
Sewage sludge-based activated carbon	Methylene blue	[24]
Banana and orange peels	Methylene blue	[50]
Bamboo dust, coconut shell, groundnut shell	Methylene blue	[51]
Sawdust and water hyacinth	Methylene blue	[52]

1.9.1.7 Membrane Filtration

This method has the ability to clarify, concentrate and, most importantly, to separate dye continuously from effluent [53]. It has some special features unrivalled by other methods; resistance to temperature, an adverse chemical environment, and microbial attack. The concentrated residue left after separation poses disposal problems, and high capital cost and the possibility of clogging, and membrane replacements are its disadvantages. This method of filtration is suitable for water recycling within a textile dye plant if the effluent contains low concentration of dyes, but it is unable to reduce the dissolved solid content, which makes water re-use a difficult task. Vacuum membrane distillation processes were used for treatment of dyed solutions contained methylene blue as a model [53].

1.9.1.8 Ion Exchange

Ion exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes [3]. Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cation and anion dyes can be removed from dye-containing effluent.

Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes. A major disadvantage is cost. Organic solvents used for regeneration are expensive and the ion exchange method is not very effective for disperse dyes [3].

1.9.1.9 Irradiation

Sufficient quantities of dissolved oxygen are required for organic substances to be broken down effectively by radiation. The dissolved oxygen is consumed very rapidly and so a constant and adequate supply is required. This has an effect on cost. Dye-containing effluent may be treated in a dual-tube bubbling reactor. This method showed that some dyes and phenolic molecules could be oxidised effectively at a laboratory scale only [3].

1.9.1.10 Radiolytic Degradation

Steady-state radiolysis experiments were performed to investigate the mechanisms of the radiolytic degradation of Acid Orange 7 (AO7) in aqueous solutions, which might be useful for the application of ionizing radiation for the remediation of azo-dye-laden wastewaters [54]. The results showed that under reductive conditions AO7 was decomposed through N=N cleavage with the formation of aniline, sodium sulfanilamide, 1-amino-2-naphthol, naphthalidine, 1,2,3,4-tetrahydro-2-naphthol, and 2-naphthol. Whereas under oxidative conditions both N=N and C–N cleavages might be the initial steps in the radiolytic degradation of AO7.

1.9.2 Biological Treatments

In recent years, a number of studies have focused on some microorganisms which are able to biodegrade and biosorb dyes in wastewaters [2]. A wide variety of microorganisms capable of decolorizing a wide range include bacteria, fungi and algae [55].

Biodegradation to complete mineralization would be an ideal method to decolourize coloured effluents. Unfortunately, however, synthetic dyes are, with very few exceptions, xenobiotic [2]. The natural systems of microorganisms in rivers and lakes do not contain enzymes which are designed by nature to degrade such compounds under aerobic conditions. Under anaerobic conditions, however, such as in the digestion of sewage sludge, dyestuff degradation takes place slowly. Biological activity, in liquid state fermentations, is incapable of removing dyes from effluent on a continuous basis. This is due to the time period of a few days required for decolourisation fermentation processes [4]. In order for this to be a viable option for industry, the dye-containing effluent must be held in large tanks; this presents problems due to the sheer site size required and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Table 1.5 shows some of the microorganisms used in treatment of dyes in literature regarding the dyes used in this study.

Table 1.5: Some literature biological treatment (Bioadsorption) of dyes investigated in this thesis

Methods of treatment	Dye	References
*Streptomyces rimosus (*dead)	Methylene blue	[56]
Ganoderma sp. WR-1(white rot fungus)	Amaranth	[57]
Mg/Pd (fungal biomass system)	Sunset yellow FCF, tartrazine	[58]
Horseradish peroxidase (HRP) of plant origin	Methylene blue, azure B	[59]
Giant duckweed (*Spirodela polyrrhiza*)	Methylene blue	[27]
Thelephora sp. (white rot fungus)	Sunset yellow FCF (orange G)	[60]
Pleurotus sajorcaju and *Phanerochaete chrysosporium*	Amaranth, ponceau 4R, tartrazine	[61]
Anaerobic Baffled reactor	Tartrazine	[62]
Phanerochaete chrysosporium lignin peroxidase (LiP)	Methylene blue, azure B	[63]
Mammalian metabolism (Non-Enzymatic)	Sunset yellow FCF	[8]
Flavodon flavus (marine fungi)	Azure B	[64]
Trametes versicolor	Amaranth	[65]
Clostridium perfringens	Amaranth, tartrazine	[66]
Arthobacter globiformis	Acridine orange	[67]
Mixed culture (aerobic/anaerobic)	Carmoisine (acid red 14), ponceau 4R	[68]
P. chrysosporium	Amaranth, Azure B, Sunset yellow FCF	[69]
Phanerochaete chrysosporium (LiP)	Azure B	[70]

1.9.3 Chemical Methods

1.9.3.1 Oxidative Processes

This is the most commonly used method of decolourisation by chemical means. This is mainly due to its simplicity of application. The main oxidising agent is usually hydrogen peroxide (H_2O_2). This agent needs to be activated by some means, for example, ultra violet light. Methods of chemical decolourisation vary depending on the way in which the H_2O_2 is activated [3]. Chemical oxidation removes the dye from the dye-containing effluent by oxidation resulting in aromatic ring cleavage of the dye molecules [3].

1.9.3.2 Fenton's reagent (H_2O_2-Fe(II) Salts)

The oxidation with Fenton's reagent based on ferrous ion and hydrogen peroxide is a proven and effective technology for destruction of a large number of hazardous and organic

pollutants [1, 71]. At pH values less than 4.0 ferrous ions decompose H_2O_2 catalytically yielding hydroxyl radicals most directly. However, at pH values higher than 4.0, ferrous ions easily form ferric ions, which have a tendency to produce ferric hydroxo-complexes. H_2O_2 is quite unstable and easily decomposes at alkaline pH [1].

One major disadvantage of this method is sludge generation through the flocculation of the ion salts and the dye molecules. The sludge, which contains the concentrated impurities, still requires disposal. It has conventionally been incinerated to produce power, but such disposal is seen by some to be far from environmentally friendly [3].

1.9.3.3 Ozonation

Ozonation, as an effective oxidation process, has found application in the degradation of a wide variety of dyes in aqueous solutions [1]. This method shows a preference for double-bonded dye molecules [2].

One major advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and with no residue or sludge formation, and also has the advantage of not producing inorganic ions.

A disadvantage of ozonation is its short half-life, typically being 20 minutes. This time can be further shortened if dyes are present, with stability being affected by the presence of salts, pH, and temperature. In alkaline conditions, ozone decomposition is accelerated, and so careful monitoring of the effluent pH is required [3]. One of the major drawbacks with ozonation is cost because continuous ozonation is required due to its short half-life [3].

1.9.3.4 Photochemical

This method degrades dye molecules to CO_2 and H_2O [72, 73] by UV treatment in the presence of H_2O_2. Degradation is caused by the production of high concentrations of hydroxyl radicals. UV light may be used to activate chemicals, such as H_2O_2, and the rate of dye removal is influenced by the intensity of the UV radiation, pH, dye structure and the dye-bath composition. Depending on initial materials and the extent of the decolourisation

treatment, additional by-products, such as, halides, metals, inorganic acids, organic aldehydes and organic acids, may be produced [3]. It has been proven that the presence of catalysts such as TiO_2 enhances the rate of photodecomposition [74]. There are advantages of photochemical treatment of dye-containing effluent; no sludge is produced and foul odours are greatly reduced. UV light activates the destruction of H_2O_2 into two hydroxy radicals:

$$H_2O_2 + h\nu \rightarrow 2\,OH^{\bullet}$$

This causes the chemical oxidation of organic material. Photochemical degradation in aqueous solution, which may occur in lakes and rivers, is likely to progress very slowly since synthetic dyes are in principle designed to possess a high stability to light. Table 1.6 shows some of the chemical oxidative methods used in treatment of dyes in literature regarding the dyes used in this study.

Table 1.6: Some of the studied chemical oxidation methods for dye removal from aqueous solutions

Methods of treatment	Dye	References
Vanadium-doped TiO_2,TiO_2, SO_4^{2-}	Methylene blue	[75]
Nanocrystalline TiO_2	Methylene blue	[76]
MnO_2 nanorods/ H_2O_2	Methylene blue	[77]
Sunlight induced degradation	Sunset yellow FCF, brilliant blue FCF	[78]
Solar energy light irradiation /TiO_2	Methylene blue	[79, 80, 73, 74]
UV/TiO_2	Amaranth	[81]
UV/TiO_2	Methylene blue	[82, 72, 83, 84]
Fenton process	Methylene blue	[71]
H_2O_2/Supported alumina	Methylene blue	[85]

1.9.3.5 Sodium hypochlorite (NaOCl)

This method causes attack at the amino group of the dye molecule by the Cl^+ and initiates and accelerates azo-bond cleavage. This method is unsuitable for disperse dyes. An increase in decolouration is seen with an increase in Cl^+ concentration. The use of Cl^+ for dye removal is becoming less frequent due to the negative effects it has when released into

waterways [3] and the release of aromatic amines which are carcinogenic, or other toxic molecules.

1.9.3.6 Coagulation

This technique uses a coagulant and produces flocs together with dye materials. The flocs are then separated from the aqueous solution by means of physical sedimentation [86]. The application of $MgCl_2$ as a coagulant has been compared with the well known coagulants such as alum and polyaluminium chloride (PAC) [37]. The results show that $MgCl_2$ is capable of removing more than 90% of the colouring material in wastewaters of a dyeing and printing mill. $MgCl_2$ is shown to be more effective in removing reactive dye than alum and polyelectrolyte (PAC) in terms of settling time and amount of alkalinity required [37].

1.9.3.7 Electro Coagulation

This is an economically feasible method of dye removal [87]. It involves the addition of ferrous sulphate and ferric chloride, allowing excellent removal of direct dyes from wastewaters. Unfortunately, poor results with acid dyes, with the high cost of the ferrous sulphate and ferric chloride, means that it is not a widely used method. The optimum coagulant concentration is dependent on the static charge of the dye in solution and difficulty in removing the sludge formed as part of the coagulation is a problem [3]. Production of large amounts of sludge occurs, and this results in high disposal costs.

1.9.3.8 Electrochemical Destruction

Electro-oxidation is a powerful technique for the purification of many kinds of wastewater [20, 88-91]. This technique has been used successfully for removing the colour of dyes from aqueous solutions [92-101]. In electro-oxidation treatment, the pollutants are destroyed by direct anodic oxidation or by an indirect oxidation process, converting all of the carbon and hydrogen atoms of the dye to carbon dioxide and water [95].

In electrochemical methods the main reagent is the electron [102], which is a "clean reagent". This makes these methods widely used in many applications such as electrodialysis, metal ion removal and recovery, electrodeionisation, and in the destruction

of toxic and non-degradable organics by direct or indirect oxidation [98]. Electrochemical treatment of wastewater offers high removal efficiencies and operates at lower temperature than non-electrochemical treatment. In addition, the method could prevent the production of unwanted side-products by controlling duration time of electrolysis, and there is little or no consumption of chemicals and no sludge build up [95]. Relatively high flow rates cause a direct decrease in dye removal, and the cost of electricity used is comparable to the price of chemicals.

Researchers used different types of anodes and electrolytes to destroy organics and dyes, and suggested that high destruction efficiency can be obtained by changing the anode materials and the electrolytes. Naumczyk et al. [103] studied the treatment of textile wastewater using Ti/RuO_2, Ti/Pt and Ti/Pt/Ir anodes. All three anodes proved to be very effective in direct or indirect oxidation of organics in the wastewater. The efficiency of organic removal followed the order: Ti/RuO_2> Ti/Pt> Ti/Pt/Ir. Abdo et al. [104] used a lead sphere anode and sodium sulphate electrolyte to destroy direct dyes but suggested that decolourisation was due to the formation of colourless compounds obtained upon rupturing the dye molecules. Rajkumar et al. [92] investigated the electrochemical degradation of reactive blue 19 using titanium based dimensionally stable anode (DSA) in the presence of chloride. They also studied the effects of various operating parameters.

Donaldson et al. [98] studied the anodic oxidation of dye molecules, methylene blue, acid blue 25, reactive blue 2, and reactive blue 15 in chloride solution. Their results showed the formation of several intermediate in the electrochemical oxidation of methylene blue from its aqueous solution. Davila et al. [100] investigated the electrochemical decomposition of textile dyes of different nature. The destruction products identified were aniline and alkyl anilines for the studied nitrogen containing dyestuffs [100]. Brillas et al. proposed reaction pathway for the mineralisation of aniline to CO_2 and NH_4^+ by anodic oxidation [105].

A brief description of the theory of this technique is in section 1.10.

1.10 BACKGROUND TO ELECTROCHEMISTRY

Electrochemistry and its application play an important role in the industrial and commercial world. The types of cell reactions are varied, ranging from simple single-phase redox reactions, to reactions, which involve a phase transition (metal deposition, gas evolution, precipitation) to multistep reactions, which combine chemical and electrochemical process [106]. These reactions occur in the wide range of applications of colour removal and effluent treatment and which is the focus for this research. This section introduces the subject area of electrochemistry; the electrochemical cell, its function and the materials, which make up its structure. In order to establish an effective electrochemical effluent treatment method, it is important to understand the basic principles involved.

1.10.1 Electrochemical Reactions and the Electrolytic Process

Electrolysis is a process in which the decomposition of a conducting solution or molten salt is carried out by passing an electric current through them. An electrochemical reaction is a reaction involving the transfer of charge as a part of a chemical reaction.

The electrolytic process requires that an **electrolyte,** an ionized solution or molten metallic salt, complete an electric circuit between two electrodes. When the electrodes are connected to a source of direct current one, called the cathode, becomes negatively (–) charged while the other, called the anode, becomes positively (+) charged. The positive ions in the electrolyte will move toward the cathode and the negatively charged ions toward the anode. This migration of ions through the electrolyte constitutes the electric current in that part of the circuit. The migration of electrons into the anode, through the wiring and an electric generator, and then back to the cathode constitutes the current in the external circuit [106].

1.10.2 Faraday's Law

The basic law of electrochemical theory is Faraday's Law, which relates the amount of charge involved in an electrochemical reaction with the number of moles of reactant reacting and the number of electrons required for the reaction.

$$Q = zmF$$

where z = number of electrons
m = number of moles
F = Faraday' s constant (= 96500 coulombs/ mole)

In addition to *Faradaic* processes that obey Faraday's Law, *non-Faradaic* processes may also occur. Typically these are processes such as adsorption that do not involve a complete transfer of charge from the solution to the metal.

1.10.3 Mechanism of Electrolysis and the Transport of Ions

Substances that yield electrically conducting solutions are known as electrolytes. Electrolysis is only possible in a cell if at least an anode and a cathode are immersed in an electrolyte solution. During electrolysis, electrons must pass from the anode to the cathode through an external electrical circuit interconnecting the two electrodes, and there must be a mechanism for charge transport between the electrons within the cell. Anions move towards the anode and cations move towards the cathode in sufficient quantity to maintain a charge balance, and to avoid a net accumulation of charge. The amount of reduction at the cathode must be equal to the amount of oxidation at the anode. Once the metal ions are discharged on the cathode surface, the solution in the immediate vicinity of the cathode is depleted in metal ions. To continue the reaction, these ions must be replenished. There are three possible methods [107] in which ions reach the electrode:

a) Convection-due to the effect of hydrodynamic flow.

b) Migration-due to the effect of the applied electric field.

c) Diffusion-due to the effect of concentration gradient in the bulk of the solution.

1.10.3.1 Convection

There are two types of convection: forced and natural. The forced convection occurs when the solution is stirred. Natural convection, on the other hand, occurs whether a solution is stirred or not. When a difference in pressure, density, or temperature exists in various parts of the electrolyte, then the liquid either begins to move as a whole or in part to counteract

the difference. For example, when ions are deposited, on the electrode the density of the solution at the electrode-solution interface is reduced. The density change causes an influx of ions from the surrounding part of the solution towards the electrode, independent of that caused by diffusion. Lower density solution in the vicinity of the electrode surface flows upward whilst the higher density solutions flow down into the bulk solution creating a movement by convection. The difference between diffusion and convection is, therefore, that diffusion occurs because of the changes in concentration of ions and convection occurs because of charge density changes [106, 107].

1.10.3.2 Migration

This involves the movement of ionic species through a solution under the influence of an applied potential in the solution. The potential gradient acts upon the ions to push the positive ions towards the negative electrode and the negative ions towards the positive electrode. If the concentration of ions reacting at the electrode is small compared to the concentration of other ions in the solution, the effect of ionic migration is negligible compared to diffusion [107].

1.10.3.3 Diffusion

Diffusion occurs as a result of concentration gradients in the electrolyte. A difference in the concentration can arise when an electrode takes ions out of a solution by electron transfer; so reducing the concentration of ions near the electrode compared with the concentration a few thousand angstroms further into the liquid. When this happens there will be a movement of ions towards the interface to fill the gap [107].

1.10.3.4 Transport of Ions in Dilute Solutions

In normal electroplating solutions with high metal ion concentration, transportation of ions does not cause problems, but in dilute solutions, with less than 1000 mg dm^{-3} metal, there are several problems. In dilute solutions there is a gradient of ionic concentrations from the bulk of the electrolyte to the surface of the electrode where the value is zero at limiting current density [108]. This is known as the boundary or diffusion layer, which is wrapped inside the blanket of thickness $\delta \cong 0.5$ mm (not stirred solution). The removal of metal ions from dilute solutions requires the boundary layer to be broken down or reduced in thickness

for electrolysis to be viable. Several factors, however, influence the thickness of the boundary layer: the ion removal rate on to the electrode, changes in ion density, the resulting convection flow, level of concentration gradient and the counter-forces of diffusion. If the thickness of the boundary layer is not reduced and the current density is increased beyond that which brings the ion concentration to zero at the electrode surface, then other competing reactions such as the evolution of hydrogen will take place thus reducing the current efficiency of the process.

On the other hand, in dilute solutions convection does not bring about mass transportation of ions to the surface of electrodes. Migration itself is insufficient to transport the ions through the barrier of the boundary layer to the surface of the electrodes.

In the case of dilute solutions, the only way to transport the ion into the boundary layer up to the electrodes is diffusion. There is a gradient of ionic concentration in the boundary layer, from that of the bulk electrolyte to that at the electrode, which is zero at limiting current density.

1.10.4 Theory of Electro-oxidation Process

Electrochemical oxidation of many organic pollutants in aqueous solutions on anode could take place by direct electron or oxygen atom transfer. In addition to direct oxidation, organic pollutants can also be treated by an indirect electrolysis generating chemical reactant to convert them into less deleterious products. Oxidation of these pollutants might go right to carbon dioxide and water via successive reactions; each of them could proceed through several steps such as mass transport, adsorption and direct or indirect reaction at the anode surface [102]. The direct electrochemical oxidation of organic compounds could generally occur via a mechanism in which the first step is the oxidation of water molecules on the electrode surface (MO_X), giving rise to formation of hydroxyl radicals according to Awad and Abo Galwa [102].

$$MO_X + H_2O \rightarrow MO_X[OH^{\bullet}] + H^+ + e^- \qquad (1)$$

The produced hydroxyl radicals can, if it is possible, oxidize the underlying oxide lattice to a higher state forming the so-called higher oxide:

$$MO_x[OH^{\bullet}] \rightarrow MO_x[O] + H^+ + e^- \qquad (2)$$

The only role of the formed higher oxide is the participation in the formation of selective oxidation of the organic pollutants (R) without complete mineralisation:

$$MO_x[O] + R \rightarrow RO + MO_x \qquad (3)$$

It is to be noted that the above route can takes place only if the transition of the underlying oxide to a higher oxidation state is possible and the electrodes of this class are called "active electrodes". However, if this is not possible, the electrogenerated hydroxyl radicals could directly oxidize the organic compound to carbon dioxide and water, effectively similar to the combustion of the organic compound:

$$MO_x[OH^{\bullet}] + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \quad (4)$$

and this class of electrodes are called "non-active electrodes"

The electrochemical cell required consists of electrodes (mesh or plate) usually a cathode made of mild steel or titanium and a non-sacrificial anode with high oxygen evolution (platinised titanium (Pt/Ti), graphite, Pb, Pb-alloy, PbO_2, SnO_2, IrO_2-coated titanium or mixed metal oxides). It is reported that these anodes make considerable voltage savings in the electrolysis and make the system more cost effective [106]. In the electrolysis, reduction generally occurs at cathodes and oxidation occurs directly or indirectly at the anodes so that, removal of undesired organic and inorganic compounds are possible. This process achieves the oxidation of organic compounds with little consumption of electrolyte and very little or no sludge production.

Indirect electrochemical oxidation of organic pollutants occurs via "*in situ*" electrogeneration of catalytic species with powerful oxidizing property capable of eliminating the detrimental pollutants from their solutions by converting them into harmless compounds. Although a large number of electrogenerated oxidants can be used such as Fenton's reagent [109] and ozone [110], hypochlorite ion is the most widely employed oxidant in wastewater treatment [20, 99, 101, 102].

Factors which have been shown to be responsible for the decolourisation at the anode in a NaCl electrolyte are as follows:

- Active chlorine formation (Cl_2, HOCl, $OCl^{\bullet}$)
- Oxygen evolution
- Dye destruction

The mechanism of the electrogeneration from a solution containing chloride ions involves two steps, the first of which is the primary oxidation of chloride ions to chlorine at the anode surface according to Awad and Abo Galwa [102]. This followed by the secondary solution phase reaction resulting in the formation of hypochlorous acid, which undergoes dissociation into hypochlorite and hydrogen ions:

At the anode:

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad (5)$$

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \qquad (6)$$

$$OH^- \rightarrow OH^{\bullet} + e^- \qquad (7)$$

At the cathode:

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \qquad (8)$$

(In electrolyte)

$$Cl_2 + 2\,OH^- \rightarrow H_2O + OCl^- + Cl^- \qquad (9)$$

Research work [87] has suggested that the most important of these factors is the formation of cathodic hypochlorite and anodic free chlorine, which act as oxidizing agents to oxidize the dye molecule.

The electrolysis of aqueous bromide solution produces bromate in a similar chemistry to that of chlorate although the disproportionation reaction between bromite ion and hypobromous acid is much faster [106].

At the cathode:

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$$

$$Br_2 + 2\,e^- \rightarrow 2\,Br^-$$

$$BrO_3^- + 6\,H^+ + 6\,e^- \rightarrow Br^- + 3\,H_2O$$

At the anode:

$$2\,Br^- \rightarrow Br_2 + 2\,e^-$$

$$Br^- + 3\,H_2O \rightarrow BrO_3^- + 6\,H^+ + 2\,e^-$$

The chemistry of the anodic oxidation of iodide solutions is analogous to that of chloride and bromide although the competing discharge of hydroxide ions to oxygen is not significant. The chemical formation of iodate from the disproportionation reaction is faster than the analogous reaction for bromate and no hypoiodite builds up in solution [106].

Goswami [111] used sodium meta-bisulphite as an electrolyte for degradation of azo dyes and claimed that $Na_2S_2O_5$ enhanced degradation due to the presence of the bisulphite ion (HSO_3^-) in the solution. The HSO_3^- was formed when the meta-bisulphite ion hydrolysed in water, and was reduced at the cathode to yield dithionite ion ($S_2O_4^{2-}$). The dithionite is a strong reducing agent, most probably because of formation of the sulphoxylate radical anion ($SO_2^{-}\bullet$) [112]. The following reactions describe the process:

$$2\,HSO_3^- + 2\,H^+ + 2\,e^- \rightarrow S_2O_4^{2-} + 2\,H_2O$$

$$S_2O_4^{2-} \rightarrow 2\,SO_2^{-}\bullet$$

The electrochemical reduction of nitrate to ammonia and nitrogen e.g.,

$$3\ NaNO_3 + 3\ H_2O \rightarrow NH_3 + N_2 + 3\ NaOH + 9/2\ O_2$$

occurs with the corresponding formation of oxygen and caustic at the anode [106].

Peroxydisulphate is formed by the anodic oxidation of a sulphate electrolyte in which the following reactions are principally involved [106]:

$$2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e^-$$

$$2\ HSO_4^- \rightarrow S_2O_8^{2-} + 2\ H^+ + 2\ e^-$$

In the aqueous electrolyte the anodic formation of oxygen will be a competitive reaction and thus the electrosynthesis requires high overpotentials. Furthermore the efficiency of the process is affected by the H^+ ion catalysed hydrolysis of persulphate ions:

$$S_2O_8^{2-} + H_2O \rightarrow HSO_4^- + HSO_5^-$$

following which the peroxymonosulphate ions can be oxidized according to:

$$HSO_5^- + H_2O \rightarrow HSO_4^- + 2\ H^+ + O_2 + 2\ e^-$$

In the present work, sodium chloride, sodium bromide, sodium iodide, sodium metabisulphite, sodium sulphate, sodium acetate, sodium nitrate and sodium carbonate were used as supporting electrolytes in the electrolytic degradation of the dyes. On the basis of the literature review, the reaction mechanisms on the formation of hypochlorite ion and free chlorine from NaCl electrolyte and the free radical anion ($SO_2^{-}\bullet$) formation from sodium meta-bisulphite electrolyte are discussed above.

But no evidence of free radical formation from sodium sulphate and sodium carbonate has been found that can enhance the degradation of the dye molecule [111]. It is postulated that

these two electrolytes were used only to make the solution conductive, and any extent of degradation of the dye achieved here was only due to evolution of free oxygen at the anodes.

1.11 AIMS AND OBJECTIVES OF THE RESEARCH WORK

The aims of this research work are:

- To highlight the problems associated with the management of textile effluent streams containing dyes.
- To optimise the electrochemical processes for the removal and destruction of synthetic textile dyes in aqueous solutions.

The main objectives of this research work are:

- To apply the electrochemical processes for the removal and destruction of synthetic food colours.
- To investigate the application of simple techniques to extract natural dye from different plants.
- To investigate the application of natural-derived colourants for dyeing textile fabrics.
- To apply the electrochemical processes for the removal for residual natural pigments and dyes in aqueous solutions.

1.12 THE SCOPE OF THIS WORK

This introductory chapter describes the background to the present work. The colour fastness assessment methods of textile fabrics are described in chapter two. It is followed by four chapters containing experimental details and the final chapter contains the conclusions of this work.

The effects of different operational parameters on the removal and degradation of aqueous solutions of methylene blue and related phnenothiazines, oxazines, azine and acridine dyes by electrochemical process are discussed in Chapter three.

Chapter four describes the electrochemical processes used for the removal and degradation of eight permitted food colours: amaranth, carmoisine, ponceau 4R, sunset yellow FCF, tartrazine, blue food colour, green food colour and yellow food colour in aqueous solutions.

Chapter five describes the processes used for the extraction of natural dyes from 53 different types of plants and one dye of animal origin. These natural dyes were used to colour three kinds of textile fabrics, paj silk (animal origin), brushed twill cotton (plant origin) and crystallized shimmering satin (synthetic). The data on colour fastness to wash and light (natural and artificial) of these natural dyes is also given in this chapter.

Chapter six describes the electrochemical treatment of aqueous solutions containing 9 natural dye extracts (spinach, green tea, saffron, turmeric, binary mixture of curcumin and annatto, beetroot, sumac, roselle and henna), and one natural animal-derived colourant (cochineal).

The conclusions of this work along with the recommendations for future work are given in chapter seven.

1.13 REFERENCES

1. S.K.A. Solmaz, A. Birgül, G.E. Üstün, T. Yonar, 2006, *Color. Technol.*, **122**, 102-109.
2. E. Forgacs, T. Cserháti, G. Oros, *Environ. Int.*, 2004, **30**, 953-971.
3. T. Robinson, G. McMullan, R. Marchant, P. Nigam, *Bioresour. Technol.*, 2001, **77**, 247-255.
4. G. Crini, *Bioresour. Technol.*, 2006, **97**, 1061-1085.
5. www.etad.com, ETAD (22/01/2006)
6. R. Anliker, *Ecotoxicol. Environ. Saf.*, 1979, **3**, 59-74.
7. F. Calbiani, M. Careri, L. Elviri, A. Mangia, L. Pistarà, I. Zagnoni, *J. Chromatogr. A*, 2004, **1042**, 123-130.
8. S. Nam and V. Renganathan, *Chemosphere*, 2000, **40**, 351-357.
9. P.F. Gordon and P. Gregory, Organic Chemistry in Colour, 1983, Springer-Verlag, Berlin, Heidelberg, New York.
10. P. Atkins, Atkins' Molecules, 2003, Cambridge University Press, Cambridge, UK.
11. R.M. Christie, Colour Chemistry, 2001, Royal Society of Chemistry, Cambridge, UK.
12. J. Tawil, Colorimetry, International Cinematographic Guild, Edited by Mark Woods. www.cameraguild.com/technology/colorimetry/colorimetry.htm, Colorimetry. (07/09/2005).
13. Colour Index, 3rd Edition, Vol.4, *The Society of Dyers and Colourists*, 1971.
14. D.R. Waring and G. Hallas, The Chemistry and Application of Dyes, 1990, Plenum Press, New York, USA.
15. E.N. Abrahart, Dyes and their Intermediates, 1977, Edward Arnold Publishers Ltd, London, UK.
16. R.L.M. Allen, Colour Chemistry, Studies in Modern Chemistry, 1971, Nelson, London, UK.
17. E.R. Trotman, Dyeing and Chemical Technology of Textile Fibres, 1964, Charles Griffin, London, UK.
18. H. Zollinger, Color Chemistry, Synthesis, Properties and Applications of Organic Dyes and Pigments, 1987, VCH, Weinheim, Germany.

19. M. Hancock, Potential for Colourants from Plant Sources in England & Wales, 1997, ST0106, Arable Crops & Horticulture Division, ADAS Boxworth, Cambridge, UK.
20. L. Szpyrkowicz, G.H. Kelsall, S.N. Kaul, M. De Faveri, *Chem. Eng. Sci.*, 2001, 56, 1579-1586.
21. A.R. Shawa, D.W. Smith, D.C. Sego, *Water Res.*, 2001, 35, 745-749.
22. R.A. Iglesias, M.F. Mora, A.M. Baruzzi, *J. Electroanal. Chem.*, 2005, 585, 113-119.
23. P. Gregory, Topics in Applied Chemistry, High-Technology Application of Organic Colorants, 1991, Plenum Press, New York, London, UK.
24. F. Rozada, L.F. Calvo, A.I. García, J. Martín-Villacorta, M. Otero, *Bioresour. Technol.*, 2003, 87, 221-230.
25. M. Wainwright, M. N. Byrne, M. A. Gattrell, *J. Photochem. Photobiol. B: Biol.*, 2006, 84, 227-230.
26. P.G. Musto, March 1994, Brunel University dissertation, (The Global Trade of Hazardous Waste), UK.
27. P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, *Environ. Pollut.*, 2003, 125, 385-392.
28. M. Hajjaji, A. Alami, A. El Bouadili, *J. Hazard. Mater.*, 2006, B135, 188-192.
29. M.A. Zanjanchi, A. Ebrahimian, Z. Alimohammadi, *Optical Materials*, 2007, 29, 794-800.
30. L.-C. Juang, C.-C. Wang, C.-K. Lee, *Chemosphere*, 2006, 46, 1920-1928.
31. B. Acemioglu, *Chem. Eng. J.*, 2005, 106, 73-81.
32. C. Namasivayam and S. Sumithra, *J. Environ. Manage. J.*, 2005, 74, 207-215.
33. C.C. Chen, Ph.D Thesis, 2004, Centre for Environmental Research, Brunel University, UK.
34. G. Atun, G. Hisarli, W.S. Sheldrick, M. Muhler, *J. Coll. Interf. Sci.*, 2003, 261, 32-39.
35. G. Atun and G. Hisarli, *Chem. Eng. J.*, 2003, 95, 241-249.
36. D. Ghosh and G. Bhattacharyya, *Appl. Clay Sci.*, 2002, 20, 295-300.
37. Y.S. Ho and C.C. Chiang, *Adsorption*, 2001, 7, 139-147.
38. A. Papadopoulos, C. Savvides, M. Loizidis, K. J. Haralambous, M. Loizidou, *Water Sci. Technol.*, 1997, 36, 377-381.

39. G. Lunn, P.J. Klausmeyer, E.B. Sansone, *Biotech. Histochem.*, 1994, 69, 45-54.
40. M. Saleem, M. Afzal, A. Hameed, F. Mahmood, *Sci. Int. (Lahore)*, 1993, 5, 323-330.
41. R. Gong, Y. Sun, J. Chen, H. Liu, C. Yang, *Dyes Pigm.*, 2005, 67, 175-181.
42. K.G. Bhattacharyya and A. Sharma, *Dyes Pigm.*, 2005, 65, 51-59.
43. V.K. Garg, M. Amita, R. Kumar, R. Gupta, *Dyes Pigm.*, 2004, 63, 243-250.
44. D.K. Singh and B. Srivastava, *Indian J. Environ Health*, 1999, 41, 333-345.
45. M.M. Nassar, *Water Sci. Technol.*, 1999, 40, 133-139.
46. V. Vadivelan and K. V. Kumar, *J. Coll. Interf. Sci.*, 2005, 286, 90-100.
47. K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, *Bioresour. Technol.*, 2003, 87, 129-132.
48. F. Banat, S. Al-Asheh, L. Al-Makhadmeh, *Process. Biochem.*, 2003, 39, 193-202.
49. K. Okada, N. Yamamoto, Y. Kameshima, A. Yasumori, *J. Coll. Interf. Sci.*, 2003, 262, 194-199.
50. G. Annadurai, R. Juang, D. Lee, *J. Hazard. Mater.*, 2002, B92, 263-274.
51. N. Kannan and M.M. Sundaram, *Dyes Pigm.*, 2001, 15, 25-40.
52. T. Al-Nabarawi and S.A. Khedr, *Adsorp. Sci. Technol.*, 2000, 18, 385-398.
53. F. Banat, S. Al-Asheh, M. Qtaishat, *Desalination*, 2005, 174, 87-96.
54. S.-J. Zhang, H.-Q. Yu, Q.-R. Li, *Chemosphere*, 2005, 61, 1003-1011.
55. Y. Fu and T. Viraraghavan, *Bioresour. Technol.*, 2001, 79, 251-262.
56. Y. Nacera and B. Aicha, *Chem. Eng. J.*, 2006, 119, 121-125.
57. S. Revankar and S.S. Lele, *Bioresour. Technol.*, 2007, 98, 775-780.
58. R. Patel and S. Suresh, *J. Hazard. Mater.*, 2006, B137, 1729-1741.
59. V.S. Ferreira-Leitão, J.G. da Silva, E.P.S. Bon, *Appl. Catal. B: Environ.*, 2003, 42, 213-221.
60. K. Selvam, K. Swaminathan, K.-S. Chae, *Bioresour. Technol.*, 2003, 88, 115-119.
61. E.P. Chagas and L.R. Durrant, *Enzyme Microb. Technol.*, 2001, 29, 473-477.
62. J. Bell, J.J. Plumb, C.A. Buckley, D.C. Stuckey, *J. Environ. Eng. (ASCE)*, 2000, 126, 1026-1032.
63. V.S. Ferreira-Leitão, D.B. Magalhaes, S.H. Kling, J.G.Jr. Da Silva, E.P.S. Bon, *Appl. Biochem. Biotechnol.- Part A*, 2000, 84-86, 255-265.
64. C. Raghukumar, *Mycol. Res.*, 2000, 104, 1222-1226.

65. J. Swamy and J.A. Ramsay, *Appl. Microbiol. Biotechnol.*, 1999, 51, 391-396.

66. R. Semde, D. Pierre, G. Geuskens, M. Devleeschouwer, A.J., Moes, *Int. J. Pharm.* 1998, 161, 45-54.

67. K. Itoh, Y. Kitade, S. Kobayashi, M. Nakanishi, C. Yatome, *Bull. Environ. Contam. Toxicol.*, 1998, 60, 781-785.

68. S. FitzGerald and P.L. Bishop, *J. Environ. Sci. Health. Part A, Environ. Sci. Eng. Toxic Hazard. Substance Control A*, 1995, 30, 1251-1276.

69. W.L. Chao and S.L. Lee, *World J. Microbiol. Biotechnol.*, 1994, 10, 556-559.

70. C. Cripps, J.A. Bumpus, S.D. Aust, *Appl. Environ. Microbiol.*, 1990, 56, 1114-1118.

71. K. Dutta, S. Mukhopadhyay, S. Bhattacharjee, B. Chaudhuri, *J. Hazard. Mater.*, 2001, B84, 57-71.

72. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Hermann, *Appl. Catal. B: Environmental*, 2001, 31,145-157.

73. C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J.-M. Hermann, *J. Photochem. Photobiol. A: Chem.*, 2003, 158, 27-36.

74. W.S. Kuo and P.H. Ho, *Chemosphere*, 2001, 45, 77-83.

75. M.M. Mohamed and M.M. Al-Esaimi, *J. Molecular Catal. A: Chem.*, 2006, 255, 53-61.

76. H. Gnaser, A. Orendorz, C. Ziegler, E. Rowlett, W. Bock, *Appl. Surf. Sci.*, 2006, 252, 6996-6999

77. W. Zhang, Z. Yang, X. Wang, Y. Zhang, X. Wen, S. Yang, *Catal. Commun.*, 2006, 7, 408-412.

78. F. Gosetti, V. Gianotti, E. Mazzucco, S. Polati, M.C. Gennaro, *Dyes Pigm.*, 2007, 74, 424-432.

79. Y.-H. Xu, L.-Y. Wang, Q. Zhang, S.-J. Zheng, X.-J. Li, C. Huang, *Mater. Chem. Phys.*, 2005, 92, 470-474.

80. M.A. Hasnat, I.A. Siddiquey, A. Nuruddin, *Dyes Pigm.*, 2005, 66, 185-188.

81. M. Karkmaz, E. Puzenat, C. Guillard, J.M. Herrmann, *Appl. Catal. B: Environ.*, 2004, 51, 183-194.

82. G. Sivalingam, K. Nagaveni, M.S. Hegde, G. Madras, *Appl. Catal. B: Environ.*, 2003, 45, 23-38.

83. T. Zhang, T. Oyama, A. Aoshima, H. Hidaka, J. Zhao, N. Serpone, *J. Photochem. Photobiol. A: Chem.*, 2001, 140, 163-172.

84. F.B. Li, G.B. Gu, G.F. Huang, Y.L. Gu, H.F. Wan, *J. Environ. Sci. (China)*, 2001, 13, 64-68.

85. I.A. Salem and M.S. El-Maazwi, *Chemosphere*, 2000, 41, 1173-1180.

86. B.H. Tan, T.T. Teng, A.K.M. Omar, *Water Res.*, 2000, 34, 597-601.

87. U.B. Ogutveren, N. Gonen, S. Kaparal, *J. Environ. Sci. Health A, Environ. Sci. Eng.*, 1992, 27, 1237-1247.

88. M.A.Q. Alfaro, S. Ferro, C.A. Mrtínez-Huitle, Y.M. Vong, *J. Braz. Chem. Soc.*, 2006, 17, 227-236.

89. S.B. Jonnalagadda and S. Nadupalli, *Talanta*, 2004, 64, 18-22.

90. G. Lissens, J. Pieters, M. Verhaege, L. Pinoy, W. Verstraete, *Electrochimica Acta*, 2003, 48, 1655-1663.

91. K. Ochr, *J. Wat. Pollut. Control Fed.*, 1978, 50, 286-289.

92. D. Rajkumar, B. J. Song, J. G. Kim, 2007, *Dyes Pigm.*, 2007, 72, 1-7.

93. V. López-Grimau and M.C. Gutiérrez, *Chemosphere*, 2006, 62, 106-112.

94. D. Dogan and H. Türkdemir, *J. Chem. Technol. Biotechnol*, 2005, 80, 916-923.

95. C. Cameselle, M. Pazos, M.A. Sanromán, *Chemosphere*, 2005, 60, 1080-1086.

96. A. Fernandes, A. Morão, M. Magrinho, A. Lopes, I. Gonçalves, *Dyes Pigm.*, 2004, 61, 287-296.

97. S. Hattori, M. Doi, E. Takahashi, T. Kurosu, M. Nara, S. Nakamatsu, Y. Nishiki, T. Furuta, M. Iida, *J. Appl. Electrochem.*, 2003, 33, 85-91.

98. J.D. Donaldson, S.M. Grimes, N.G. Yasri, B. Wheals, J. Parrick, W.E. Errington, *J. Chem. Technol. Biotechnol.*, 2002, 77, 756-760.

99. J. P. Lorimer, T. J. Mason, S. S. Phull, *Ultrasonics Sonochemistry*, 2000, 7, 237-242.

100. M.M. Davila-Jimenez, M.P. Elizalde-Gonzalez, A. Gutierrez-Gonzalez, A.A. Pelaez-Cid, *J. Chromatogr. A*, 2000, 889, 253–259.

101. S. J. Allen, K. H. Khader, M. Bino, *J. Chem. Tech. Biotechnol.* 1995, 62, 111-117.

102. H.S. Awad, N. Abo Galwa, *Chemosphere*, 2005, 61, 1327-1335.

103. J. Naumczyk, L. Szpyrkowicz, F. Zilio-Grandi, *Wat. Sci. Tech.*, 1996, 34, 17-24.

104. M.S.E. Abdo and S.R. Almeeri, *J. Environ. Sci. Health*, 1987, A22, 27-45.

105. E. Brillas, E. Mur, R. Sauleda, L. Sànchez, J. Peral, X. Domènech, J. Casado, *Appl. Catal. B: Environ.*, 1998, 16, 31-42.
106. K. Scott, Electrochemical Processes for Clean Technology, 1995, Royal Society of Chemistry, Newcastle upon Tyne, UK.
107. A.C. Fisher, Electrode Dynamics, 2000, Oxford Science Publications, Zeneca, Oxford, UK.
108. N.G. Yasri, Ph.D Thesis, 2000, Centre for Environmental Research, Brunel University, UK.
109. K. Dutta, S. Mukhopadhyay, S. Bhattacharjee, B. Chaudhuri, *J. Hazard. Mater.*, 2001, B 84, 57-71.
110. A. de O. Martins, V. M. Canalli, C.M.N. Azevedo, M. Pires, *Dyes Pigm.*, 2006, 68, 227-234.
111. N. Goswami, PhD Thesis, 2002, Centre for Environmental Research, Brunel University, UK.
112. A. Reife and C.M. Freeman, Environmental Chemistry of Dyes and Pigments; 1996, Wiley-Interscience, John Wiley & Sons, New York, USA.

CHAPTER 2

ANALYTICAL METHODS

2.1 THE METHODS TO MEASURE COLOUR FASTNESS OF TEXTILES

Many of the conditions in which textiles are used, processed or stored can have a detrimental effect on the colour of the textile. Typical examples are colour bleeding, loss or transfer to other adjacent textiles, in washing, when wet from the rain, after swimming or with perspiration. The dye, colour, can be destroyed or changed by the action of light and chemicals found in common household cleaning agents and atmospheric contaminants. The ability of the coloured textiles to withstand these various changes is called its Colour Fastness Properties. It should be noted that to date there is no such thing as a completely colour fast textile [1, 2]. It is always possible to find conditions under which the dyes used to colour the textiles can be destroyed or made to bleed. For this reason when coloured textiles that have been used successfully under specific conditions the fastness should be reappraised if the conditions change. For example fashion wear used for industrial/corporate wear purposes.

The methods of physical tests do not cover tests to satisfy final consumer, e.g. washing, perspiration, light fastness are only required. But also tests for the reaction of colour to production processing like fusing, steaming or milling of wool and others determine properties which are important to the dyer and finisher.

2.1.1 The History of Colour Fastness Test Methods

Tests to evaluate the colour fastness of textiles have been in the UK since 1934, when the Society of Dyers and Colourists (SDC), Bradford, first published some basic test methods. Other organisations such as the American Association of Textiles Chemists and Colourists (AATCC), British Standards Institution (BSI) and other countries have also introduced test methods over the years. These test methods are often referred to as 'Standards', which detail a procedure from which consistent, reproducible and meaningful results can be obtained. The standards do not generally specify performance requirements [1].

With the formation of the International Standard Organisation (ISO) in the 1940's, truly international methods appeared. Most of these methods have been adopted for use in all European Union countries. Many countries still retained their own national standards. The

numbering of these standards therefore became complicated. Many EU member states have retained a country prefix in addition to the European/International Standard reference [1]. For example, Colour Fastness to Rubbing:

BS EN ISO 105 X12 (UK)

DIN EN ISO 105 X12 (Germany)

NF EN ISO 105 X12 (France)

It is important to note that all three of these standards are technically the same [1].

A hydro thermograph is used to measure the temperature and humidity of the operating laboratory conditions (Plate 2.1) which is the international standard [1].

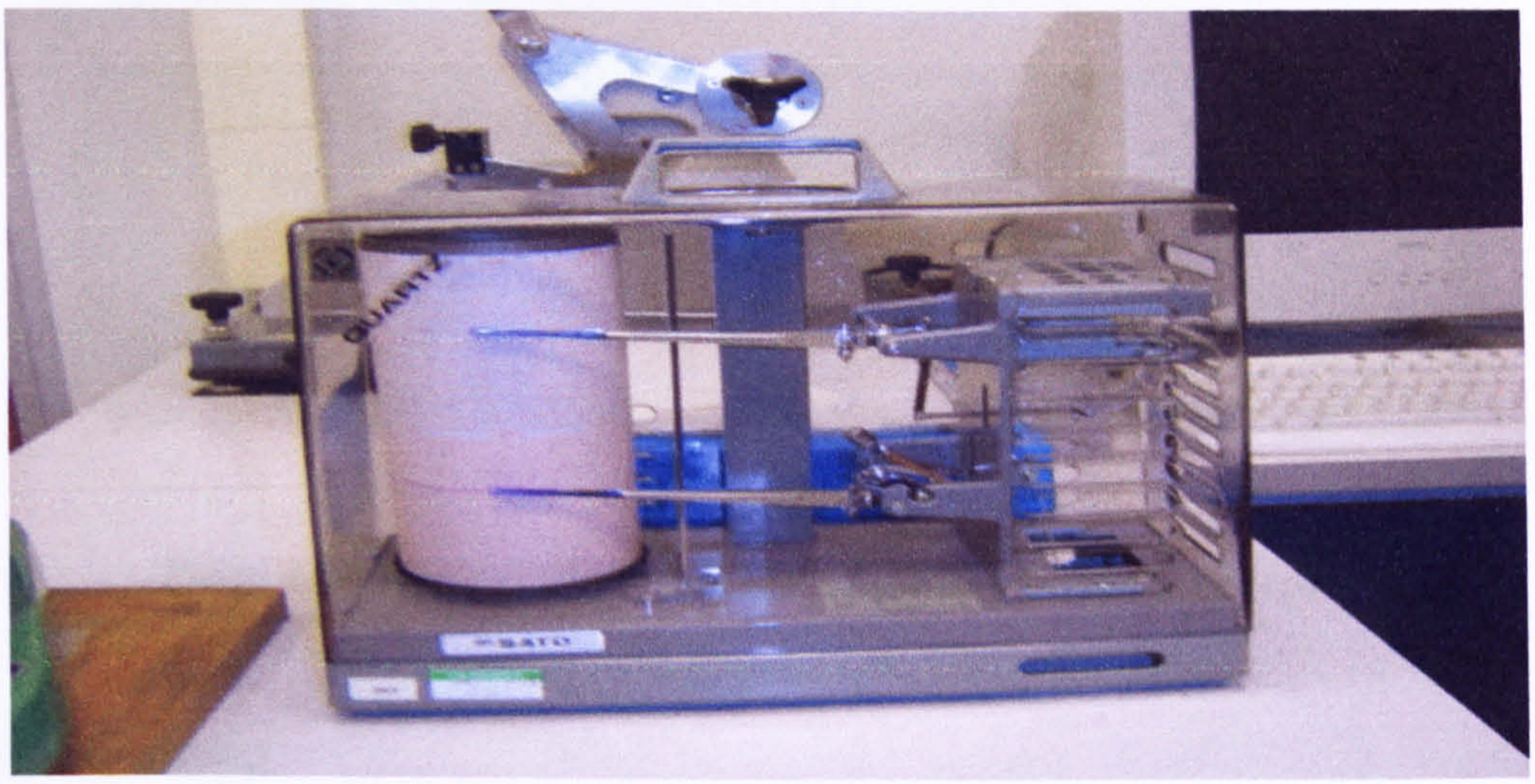


Plate 2.1: Hydro thermograph for measuring humidity and temperature

Below are the most common colour fastness tests carried out for most retail groups in the UK and Europe.

2.1.2 Colour Fastness Assessments

Colour fastness means the resistance of the hue of textiles to the different agents to which they may be exposed during manufacture and subsequent use [1, 2].

The colour change and potential to stain other fabrics are graded using a 1-5 scale. The tested samples (often 40 mm × 100 mm) are visually assessed against a series of pairs of

grey chips (Plate 2.2) with an increasing difference in colour between 5 no difference (good) to 1 the greatest difference (poor). Two sets are used, one for colour change, ISO 105, and one for staining, ISO 105 A03. Instrumental methods are also available for grading specified lighting illuminants and sample presentation. Samples tested to the colour fastness to light method are assessed by a series of blue standards described in section 2.2.4.

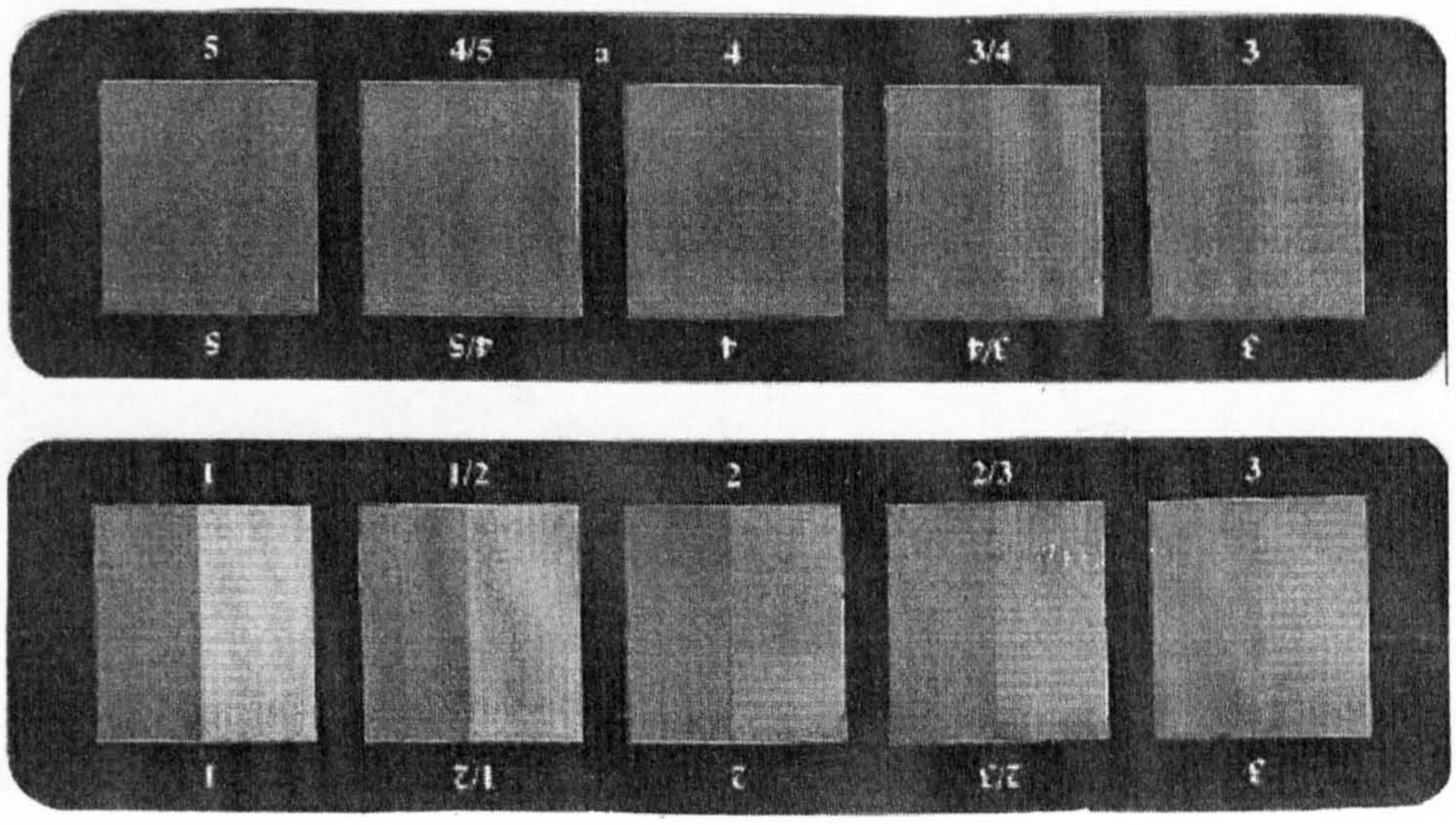


Plate 2.2: Grey scale chips for assessing change in colour

2.1.3 Cross Staining

The methods of testing dyes as to behaviour toward each of the various agents are as follows:

A specimen of dyed textile in intimate contact with an undyed specimen of the same or a different textile is subjected, on the laboratory scale, to conditions simulating those met with in processing or use. In all cases the change in colour of the dyed specimen and, where appropriate, the staining of the undyed cloths, are assessed visually using the standard grey scale [1, 2]. In certain cases, e.g., bleach fastness, gas fading, there is no need to have undyed cloths present, only the change in colour being relevant.

It is now common practice to use a multifibre strip typically 40 mm × 100 mm, containing different fibres rather than single fibre adjacent fabrics [1]. The most common type used in

Europe is type DW, which contains Diacetate, Cotton, Nylon, Polyester, Acrylic and Wool (Plate 2.3). Other types of multifibre strips are available, some of which contain different fibres. Not all multifibre strips achieve the same results when tested side by side, so it is important that the correct type is used.

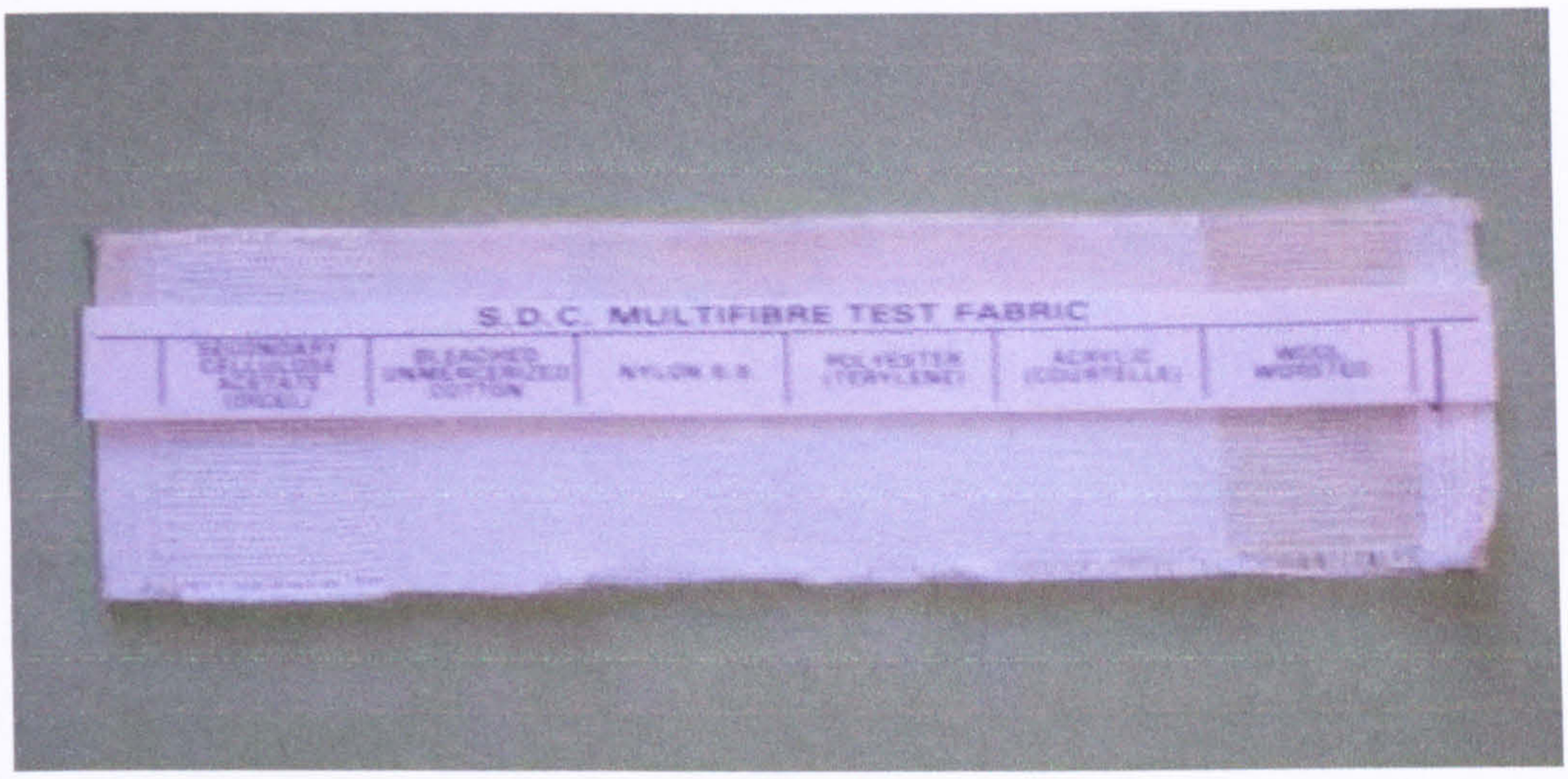


Plate 2.3: DW multifibre test fabric strip

2.1.4 Colour Fastness to Light (BS EN ISO 105 B02)

The test is used to determine if a textile changes colour or if the colour is destroyed by the action of daylight. A specimen of the dyed or printed textile is exposed to daylight under standard conditions, including protection from rain, along with eight dyed wool standards (Plate 2.4) [2].

It can be seen from Plate 2.4 and Table 2.1 that the standard wool dyes are all blue dyes. This at first sight may appear strange when one considers that dyes of every hue, applied on different substrates, have to be tested for light fastness.

The change in colour is assessed by eye by reference to five pairs of grey dyed chips, each pair representing a visual difference and contrast. By this means the degree of fading of any hue can be assessed, via the standard grey scale (Plate 2.2), in relation to the official standards [2].

The process of fading in daylight is generally slow and tests may take months to complete. Laboratory instruments have been designed and are in use in which intense artificial light is employed to accelerate the fading process. Such instruments are for the most part used comparatively [2].

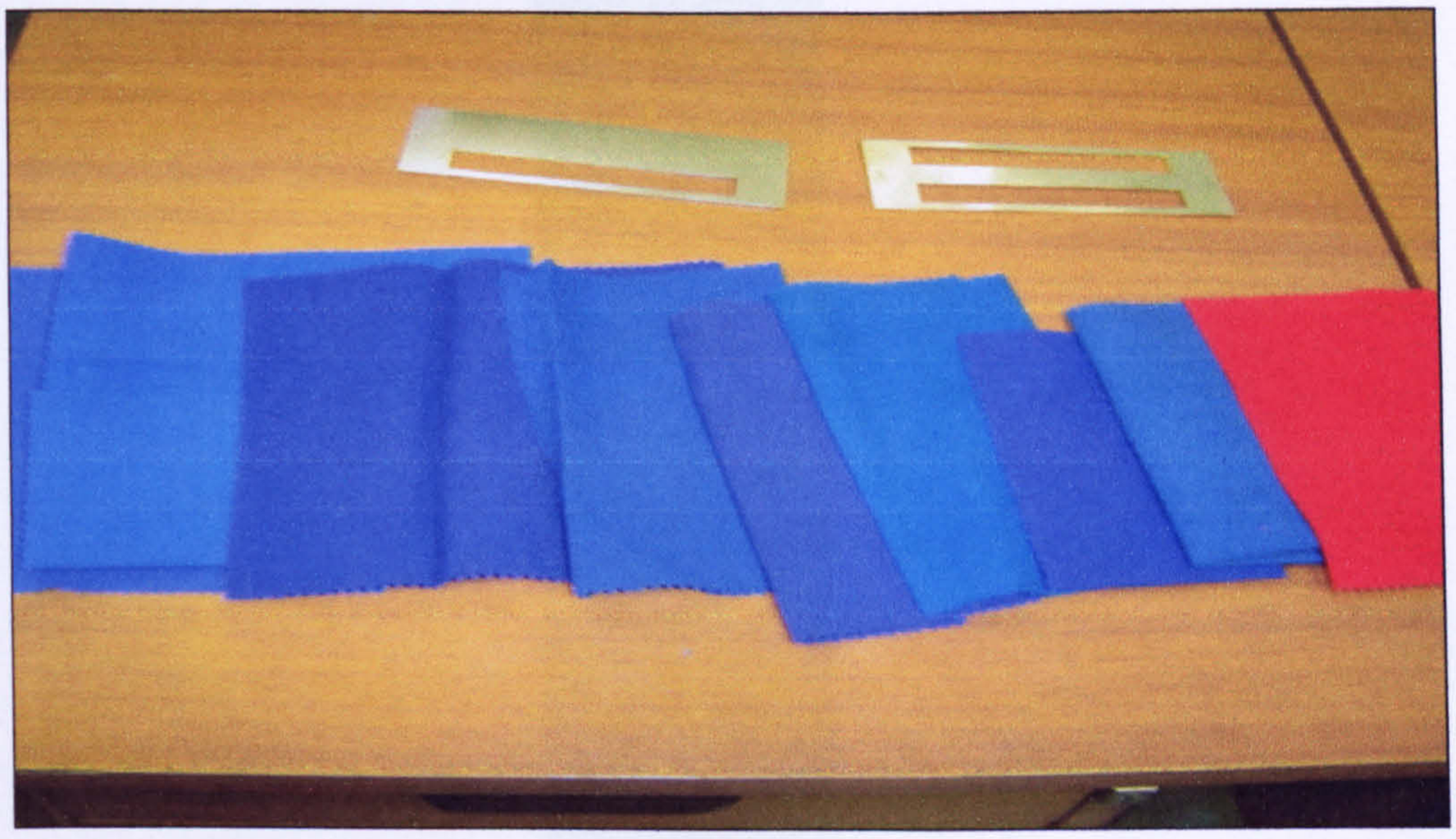


Plate 2.4: 1-8 Scale of blue standards and humidity control fabric B02

Table 2.1: List of standard wool dyes [2]

Light fastness rating	Dye	C.I. designation	C.I. number	Chemical class
1	Acilan brilliant blue FFR	Acid blue 104	42735	Triarylmethane
2	Acilan brilliant blue FFB	Acid blue 109	42740	Triarylmethane
3	Coomassie brilliant blue R	Acid blue 83	42660	Triarylmethane
4	Supramin blue EG	Acid blue 121	50310	Azine
5	Solway blue RN	Acid blue 47	62085	Anthraquinonoid
6	Alizarin light blue 4GL	Acid blue 23	61125	Anthraquinonoid
7	Soledon blue 4BC Powder	Solubilised vat blue 5	73066	Indigoid
8	Indigosol blue AGG	Solubilised vat blue 8	73801	Indigoid

An artificial daylight is achieved by use of a 'filtered xenon arc' light source (the xenon lamp has an emission wavelength profile close to daylight) and samples are exposed at a controlled temperature and humidity (Plate 2.4). Colour fastness to light in Europe is assessed using a 1-8 scale of blue standards (1 being very low fastness and 8 being

excellent fastness) which fade at predetermined geometric intervals. These blue standards (often referred to as Blue Wool or Pigment Print) are simultaneously exposed with the test specimens to the light source (Plate 2.5) [1].

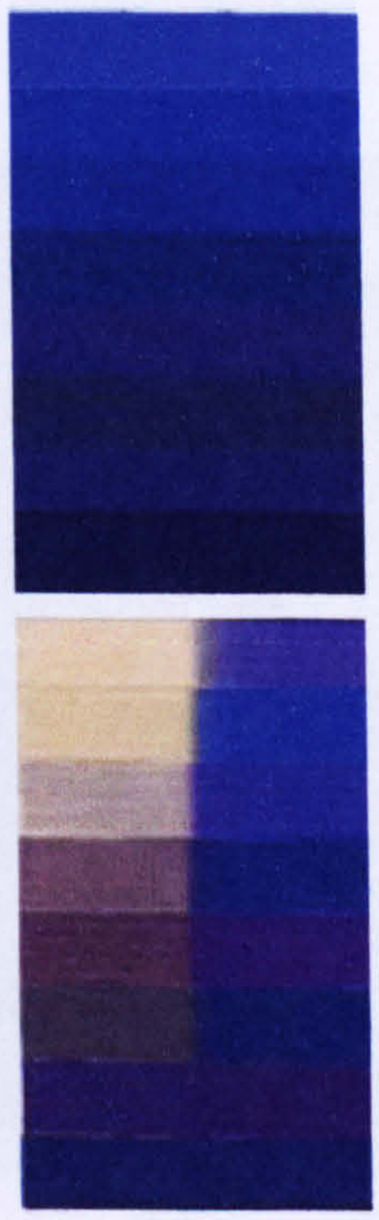


Plate 2.5: 1-8 Scale of blue standards before and after exposing to light source

The humidity control fabric (Plate 2.4) is an azoic dyed cotton fabric with specified fading properties, which varies with the amount of relative humidity [3]. It is used as a calibration tool for light fastness testing. When the humidity of the light fastness testing machine is correctly set it will fade at an identical rate to the light fastness standard Number 5.

For general apparel, retailers usually specify a standard of 4 as a minimum requirement. For some apparel end use e.g., outwear, a minimum standard of 5 is required, whilst home wear is often expected to achieve a standard of 5 or 6 [1]. The blue standards are faded to a predetermined contrast as assessed using the grey scale for colour change. When the correct level of fading on the blue standard has been achieved, the test specimens and blue standards are removed from the light source. The final result allocated to the test specimens is the number of the blue standard that shows the same degree of fading as the specimen. The minimum specimen size is 10 mm × 45 mm.

The process of fading in daylight is generally slow and tests may take months to complete. Laboratory instruments have been designed and are in use in which intense artificial light is employed to accelerate the fading process (Plate 2.6). Such instruments are for the most part used comparatively [2].

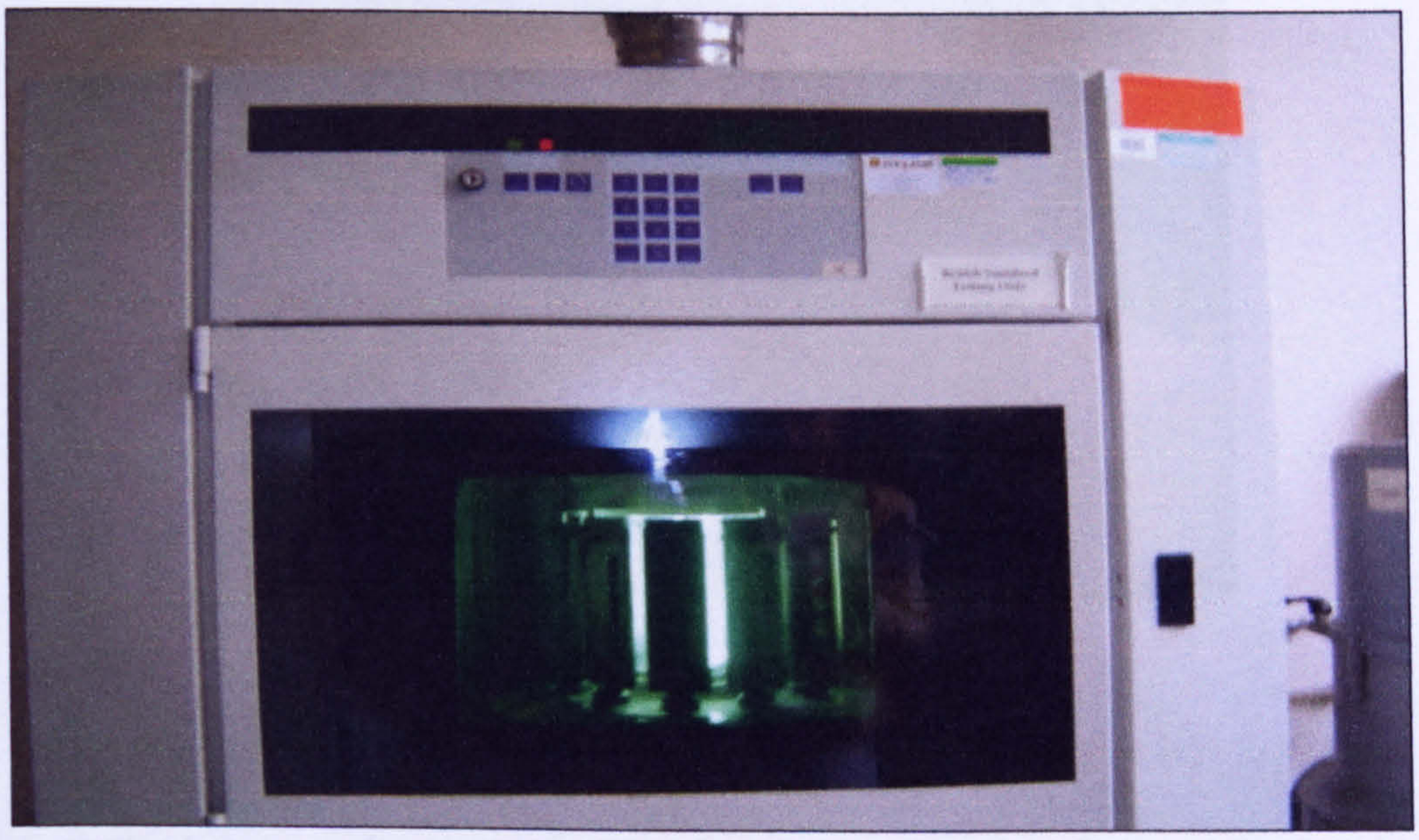


Plate 2.6: Fabric samples exposed to a filtered xenon arc light source

2.1.5 Colour Fastness to Washing BS EN ISO 105

2.1.5.1 Domestic and Commercial Laundering C01 to C05 (soap), C06 (phosphate detergent) C08 (non phosphate detergent) C09/UK-TO

A range of international tests are available for use. The tests are used to determine the colour change and staining potential of dyed material when washed under standard conditions (Plate 2.7) [1].

The standards numbered C01 to C05 use a wash solution of soap and 'washing soda'. These tests do not represent current washing practice and may therefore give misleading results. These standards are rarely used nowadays.

Plate 2.7: Textile washing machine

The C06 method uses a detergent (rather than a soap) and sodium perborate in the test solution and incorporates a range of different temperatures and conditions relating to domestic and commercial laundering using traditional phosphate based detergents. This is the test procedure that is most commonly specified by retailers [1] although it is very likely that this will change in the next few years, as the method does not indicate how the colour will perform with low temperature bleach activators.

The latest development is the C08 standard, which was published during 2001. This is a new test, similar to the C06 test but using a non-phosphate detergent, typical of today's domestic detergent formulations.

The C09 test determines the effect of bleach activated detergents on the long term colour stability of specimens washed at low temperatures. This single test method predicts the colour loss that will occur over 10 to 20 domestic washes. Assessment of the staining potential is not evaluated within this test-no multifibre strip is added.

2.1.5.2 Hand Washing

Dyed and undyed samples in contact are agitated in a soap solution, rinsed and dried. Change in colour of the dyed samples and degree of staining of the undyed samples are assessed in the normal way [2].

A visit and tour of testing laboratories was made to Precision Processes Textiles (PPT) in Ambergate, Derbyshire on 16th August 2006. Sections 2.1.6-2.1.11 detail some of the tests and instruments used in assessing the durability of dyed textile fabrics.

2.1.6 Colour Fastness to Dry Cleaning (BS EN ISO 105 D01)

The test indicates the colour change and the colour transfer into dry cleaning solvent (perchloroethylene). Some of the retailer specific tests also include multifibre strip to assess the staining potential onto other fibres, and sometimes this detects very poor fastness [1]. The test, however, may not always be representative of the procedures used in professional dry cleaning services.

2.1.7 Colour Fastness to Water (BS EN ISO 105 E01)

This test stimulates the potential for cross staining when a wet coloured textile is in intimate contact with another. It can give an indication of the possible staining that may occur if the wearer perspires [1], but it will not predict the colour change of some textiles due to the action of chemicals in the perspiration. It may be useful for detecting cross staining when garments are professionally 'wet' cleaned.

A specimen of the textile in contact with the adjacent fabric is immersed in water, drained and placed between two plates under a specified pressure [4]. The specimen and the adjacent fabrics are dried separately. The change in colour of the specimen and the staining of the adjacent fabrics are assessed with grey scales. The test duration under pressure is 4 hours at a temperature of 37°C, a suitable testing device is a Perspirometer.

2.1.8 Colour Fastness to Perspiration (BS EN ISO 105 E04)

This test stimulates the potential for cross staining when a coloured textile wetted with perspiration is in intimate contact with another [1]. The test is carried out in both acid and alkaline artificial perspiration solutions of histidine (α-amino-β-(iminazol-4-yl) propionic acid) to account for the differences between different sections of the population (Plate 2.8) [2, 4].

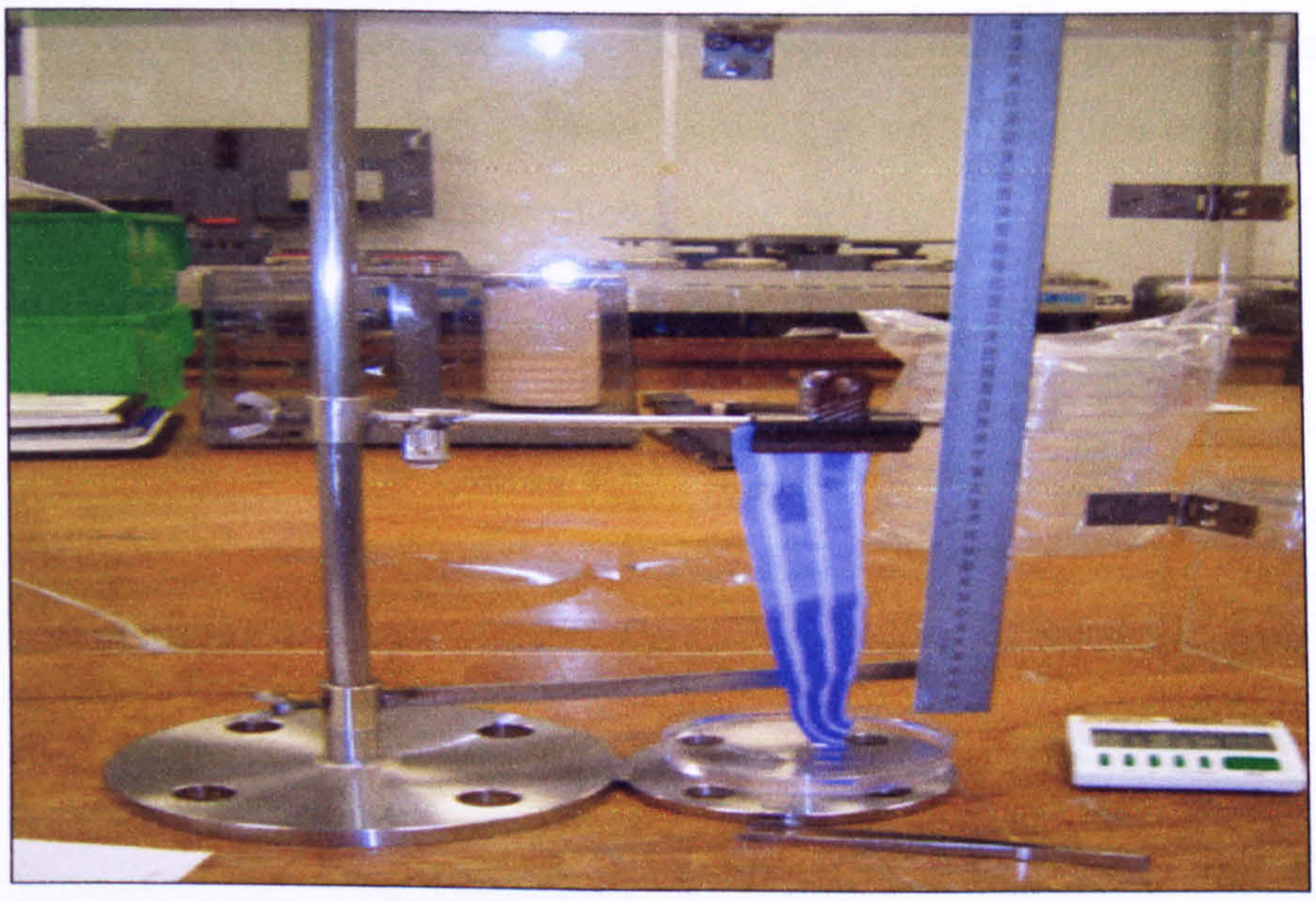


Plate 2.8: Wick tester for measuring perspiration

2.1.9 Colour Fastness to Water Spotting (BS EN ISO 105 E07)

The colour fastness to water spotting is the resistance to the action of water drops on dyed fabric surfaces [1]. A sample of the fabric has 2 water drops placed on the surface. One drop is dried after 30 minutes with absorbent paper and the other left for 16 hours. The change of colour of the fabric sample is evaluated using the change of colour Grey Scale.

2.1.10 Colour Fastness to Chlorinated Water (BS EN ISO 105-EO3)

This method determines the resistances of the colour of textiles to the action of active chlorine in concentrations such as are used to disinfect swimming-bath water. A specimen of the textile is treated with a weak chlorine solution of a given concentration and dried. The change in colour of the specimen is assessed with the grey scale. The test duration is 1

hour at a temperature of 27°C; a suitable testing device is a Gyrowash as used for the colour fastness to washing tests [5].

2.1.11 Colour Fastness to Rubbing (BS EN ISO 105 X12)

This method is intended for determining the resistance of the colour of textiles to rubbing off and staining other materials when it is worn [1]. Specimens of the textile are rubbed with dry rubbing cloth and with wet rubbing cloth. Physical movement creates a rubbing action against adjacent fabrics or garments (Plate 2.9). The testing device known as a crock meter [5] comprises a rubbing finger cylinder moving to and from in a straight line along a 10 cm track on the specimen with a downward force of 9 N.

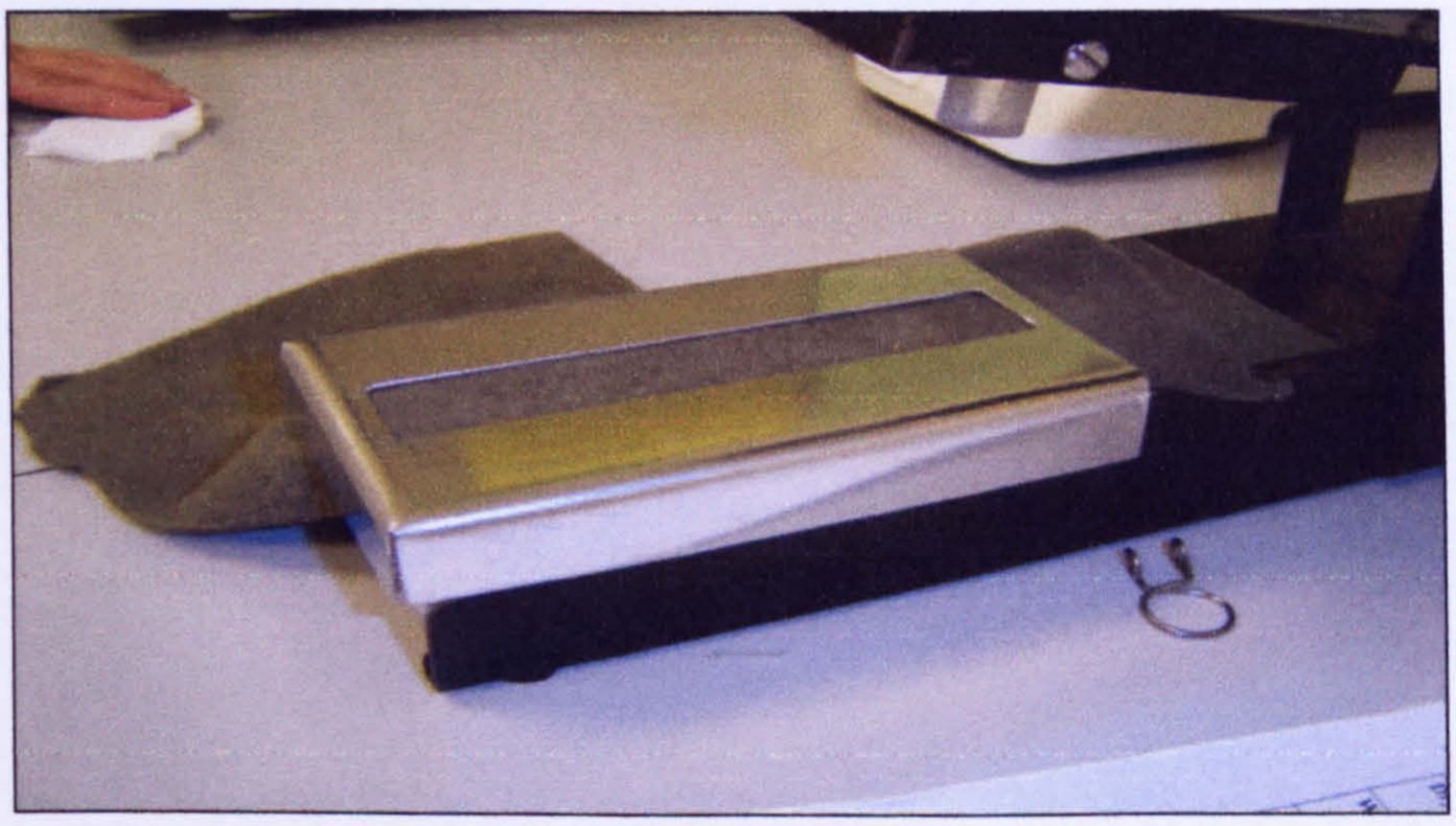


Plate 2.9: Rubbing tester against fabric for colour fastness

The test duration is 10 times to and from in 10 seconds. The test does not assess the appearance of the area that has been rubbed on a sample, which can sometimes show 'frosting'. The staining of the rubbing cloths is assessed with the grey scale [5].

2.2 REFERENCES

1. K. Wilkinson, A Division of Specialised Technology Resources, Precision Processes Textiles Ltd., Derby, UK.
2. E.N. Abrahart, Dyes and their Intermediates, 1977, Edward Arnold Publishers Ltd., London, UK.
3. www.sdcenterprises.co.uk/products/lightfastness.asp, (10/09/2007).
4. E.R. Trotman, Dyeing and Chemical Technology of Textile Fibres, 1964, Charles Griffin, London, UK.
5. www.analytical-s.co.uk/tests%20info.htm, (10/09/2007).

CHAPTER 3
DECOLOURIZATION STUDIES OF SYNTHETIC DYES

3.1 INTRODUCTION

The widespread conscientiousness of the need to avoid and minimize environmental contamination has greatly increased the interest in the elimination of hazardous organic compounds, including dyes, present in a wide range of industrial effluents [1, 2].

Different types of dyes are being used in large quantities in various industries including the textile industry. The residual concentrations of these dyes are commonly present in industrial effluents mainly coming from textile plants [2-4]. Effluents containing dyes readily demand attention because their intense colour even at high dilution means they are highly visible and affect the water transparency and can alter biological cycles [5-7]. For these reasons, dye containing effluents have attracted the attention of researchers and environmentalists alike, searching for alternatives to avoid and/or minimize their polluting potentials [1, 8].

A literature review on this subject matter has revealed the importance of various approaches to handle the wastewater streams containing dyes [9]. Technological systems for the removal of different types of dyes can be divided into a) physical methods, b) biological methods and c) chemical methods. Physical methods include adsorption on mango pit [10], date pit and olives stones [11], passion fruit and mandarin peels [12], rice straw [13], sand [14] and Fe (III)/Cr (III) hydroxide sludge [7]. Biological methods include biodegradation and biosorption [15-17]. Chemical methods such as Fenton's reagent [18, 19] and other oxidation procedures [20] are the most frequently used.

Recently, photocatalytic degradation has received great attention for the removal of a commercial dye, methylene blue, from aqueous media [9, 11, 21-28]. Combined photo-electrochemical methods have also been used for the removal of methylene blue [2, 29].

In the last decade, advanced oxidation processes (AOPs) were widely used for the treatment of wastewater since they were able to cause the destruction of organic pollutants in aqueous solution [30-35]. Among these advanced oxidation processes, electrochemical

treatment has received greater attention in recent years due to its unique features, such as versatility, energy efficiency, automation and cost effectiveness [36, 37].

In electrochemical techniques, the main reagent is the electron, called a 'Clean Reagent' because it degrades all the organics present in the effluent without generating any secondary pollutant or by-product/sludge [36, 38]. Eventually, the dye is converted directly into CO_2 and H_2O; a process commonly referred to as electrochemical mineralization or combustion [9]. The electrochemical technique offers high removal efficiencies and has lower temperature requirements compared to non-electrochemical treatments. In addition to the operating parameters, the rate of pollutant degradation depends on the anode material. Above all, the electrochemical reactors are compact, simple and the rate of pollutants removal is very rapid [39].

When the electrochemical reactors operate at high cell potential, the anodic process occurs in the potential region of water discharge, and hydroxyl radicals are generated [6, 34, 37, 40, 41]. On the other hand, if chloride is present in the electrolyte, an indirect oxidation via active chlorine can be operative [4, 5, 42, 43].

Methylene blue is a cationic phenothiazine dye, used extensively for dyeing and printing cotton, wool and silk [11]. Methylene blue has been widely used in biomedical research [44], and was the lead compound in several important clinical areas [45-50] because of its antiseptic properties [51]. The presence of this dye in wastewater may cause effect in the eye, or nausea, vomiting and diarrhea [11] and other effects [52, 53].

Although there is extensive literature available on electrochemical treatment of wastewater containing dyes [1, 4-6, 8, 31-33, 39, 40, 43, 54-57], few studies have been devoted to cationic dyes such as methylene blue or related phenothiazine dyes [38, 58, 59]. In the present work, investigations of the decolourisation of aqueous solutions of methylene blue and related phnenothiazines, oxazines, azine and acridine dyes by electrochemical process were undertaken and the effects of different operational parameters on the removal of these dyes were studied.

The phenothiazinium dyes were first synthesised in the late 19th century - e.g. both methylene blue (Caro) and thionine (Lauth) in 1876 [60].

Oxazines represent one of the oldest classes of delocalized cationic dyes. They are bright, intense dyes with moderate to good light fastness properties [61]. They are related to thiazine dyes by replacement of sulphur in the hetero ring by oxygen.

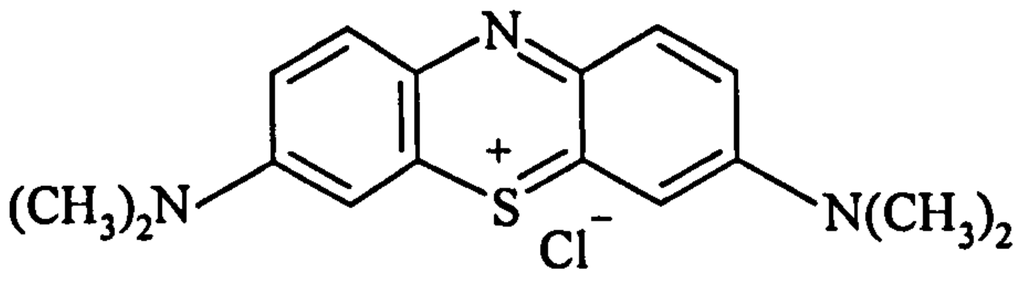
The main objectives of this research work are:

- To investigate the optimum conditions for complete colour removal and degradation of methylene blue by using the electrochemical processes.
- To apply the optimised operational parameters to the colour removal for related dyes.
- To study the effect of substituents on the aromatic rings of phenothiazine dyes (e.g. methyl and nitro groups), and the hetero atoms of phenothiazine, oxazine, azine and acridine dyes by using the electrochemical processes.

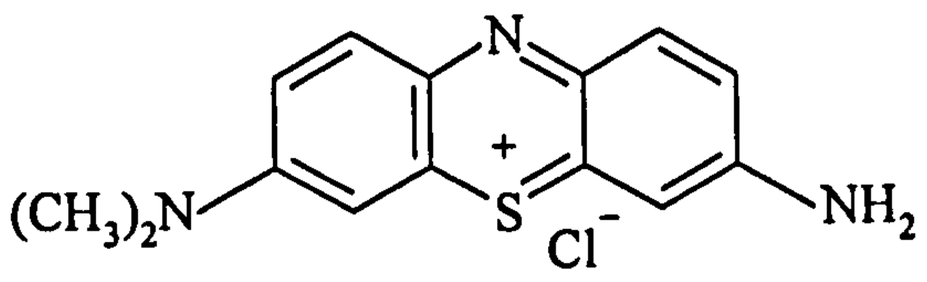
3.2 EXPERIMENTAL

3.2.1 Dyes and Chemicals

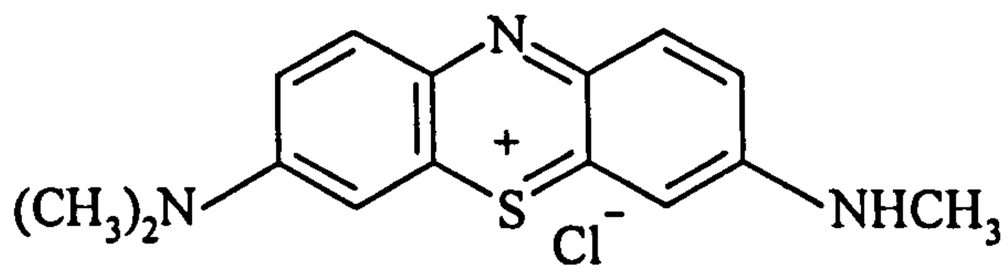
Methylene blue, azure A, azure B, azure C, toluidine blue O, new methylene blue, 1, 9-dimethyl methylene blue, thionine, methylene violet, resorufin, neutral red and acridine orange were all purchased from Sigma-Aldrich Chemicals (Gillingham, UK) and methylene green and Nile blue were obtained from Acros Organics.



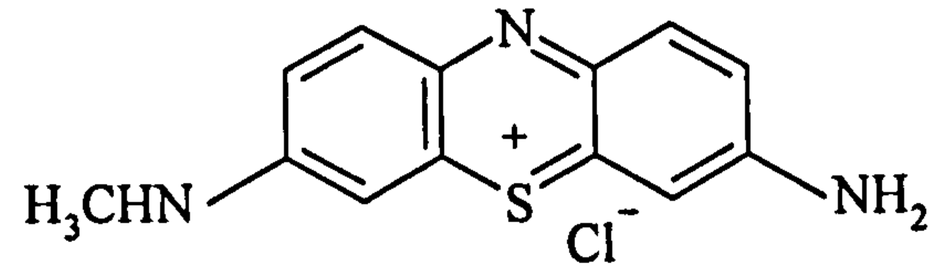
Methylene blue
(MB)



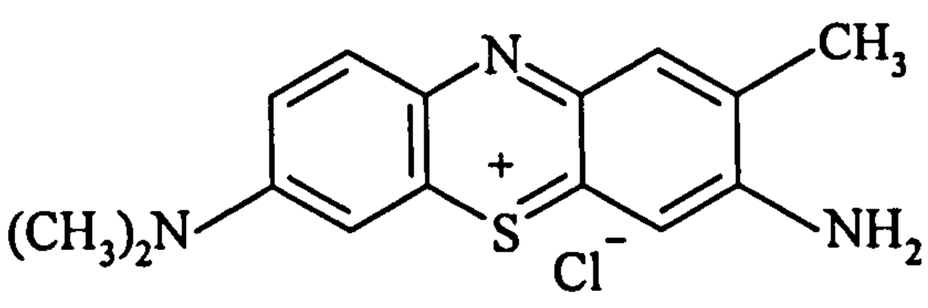
Azure A
(AA)



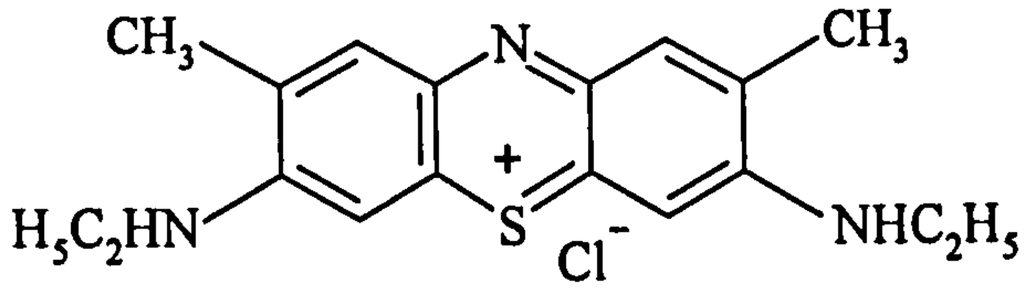
Azure B
(AB)



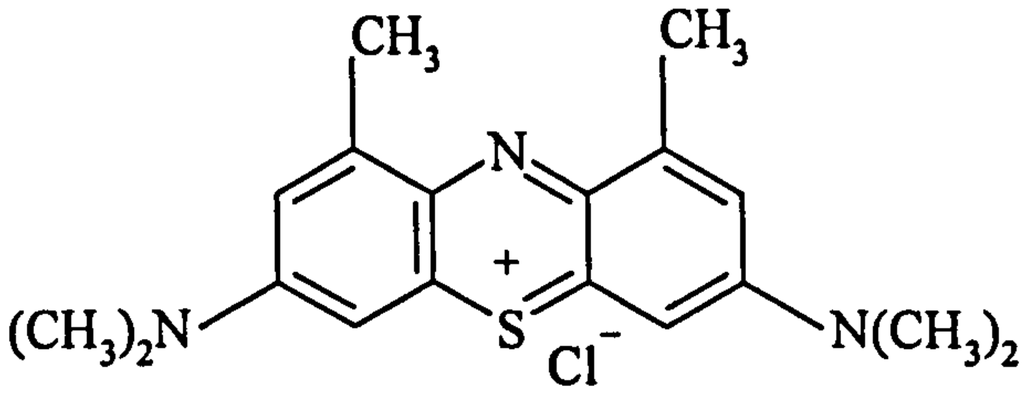
Azure C
(AC)



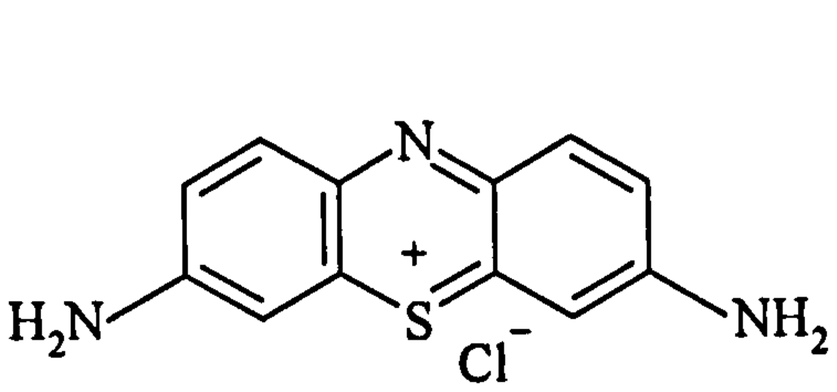
Toluidine blue O
(TBO)



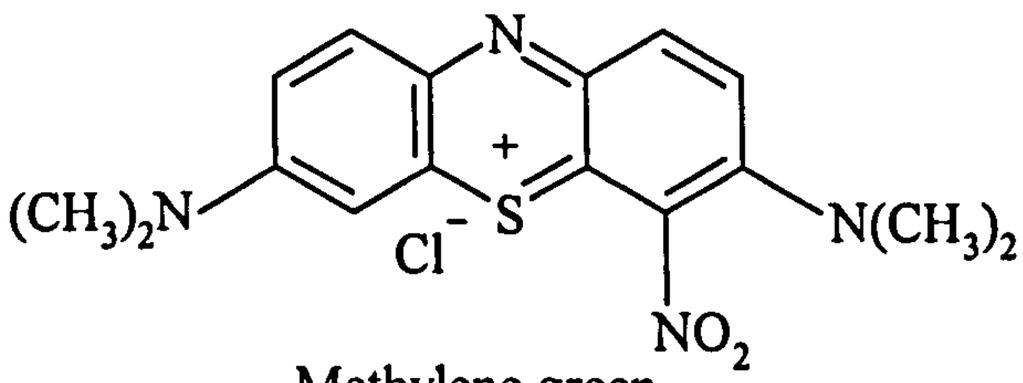
New methylene blue
(NMB)



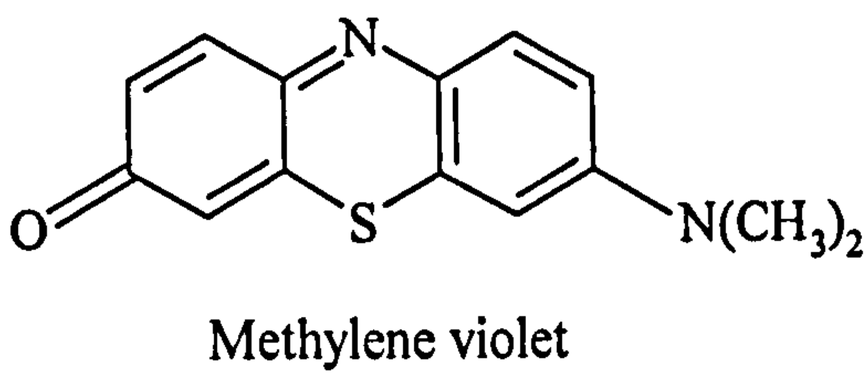
Dimethyl methylene blue
(DMMB)



Thionine
(TH)



Methylene green
(MG)



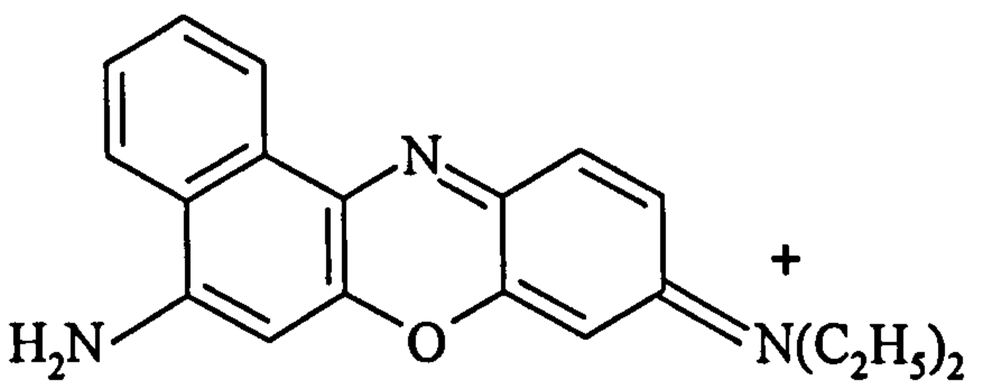
Methylene violet
(MV)

Figure 3.1: Chemical structures of phenothiazine dyes investigated in this study

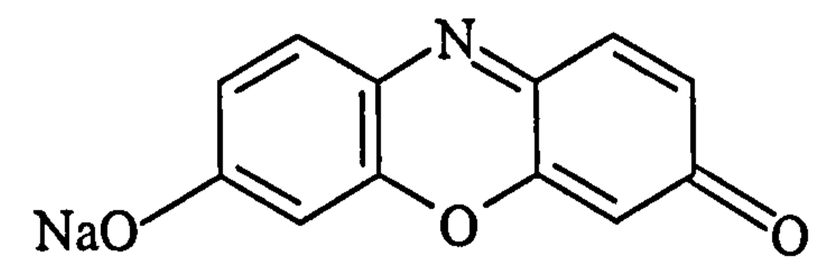
Figure 3.1 shows the chemical structures of methylene blue and related phenothiazine dyes and Figure 3.2 shows the chemical structures of oxazines, azine and acridine dyes. Table

3.1 summarises some of the health hazards and side effects of the investigated dyes in this study. All dyes were used without any further purification.

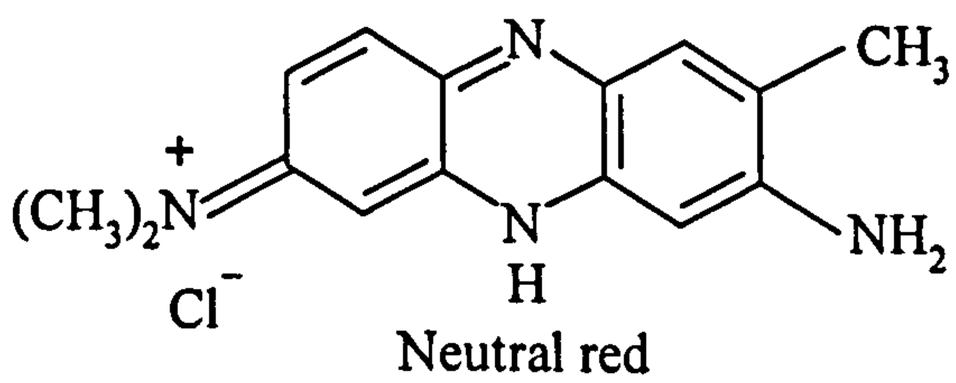
Several supporting electrolytes such as Na_2CO_3, CH_3COONa, $NaNO_3$, $Na_2S_2O_5$, Na_2SO_4, NaBr, NaI and NaCl have been employed to elucidate their influence on the electrochemical treatment. Chlorine gas was obtained from BOC Special Products, UK and dissolved in cold distilled water to obtain Chlorine water (Cl_2/H_2O) which was used to decolourise dyes from aqueous solutions. All other chemicals were of analytical reagent grade and used as supplied. Distilled water was used to prepare all solutions, and deionised water was used in TOC analysis.



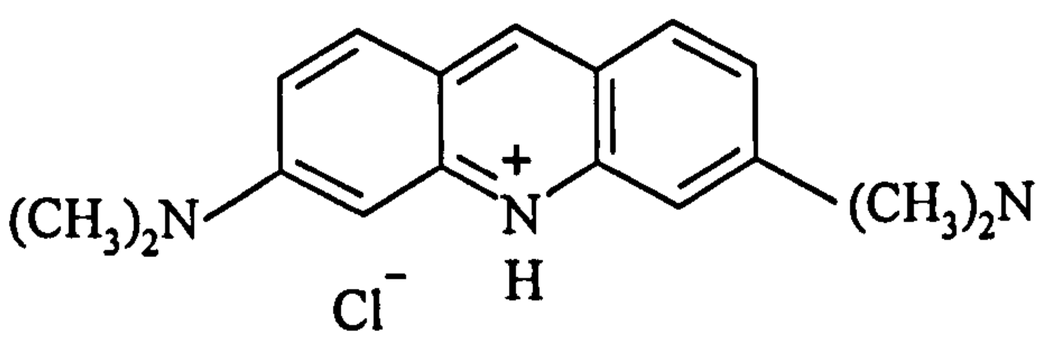
Nile blue
(NB)



Resorufin
(RS)



Neutral red
(NR)



Acridine orange
(AO)

Figure 3.2: Chemical structures of oxazines (Nile blue and resorufin), azine (neutral red) and acridine (acridine orange)

Table 3.1: Health hazard and side effects of the investigated dyes in this study

Dye	Colour index	Status	Comment
AA	52005	I	Harmful [62]
AB	52010	I	Harmful [62]
AC	52005	P	Cellular damage in vitro tests [63]
MB	52015	F+I+T+P	May cause dryness of mouth, flushed skin, rapid pulse, blurred vision, dizziness, haemolytic anaemia, cyanosis and methaemaglobinaemia. Animal mutagen, moderately to highly toxic, may cause Heinz bodies haemolytic anaemia, contact can cause staining of the eye, stinging and lacrimation, risk of DNA damage [64, 65, 66]
NMB	52030	I	Hazard in contact with eyes and skin [62]
DDMB	n.a.	I	Harmful, possible mutagen [67]
TBO	52040	I+T+P	Harmful, animal mutagen, combustible, blood and gastrointestinal disorder reports [62, 64, 68, 69]
NR	50040	I+T	Dermatitis and combustible, harmful [62, 64, 69, 70]
TH	52000	I +T	Harmful [62]
NB	51180	I + T	Insufficient data [64, 69]
RS		I	Harmful [62]
AO	46005	I+T+P	Combustible, cause hypersensitivity reactions mutagen and harmful [62, 64, 69]
MG	52020	I+	Harmful [67]
MV	52041	U	Hazard properties not established [69]

T = Toxic, F = Flammable, P = Probable carcinogen, U = Unknown, I = Irritant,
n.a. = not available

3.2.2 Experimental Set-up for Electrolysis of Phenothiazine, Oxazine, Phenazine and Acridine Dyes

The electrolytic cell consists of a Pyrex beaker of 5 L capacity (Plate 3.1). The cell contained three circular electrodes (two mixed metal oxide coated mesh anodes and a stainless steel mesh cathode). The lay out arrangement of these were: anode – cathode – anode with 2 cm gap between them. The dimensions of the mesh cathode was 7.0 cm × 23.5 cm (height × diameter) and dimensions of the two mesh anodes were 7.0 cm × 13.0 cm and 7.0 cm × 33 cm (height × diameter) respectively.

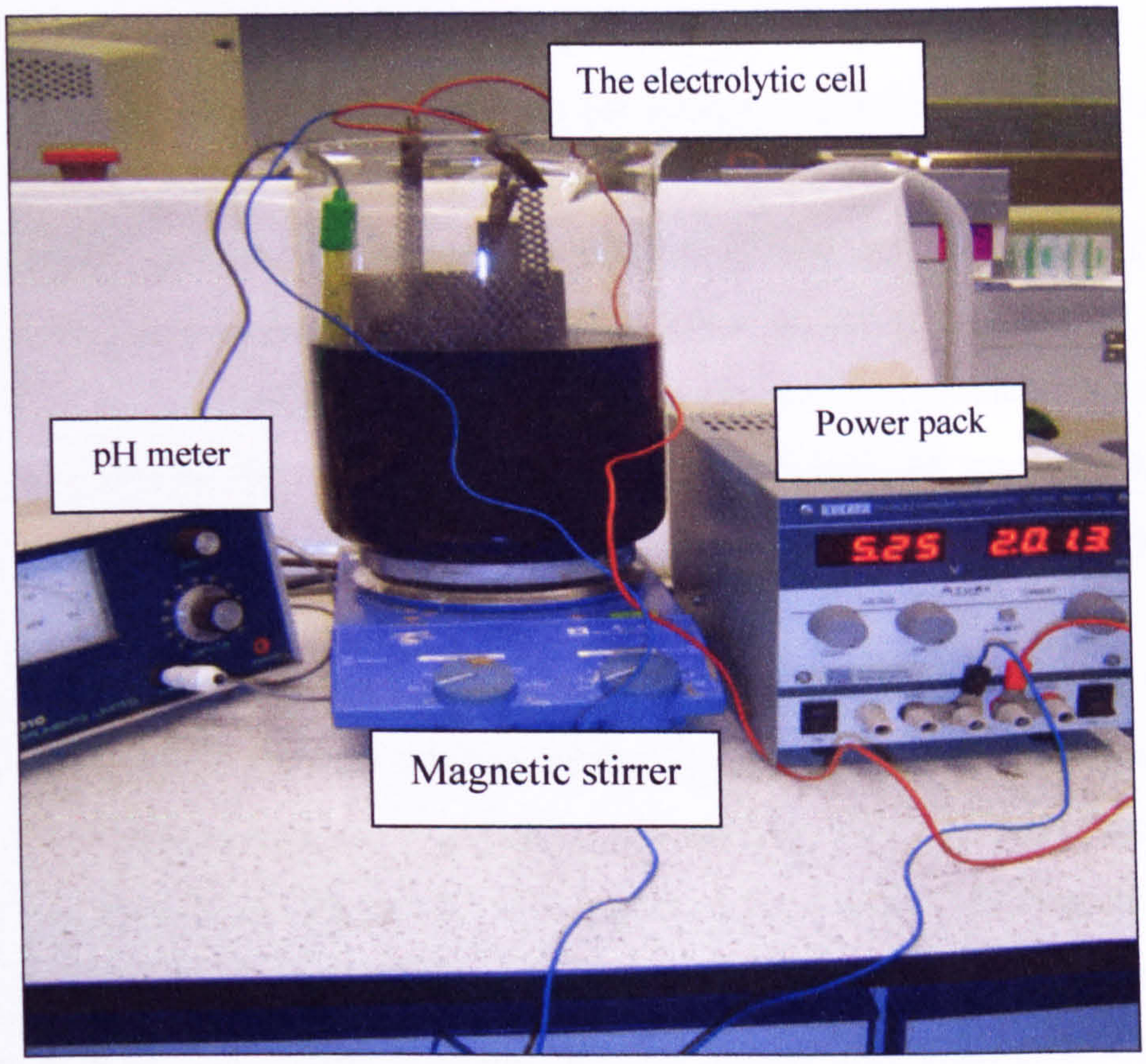


Plate 3.1: Experimental set-up for electrolytic oxidation of phenothiazine, oxazine, phenazine and acridine dyes

All experiments were conducted at ambient temperature. A DC power supply (Thurlby model PL154, RS Components, Ltd., England), having an input of 230 V and variable output of 0-15 V with maximum current of 4 A was used as a direct current source. Magnetic stirring (KIKA RO8 model, Germany) was used in order to keep the solutions in the compartment well-mixed during electrochemical oxidation.

3.2.3 Apparatus and Analysis

The centrifuge used was a Cenatur with speed (2500 rev/ minute). The pH meter was Mettler delta (Toledo) 320 Model pH–meter, calibrated with buffer solution (pH 4 and pH 7 ± 0.05). A Perkin-Elmer Lambda 9 UV-visible Spectrophotometer was used in this work for the determination of dye concentrations at the maximum absorbance in the range of 225-725 nm. Total organic carbon (TOC) was determined by using a model 700 (O.I. Corporation) TOC analyzer.

High performance liquid chromatographic (HPLC) system equipped with a UV detector (Cecil 1100) and operated at 290 or 340 nm (or otherwise specified) wavelength was used to monitor the degradation reaction. The system contains a column (12.5 cm long and 4.5 mm in diameter) packed with spherisorb octadecylsilane (ODS-2) 5μm (C_{18} packing, Restek), a silica based packing, with a reversed-phase eluent of acetonitrile: water (90/10 v/v) or (70/30 v/v) and flow-rate 1 ml/min.; column temperature, ambient; injection volume, 20 μl via a Rheodyne valve, detection wavelength 290 and 340 nm; detector sensitivity 0.05-0.2 a.u.f.s (absorbance unit full scale); chart speed, 5 mm/min., recorder setting 10 Mv.

Two litres of solutions of each dye were prepared by dissolving the required amount of the dye in distilled water to make a 50 mg/l of dye solution or as otherwise specified. At the beginning of each experiment the electrolytic cell was filled with 2 litres of dye solution and the required amount of the electrolyte was added to the solution. During the experiments, the pH of the solution was monitored constantly. Experiments were performed in duplicate (replicate in case of electrolysis of MB in aqueous solutions of NaI, NaBr, CH_3COONa and Na_2CO_3) and found to be reproducible.

About 20 ml of the solution was sampled at predetermined intervals from the middle part of the electrolytic cell by a glass pipette. The samples were analysed by UV/visible spectrometer, HPLC and TOC analysis. Decrease in the intensity of absorbance at the visible range λ_{max} or in the HPLC chromatograms of the investigated dyes were taken as an indication of decolourisation due to transformation of dyes.

In some selected experiments the aqueous solutions resulting from electrochemical treatment were also analyzed by TLC. The thin layer chromatography (TLC) utilized commercial fluorescent silica gel (7.5 cm × 2.5 cm) plates or alumina coated on aluminium sheet (60 F_{254}, neutral type). Preparative silica gel was also used in some analysis. The analysis for the products from electrolysis used chloroform: ethyl acetate (94:6), and for the original dyes a mixture of (dichloromethane: methanol: acetic acid (7: 3:1) was employed.

3.3 RESULTS AND DISCUSSION

The research work described in this chapter is divided into three sections (i) optimization of the conditions for colour removal and destruction of the phenothiazine dye methylene blue as a model by an electrochemical process, (ii) investigation of the effect of substituents variation on the colour removal and degradation of related phenothiazine dyes by the electrochemical process (iii) investigation of the effect of altering the heteroatom of the phenothiazine chromophore on the colour removal and degradation of the related oxazine, azines and acridine dyes by the electrochemical process.

3.3.1 ELECTROCHEMICAL DEGRADATION OF METHYLENE BLUE

The main purpose of this study was to decolourise and degrade, as much as possible, the model solutions of methylene blue dye. To achieve this, the following studies were carried out sequentially to establish the optimum operational conditions. Some selected studies were repeated more than twice to be sure of the repeatability of the results.

3.3.1.1 The Effect of Electrolyte Type on the Electrochemical Degradation and Colour Removal of Methylene Blue

To investigate the effects of different types of supporting electrolytes on the decolourisation process of methylene blue (50 mg/l), sodium acetate, carbonate, nitrate, meta-bisulphite, sulphate, bromide, iodide and chloride, each of which had a concentration of 5 g/l were used. The pH of the solution was monitored during the electrolysis and the current input was 1.5 A, or otherwise specified. The results obtained from the experiments are summarised in each of the following sections.

The effect of sodium acetate on the electrolytic degradation/removal of methylene blue

The HPLC chromatograms of methylene blue, in the absence of CH_3COONa, showed very small peaks which are not fully resolved specially when acetonitrile: H_2O (90: 10) mixture was used as a solvent system (Figure 3.3). These results indicated that the HPLC column was unable to separate and analyse the ionized species of methylene blue. These results are in agreement with the previous studies [59, 71, 72] which also indicated that the ionized species of methylene blue can not be separated under the condition studied in this work.

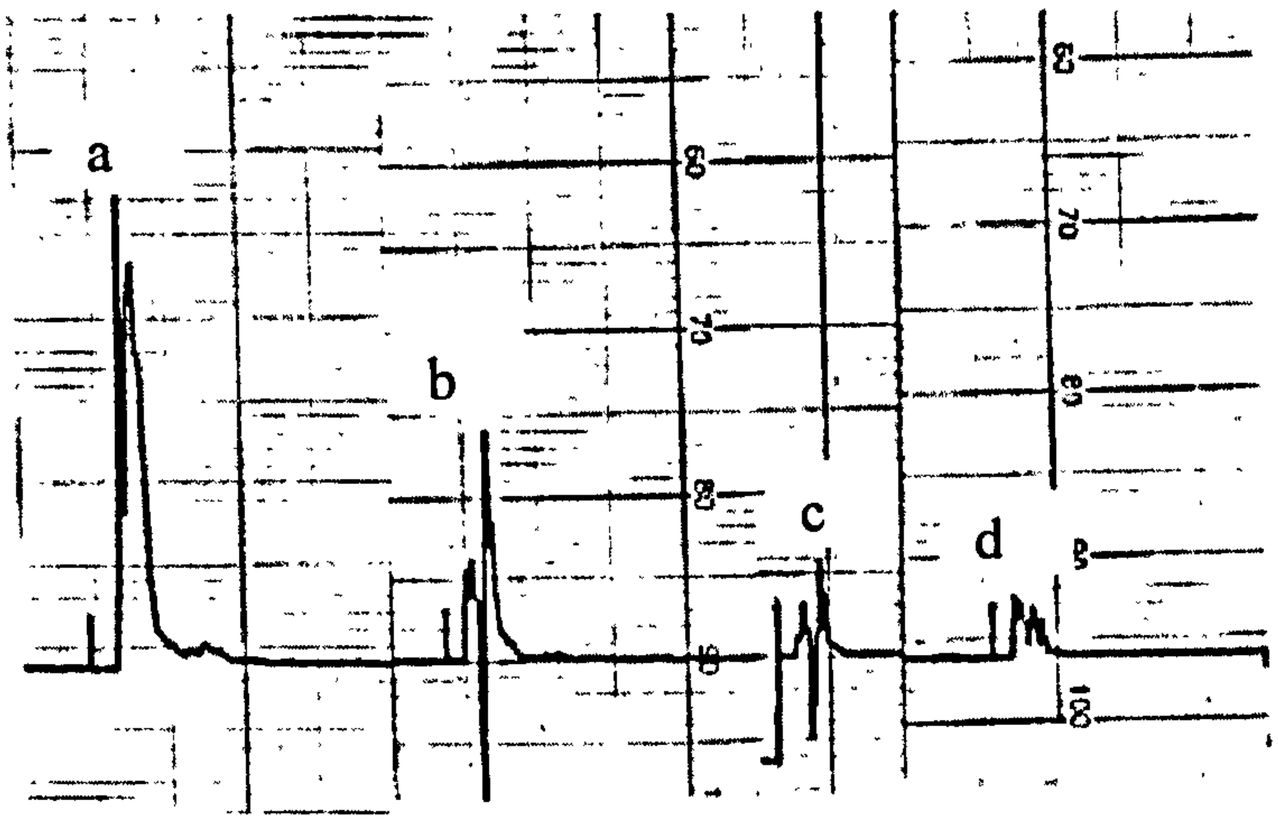


Figure 3.3: HPLC chromatogram of methylene blue (50 mg) at 290 nm

a) in H_2O); b) in acetonitrile: H_2O (90: 10)

(sensitivity 0.02); c) in acetonitrile: H_2O (90: 10)

(sensitivity 0.05); d) in acetonitrile: H_2O (90: 10) (sensitivity: 0.1)

The electrolysis of MB in the presence of CH_3COONa was investigated over 720 minutes at natural pH (8.6-7.0). It was observed that the colour of the solution disappeared after 720 minutes (Table 3.2). However, the TOC results indicated that only 35% of the organic carbon was removed after 720 minutes electrolysis (Table 3.3).

The HPLC chromatogram of the dye solution (Figures 3.4) before electrolysis showed a peak with retention time (RT) of 1.1 minute. This peak is attributed to the aqueous sodium acetate solution (Figures 3.4a). The height of this peak increased after 60 minutes then decreased slowly during the electrolysis process. The HPLC results showed that methylene blue was not eluted under these conditions, suggesting that it is a charged moiety and remains in the column [59, 71, 72]. The same condition was applied to observe the dye breakdown products obtained during the anodic oxidation process. After 60 minutes of electrolysis, a second peak appeared at the retention time of 3.2 minute, however, this peak almost disappeared after 180 minutes. The second weak peak appeared after 300 minutes electrolysis treatment with shorter retention times (RT: 0.7 minute) than sodium acetate and intensity of this peak increased with electrolysis treatment time.

The results obtained from TOC data and HPLC chromatograms confirmed that the product formed after 60 minutes was further broken during the electrolytic process, while the product formed after 240 minutes electrolysis remained in solution as electrolysis progressed.

Table 3.2: Electrochemical decolourisation of methylene blue in aqueous sodium acetate

Time (min)	pH	Voltage (V)	Colour
0	8.6	4.50	Dark blue
60	11.6	4.70	Dark blue
120	10.0	4.80	Dark blue
240	7.8	4.80	Dark blue
360	7.5	5.00	Blue
480	7.0	5.00	Light blue
720	7.0	5.00	Colourless

Conditions: current, 1.50 A; temperature, ambient; concentration (MB, 50 mg/l; CH_3COONa, 5 g/l)

Table 3.3: The TOC values during the electrolysis of methylene blue (50 mg/l) in aqueous sodium acetate (5 g/l) solution

Time (min)	TOC (ppm)	% Degradation
0	2060	0
60	1685	18
120	1625	21
240	1570	24
360	1550	25
480	1535	26
720	1333	35

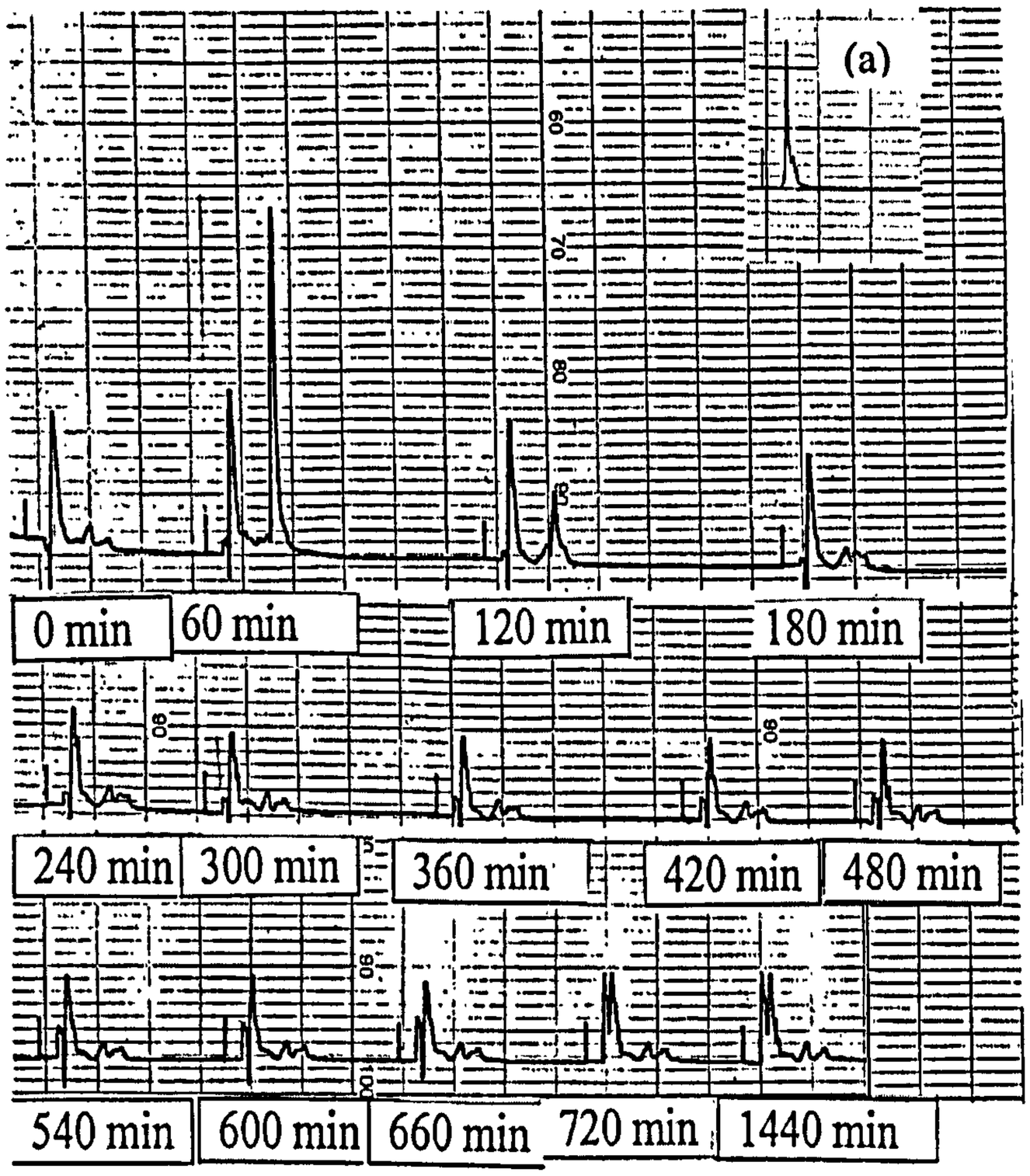


Figure 3.4: HPLC chromatogram during the electrolysis of MB in aqueous CH_3COONa solution at 290 nm, (a) HPLC of aqueous sodium acetate solution

The effect of sodium carbonate on the degradation of methylene blue

The effect of Na_2CO_3 on the degradation of MB by the electrolytic process was investigated over 540 minutes with natural pH (11.6-11.3) (Table 3.4). The original dark blue colour faded gradually during 480 minutes electrolysis and finally discharged after 540 minutes with only 13% TOC removed (Table 3.5).

The HPLC chromatograms during the electrolysis of MB in aqueous Na_2CO_3 solution at 290 nm (Figures 3.5) characterized by a high intensity peak with retention time 2.7 minutes which decreased gradually and almost disappeared after 360 minutes electrolysis. This peak could be attributed to the aqueous solution of sodium carbonate (Figure 3.7). The results obtained from HPLC showed that MB is not eluted using the applied conditions and is retained in the column (Figures 3.5). The HPLC chromatograms during the electrolysis of

MB in aqueous Na_2CO_3 solution at 340 nm (Figures 3.6) showed a sharp low intensity peak, which decreased and disappeared after 240 minutes electrolysis. The results also showed degradation product formed after 30 minutes electrolysis, which increased during the 300 minutes electrolysis, then decreased slowly during the remaining treatment time (540 minutes).

No evidence of free radical formation from sodium carbonate has been found in the literature that can enhance the degradation of the dye molecules [72]. The addition of sodium carbonate only makes the solution conductive, and the degradation of the dye achieved here was due to the evolution of free oxygen from water at the anodes.

Table 3.4: Electrochemical decolourisation of methylene blue (MB) in aqueous sodium carbonate

Time (min)	pH	Voltage (V)	Colour
0	11.6	4.07	Dark blue
30	11.8	4.08	Dark blue
60	11.7	4.08	Dark blue
120	11.7	4.09	Blue
180	11.8	4.11	Blue
240	11.7	4.15	Blue
300	11.6	4.17	Light blue
360	11.6	4.18	Light blue
480	11.4	4.23	Pale blue
540	11.3	4.24	Colourless

Conditions: current, 1.5 A; temperature, ambient; concentration (MB, 50 mg/l; Na_2CO_3, 5 g/l)

Table 3.5: The TOC values during the electrolysis of methylene blue (50 mg/l) in aqueous sodium carbonate (5 g/l) solution

Time (min)	TOC (ppm)	% Degradation
0	328	0
60	321	02
120	314	04
240	308	06
300	299	09
360	291	11
480	289	12
540	285	13

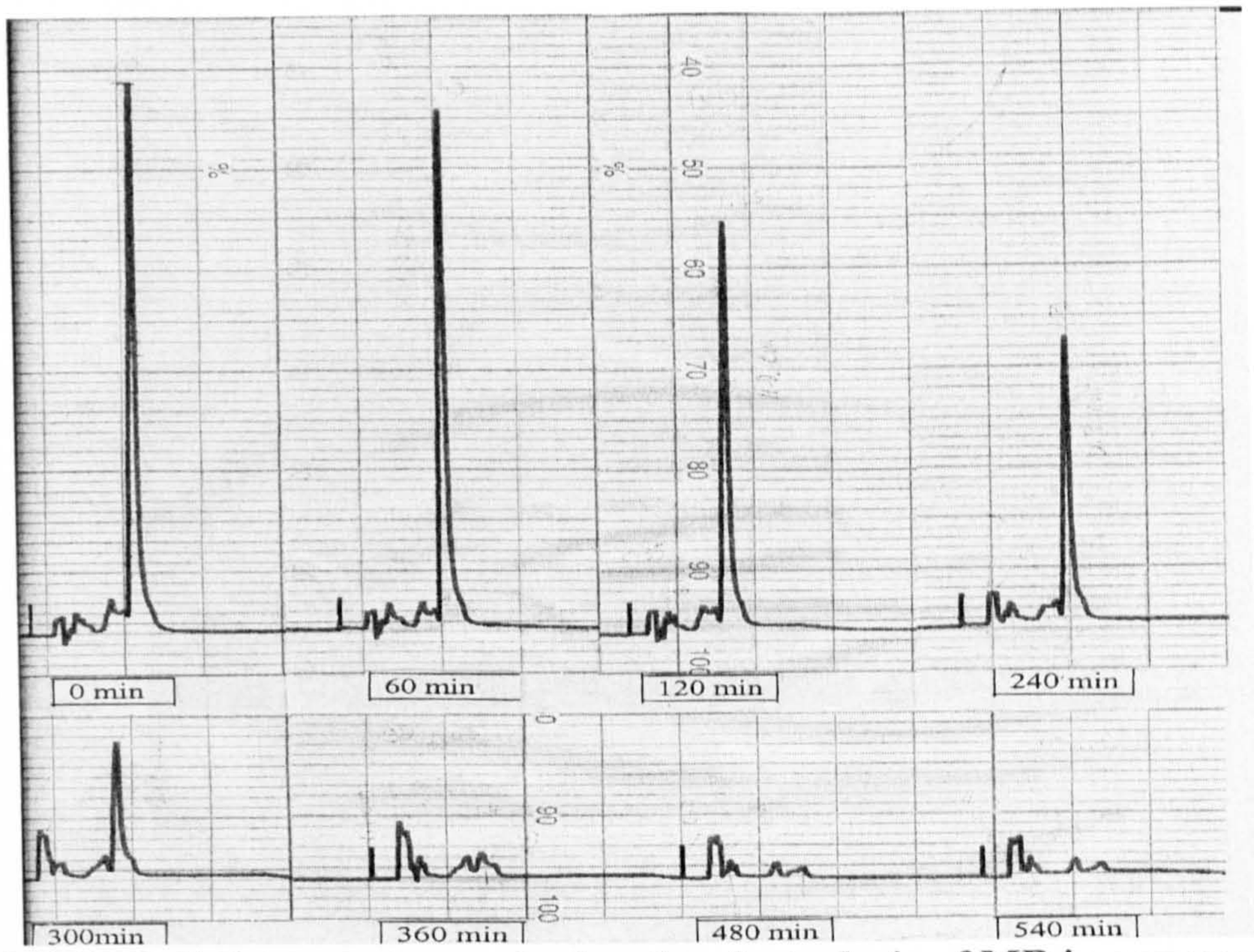


Figure 3.5: HPLC chromatogram during the electrolysis of MB in aqueous Na_2CO_3 solution at 290 nm. (Solvent; acetonitrile: H_2O (90:10), sensitivity: 0.1).

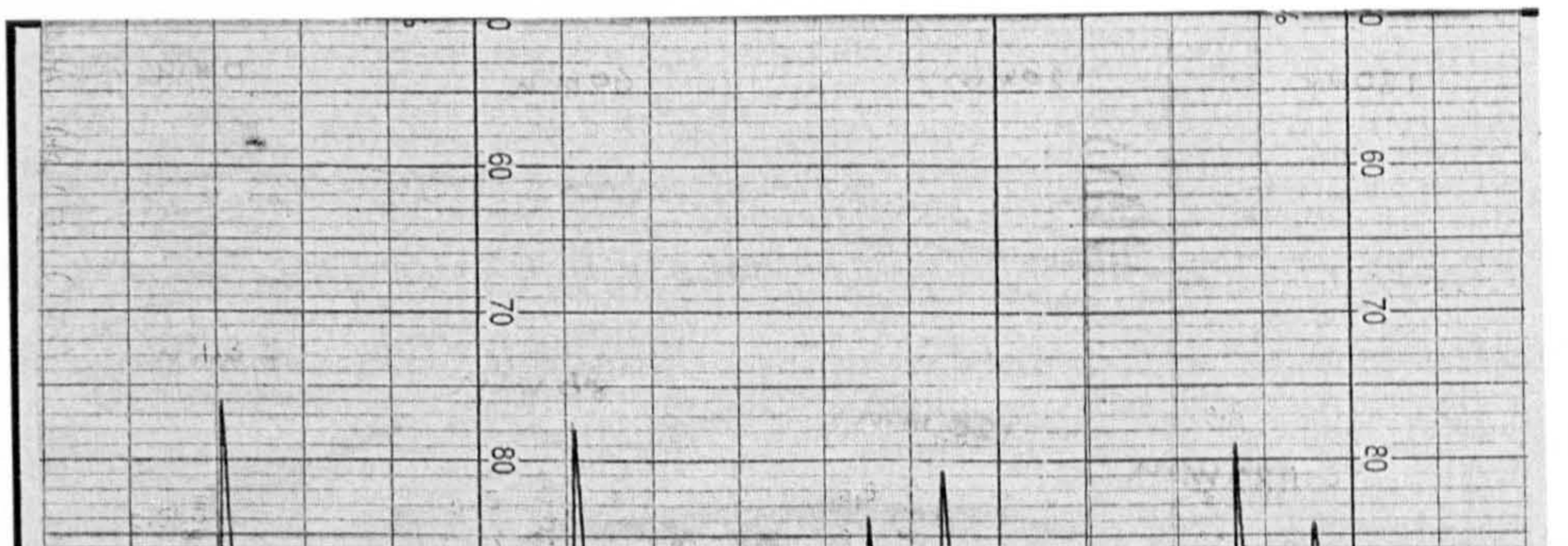


Figure 3.6: HPLC chromatogram during the electrolysis of MB in aqueous Na_2CO_3 solution at 340 nm. (Solvent; acetonitrile: H_2O (90:10), sensitivity: 0.1)

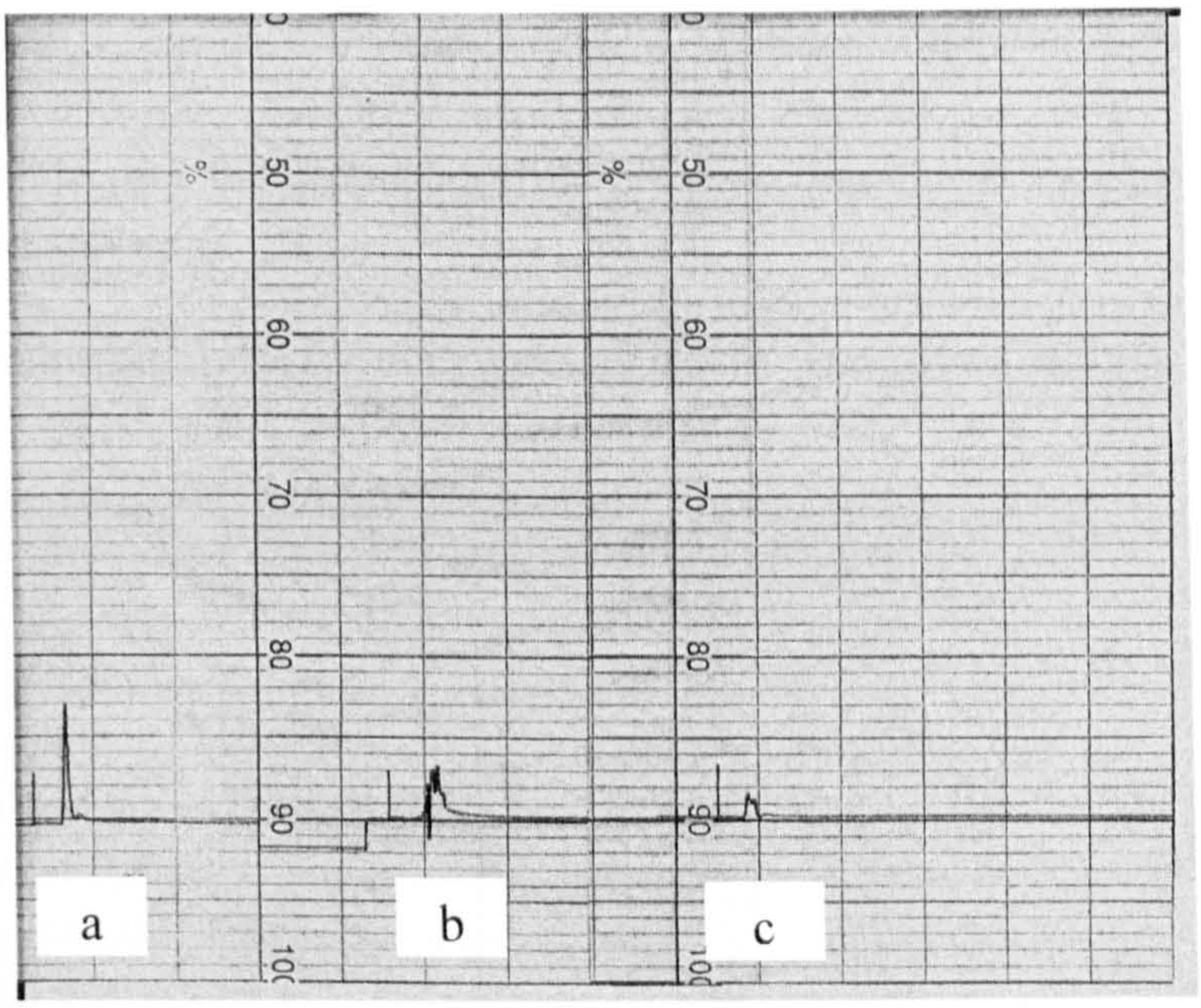


Figure 3.7: HPLC chromatogram of aqueous Na_2CO_3 solution

a) at 290 nm, using acetonitrile: H_2O (70:30), sensitivity: 0.1, b) at 290 nm using acetonitrile: H_2O (90:10), sensitivity: 0.1, and c) at 340 nm using acetonitrile: H_2O (90:10), sensitivity: 0.1

The effect of sodium nitrate on the degradation of methylene blue

The pH during the electrolysis of MB in aqueous $NaNO_3$ solution increased markedly from a value of 5.3 to a value of 12.0 after 120 minutes (Table 3.6). This increase to a major extent can be explained by formation of basic intermediates in the electrolysed solution. The blue colour solution of MB faded gradually to pale turquoise after 360 minutes electrolysis and a complete discharge of the blue colour occurred after 1440 minutes (Plate 3.2). The decolourisation of MB in the presence of $NaNO_3$ solution may be due to indirect oxidation processes promoted by the action of electro-generated ozone as suggested by Andrade et al. [2] in their finding regarding the electrochemical degradation of blue reactive 19 dye.

It was also observed that the solution turned pale yellow at 480 minutes electrolysis which suggests that nitrogen oxide vapours were evolved during the course of electrolysis [73] due to the electrochemical reduction of nitrate to ammonia and nitrogen e.g.,

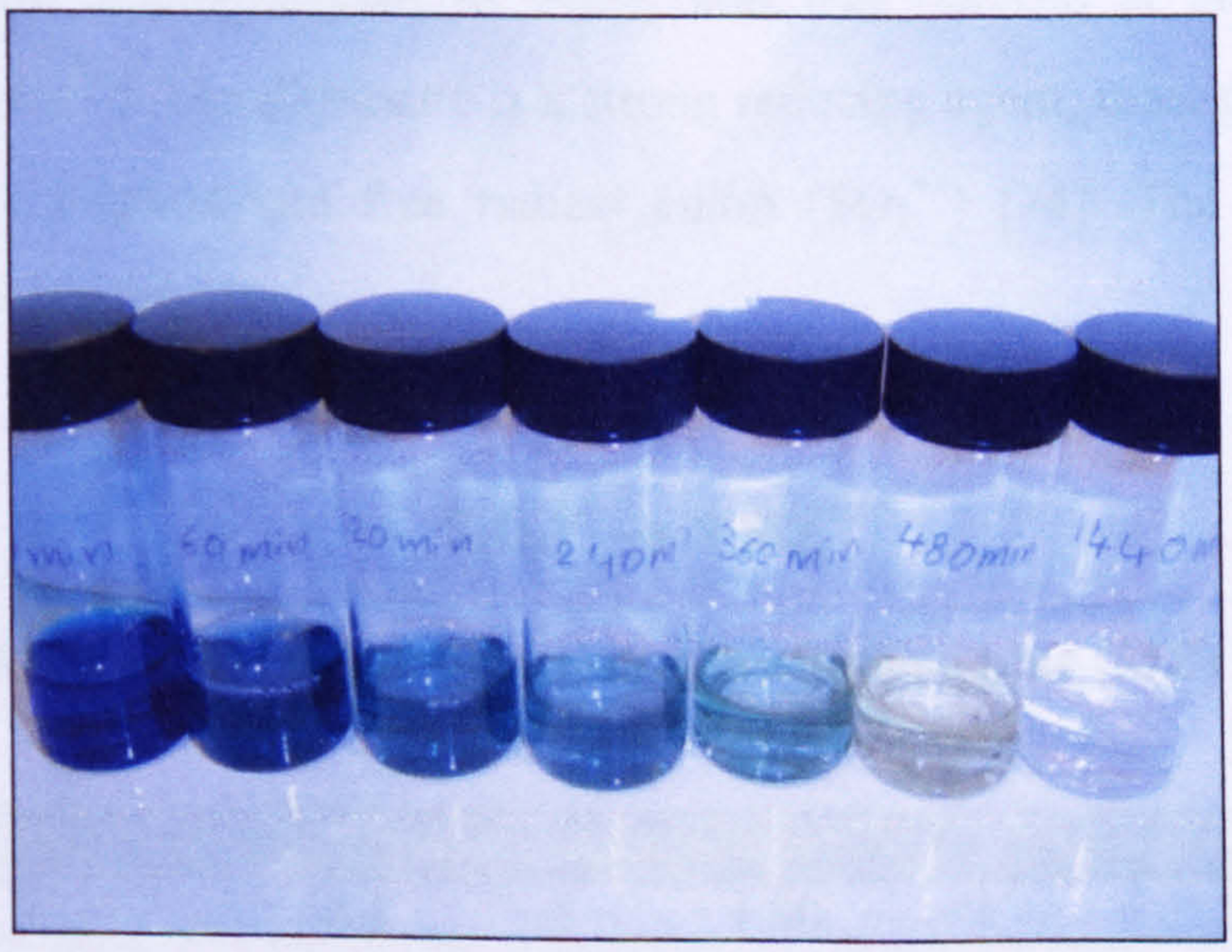
$$3NaNO_3 + 3H_2O \longrightarrow NH_3 + N_2 + 3\ NaOH + 9/2\ O_2$$

which occurs with the corresponding formation of oxygen and caustic at the anode as suggested by Scott et al. [73].

Table 3.6: Electrochemical decolourisation of methylene blue (MB) in aqueous sodium nitrate solution

Time	pH	Voltage (V)	Colour
0	5.3	4.73	Blue
15	3.0	4.65	Blue
30	10.2	4.68	Blue
60	11.9	4.73	Grey blue
120	12.0	4.77	Light blue
240	12.0	4.75	Pale blue
300	12.2	4.78	Pale grey blue
360	12.2	4.80	Pale turquoise
480	12.0	4.85	Pale yellow
1440	12.2	4.85	Colourless

Conditions: current, 1.5 A; temperature, ambient; concentration (MB, 50 mg/l; $NaNO_3$, 5 g/l)



Plates 3.2: The change of colour during the electrochemical degradation of methylene blue in aqueous sodium nitrate solution

The effect of sodium metabisulphite on the degradation of methylene blue

The results obtained during the electrolytic treatment of MB in aqueous $Na_2S_2O_5$ solution showed that the colour removal was very slow during the 480 minutes (Plate 3.3) but extending the electrolysis time to 1800 minutes resulted in discharge of the original blue

(Table 3.7), however the blue colour was restored when the electrolysis was stopped. The restoration of the colour in the samples taken for analysis was also observed when left exposed to the light (the samples were tightly closed). The initial pH of the solution 4.4 dropped to 1.9 during the 1800 minutes.

The HPLC chromatogram of MB in aqueous $Na_2S_2O_5$ solution at 340 nm, using solvent system, acetonitrile: water (70: 30) and sensitivity: 0.1 (Figure 3.8) showed two peaks with retention times RT: 0.7 and 1.0 minute (a shoulder with low intensity). The peak with RT: 0.7 minute increased gradually during the 180 minutes electrolysis, then decreased slowly during the remaining electrolysis treatment. The peak at RT: 1.0 minute disappeared after 120 minutes electrolysis.

It could be concluded that sodium meta-bisulphite enhanced the degradation due to the presence of the bisulphite ion (HSO_3^-) in the solution [72]. The HSO_3^- was formed when the metabisulphite ion hydrolysed in water, and was reduced at the cathode to yield dithionite ion ($S_2O_4^{2-}$). The dithionite is a strong reducing agent, most probably because of formation of the sulphoxylate free radical anion ($SO_2^{\bullet-}$) [74]. The following reaction schemes describe the process:

$$2\,HSO_3^- + 2\,H^+ + 2\,e^- \rightarrow S_2O_4^{2-} + 2\,H_2O$$

$$S_2O_4^{2-} \rightarrow 2\,SO_2^{\bullet-}$$

Table 3.7: Electrochemical decolourisation of methylene blue (MB) in aqueous sodium metabisulphite

Time	pH	Voltage (V)	Colour
0	4.4	4.80	Blue
30	2.7	4.70	Light blue
60	2.4	4.60	Turquoise
120	2.3	4.50	Turquoise
180	2.2	4.50	Light yellow
240	2.0	4.40	Light yellow
360	2.0	4.40	Light green
480	2.0	4.40	Light green
1440	1.9	4.40	Light green
1800	1.9	4.40	Colourless

Conditions: current, 1.5 A; temperature, ambient; concentration (MB, 50 mg/l; $Na_2S_2O_5$, 5 g/l)

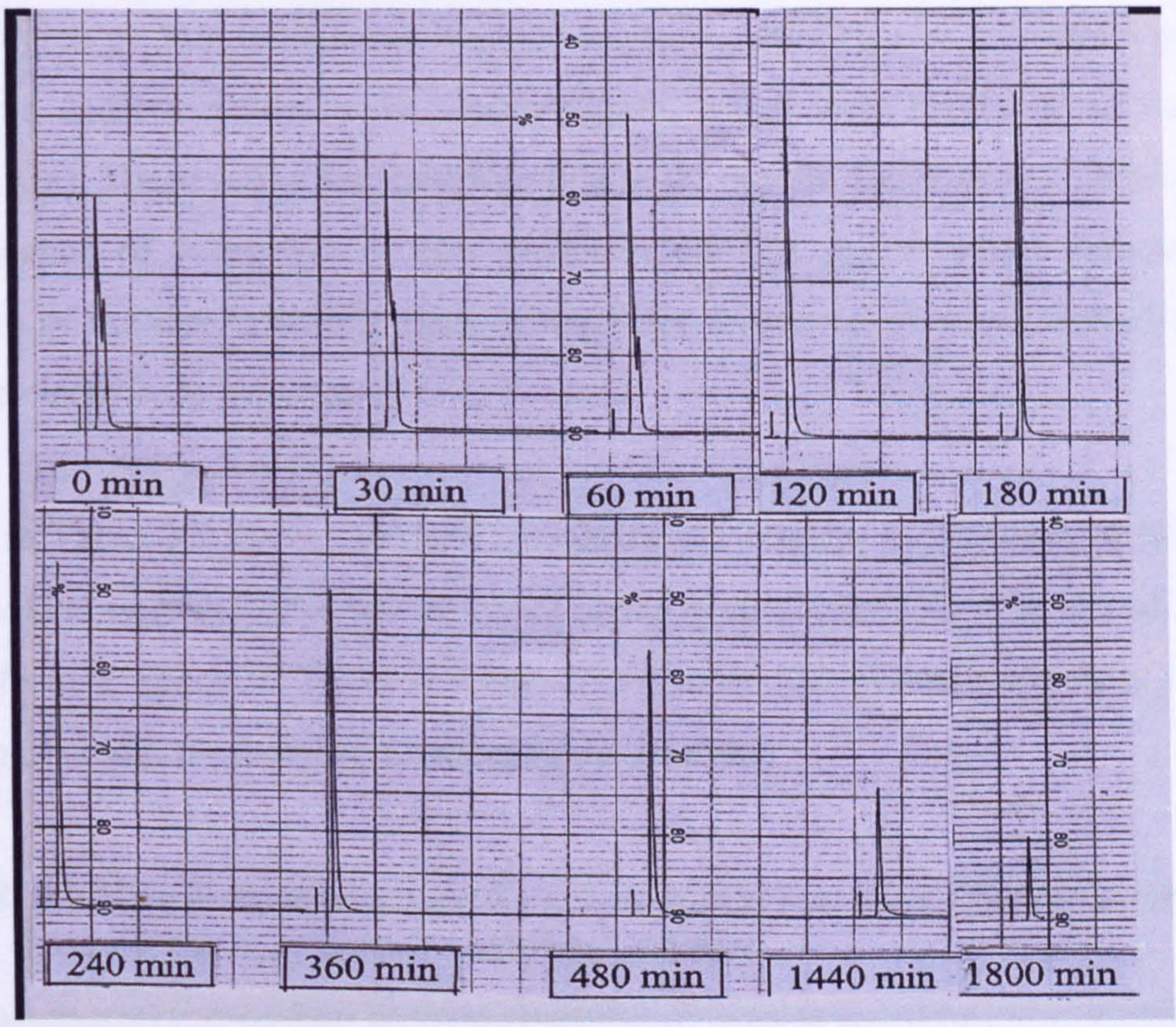
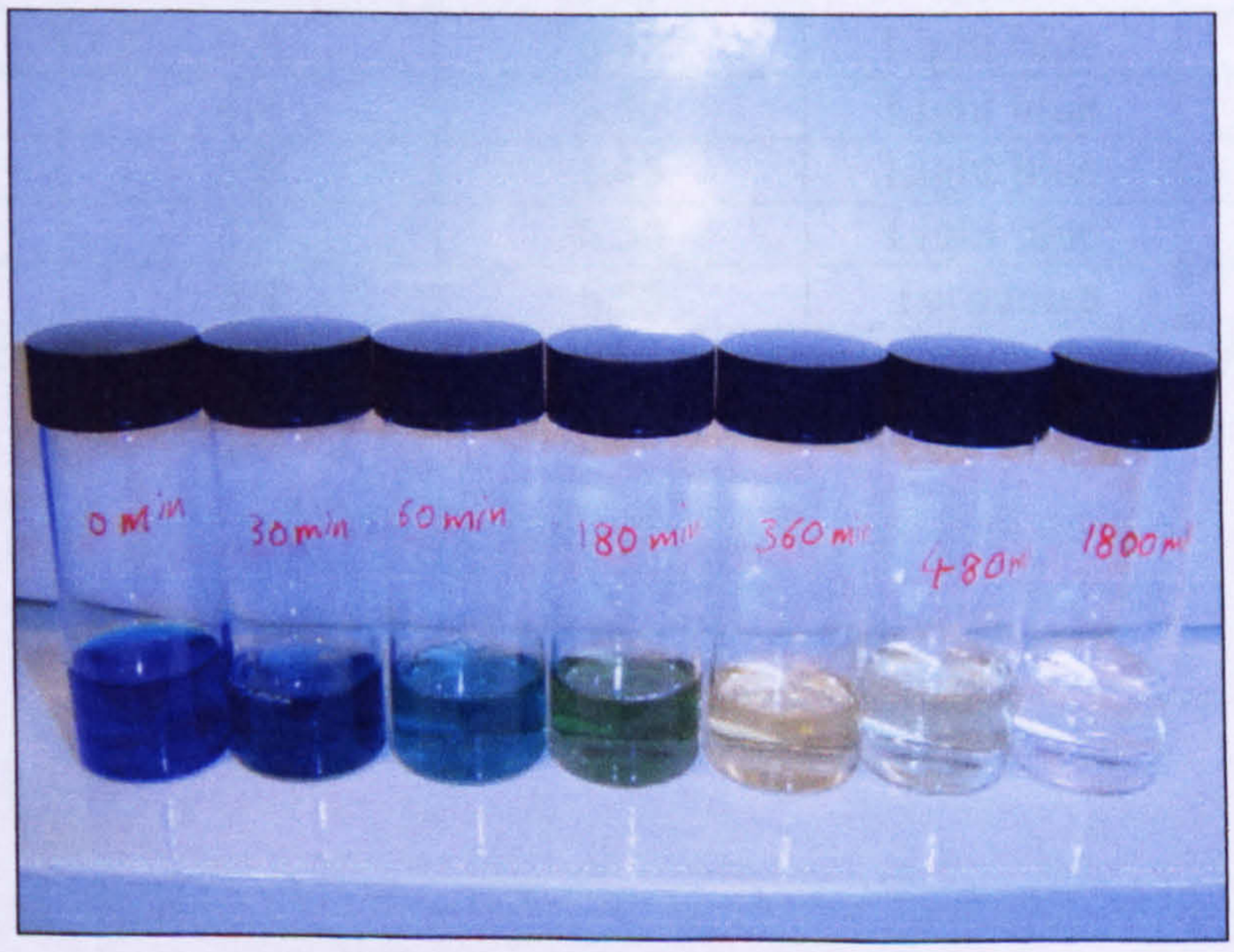


Figure 3.8: HPLC chromatogram during the electrolysis of MB in aqueous $Na_2S_2O_5$ solution at 340 nm



Plates 3.3: The change of colour during the electrochemical degradation of methylene blue in aqueous sodium metabisulphite solution

The effect of sodium sulphate on the degradation of methylene blue

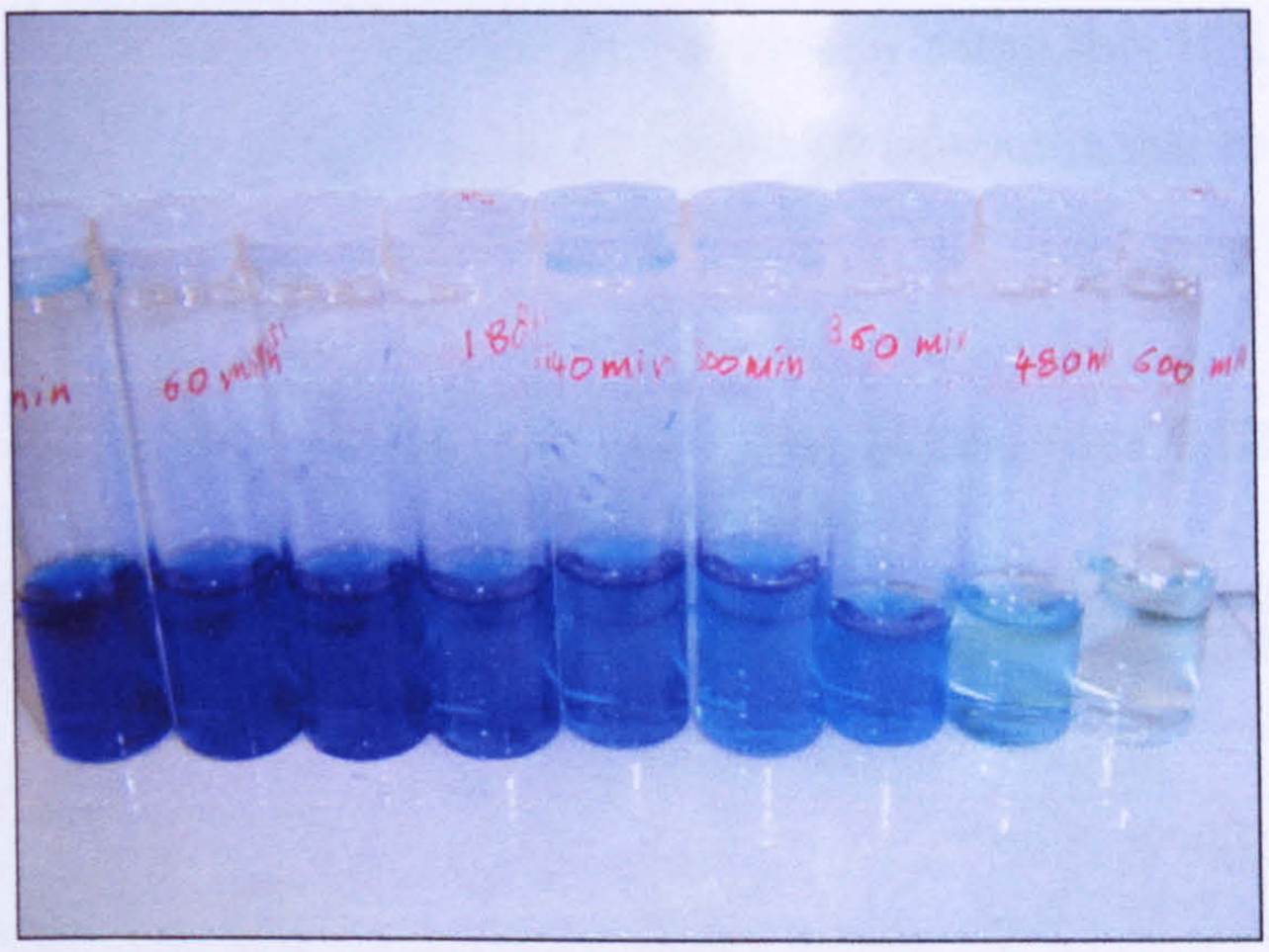
The UV region of MB in aqueous Na_2SO_4 solution exhibited two absorption peaks at 259 and 298 nm and two peaks in the visible region, which were located at 625 and 675 nm (Figure 3.13a). These peaks decreased gradually during the 480 minutes electrolysis. There is no evidence of formation of new peaks in the UV region which indicates that the destruction of the dye is taking place without the formation of any intermediate products during the electrolytic process.

The data in Table 3.8 show a gradual change of the original blue colour to turquoise with 91% of colour removal after 480 minutes electrolysis (Plate 3.4). The pH of the solution dropped from a value of 7.8 to a value of 4.0 after 120 minutes which is indicative of formation of acidic products in the electrolyte solution.

Table 3.8: Electrochemical decolourisation of methylene blue (MB) in aqueous sodium sulphate solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.8	6.71	Blue	0
30	7.7	6.58	Blue	17
60	8.4	6.56	Blue	33
120	4.0	6.46	Blue	44
180	4.9	6.45	Light blue	49
240	4.4	6.45	Light blue	57
300	5.8	6.45	Light blue	63
360	5.9	6.50	Light blue	73
480	5.9	6.55	Turquoise	91

Conditions: current, 2.0 A; temperature, ambient; concentration (MB, 50 mg/l; Na_2SO_4, 5g/l)



Plates 3.4: The change of colour during the electrochemical degradation of methylene blue in aqueous sodium sulphate

The effect of sodium bromide on the degradation of methylene blue (MB)

The UV-Visible spectrum (Figure 3.13b) shows three absorption peaks at 234, 258 and 299 nm in the UV region and two peaks located at 621 nm and 676 nm in the visible region. The peaks in the visible decreased rapidly and reached 97% colour removal within 5 minutes (Table 3.9). Although the complete removal of colour was achieved within a short period of time, only 34% of TOC was removed during 360 minutes electrolysis (Table 3.10). The peak at 299 decreased only slightly. An increase in intensity occurred at 234 nm and a shift to longer wavelength was observed. This indicated the formation of new organic materials. The results also showed that after 30 minutes a yellow solution formed which remained during the electrolytic process, but discharged completely within couple of weeks (Plate 3.5). This indicates that toxic bromine vapours evolved during the electrolytic process. The pH increased from 7.9 to 10.0 and 9.4 after 15 and 480 minutes.

The HPLC chromatogram of MB during the electrolysis treatment in aqueous NaBr solution at 290 nm using acetonitrile: water (70:30) system and sensitivity 0.5 (Figure 3.9) shows breakdown products (RT: 1.1, 1.4, 1.6, 3.2, 3.9, 4.3 and 4.6 minutes) formed after 5 minutes electrolysis. These products disappeared after 30 minutes. However the peaks with RT: 1.1 and 1.4 minute increased gradually with electrolysis process. The HPLC results

also showed that MB is not eluted before electrolysis using this HPLC conditions system (Figure 3.9) and that the peaks with RT: 1.1 and 1.4 minute is due to the NaBr in solution (Figure 3.12a).

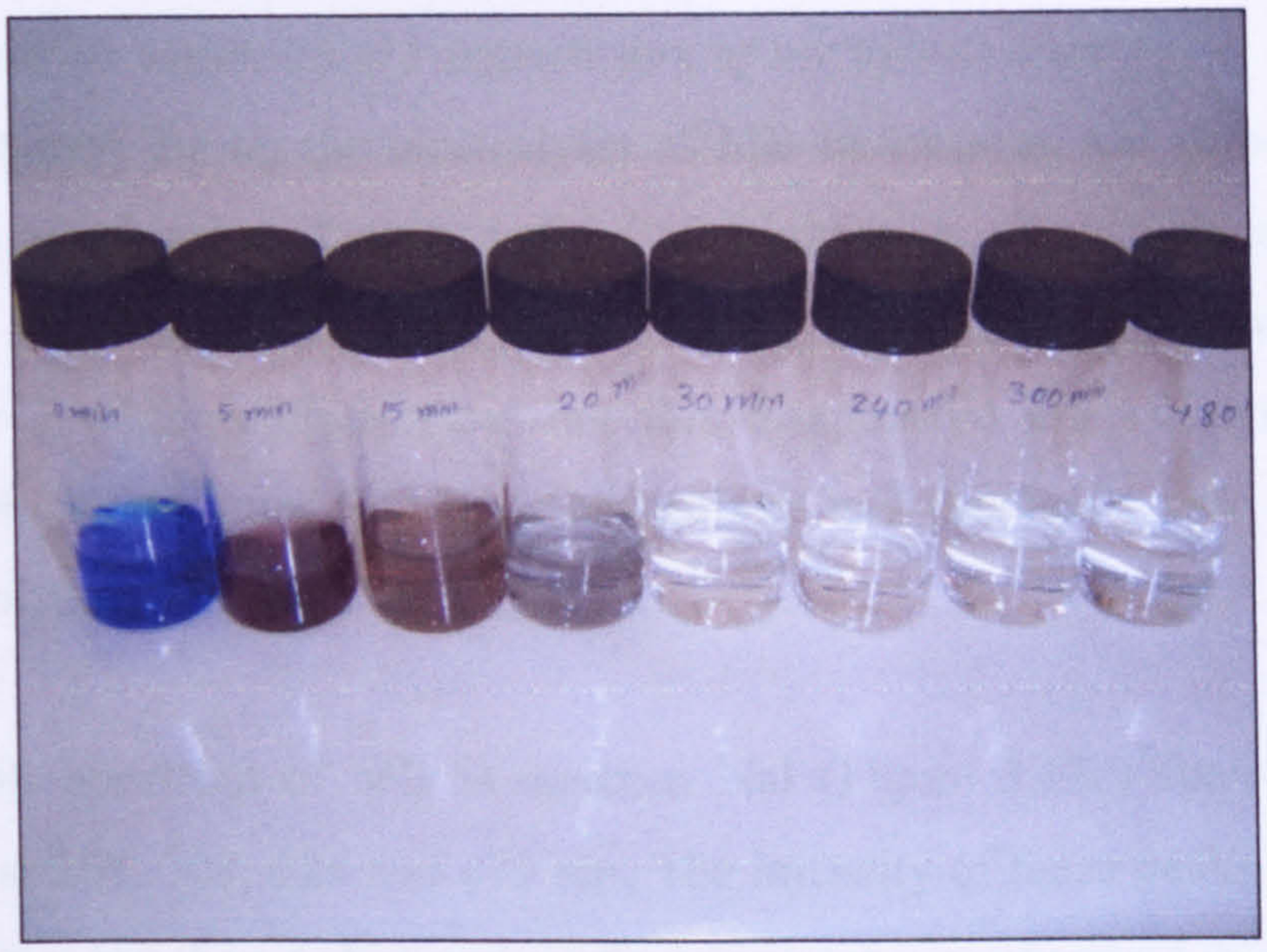
Table 3.9: Electrochemical decolourisation of methylene blue (MB) in aqueous sodium bromide solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.8	4.24	Blue	0
5	8.5	4.26	Violet	97
15	10.0	4.33	Smoke violet	98
20	9.8	4.76	Light grey	98
30	9.5	4.83	Colourless	99
480	9.4	5.16	Colourless	100

Conditions: current, 1.5 A; temperature, ambient; concentration (MB, 50 mg/l; NaBr, 5 g/l)

Table 3.10: The TOC values during the electrolysis of methylene blue (50 mg/l) in aqueous sodium bromide (5 g/l) solution

Time (min)	TOC (ppm)	% Degradation
0	19.55	0
5	19.25	04
15	18.35	06
20	14.75	25
30	14.05	28
120	13.50	31
180	13.35	32
240	13.25	32
300	13.20	33
360	13.00	34



Plates 3.5: The change of colour during the electrochemical degradation of methylene blue in aqueous sodium bromide

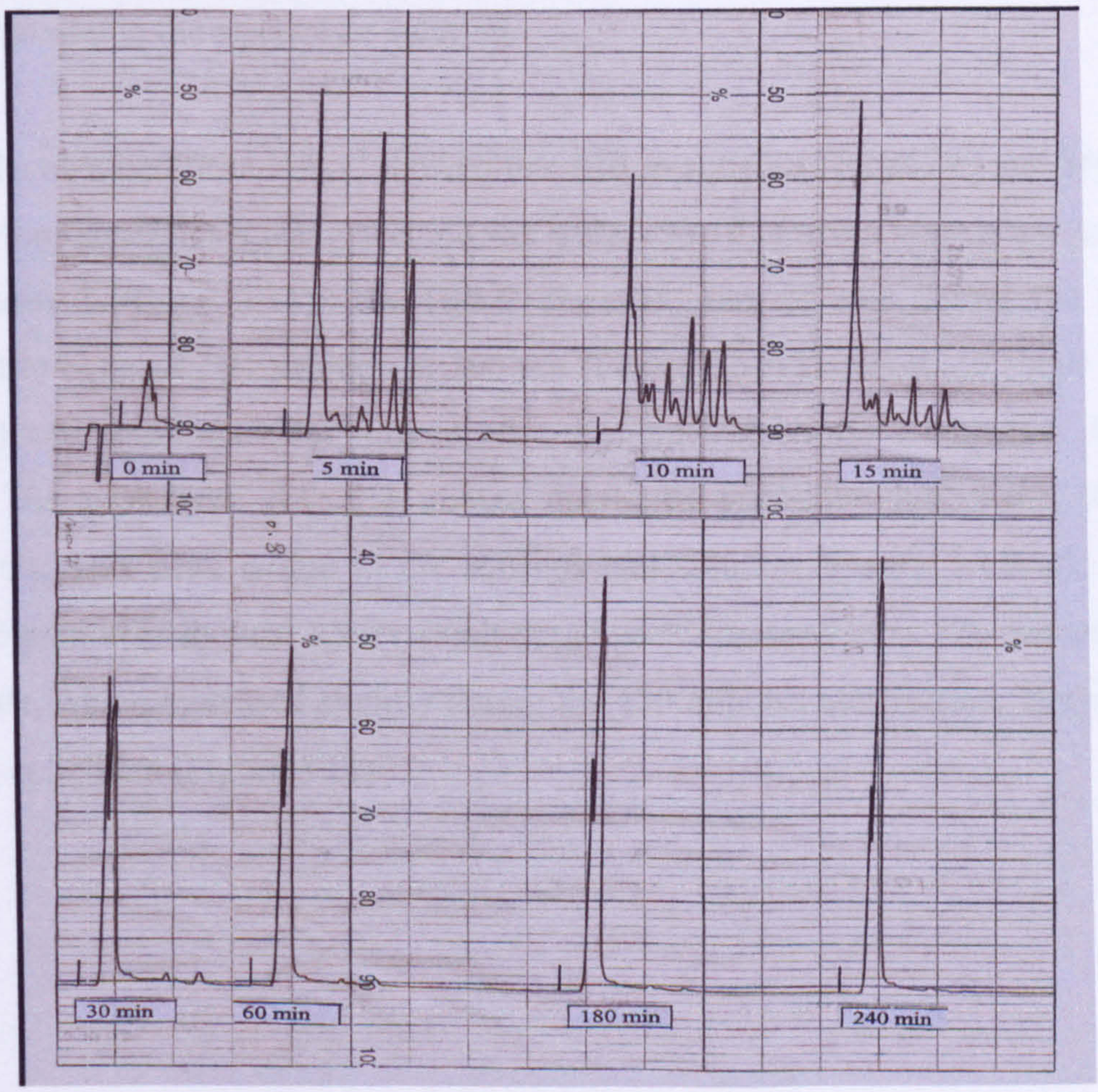


Figure 3.9: HPLC chromatogram during the electrolysis of MB in aqueous NaBr solution at 290 nm

The effect of sodium iodide on the degradation of methylene blue

The results obtained during the electrolysis of MB in aqueous NaI solution (Table 3.11) show that 91% of colour was removed after 240 minutes and this remained the same during the following 360 minutes of electrolysis time. The formation of a black residue was observed after 2 minutes electrolysis but this disappeared after 60 minutes. The blue solution became yellow after 5 minutes electrolysis and eventually pale green during 360 minutes electrolysis.

The UV-Visible spectrum of MB in aqueous NaI (Figure 3.13c) shows four absorption peaks located at 269, 303, 624 and 675 nm. The intensity of these peaks decreased rapidly within 30 minutes but then a slow and gradual decrease was observed during the remaining 240 minutes. The peaks in the visible region showed an increase in the intensity and a blue shift occurred after 300 minutes electrolysis. The UV region also showed the remains of organic material in the electrolyte solution.

The results obtained from HPLC showed that MB in aqueous NaI at 290 and 340 nm is not eluted before electrolysis using acetonitrile: water (90:10) solvent system and at sensitivity 0.1 (Figures 3.10 and 3.11). The HPLC chromatogram of MB during the electrolysis treatment in aqueous NaI solution at 290 nm (Figure 3.10) shows sharp single peak (high intensity) and small shoulder formed after 2 minute electrolysis with RT: 1.7 and 1.9 minute. The peak with RT: 1.7 minute decreased gradually during the 480 minutes electrolysis. This peak is due to the aqueous NaI solution (Figure 3.12b-d). The HPLC chromatogram also showed a very small broad peak appeared after 120 minutes with RT: 2.1 minute, which increased slightly during the 480 minutes electrolysis. The same results obtained at 340 nm (Figure 3.11)

Table 3.11: Electrochemical decolourisation of methylene blue (MB) in aqueous sodium iodide solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.7	6.05	Blue	0
5	10.5	6.08	Yellow	72
30	8.7	5.90	Yellow	83
60	8.6	5.72	Yellow	88
120	8.5	5.79	Yellow	89
180	8.6	5.79	Olive green	90
240	8.6	5.82	Pale green	91

Conditions: current, 2.0 A; temperature, ambient; concentration (MB, 50 mg/l; NaI, 5 g/l)

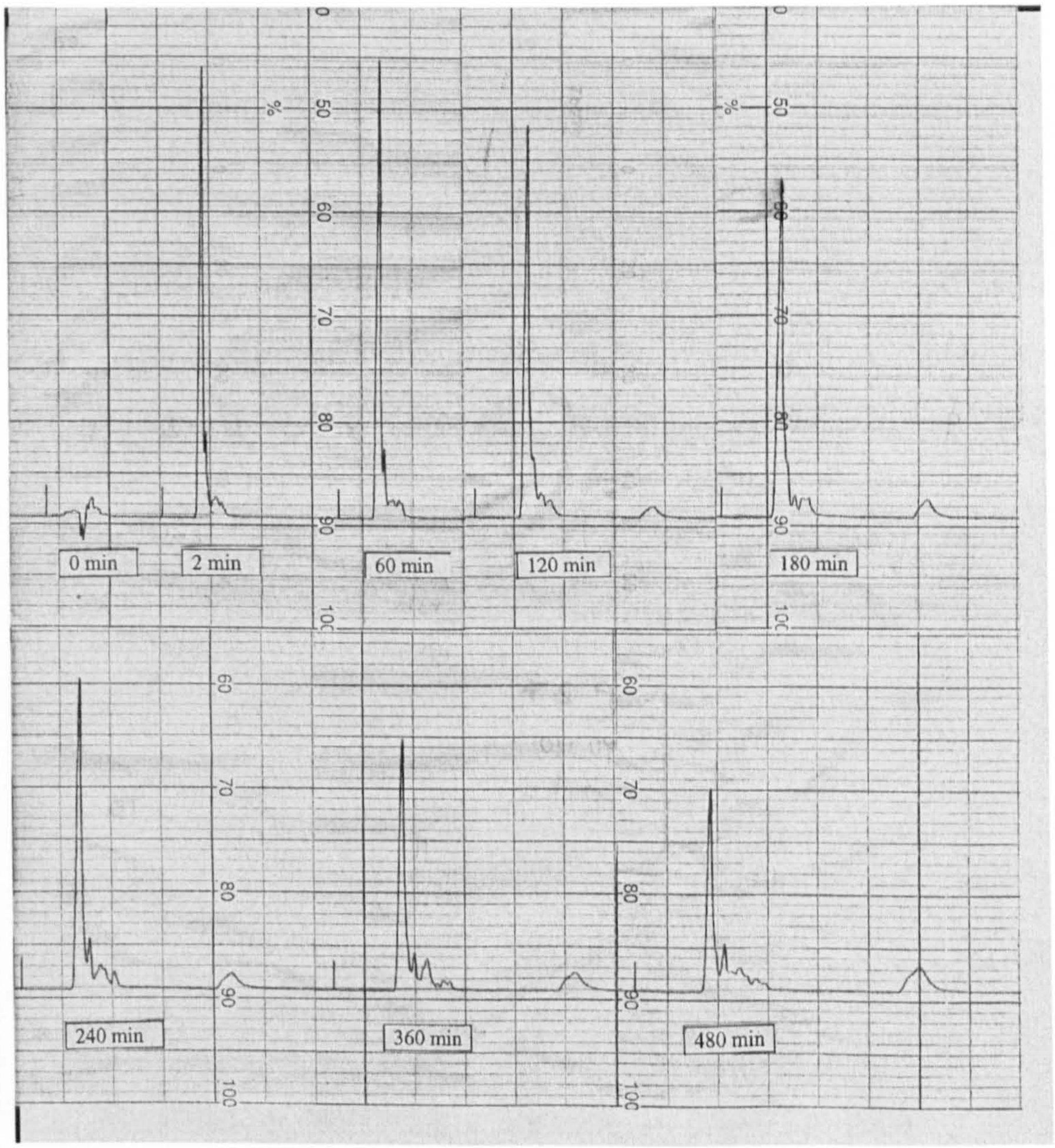


Figure 3.10: HPLC chromatogram during the electrolysis of MB in aqueous NaI solution at 290 nm

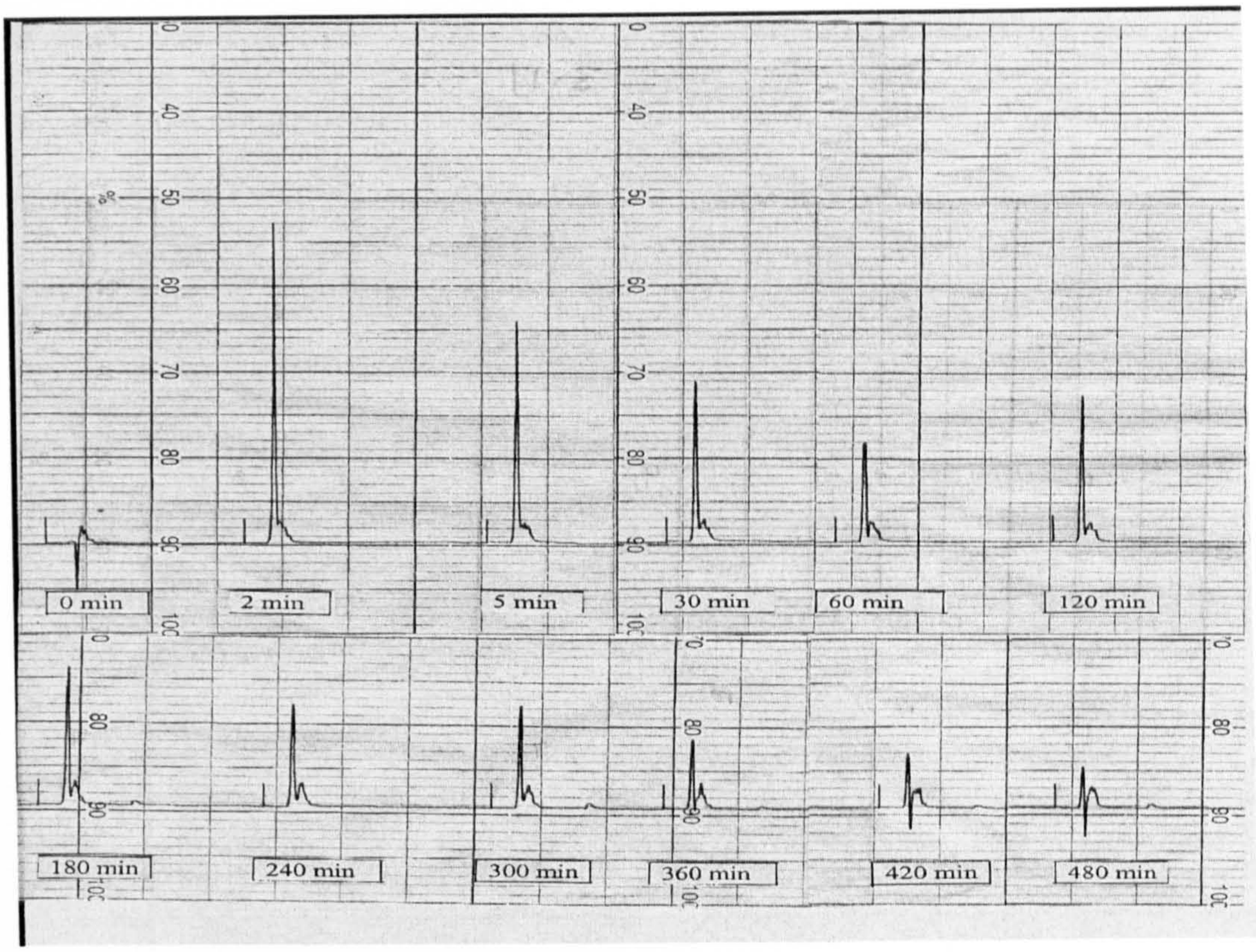


Figure 3.11: HPLC chromatogram during the electrolysis of MB in aqueous NaI solution at 340 nm

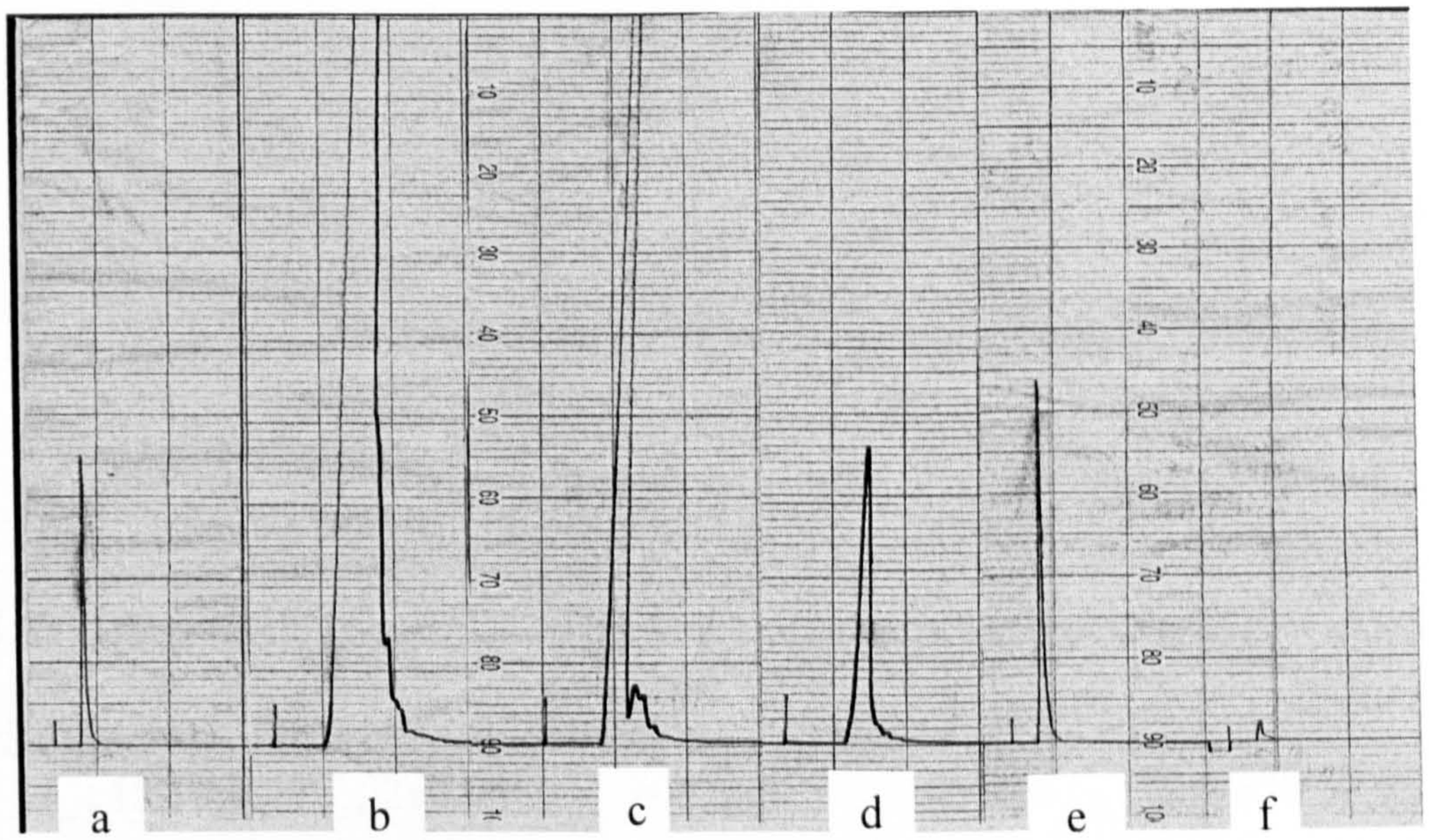


Figure 3.12: HPLC chromatogram of aqueous a) NaBr at 290 nm, sensitivity: 0.2†, **b) NaI** at 290 nm, 0.05† **c) NaI** at 290 nm, 0.2† **d) NaI**, 0.5, **e) NaCl** at 290 nm, 0.2†, **f) NaCl solutions** at 340 nm, 0.2†; solvent, acetonitrile: H_2O (70: 30), sensitivity†

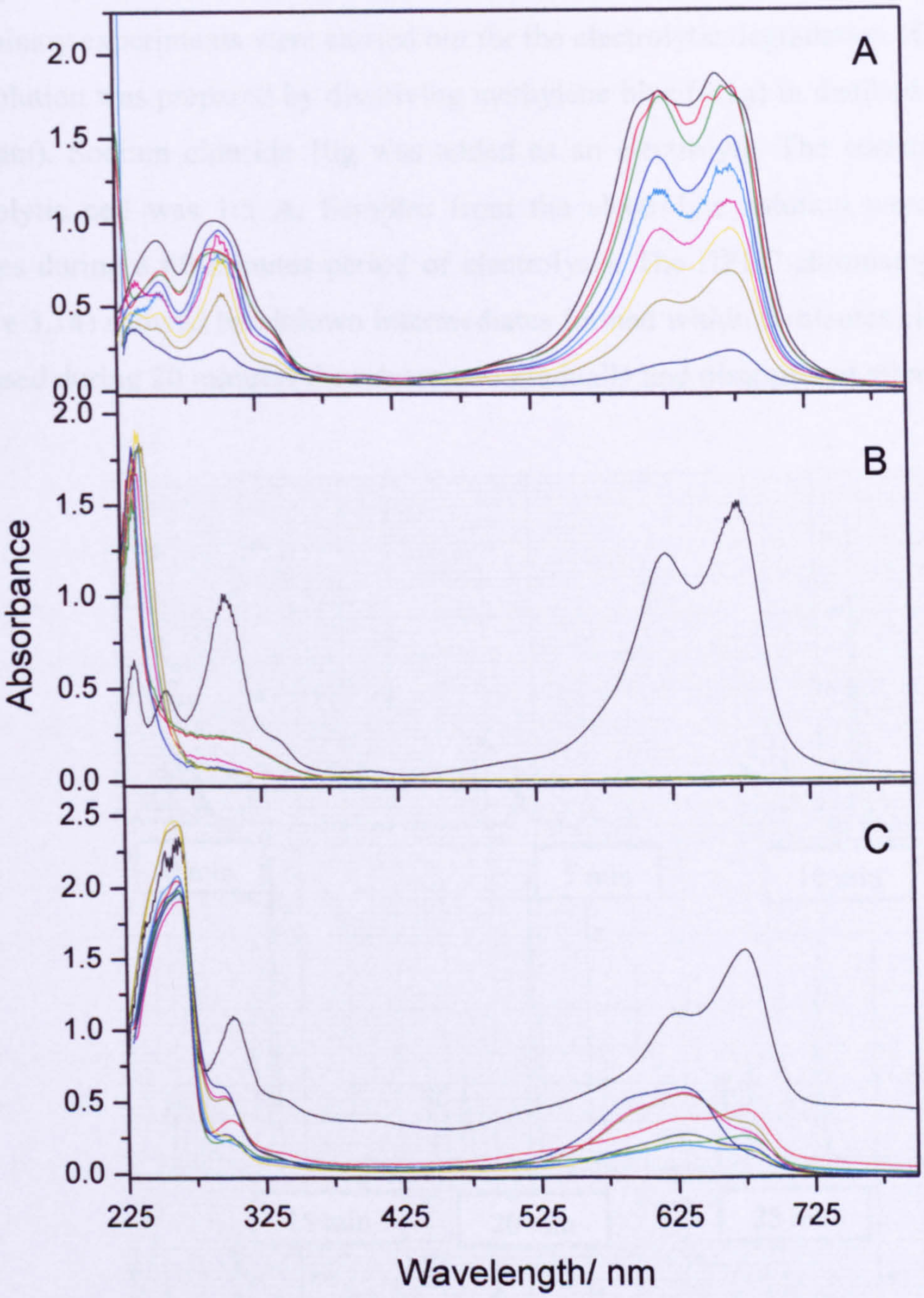


Figure 3.13: UV-Visible spectra showing the electrolytic destruction of methylene blue in:

A) Na_2SO_4 Solution. Electrolysis time: 0 min____, 30 min____, 60 min____, 120 min____, 180 min____, 240 min____, 300 min____, 360 min____ and 480 min____.

B) NaBr solution. Electrolysis time: 0 min____, 05 min____, 30 min____, 120 min____, 180 min____, 240 min____, 300 min____ and 480 min____.

C) NaI solution. Electrolysis time: 0 min____, 05 min____, 30 min____, 60 min____, 120 min____, 240 min____, 300 min____, 360 min____ and 480 min____.

The effect of sodium chloride on the degradation of methylene blue

Preliminary experiments were carried out for the electrolytic degradation of methylene blue. The solution was prepared by dissolving methylene blue (0.1g) in distilled water (2 litres), (50 ppm). Sodium chloride 10g was added as an electrolyte. The current input into the electrolytic cell was 1.5 A. Samples from the electrolyte solution were taken every 5 minutes during a 60 minutes period of electrolysis. The HPLC chromatogram at 290 nm (Figure 3.14) showed breakdown intermediates formed within 5 minutes electrolysis which increased during 20 minutes then decreased gradually and disappeared after 55 minutes.

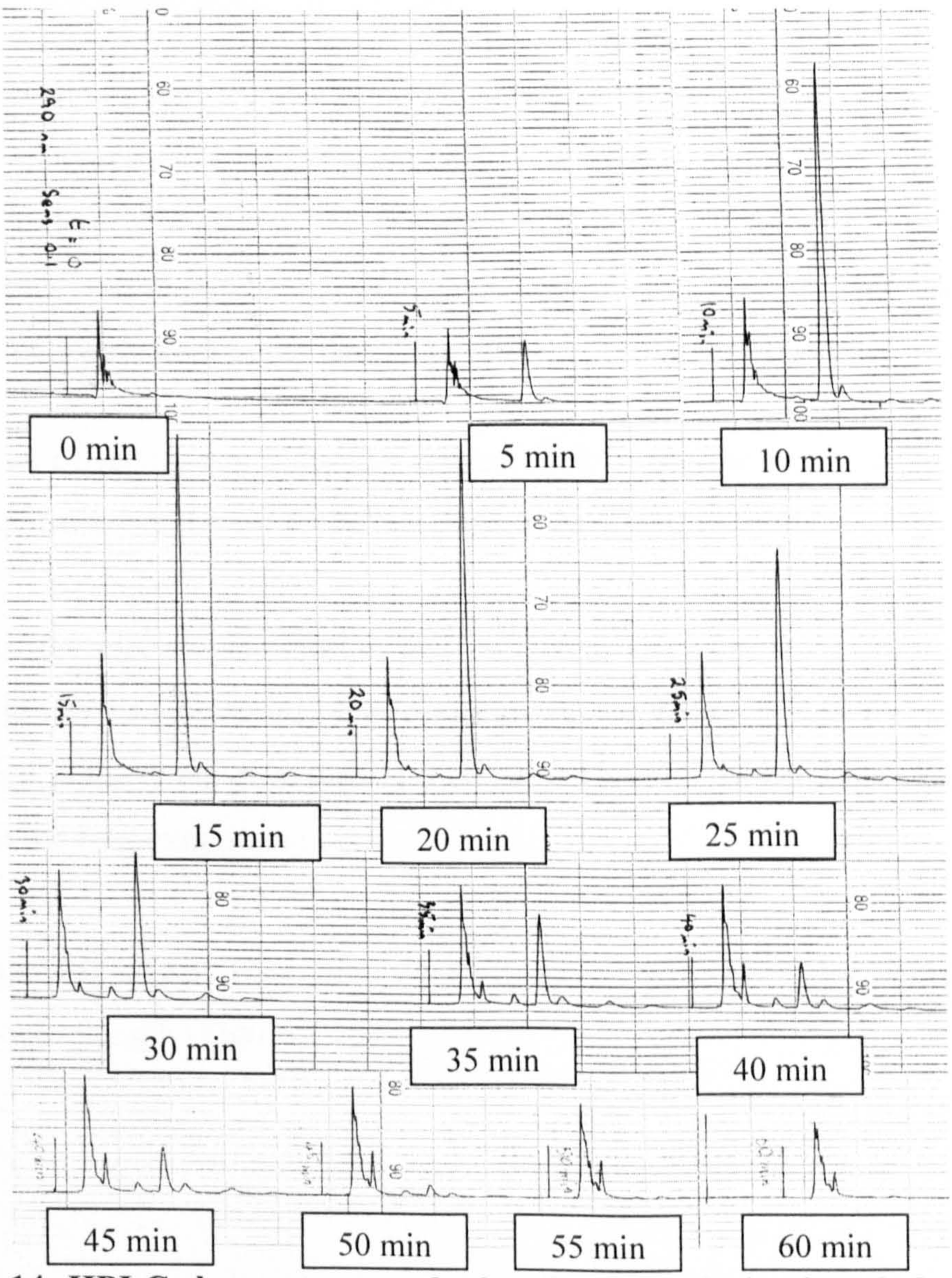


Figure 3.14: HPLC chromatogram during the electrolysis of methylene blue in aqueous NaCl for 60 minutes

The electrolysed solution (2 litres) was collected, and kept overnight, during which time precipitation had occurred. The precipitate was centrifuged, separated from solution and then dried in the oven (100C° to remove excess water). The precipitate was then dissolved in methanol. Thin layer chromatography of the residual precipitate gave one dark pink spot with R_f=0.89 compared with the methylene blue before electrolysis gave 2 spots, the main spot with R_f =0.75, the second spot was more polar R_f = 0.66. This result from TLC indicates that methylene blue may have contained azure A as reported in literature [71]. The system used for TLC was methanol: dichloromethane: acetic acid (7:9:1), (alumina 60 F_{254}, neutral type).

The aqueous solution obtained after separating the precipitate was left on the bench for two weeks, during this time more precipitates were accumulated. These were centrifuged again, and collected and combined with the first precipitate. The separated solution from above turned light blue on exposure to air, when compared with the samples taken from electrolysis which were kept in the dark. The latter are still colourless after months

The electrolysis of methylene blue was carried again using the same procedure as in the previous experiment, but the electrolysis was stopped after 15 minutes.

The 2 litres of the electrolyte solution was collected, and kept for 1440 minutes, during which a precipitate had occurred. The solution was centrifuged, and the precipitate was separated, dried in the oven, dissolved in methanol. The TLC showed the same spot, which was formed in the first experiment.

A sample of electrolysed solution after stopping the electrolysis was analysed with HPLC, with variable wavelength (Figure 3.15).

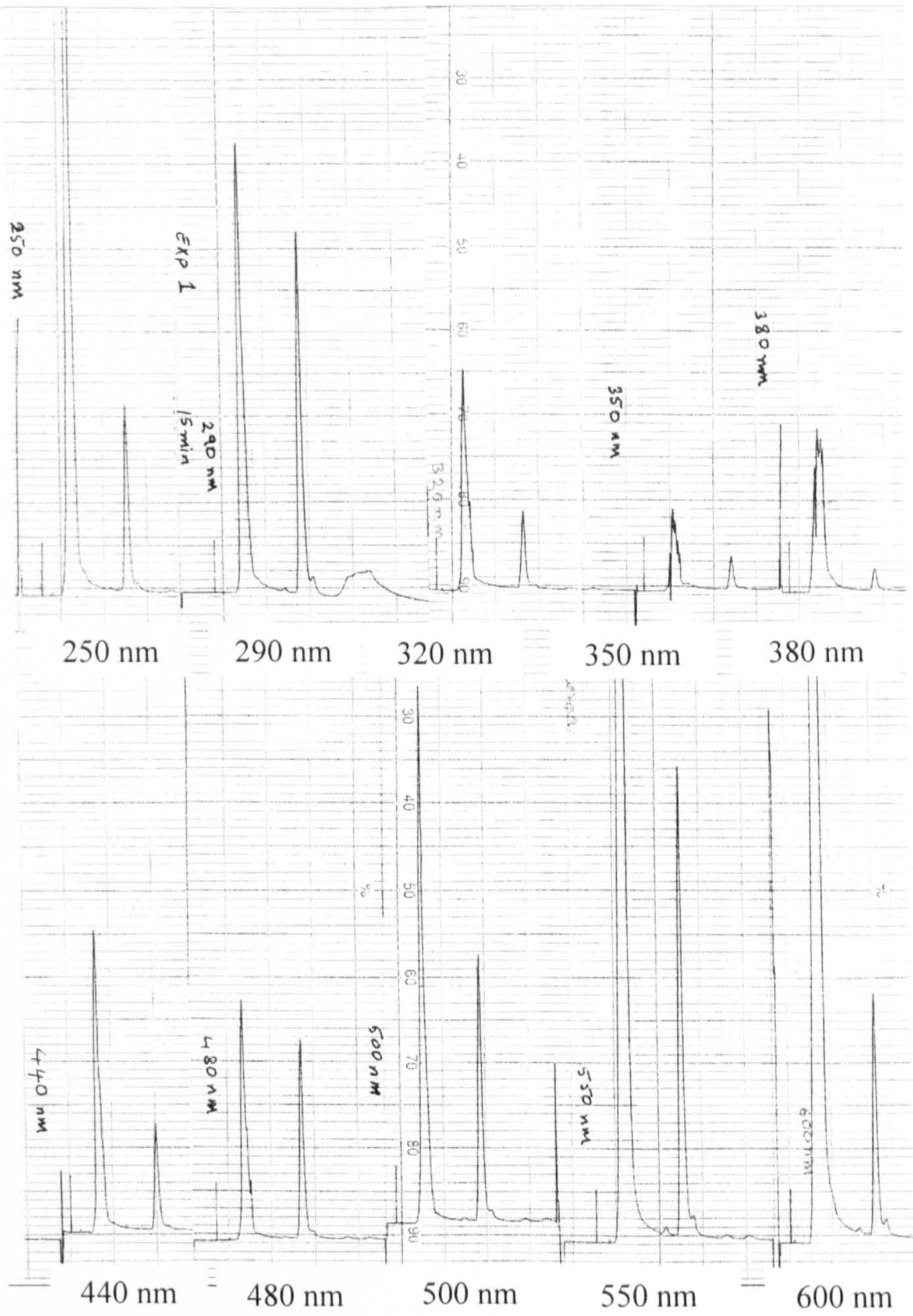


Figure 3.15: HPLC chromatogram of 15 minutes sample taken (during the electrolysis of methylene blue in aqueous NaCl) in varied wavelength (230-600 nm)

Another sample of the residual precipitate was dissolved in small amounts of distilled water and then shaken with the same amounts of the dichloromethane. The aqueous phase was dissolved in acetonitrile, and HPLC was carried on the resultant solution (Figure 3.16a). The organic phase was dried over anhydrous sodium sulphate, centrifuged and the filtered. The filtrate was dried with nitrogen gas and the residue dissolved in acetonitrile: water

(90:10) mixture and then injected into the HPLC instrument (Figure 3.16b). The chromatogram of this residue showed more than eight peaks corresponding to the formation of intermediate products. These results are in accordance with the earlier work reported by Donaldson et al. [59].

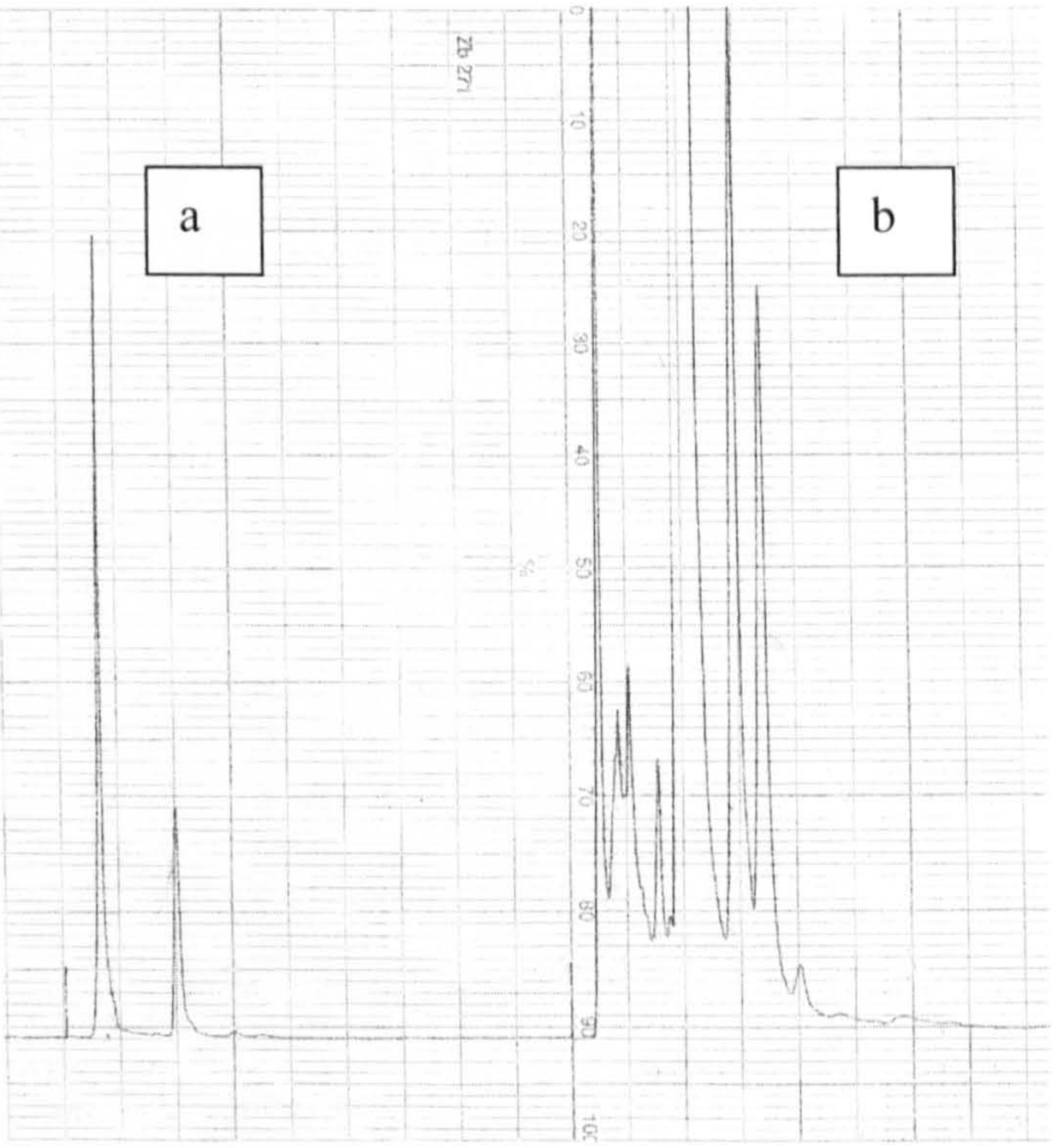


Figure 3.16: **a)** HPLC chromatogram of aqueous phase after removal of the precipitate (taken from electrolysis of methylene blue in aqueous NaCl over 15 minutes electrolysis), **b)** organic phase after drying with sodium sulphate & centrifuge, drying with N_2

The remaining residual precipitate, which was separated from the electrolyte solution by centrifugation, was dissolved in 150 ml of distilled water, adjusted to pH 7.9, then extracted with dichloromethane (50 ml × 6). A magenta coloured material was partitioned into the organic phase, which was dried with anhydrous sodium sulphate, filtered, and then concentrated under vacuum. The TLC gave seven pinks to violet spots (R_f = 0.42, 0.44, 0.52, 0.53, 0.64, 0.77, 0.86). There was a blue spot retained on the base line of the TLC. The TLC system was methanol: dichloromethane: acetic acid (3:7:1). The silica used was preparative silica gel G. The aqueous phase (light blue solution), was adjusted to pH 7.9, and then re-extracted with dichloromethane (25 ml × 6). A violet colour resulted in the

organic phase, which was dried with anhydrous sodium sulphate. While passing it through a filter paper (Whitman no. 541; hardened asheless), the colour of the solution changed from violet to indigo blue.

Figure 3.17 a and b shows the HPLC chromatogram of methylene blue (50 mg/l) and (50 mg/10ml) in aqueous solution of NaCl at 290 nm and sensitivity: 0.02.

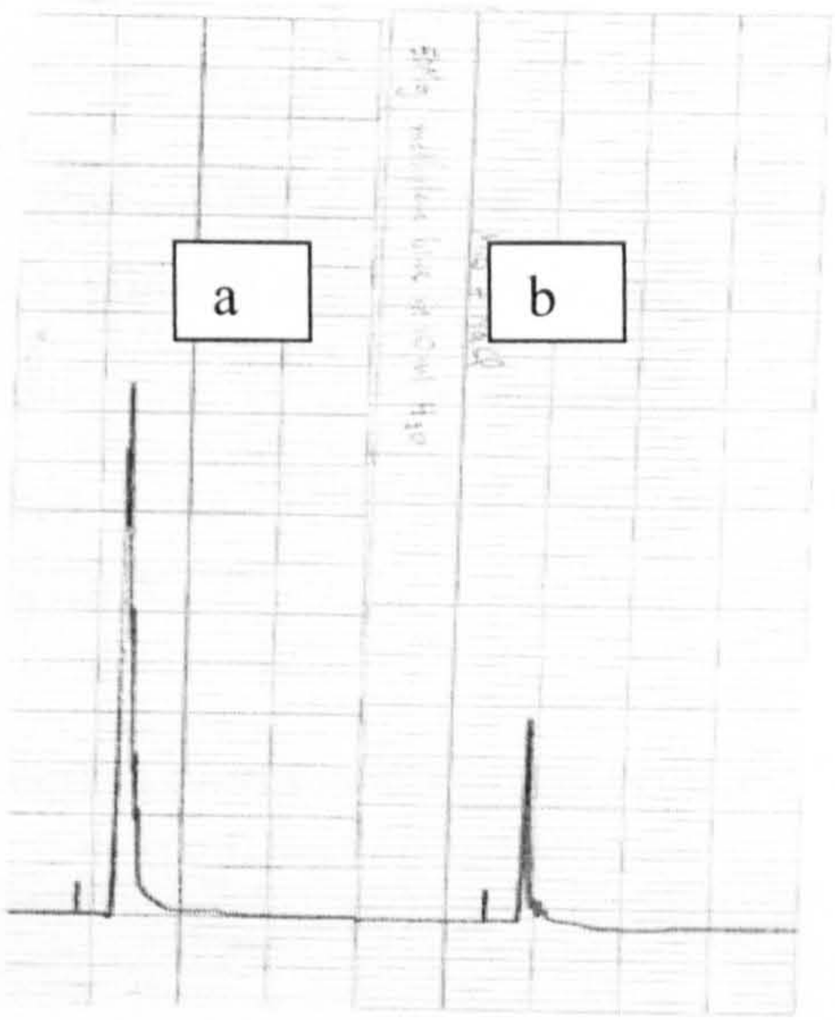


Figure 3.17: HPLC chromatogram of methylene blue in aqueous solution of NaCl at 290 nm, sensitivity: 0.02, a) MB (50 mg/l), b) MB (50 mg/10 ml)

A third experiment was conducted for the electrolysis of methylene blue (50 mg/l) using the same procedure as in the previous experiment, but the electrolysis was run for 480 minutes at current input 2.0 A (Table 3.12). The UV-visible spectrum of MB in aqueous NaCl solution before electrochemical treatment (Figure 3.20A) shows two peaks in the visible region (λ_{max} 626 and 678 nm) and two peaks in the UV region (258 and 299 nm). All the peaks decreased within 30 minutes electrolysis with 97% of colour removal achieved and the original blue colour faded into turquoise, which then discharged after 60 minutes. The results obtained also show the appearance of a new peak at 303 nm after 240 minutes. The intensity of the peak at 303 nm increased with the electrolysis time progress.

Table 3.12: Electrochemical decolourisation of methylene blue (MB) in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.2	4.88	Blue	0
30	7.0	5.02	Turquoise	97
60	6.9	5.09	Colourless	98
120	6.9	5.10	Colourless	98

Conditions: current, 2.0 A; temperature, ambient; concentration (MB, 50 mg/l; NaCl, 5 g/l)

The aim was to convert all of the carbon and hydrogen atoms of the dye to CO_2 and water, but there is evidence for the formation of colourless intermediates [59, 71] in the presence of chloride ions, of chlorinated organic products. Donaldson et al. [59] reported the formation of seven neutral compounds and two charged intermediates in the early stages of electro-oxidation of methylene blue [3, 7-bis(dimethylamino) phenothiazinium chloride] (Table 3.13). In their study they identified one intermediate as 4, 6-dichloro-7-dimethylamino-3*H*-phenothiazin-3-one.

Table 3.13: Some of the electrochemical methods studied for methylene blue removal from aqueous solutions

Methods of treatment/ Mechanism	Electrode type	Electrolyte/ reagent	Degradation products	References
Direct Electrolysis [a]	Boron doped diode (BDD)	Na_2SO_4	n.a.	[58]
Indirect Electrolysis	$Ti/TiRuO_2$ Stainless steel cathode (both cases)	$NaCl/Na_2SO_4$		
Anodic Oxidation	Mixed metal oxide anode/titanium mesh cathode	NaCl	7 neutrals and 2 charged intermediates	[59, 71]
Photo-electrochemical	Stainless steel		Cl^-, NH^{4+}, NO^{3-}, SO_4^{2-}	[38]
Electrogenerated oxygen or chlorine	Platinum	KCl	n.a.	[75]
Electrolysis	Mixed metal oxide anode/titanium mesh cathode	NaCl, NaI, NaBr, $NaNO_3$, $NaCO_3$, Na_2SO_4, $Na_2S_2O_5$, CH_3CO_2Na	n.a.	This study

[a] MB prepared in 0.5 M Na_2SO_4, n.a. not available or not identified

The effect of NaCl on the degradation of methylene blue $ZnCl_2$

The UV-visible spectrum of MB $ZnCl_2$ in aqueous NaCl solution before electrochemical treatment (Figure 3.20B) shows two peaks in the visible region (λ_{max} 625 and 675 nm) and two peaks in the UV region (258 and 299 nm). All the peaks decreased within 15 minutes electrolysis with 94% of colour removal achieved and the original blue colour faded into turquoise, which then discharged after 30 minutes (Table 3.14). The formation of a large quantity of purplish brown residue was also observed after 15 minutes electrolysis which decreased with the progress of electrolysis process.

The results obtained also show the appearance of new peaks at 478 nm after 15 minutes and at 303 nm after 180 minutes. The intensity of the peak at 303 nm increased with the electrolysis time progress.

HPLC analysis during the electrolysis of MB $ZnCl_2$ in aqueous NaCl solution (Figures 3.18 and 3.19) before electrolysis treatment at 290 nm produced four peaks with retention time (RT: 2.2, 2.4, 2.8 and 3.1 minutes) and three peaks (RT: 2.4, 2.6 and 2.9 minutes) eluted at 360 nm. The HPLC chromatogram also showed the formation of additional distinguished peak after 15 minute electrolysis treatment with RT: 5.8 minutes eluted at 290 nm (very low intensity when eluted at 340 nm), which disappeared completely after 180 minutes electrolysis treatment, indicating further breakdown. However, the HPLC chromatogram and the UV region shows organic material remain in the solution.

Table 3.14: Electrochemical decolourisation of methylene blue $ZnCl_2$ in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	Degradation %
0	6.7	4.58	Blue	0
15	9.3	4.73	Turquoise	94
30	7.4	4.78	Colourless	98
60	6.2	4.83	Colourless	99
120	7.6	4.72	Colourless	100

Conditions: current, 1.5 A; temperature, ambient; concentration (MB $ZnCl_2$ 50 mg/l; NaCl, 5 g/l)

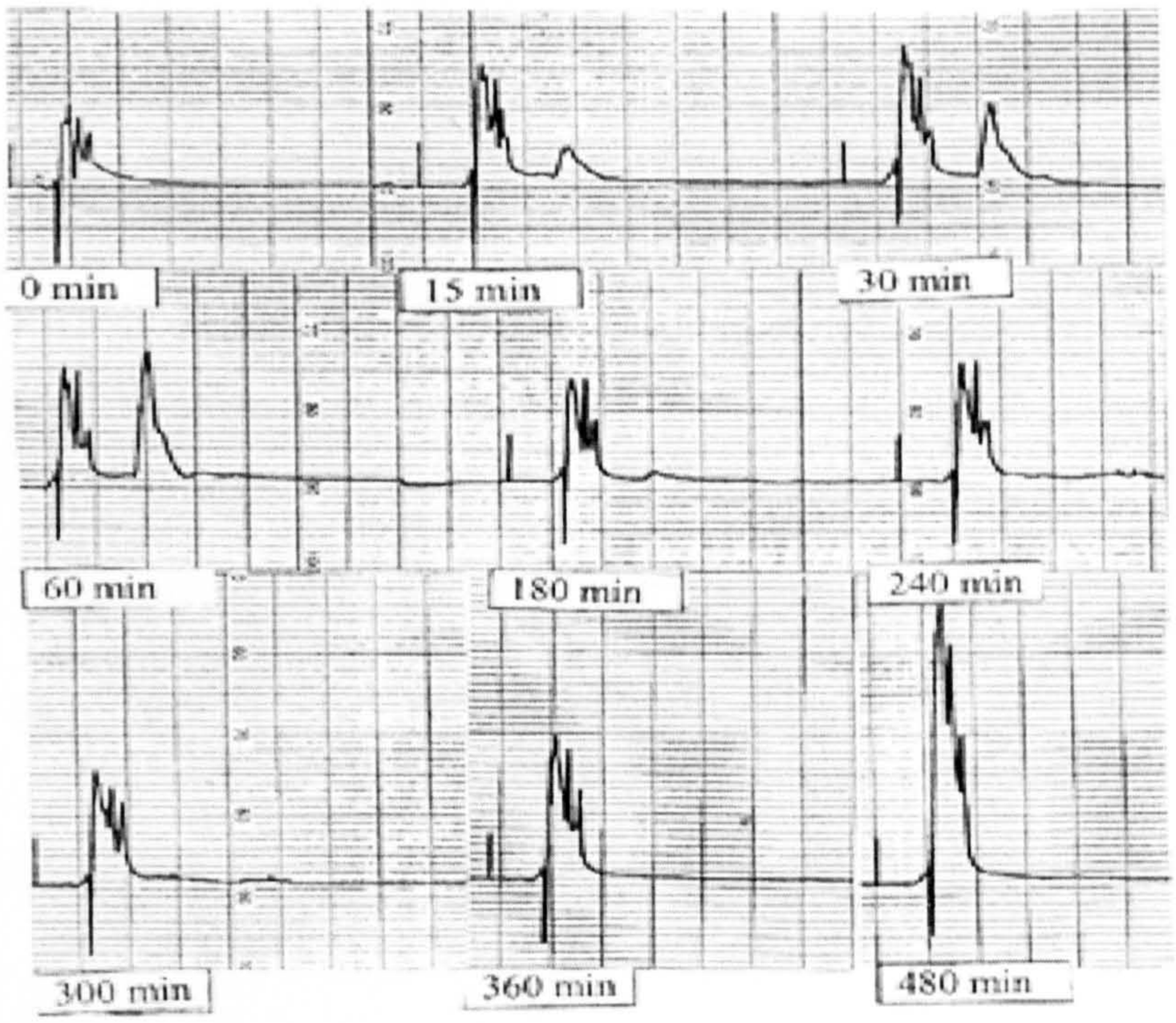


Figure 3.18: HPLC chromatogram during the electrolysis of MB $ZnCl_2$ in aqueous NaCl solution at 290 nm, solvent; acetonitrile: water (90: 10), sensitivity: 0.05

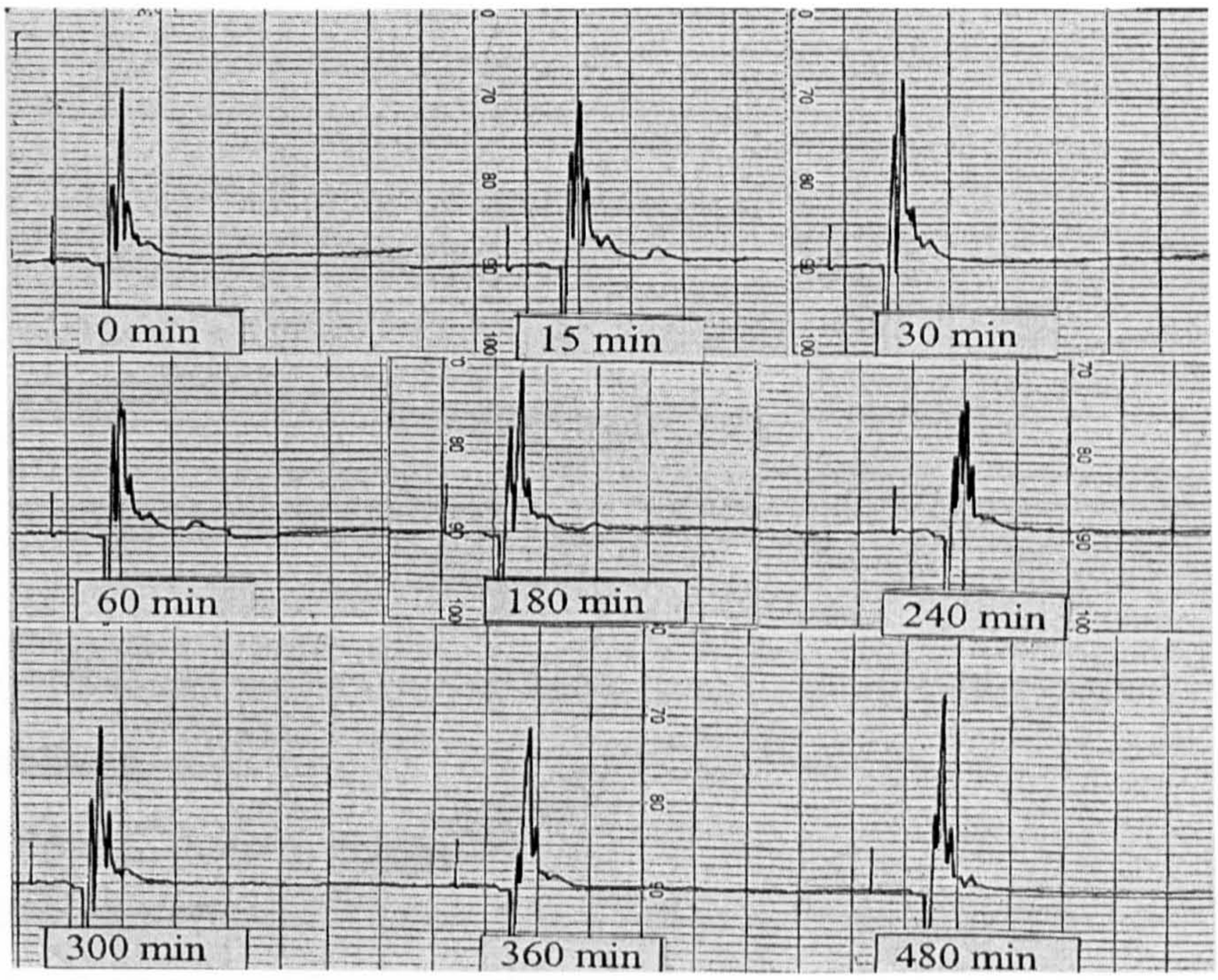


Figure 3.19: HPLC chromatogram during the electrolysis of MB $ZnCl_2$ in aqueous NaCl solution at 340 nm, solvent, acetonitrile: water (90: 10), sensitivity: 0.02

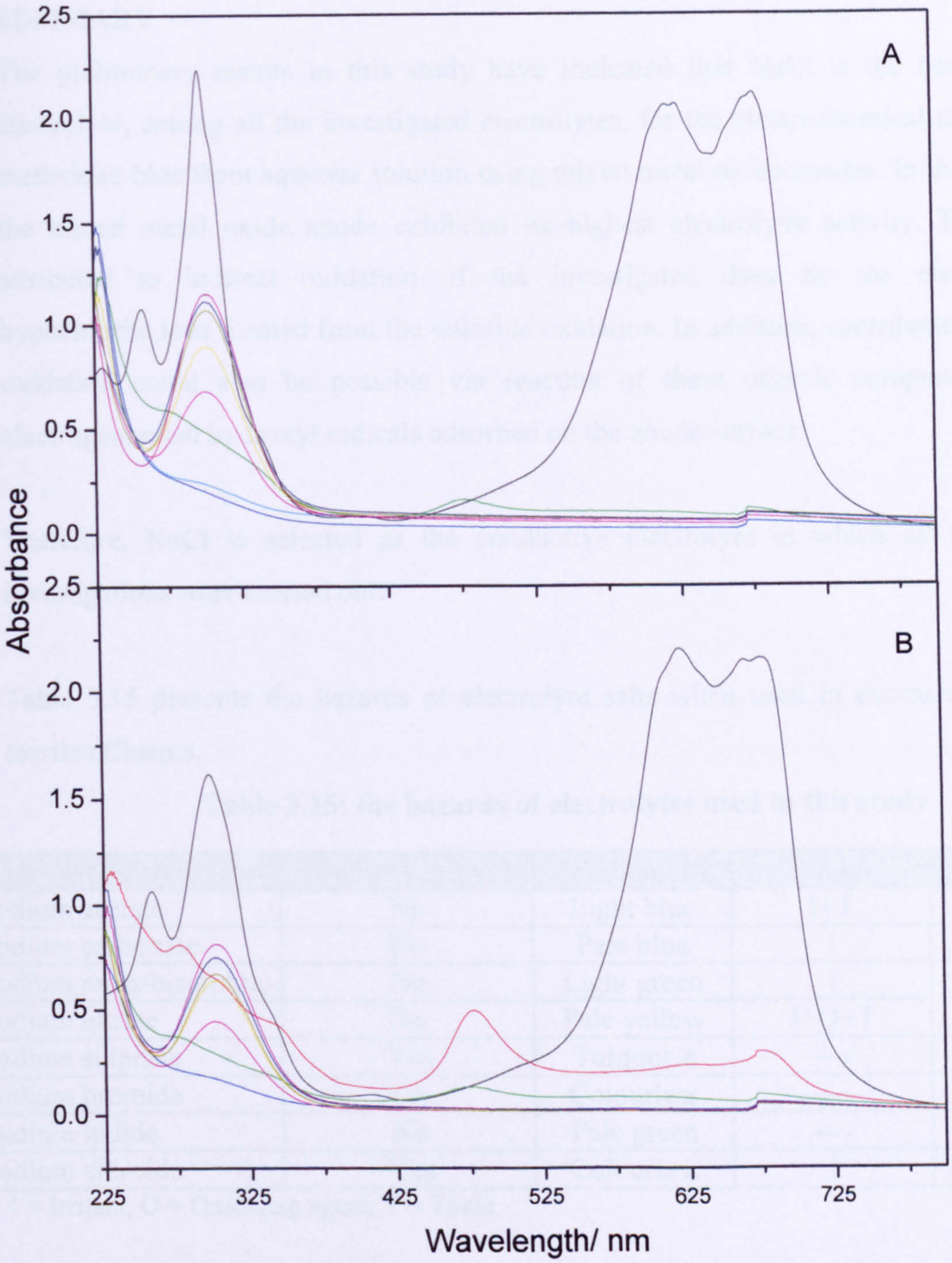


Figure 3.20: UV–visible spectra during the electrolysis of A) methylene blue in aqueous sodium chloride solution: Electrolysis Time: 0 min____, 30 min____, 60 min____, 120 min____, 180 min____, 240 min____, 300 min____, 360 min____, 480 min ____,

and B) methylene blue $ZnCl_2$ in aqueous sodium chloride solution:

Electrolysis Time: 0 min____, 15 min____, 30 min____, 60 min____, 180 min____, 240 min____, 300 min____, 360 min____, 480 min ____.

SUMMARY

The preliminary results in this study have indicated that NaCl is the best conductive electrolyte, among all the investigated electrolytes, for the electrochemical degradation of methylene blue from aqueous solution using mixed metal oxide anodes. In this electrolyte, the mixed metal oxide anode exhibited its highest electrolytic activity. This could be attributed to indirect oxidation of the investigated dyes by the electrogenerated hypochlorite ions formed from the chloride oxidation. In addition, contribution from direct oxidation could also be possible via reaction of these organic compounds with the electrogenerated hydroxyl radicals adsorbed on the anode surface.

Therefore, NaCl is selected as the conductive electrolyte in which all the following investigations were carried out.

Table 3.15 presents the hazards of electrolyte salts when used in excessive amounts in textile effluents.

Table 3.15: the hazards of electrolytes used in this study

Electrolyte	Colour removal	Final colour	State	Comment
Sodium acetate	No	Light blue	I+T	Mildly toxic
Sodium carbonate	No	Pale blue	I	Severe irritant
Sodium meta-bisulphite	No	Light green	I	Corrosive
Sodium nitrate	No	Pale yellow	I+O+T	Dermatitis
Sodium sulphate	Yes	Turquoise	----	----
Sodium bromide	Yes	Colourless	----	Toxic vapours
Sodium iodide	No	Pale green	----	Toxic vapours
Sodium chloride	Yes	Colourless	I	Animal mutagen

I = Irritant, O = Oxidising agent, T = Toxic

3.3.1.2 The Effect of the Sodium Chloride Electrolyte Concentration on the Colour Removal of Methylene Blue

The effect of NaCl concentration (5.0, 10.0 and 15.0 g/l) on the electrolysis of (50 mg/l) MB in aqueous solution was investigated at pH 6.0-8.6 and current 1.5 A (Table 3.16). Figure 3.21 (A-C) illustrates the UV-Visible spectra changes during the electrolytic destruction of MB in (5 and 15 g/l) NaCl solutions over 480 minutes and with 10 g/l NaCl over 600 minutes.

The data in Table 3.16 show that after 15 minutes the percentage removal was 48%, 96% and 98% when the NaCl concentration was 5.0, 10.0 and 15.0 g/l respectively. After 30 minutes electrolysis the colour removal was 95%, 99% and 99% for 5.0, 10.0 and 15.0 g/l NaCl respectively. The result show that an increase in the chloride concentration to 10 g/l accelerated the electrochemical decolourisation largely during the 15 minutes electrolysis and slightly after 30 minutes electrolysis, while a further increase in the chloride concentration to 15 g/l had only a slight influence on the colour removal and consequently 5 g/l of chloride ions was used for the subsequent experiments.

During the 15 and 30 minutes electrolysis a new peak appeared at 480 nm, which declined after 60 minutes, and totally disappeared after 120 minutes. The appearance of absorption peak at 303 nm occurred after 60 minutes when 10-15 g/l NaCl was used and after 120 minutes when 5 g/l NaCl was used. This intensity of this peak decreased after 480 and 600 minutes electrolysis when 10 and 5g/l NaCl was used. This result indicates that increasing the NaCl concentration also accelerated the formation of new feature in the UV region. Furthermore, extending the time of electrolysis destroy this feature. This may be explained in another way, that the methylene blue was oxidised firstly to colourless intermediates and then to carbon dioxide.

In the indirect electrolysis the organic pollutants are mainly oxidised in the bulk of the solution by chemical reaction with the electrogenerated active species and therefore the oxidation rate depends on the concentration of chloride ions that are oxidised to active chlorine at the anode surface (reactions (2), (3) and (4)) and the applied current [58]

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \quad (2)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (3)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (4)$$

$$Cl_2 + H_2O \Leftrightarrow HCl + HOCl$$

Table 3.16: Effect of sodium chloride concentration during the electrochemical decolourisation of methylene blue

Time (min)	% Removal		
	5 g/l NaCl	10 g/l NaCl	15 g/l NaCl
15	48	96	98
30	95	99	99
60	99	99	100
120	100	100	100

Conditions: current, 1.5 A; temp., ambient; concentration (MB, 50 mg/l ; NaCl, 5, 10 & 15 g/l)

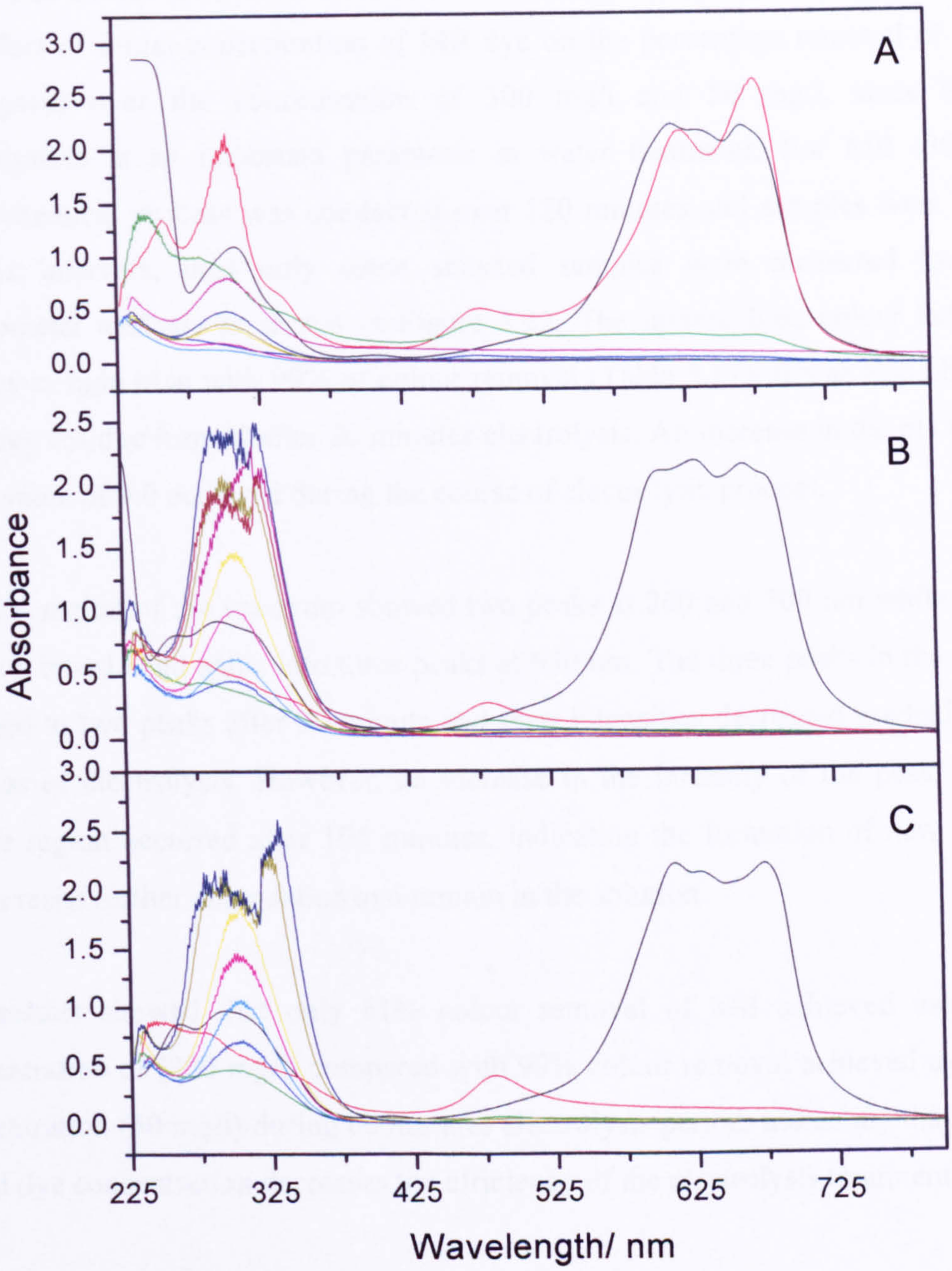


Figure 3.21: UV-Visible spectra showing the electrolytic destruction of methylene blue in:

A) (5 g/l) NaCl Solution. Electrolysis time: 0 min____15 min____, 30 min____, 60 min____, 120 min___, 180 min___, 240 min____, 300 min____, 360 min____ and 480 min____.

B) (10 g/l) NaCl solution. Electrolysis time: 0 min____, 15 min____, 30 min____, 45 min____, 60 min____, 90 min___, 120 min____, 240 min____, 360 min____, 480 min and 600 min____.

C) (15 g/l) NaCl solution. Electrolysis time: 0 min____, 15 min____, 30 min____, 45 min____,60 min____, 75 min___, 90 min____, 240 min____ and 480 min____.

3.3.1.3 The Effect of the Dye Concentration on the Percentage Removal

The effect of initial concentration of MB dye on the percentage removal of the dye was investigated over the concentration of 300 mg/l and 50 mg/l, since the pollutant concentration is an important parameter in water treatment. For MB (300 mg/l) the electrochemical process was conducted over 120 minutes and samples were taken with 5 minutes intervals, thus only some selected samples were measured for UV-visible spectrometer analysis as shown in Figure 3.22. The intense blue colour faded after 100 minutes to light blue with 90% of colour removal (Table 3.17). It was also observed that a blue grey residue formed after 20 minutes electrolysis. An increase in the pH from value of 6.8 to value of 9.0 occurred during the course of electrolytic process.

The UV region of the spectrum showed two peaks at 260 and 300 nm while in the visible region a broad band splits into three peaks at 630 nm. The three peaks in the visible region changed to two peaks after 30 minute and their intensities decreased gradually during 100 minutes of electrolysis. However, an increase in the intensity of the peak located in the visible region occurred after 105 minutes, indicating the formation of new intermediates, which resist further degradation and remain in the solution.

The results showed that only 61% colour removal of MB achieved using initial dye concentration of (300 mg/l) compared with 99% colour removal achieved using initial dye concentration (50 mg/l) during 60 minutes electrolysis period, indicating that increasing the initial dye concentration decreases the efficiency of the electrolysis treatment.

Table 3.17: Electrochemical decolourisation of (300 mg/l) methylene blue (MB) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	(%) Removal
0	6.8	5.65	Dark blue	0
30	9.0	5.70	Navy violet	46
60	9.0	5.76	Navy violet	61
90	8.5	5.79	Blue	87
100	9.0	5.87	Light blue	90

Conditions: current, 1.5 A; temperature, ambient; concentration (MB 300 mg/l; NaCl, 5 g/l)

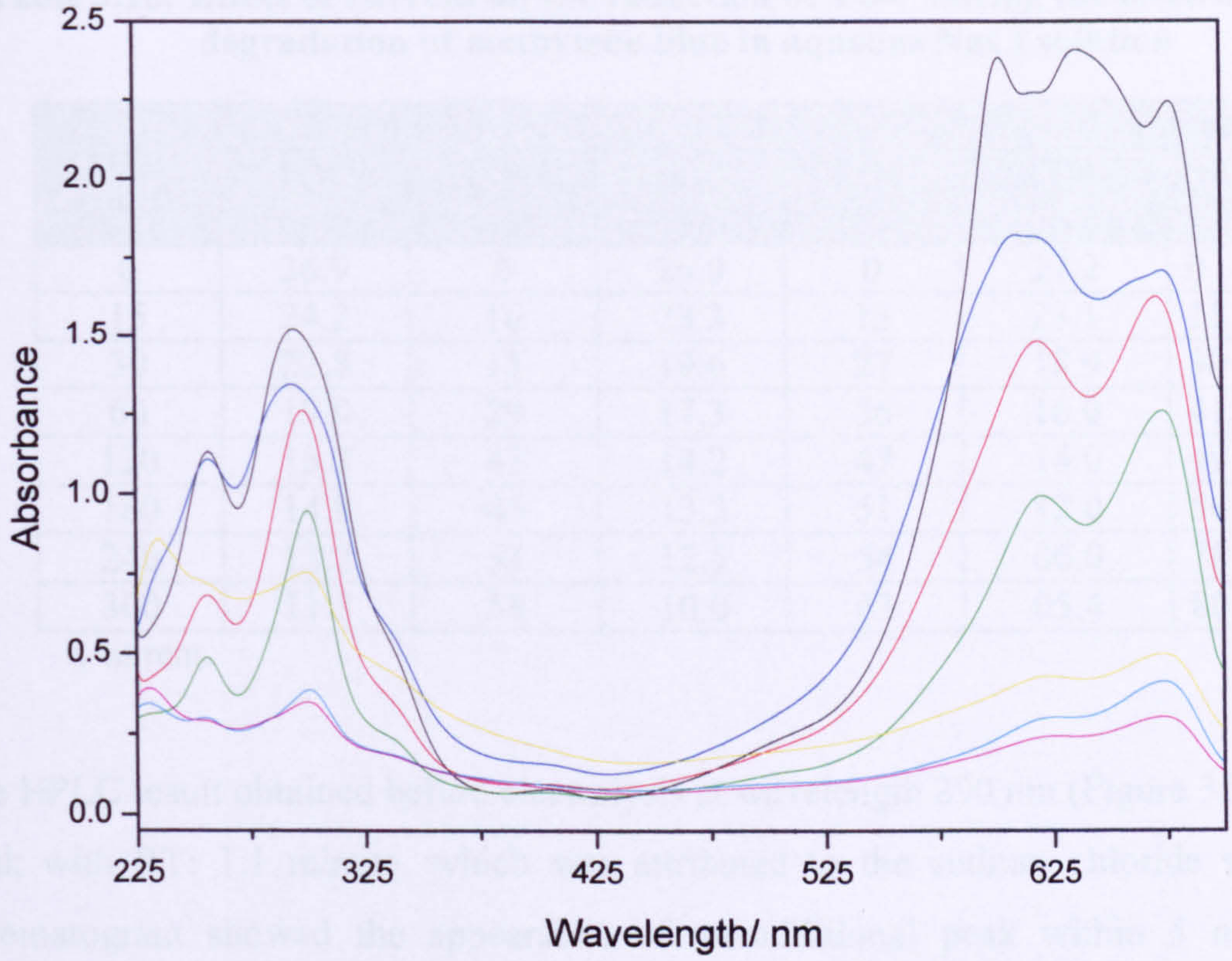


Figure 3.22: UV–Visible spectra during the electrochemical degradation of (300 mg/l) methylene blue in aqueous sodium chloride solution

Electrolysis time: 0 min ____, 30 min____, 45 min____, 60 min____, 90 min____, 100 min ____and 105 min____

3.3.1.4 The Effect of Current on the Percentage on the Colour Removal of Methylene Blue

The effect of current input (0.5, 1.5 and 2.0 A) on the electrolysis of MB (50 mg/l) in aqueous sodium chloride (5 g/l) solution was carried out. All experiments were run at natural pH. The data in Table 3.18 presents the effect of the current input on the reduction of TOC during the electrochemical degradation of MB dye.

The highest removal of TOC (80%) and the least removal of TOC (58%) after 300 minutes electrolysis are achieved at 2.0 A and 1.5 A respectively (Table 3.18). As expected, increasing the current resulted in a faster decolourisation of the dye solution, due to a greater charge entering the cell and electrogenerating more active chlorine.

Table 3.18: Effect of current on the reduction of TOC during the electrochemical degradation of methylene blue in aqueous NaCl solution

Time (min)	I- 0.5 A		I- 1.5 A		I- 2.0 A	
	TOC (ppm)	TOC (%)	TOC (ppm)	TOC (%)	TOC (ppm)	TOC (%)
0	26.9	0	26.9	0	27.2	0
15	24.2	10	23.3	13	23.1	15
30	22.8	15	19.6	27	18.9	30
60	19.0	29	17.3	36	16.0	41
120	15.3	43	14.2	47	14.0	49
180	14.8	45	13.2	51	12.0	56
240	13.2	51	12.5	54	06.0	78
300	11.3	58	10.0	63	05.4	80

I, current.

The HPLC result obtained before electrolysis at wavelength 290 nm (Figure 3.23) showed a peak with RT: 1.1 minute, which was attributed to the sodium chloride solution. The chromatogram showed the appearance of an additional peak within 5 minute which increased during 20 minutes electrolysis, then decreased gradually and finally disappeared after 360 minutes electrolysis.

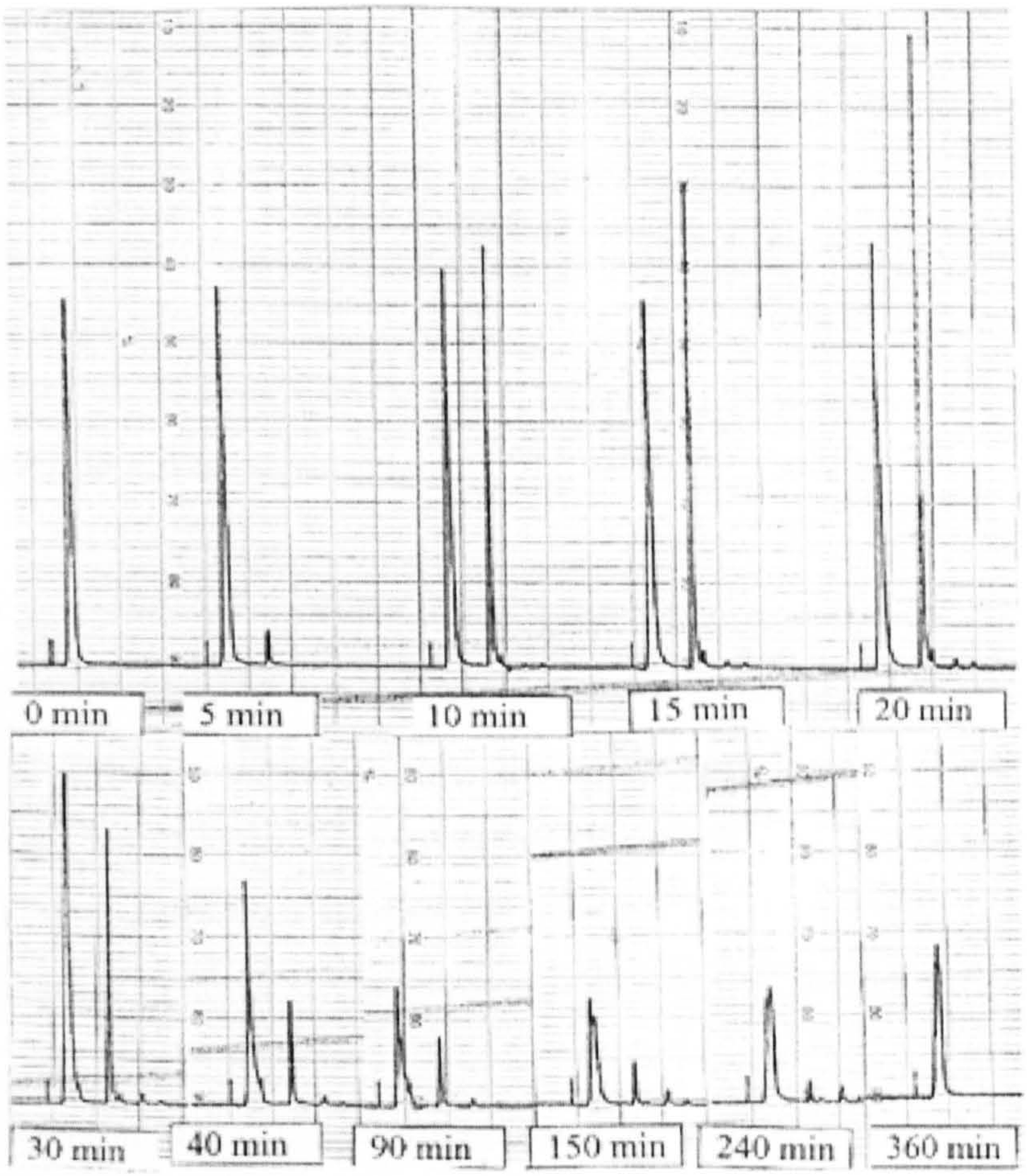


Figure 3.23: HPLC chromatogram during the electrolysis of methylene blue in aqueous NaCl for 360 minutes,

3.3.1.5 The Effect of Chlorine Water on the Colour Removal of Methylene Blue

The effect of direct chlorine water (Cl_2/ H_2O) addition on colour removal was also studied without electrolysing the dyeing solution. To a solution of methylene blue (1000 mg/l), Cl_2/ H_2O (500 ml) was added drop wise under well mixed conditions, until the blue colour of methylene blue disappeared. Samples were taken every 5 minutes for a period of 90 minutes. A dull green precipitate formed in these samples after 15 minute, which turned grey-violet after 240 minutes. Some selected samples were taken for TLC, HPLC and UV-visible analysis.

The HPLC chromatogram (Figure 3.24) shows that methylene blue retains in the column and is not eluted before the addition of Cl_2/ H_2O. The same condition was applied to observe the dye breakdown products and a number of peaks appeared in the chromatogram between 5 to15 minutes reaction with RT: 1.0, 1.2, 1.5, 2.2, 3.0, 4.2, 4.9, 5.2, 6.5, 6.6, 8.2 and 9.2. These peaks were decreased gradually and disappeared after 60 minutes reaction period, except for the peaks with RT: 1.0 and 1.5 (shoulder) which increased during the 30 minutes period then decreased with reaction progress. This peak could be due to the generated hypochlorite radical during the addition of Cl_2/ H_2O.

The UV–visible spectrum of methylene blue upon reaction with Cl_2/ H_2O (Figure 3.25) shows two peaks at 245 and 285 nm in the UV region and one broad peak, which centred at 638 nm. These peaks were decreased and shifted to longer wavelenght after 5 minutes reaction. However, an increase in absorption in the visible region occurred after 240 minutes reaction which indicate the formation of degradation intermediates. The UV region also shows that organic material remain in the solution during the reaction process.

The UV-visible spectra, HPLC chromatogram and the TLC (Plates 3.6) confirm that more intermediates were formed during the addition of chlorine water to methylene blue than in the electrolytic degradation of methylene blue in aqueous NaCl solution. This could be explained by large amount of hypochlorite radicals generated upon direct addition of Cl_2/ H_2O compared to hypochlorite generated by electrolytic oxidation treatment.

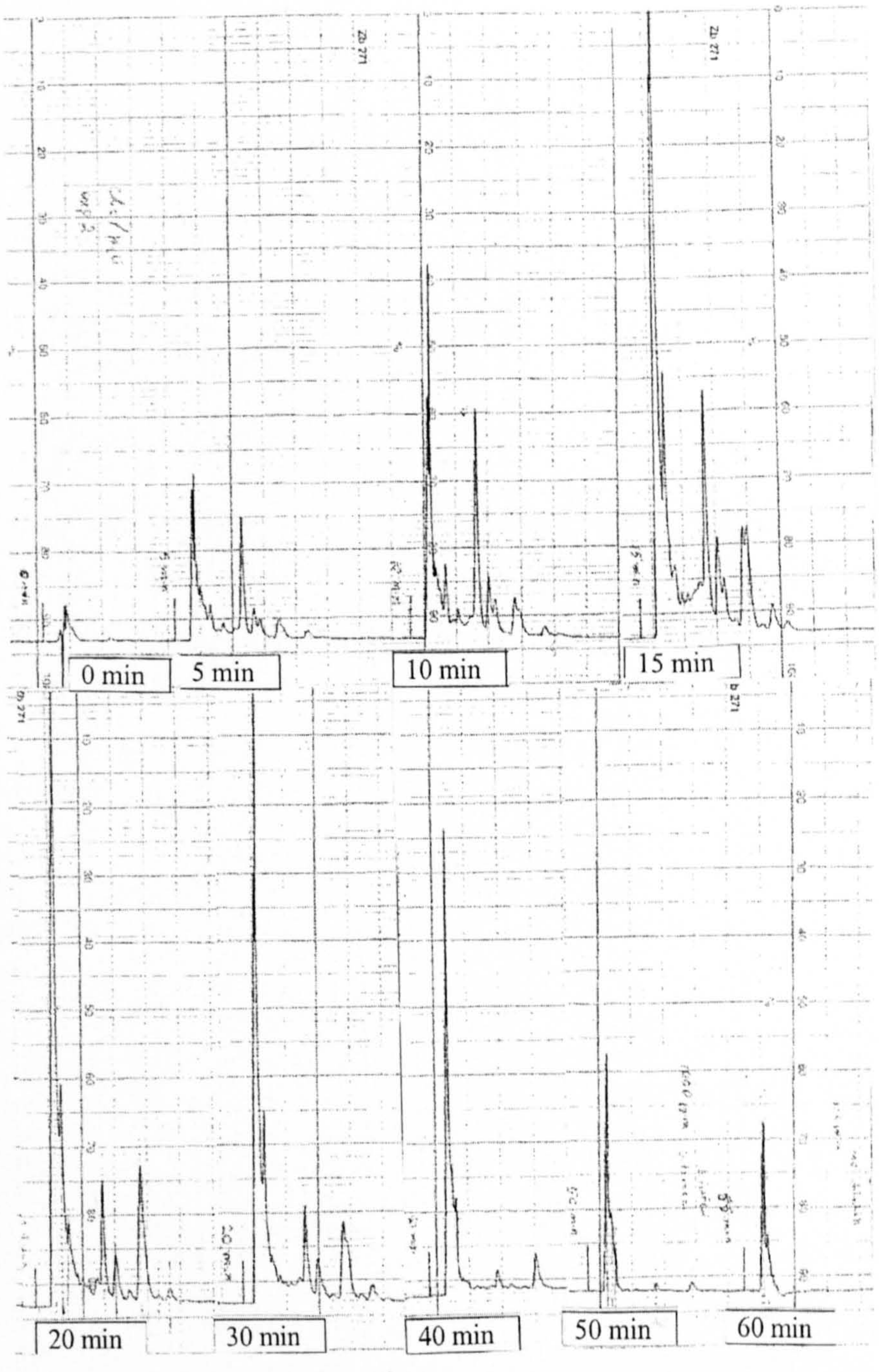
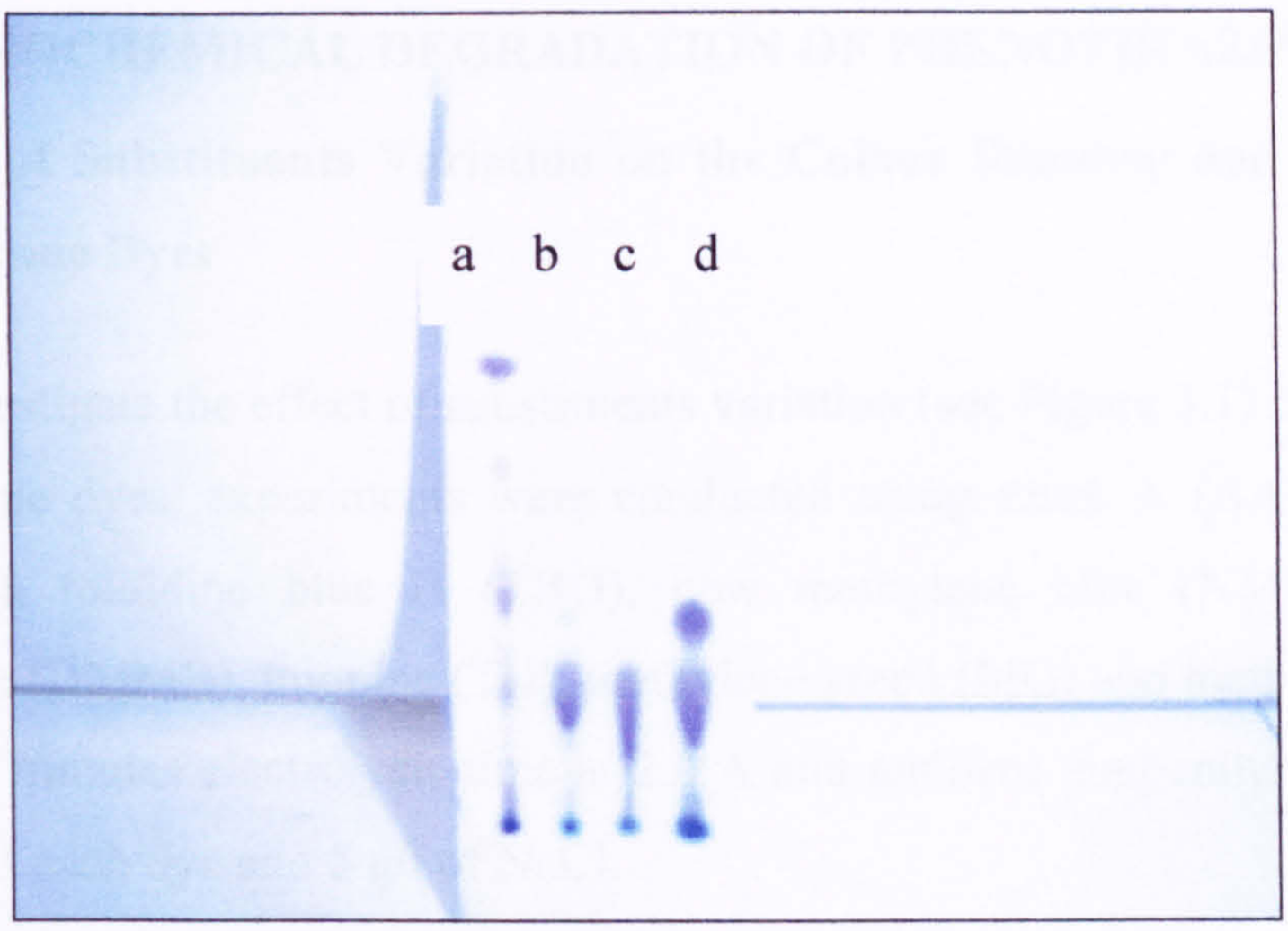


Figure 3.24: HPLC chromatogram during the addition of Cl_2/ H_2O to an aqueous solution of methylene blue



Plates 3.6: The TLC chromatogram of a) products from reaction of chlorine water with methylene blue and of b, c, d) products from the electrochemical degradation of methylene blue in aqueous sodium chloride

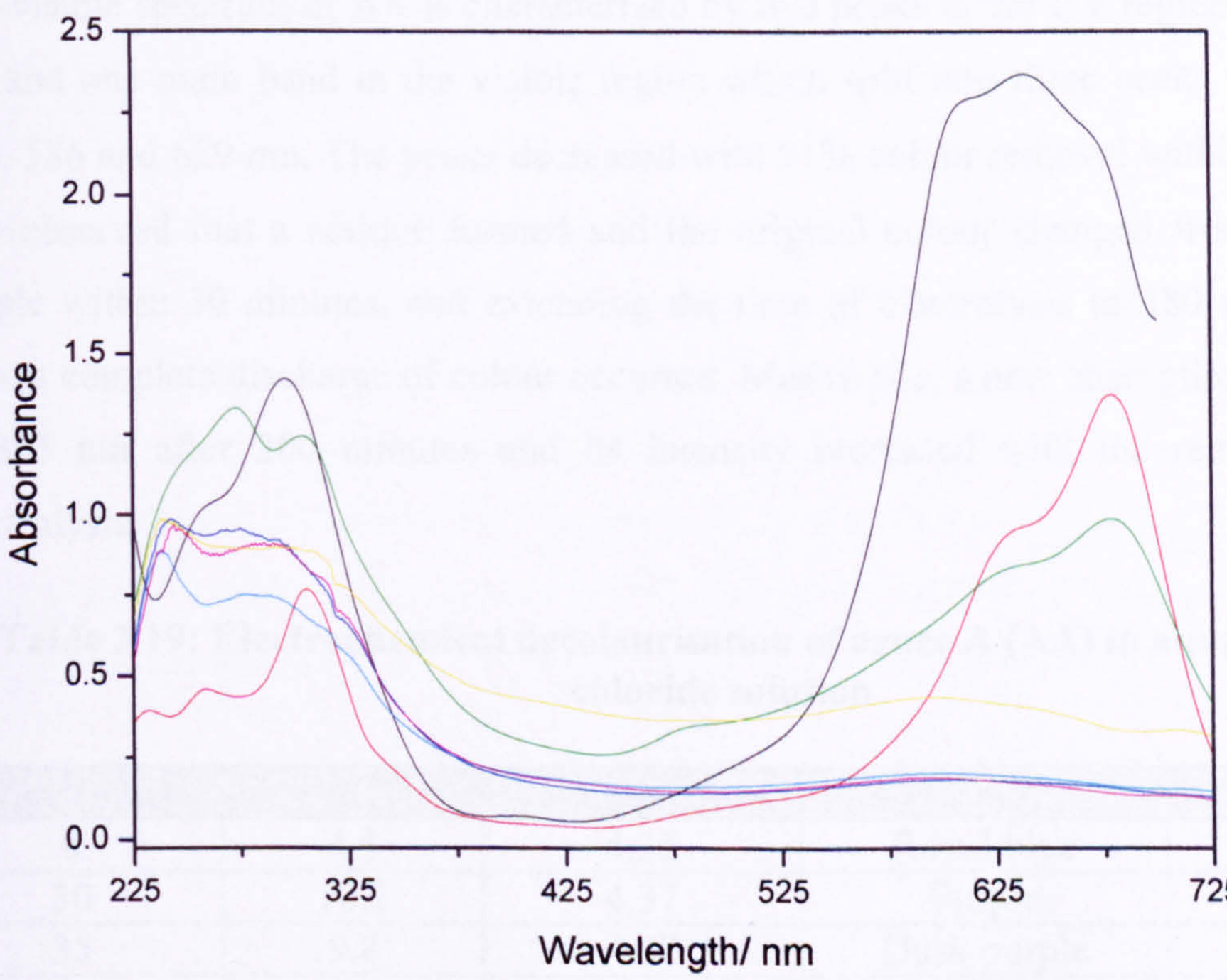


Figure 3.25: UV–visible spectra of methylene blue during reaction with Cl_2/ H_2O
Electrolysis time: 0min____, 5 min____, 15 min____, 20 min____, 30 min____, 60 min___, and 240 min____.

3.3.2 ELECTROCHEMICAL DEGRADATION OF PHENOTHIAZINE DYES

3.3.2.1 Effect of Substituents Variation on the Colour Removal and Degradation of the Phenothiazine Dyes

In order to investigate the effect of substituents variation (see Figure 3.1) on the destruction of phenothiazine dyes, experiments were conducted using azure A (AA), azure B (AB), azure C (AC), toluidine blue O (TBO), new methylene blue (NMB), 1,9-dimethyl methylene blue (DMMB), thionine (TH), methylene green (MG) and methylene violet (MV) dyes over 480 minutes electrolysis time at 2.0 A and ambient temperature and natural pH with 50 mg/l of each dye and 5 g/l of NaCl.

The electrolytic removal of azures A (AA)

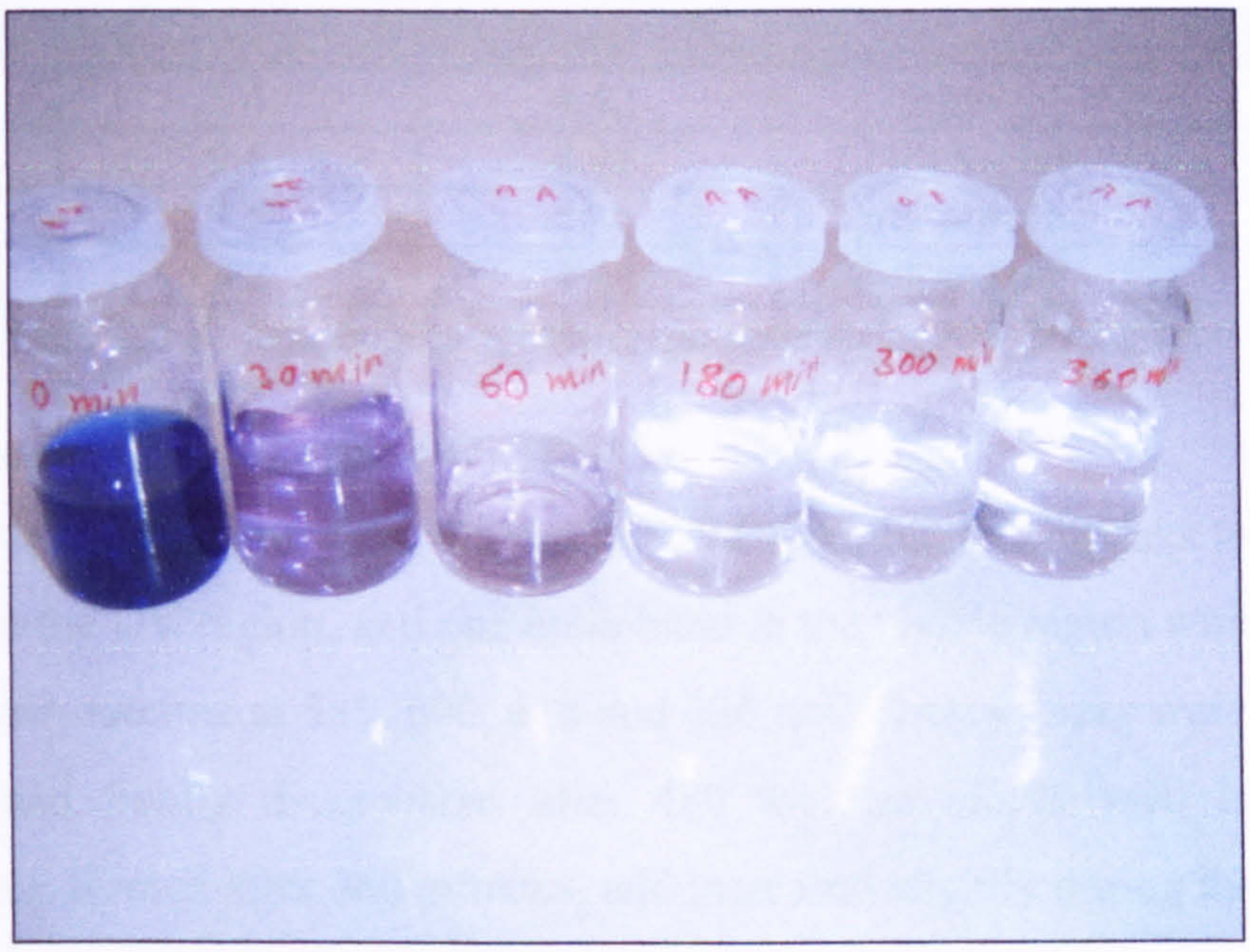
The data in Table 3.19 and Figure 3.26A show the electrolytic conditions and the UV-visible spectrum during the electrolytic destruction of AA in aqueous NaCl solution. The UV-visible spectrum of AA is characterized by two peaks in the UV region at 258 and 297 nm and one main band in the visible region which split into three peaks with maxima at 574, 586 and 629 nm. The peaks decreased with 91% colour removal within 30 minutes. It was observed that a residue formed and the original colour changed from royal blue to purple within 30 minutes, and extending the time of electrolysis to 480 minutes showed almost complete discharge of colour occurred. Meanwhile, a new absorption peak appeared at 303 nm after 300 minutes and its intensity increased with the remaining time of electrolysis.

Table 3.19: Electrochemical decolourisation of azure A (AA) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.5	4.35	Royal blue	0
30	10.2	4.37	Purple	91
35	9.8	4.37	Dusk purple	96
60	9.5	4.37	Brown purple	98
120	8.2	4.35	Pale purple	99
180	9.2	4.33	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (AA, 50 mg/l; NaCl, 5 g/l)

The pH of the solution increased from acidic 4.5 to basic value 10.2 within 30 minutes electrolysis then it dropped slightly and gradually to 8.2 in 120 minutes, increased again to 10.0 at 480 minutes. Plate 3.7 shows the change of colour during the electrochemical degradation of azure A in aqueous sodium chloride.



Plates 3.7: The change of colour during the electrochemical degradation of azure A in aqueous sodium chloride

The electrolytic removal of azures B (AB)

The data in Table 3.20 summarise the experimental conditions and Figure 3.26B shows the changes in the UV-Visible spectrum of AB during the electrolytic destruction in aqueous NaCl solution respectively.

Two sharp peaks were observed in the UV region spectrum of azure B located at 256 and 299 nm, and one main band which split into three maxima at 599 (small shoulder), 609 and 655 nm. These peaks declined within 30 minutes and finally disappeared with 100% colour removal reached after 120 minutes electrolysis. Meanwhile, a new absorption peak appeared at 303 nm after 120 minutes and its intensity increased slightly as the electrolytic process progressed. A rise in the pH value from 5.4 to 9.6 occurred within 30 minutes

electrolysis, after which decreased gradually and stayed close to 8.5 during the electrolysis period (Table 3.20).

Table 3.20: Electrochemical decolourisation of azure B (AB) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.4	4.42	Blue	0
30	9.6	4.48	Light violet	96
60	9.5	4.46	Pale purple	97
120	8.2	4.44	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (AB, 50 mg/l; NaCl, 5 g/l)

The electrolytic removal of azures C (AC)

The UV-visible spectrum of azure C (Figure 3.26C) exhibited two peaks located at 299 nm and 255 nm in the UV region, and one main band in the visible region which split into four peaks with their maxima at 585, 600, 618 and 626 nm. Theses peaks were declined within 30 minutes and finally disappeared after 480 minutes electrolysis. However, a new absorption peak formed after 360 minutes, and increased slightly during the remaining time of electrolysis.

The results obtained showed (Table 3.21) that 100% discharge of the original blue purple colour of AC occurred during after 120 minutes electrolysis. The pH of the solution increased from 5.9 to 7.3 during the 480 minutes electrolysis.

Table 3.21: Electrochemical decolourisation of azure C (AC) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.9	4.80	Blue purple	0
30	6.2	4.70	Dusky purple	94
60	5.9	4.76	Dusky purple	97
120	6.2	4.75	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (AC, 50 mg/l; NaCl, 5 g/l)

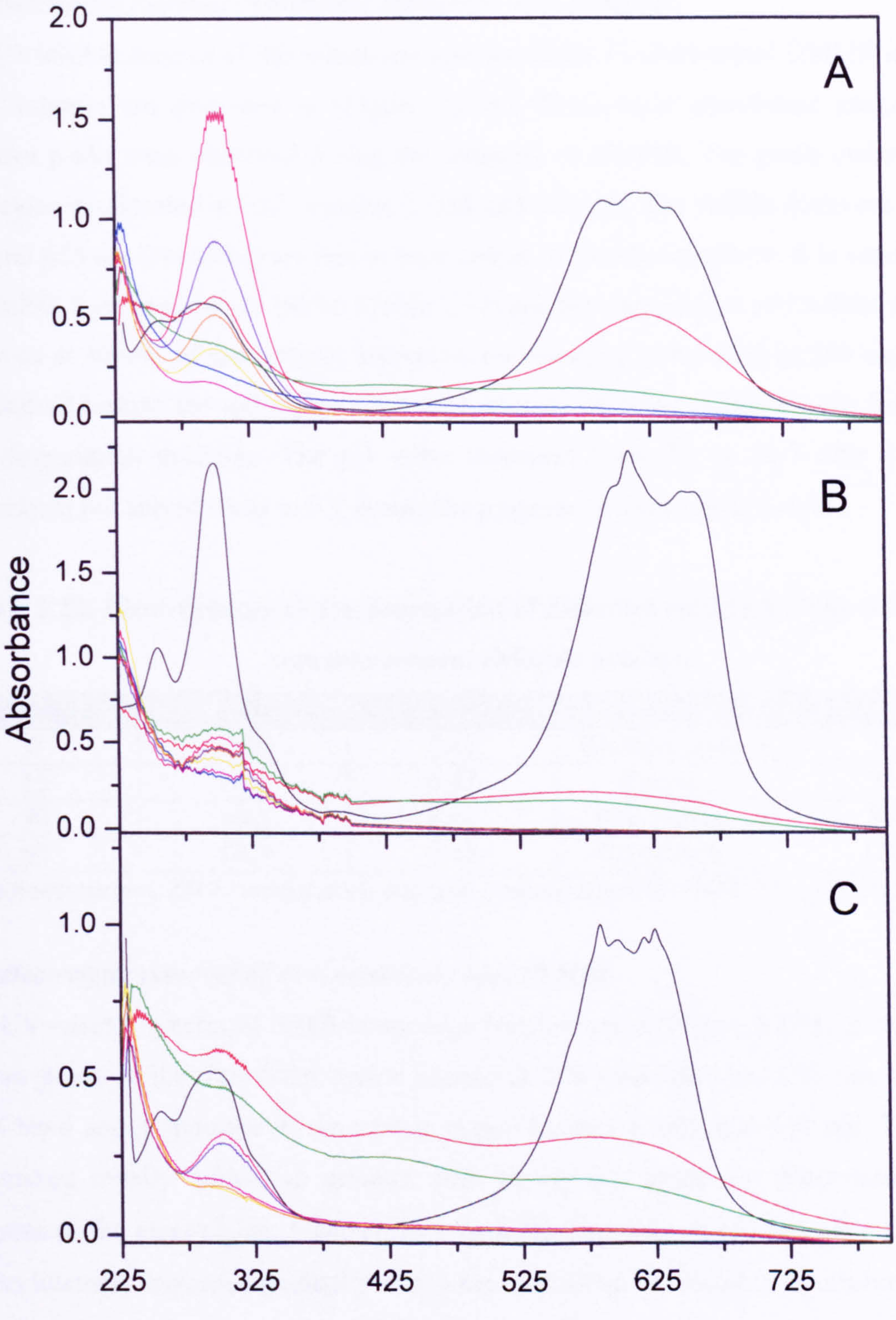


Figure 3.26: UV-Visible spectra showing the electrolytic destruction of (A) azure A, (B) azure B and (C) azure C in aqueous sodium chloride solution

Time of electrolysis: 0min ____ , 30 min____, 60 min____, 120 min____, 180 min____, 240 min____, 300 min____, 360 min____ and 480 min____.

The electrolytic removal of dimethyl methylene blue (DMMB)

The UV/visible spectra of the initial and various stages of electrolysis DMMB in aqueous NaCl solution are presented in (Figure 3.27A). Three main absorbance peaks and two shoulder peaks were observed during the scanning of DMMB. The peaks observed in the UV region are located at 232 (shoulder), 258 and 292 nm. The visible peaks are located at 590 and 656 nm (shoulder) are due to blue colour of the chromophore. It is clear that both the visible light absorbance (98%) (Table 3.22) and the degradation of DMMB structure is achieved at 30 min of electrolysis. However, the intensity of the peak at 258 nm increased and shifted toward the red region (304 nm) after 60 minutes, indicating the formation of new degradation products. The pH value increased from 9.6 to 10.7 after 15 minutes electrolysis but stayed close to 9.7 during the progress of electrolysis process.

Table 3.22: Electrochemical decolourisation of dimethyl methylene blue (DMMB) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	9.6	4.41	Bluish-purple	0
15	10.7	4.47	Purple	95
30	10.5	4.44	Pale purple	98
60	10.3	4.46	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (DMMB, 50 mg/l; NaCl, 5 g/l)

The electrolytic removal of new methylene blue (NMB)

The UV–visible spectra of NMB in aqueous NaCl solution (Figure 3.27B) is characterised by two peaks in the ultraviolet region located at 260 (shoulder) and 293 nm, and by one main band and a shoulder in the visible region located at 601 and 644 nm. These peaks diminished rapidly within 15 minutes then slowly and gradually disappeared with the progress of the electrolysis. Meanwhile, a new band appears at 303 nm after 120 minutes and its intensity increased gradually within the remaining 480 minutes electrolysis time.

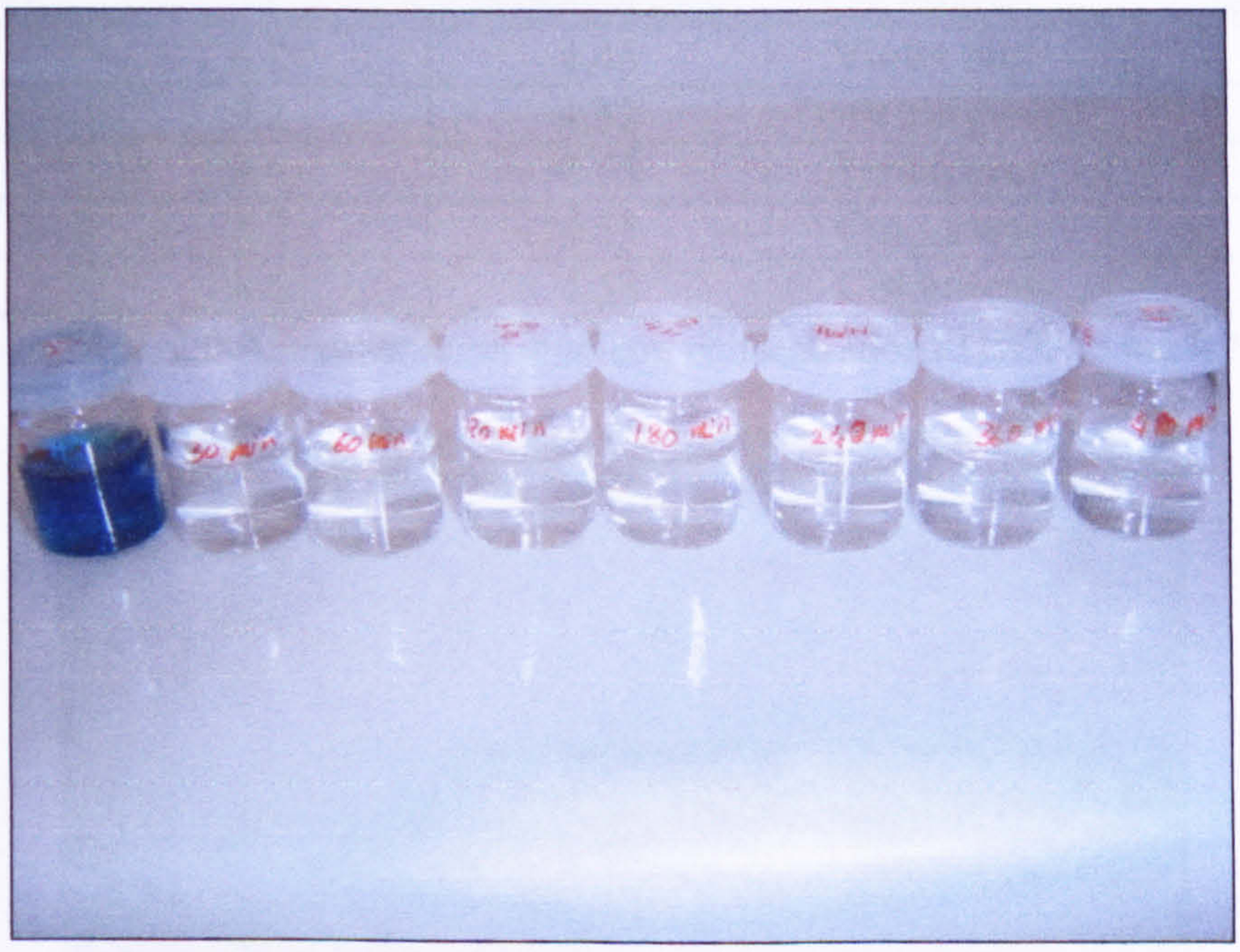
It was also observed that the original dark blue colour changed to brown purple after 15 minutes electrolysis (Table 3.23) and extending the experimental time to 480 minutes showed that the colour gradually changed to light burgundy. However, the colour discharged completely when samples were left overnight with (Plate 3.8) colour removal of

96% being achieved after 30 minutes. A rise in the pH from 8.0 to 10.4 occurred after 30 minutes then decreased to the value 8.6 during the remaining time of 480 minutes electrolysis.

Table 3.23: Electrochemical decolourisation of new methylene blue (NMB) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	8.0	4.36	Dark blue	0
15	10.2	4.46	Brown purple	93
30	10.4	4.47	Colourless	96
120	8.6	4.47	Colourless	98

Conditions: current, 2.0 A; temperature, ambient; concentration (NMB, 50 mg/l; NaCl, 5 g/l)



Plates 3.8: The change of colour during the electrochemical degradation of new methylene blue in aqueous sodium chloride

The electrolytic removal of toluidine blue O (TBO)

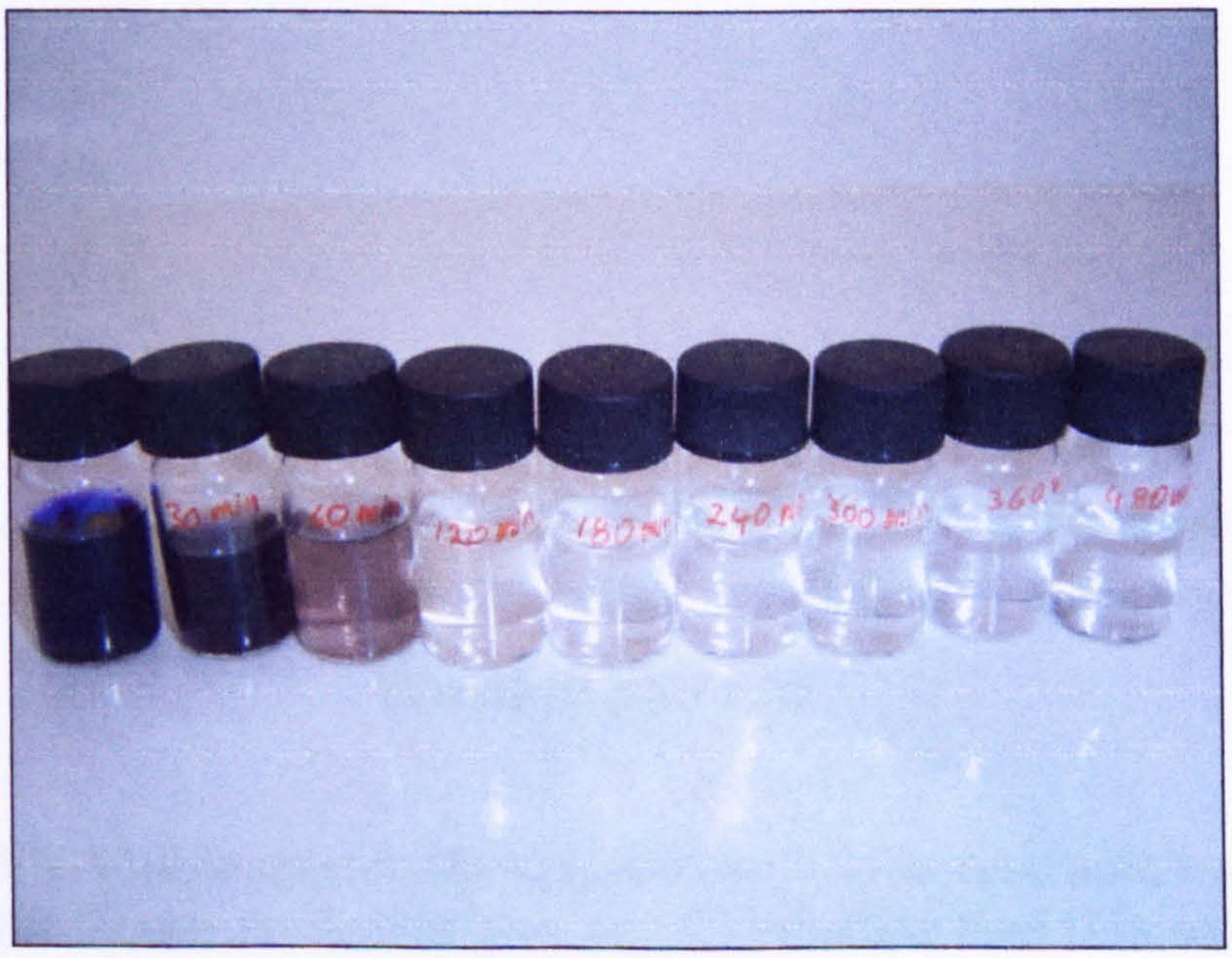
The changes in the UV-Vis spectra of the TBO dye solution as a function of electrolysis time are depicted in (Figure 3.27C). As could be observed from these spectra, before the treatment, the absorption spectrum of TBO in aqueous NaCl solution was characterized by

three absorption peaks in the ultraviolet region, two shoulders at 235, 255 nm, and one main peak at 292 nm. The visible region of the TBO spectrum shows two peaks at 597 nm and 641 (shoulder) nm. The peaks at 255, 292 597 and 641 nm diminished and finally disappeared completely under 480 minutes of electrolysis, indicating a rapid degradation of TBO (Plate 3.9). The intensity of the peak at 235 nm gradually decreased during the reaction which indicated the destruction of the phenothiazine rings. The data in Table 3.26 show that 99% of colour removal is achieved during the course of electrolysis process. Although the initial and final pH value was 6.2, but fluctuated during the reaction and stayed close to 8 during the 360 minutes (Table 3.24).

Table 3.24: Electrochemical decolourisation of toluidine blue O (TBO) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.2	4.45	Violet blue	0
30	9.2	4.52	Dark burgundy	91
60	8.6	4.53	Brown grey	95
120	8.2	4.53	Colourless	97
480	8.6	4.53	Colourless	99

Conditions: current, 2.0 A; temperature, ambient; concentration (TBO, 50 mg/l; NaCl, 5 g/l)



Plates 3.9: The change of colour during the electrochemical degradation of toluidine blue O in aqueous sodium chloride

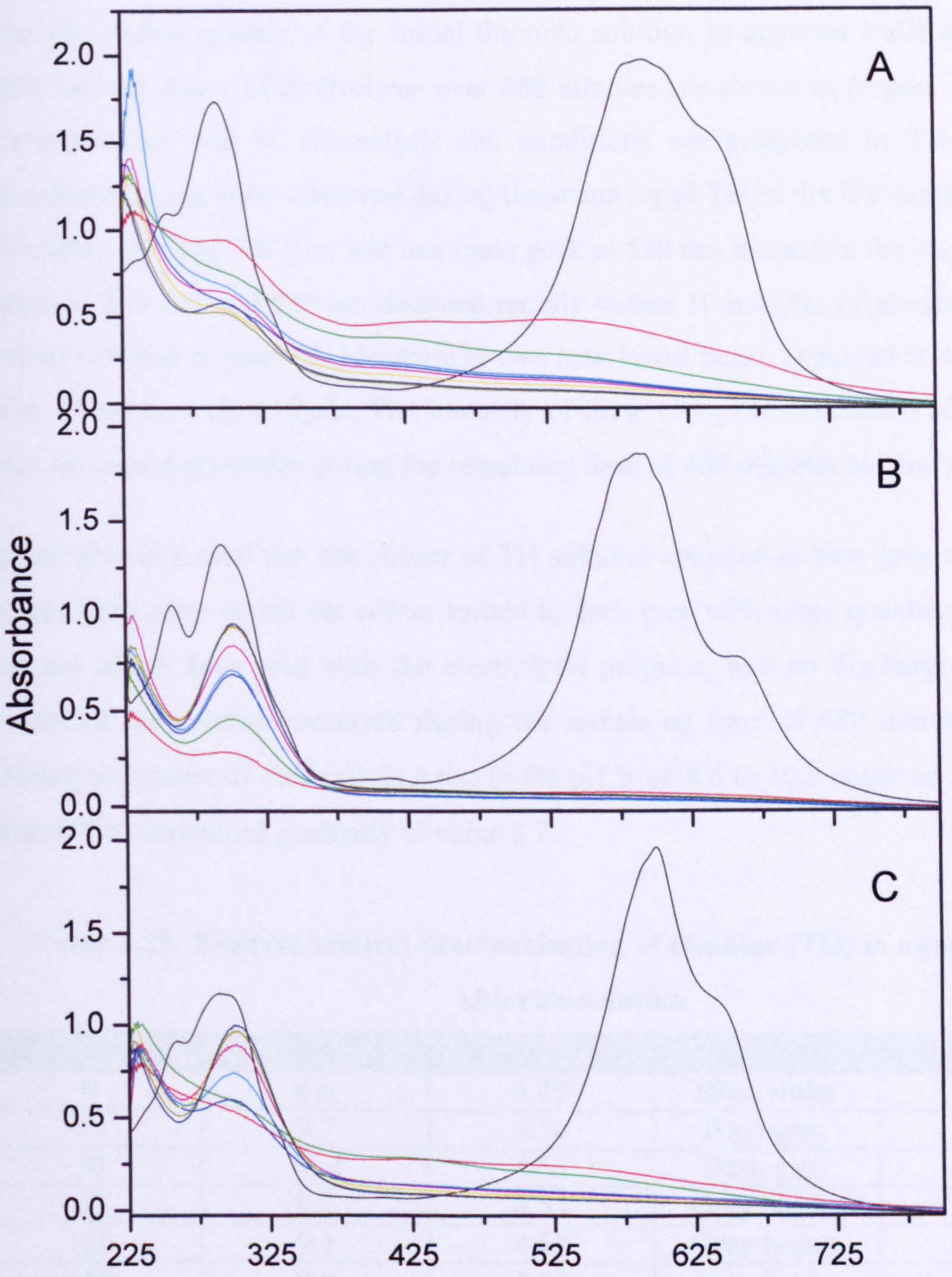


Figure 3.27: UV-Visible spectra showing the electrolytic destruction of A) dimethyl methylene blue B) new methylene blue and C) toluidine blue O in aqueous sodium chloride solution.

Electrolysis time: 0 min____, 30 min____, 60 min____, 120 min____, 180 min____, 240 min ____, 300 min____, 360 min____ and 480 min____

The electrolytic removal of thionine (TH)

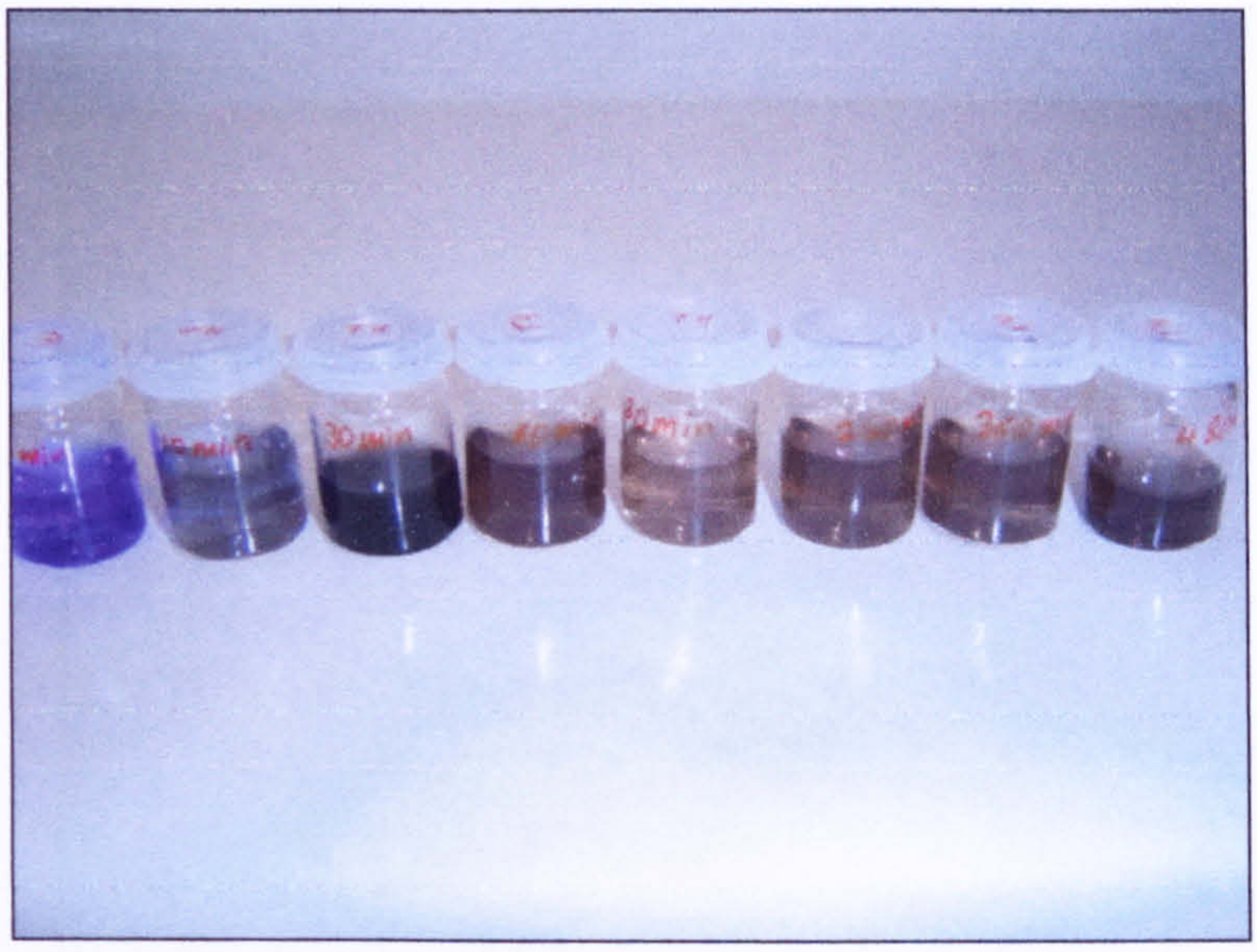
The UV-visible spectra of the initial thionine solution in aqueous NaCl and the changes after various stages of electrolysis over 480 minutes are shown in (Figure 3.28A), and the corresponding data of electrolysis run conditions are presented in Table 3.25. Three absorbance peaks were observed during the scanning of TH in the UV region at 231 (small shoulder), 249 and 301 nm, and one main peak at 589 nm located in the visible region. The peaks at 249 301 and 589 nm declined rapidly within 10 minutes of electrolysis with 91% colour removal is reached. Meanwhile, two new broad peaks appeared at 432 nm, 303 nm after 10 minutes electrolysis. The intensity of these two peaks increased after 120 minutes then decreased gradually during the remaining time of 480 minutes electrolysis.

It was also observed that the colour of TH solution changed to blue grey after 10 minutes electrolysis, after which the colour turned to dark grey with large quantity of grey residue formed which decreased with the electrolysis progress, and no discharge of grey brown colour of the solution occurred during the remaining time of 480 minutes (Plate 3.10). During the course of electrolysis a rise in the pH from 6.6 to 10.2 occurred after 30 minutes, after which decreased gradually to value 8.7.

Table 3.25: Electrochemical decolourisation of thionine (TH) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.6	4.49	Blue violet	0
10	9.7	4.54	Blue grey	83
30	10.2	4.53	Dark grey	83
60	9.2	4.53	Grey brown	84
120	9.4	4.51	Grey brown	85
180	9.0	4.52	Grey brown	86
240	8.2	4.52	Grey brown	89
300	8.5	4.53	Grey brown	89
360	8.7	4.55	Grey brown	90
480	8.7	5.56	Grey brown	91

Conditions: current, 2.0 A; temperature, ambient; concentration (TH) 50 mg/l; NaCl, 5 g/l)

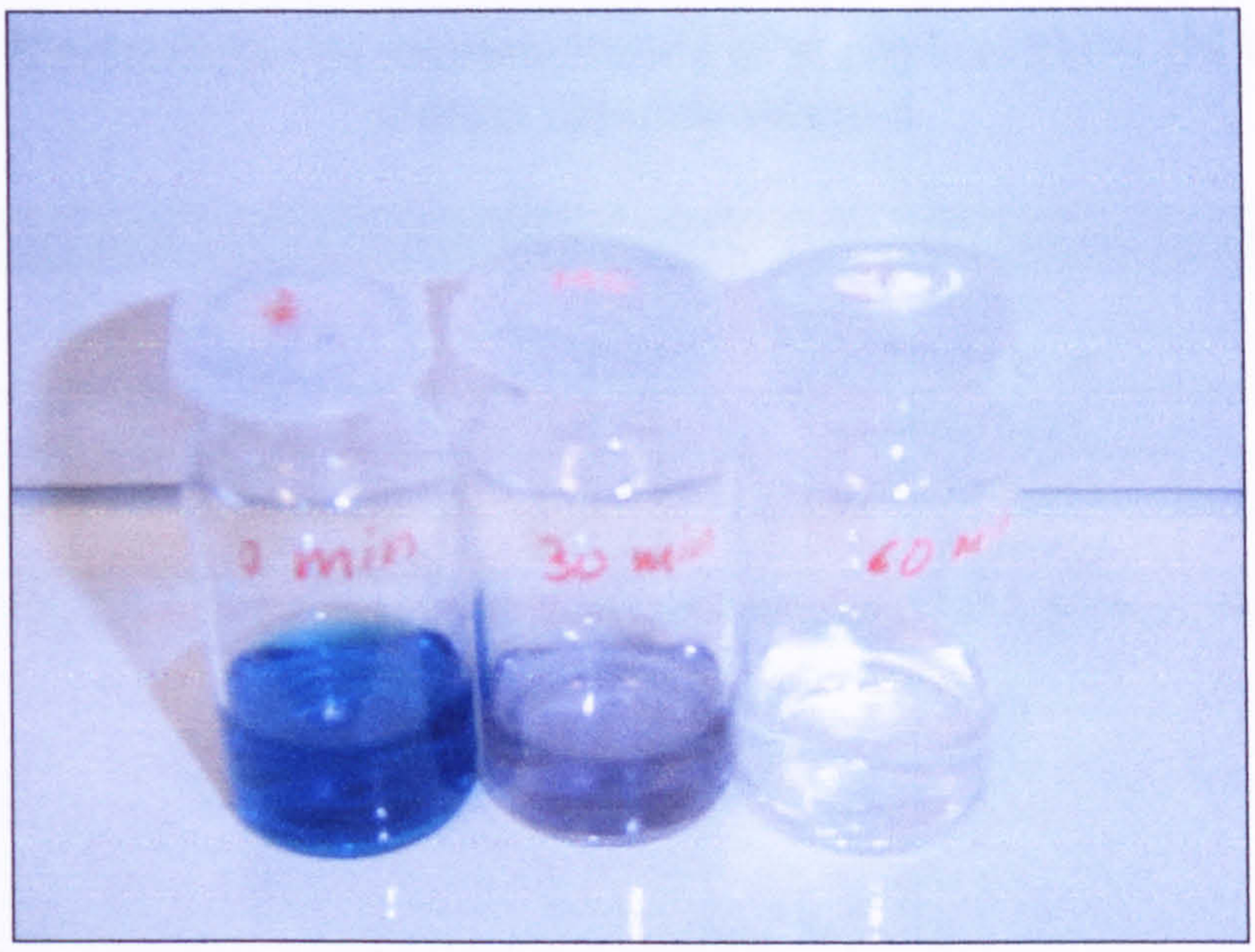


Plates 3.10: The change of colour during the electrochemical degradation of thionine in aqueous sodium chloride

The electrolytic removal of methylene green (MG)

The UV-Visible spectra during the electrolytic destruction of methylene green in aqueous NaCl solution (Figure 3.28B) exhibited absorption peaks at 260 (shoulder), 290 and 334 nm, which located in the UV region. The visible region showed two absorption bands at 454 nm (low intensity) and between (620-668) nm. The latter band split into two peaks at 624 and 662 nm. It can be seen from (Figure 3.28B) that all the peaks decreased dramatically and colour removal (100%) is achieved in 60 minutes (Table 3.26). Meanwhile, a new peak appeared at 303 nm after 120 minutes which increased slightly during the remaining time of electrolysis, indicating formation of new degradation products. The pH value increased from 7.6 to 8.6 during the reaction.

The change of colour during the electrochemical degradation of methylene green in aqueous sodium chloride is shown in Plate 3.11.



Plates 3.11: The change of colour during the electrochemical degradation of methylene green in aqueous sodium chloride

Table 3.26: Electrochemical decolourisation of methylene green (MG), in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.6	4.37	Dark turquoise	0
30	8.0	4.47	Very light grey	99
60	8.6	4.45	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (MG, 50 mg/l; NaCl, 5 g/l)

The electrolytic removal of methylene violet (MV)

The UV/visible spectra of MV are characterized (Figure 3.28C) by one peak in the UV region located at 294 and two peaks in the visible region located at 593 and 627 nm. Although 98% of colour was removed and discharged after 30 minutes, meanwhile, the intensity of the peak at 294 nm increased and shifted to 303 nm, after 30 minutes, indicating the formation of degradation products. A rise in the pH (5.0-9.2) of the solution was observed during the course of electrolysis from acidic to basic (Table 3.27), indicating the formation of basic organic residues.

Table 3.27: Electrochemical decolourisation of methylene violet (MV) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.0	4.33	Blue	0
1	8.3	4.37	Light blue	18
15	9.5	4.44	Pale blue	87
30	9.7	4.49	Colourless	98
60	9.9	4.47	Colourless	99

Conditions: current, 2.0 A; temperature, ambient; concentration (MV, 50 mg/l; NaCl, 5 g/l)

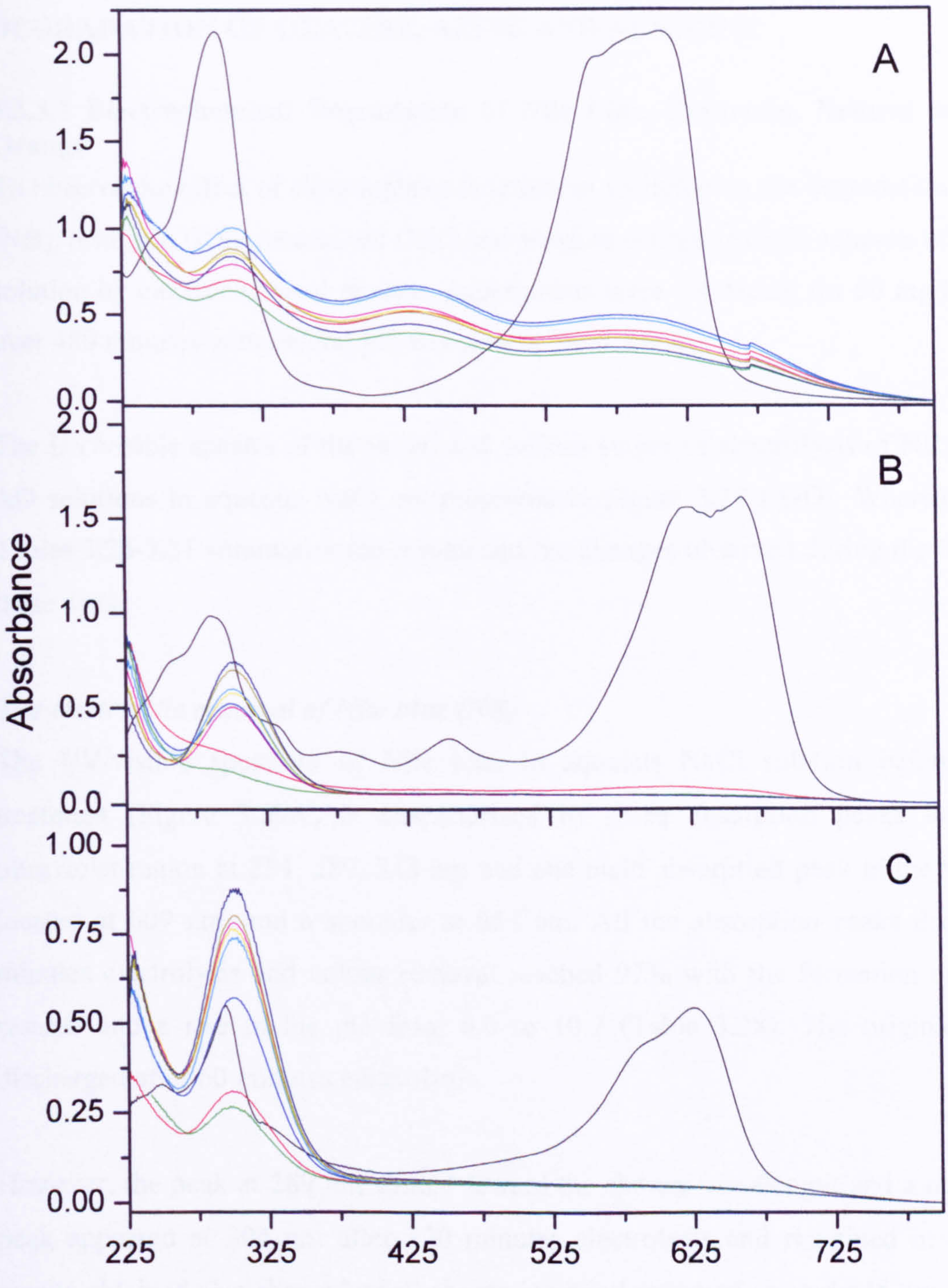


Figure 3.28: UV-Visible spectra showing the electrolytic destruction of A) thionine B) methylene green and C) methylene violet in aqueous NaCl solution.

Electrolysis time: 0 min____, 30 min____, 60 min____, 120 min____, 180 min____, 240 min____, 300 min____, 360 min____ and 480 min____.

3.3.3 EFFECT OF CHROMOPHORE HETEROATOM VARIATION ON THE DEGRADATION OF OXAZINE, AZINE AND ACRIDINE

3.3.3.1 Electrochemical Degradation of Nile Blue, Resorufin, Neutral and Acridine Orange

To observe the effect of chromophore heteroatom variation on the degradation of Nile blue (NB), resorufin (RS), neutral red (NR) and acridine orange (AO) in aqueous of NaCl (5 g/l) solution by electrochemical process, experiments were conducted for 50 mg/l of each dye over 480 minutes with natural pH and current input 2.0 A.

The UV/visible spectra of the initial and various stages of electrolysis of NB, Re, NR and AO solutions in aqueous NaCl are presented in Figure 3.29 (A-D). Whereas the data in Tables 3.28-3.31 summarise the results and the changes observed during the destruction of these dyes.

The electrolytic removal of Nile blue (NB)

The UV/visible spectrum of Nile blue in aqueous NaCl solution before electrolytic treatment (Figure 3.29A) is characterized by three absorption peaks located in the ultraviolet region at 234, 289, 343 nm and one main absorption peak in the visible region located at 609 nm, and a shoulder at 654 nm. All the absorption peaks decreased in 30 minutes electrolysis and colour removal reached 97% with the formation of grey purple residue and a rise in the pH from 8.0 to 10.2 (Table 3.28). The original colour was discharged after 60 minutes electrolysis.

However, the peak at 289 nm shifted toward the shorter wavelength and a new absorption peak appeared at 304 nm after 120 minutes electrolysis and remained in solution. The results obtained also showed small absorption band appeared around 445 nm. These results indicate that degradation products formed and remained in the solution.

Table 3.28: Electrochemical decolourisation of Nile blue (NB) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	8.0	4.35	Blue	0
30	10.2	4.45	Pale pink	97
60	10.0	4.45	Colourless	99
120	10.0	4.41	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (NB, 50 mg/l; NaCl, 5 g/l)

The electrolytic removal of resorufin (RS)

Resorufin in aqueous NaCl solution exhibited two absorption peaks at 248 and 303 nm (shoulder) located in the UV region and two peaks at 548 (shoulder) and 582 nm located in the visible region (Figure 3.29B). These peaks diminished after 30 minutes with only 65% colour removal and finally disappeared completely under 480 minutes of electrolysis with about 100% colour removal. After 30 minutes electrolysis, the pH increased from 8.3 to10.3 (Table 3.29) and the original colour of the solution changed from purplish red to purple (Plate 3.12). A complete removal of resorufin colour was achieved after 60 minutes. However, a hyperchromic effect observed around 300 nm during the 480 minutes electrolysis indicating the formation of new degradation products.

Plates 3.12: The change of colour during the electrochemical degradation of resorufin in aqueous sodium chloride

Table 3.29: Electrochemical decolourisation of resorufin (RS) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	8.3	4.42	Purple-red	0
30	10.3	4.53	Purple	65
60	9.6	4.57	Colourless	99
120	8.7	4.51	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (RS, 50 mg/l; NaCl, 5 g/l)

The electrolytic removal of neutral red (NR)

The UV/visible spectrum of neutral red in aqueous NaCl solution showed only two absorption peaks at 288 and 527 nm (Figure 3.29C). After 30 minutes electrolysis both the peaks decreased rapidly with 96% colour removal achieved. A rise in the pH from slightly acidic 5.7 to basic 10.0 medium occurred after 30 minutes. The scarlet red colour of neutral red turned to pale yellow and a reddish brown precipitate formed at 30 minutes which faded to pale yellow after 60 minutes (Table 3.30). However, degradation products appeared after 120 minutes giving rise to absorption at 300 nm. The intensity of this peak increased during the 480 minutes electrolysis process.

Table 3.30: Electrochemical decolourisation of neutral red (NR) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.7	4.52	Scarlet red	0
30	10.0	4.52	Pale brown	96
60	9.6	4.53	Pale yellow	99
120	8.5	4.55	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (NR, 50 mg/l; NaCl, 5 g/l)

The electrolytic removal of acridine orange (AO)

Two absorbance peaks were observed during the scanning of acridine orange in aqueous NaCl solution. The peak observed in the UV region at 280 nm and the visible peak at 486 nm (Figure 3.29D). A rapid decrease in the intensity of the peak at 486 nm occurred after 30 minutes electrolysis. The peak at 280 nm gradually decreased and shifted to the shorter wavelength during the electrolysis (Figure 3.36D).

The orange colour of AO discharged in 60 minutes. The pH increased from a value of 5.4 to a value of 8.7 after 30 minutes then varied slightly during the remaining time of electrolysis process (Table 3.31). Although about 98% of colour removal achieved in less than 30 minutes, however, new absorption band appeared at 294 nm after 120 minutes, indicating the formation of intermediate degradation products.

Table 3.31: Electrochemical decolourisation of acridine orange (AO) in aqueous sodium chloride solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.4	4.28	Orange	0
30	8.7	4.55	Pale yellow	98
60	8.2	4.52	Colourless	99
120	8.0	4.75	Colourless	99

Conditions: current, 2.0 A; temperature, ambient; concentration (AO, 50 mg/l; NaCl, 5 g/l)

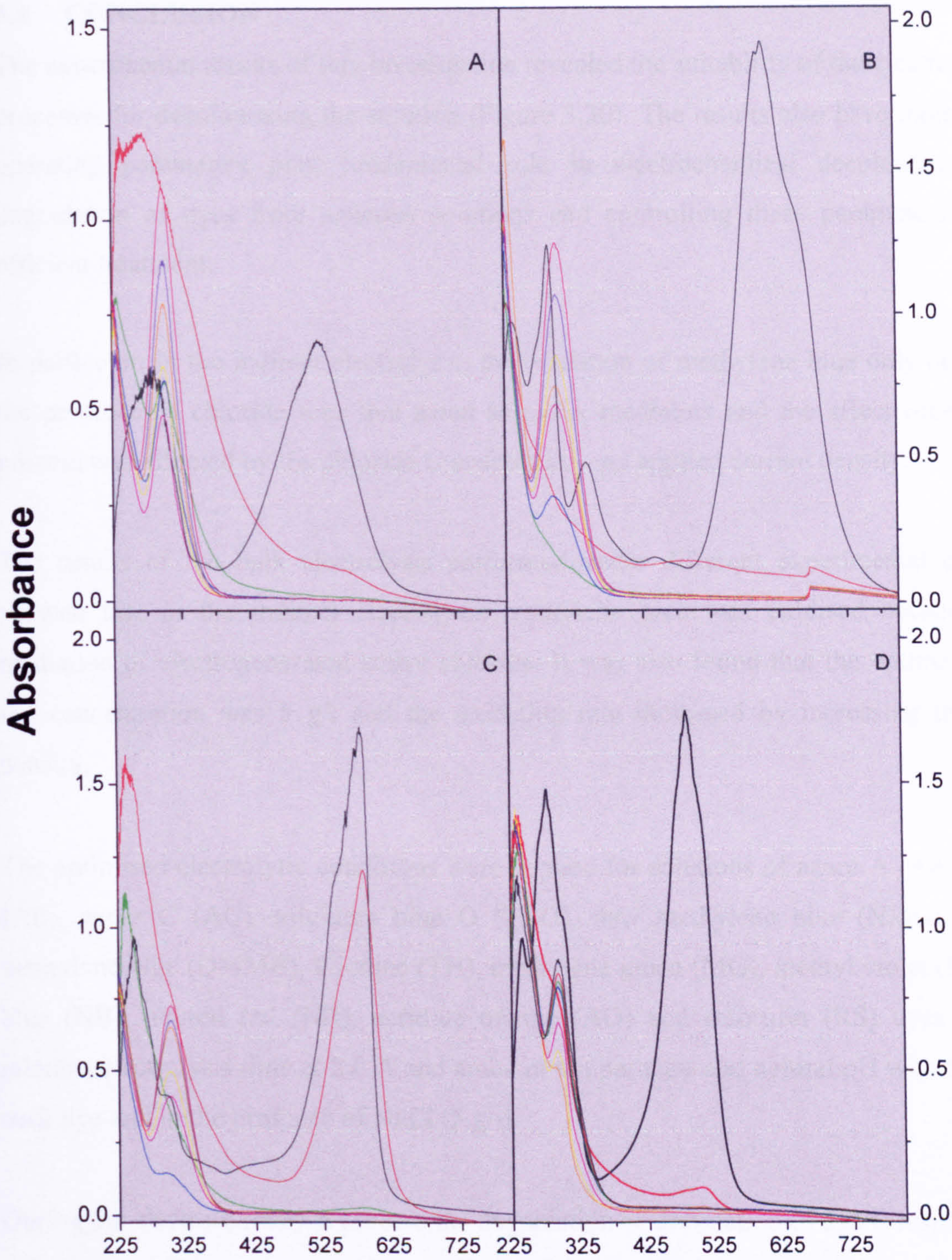


Figure 3.29: UV-Visible spectra showing the electrolytic destruction of A) resorufin, B) Nile blue C) neutral red and D) acridine in aqueous NaCl solution.

Electrolysis time: 0 min____, 30 min____, 60 min____, 120 min____, 180 min____, 240 min____, 300 min____, 360 min____ and 480 min____.

3.4 CONCLUSION

The experimental results of this investigation revealed the suitability of the electrochemical processes for decolourising the solution (Figure 3.30). The results also have indicated that operating parameters play fundamental role in electrochemical decolourisation and degradation of dyes from aqueous solutions and controlling these parameters leads to efficient treatment.

In particular, in the indirect electrolysis, the oxidation of methylene blue only occurred in the presence of chloride ions that acted as redox mediators and the effectiveness of the process was affected by the chloride concentration and applied current density.

The results of the bulk electrolysis performed under different experimental conditions showed that in the indirect electrolysis methylene blue was oxidised because of the mediation of electrogenerated active chlorine. It was also found that the optimal chloride ion concentration was 5 g/l and the oxidation rate increased by increasing the current density.

The optimised electrolytic conditions were applied for solutions of azure A (AA), azure B (AB), azure C (AC), toluidine blue O (TBO), new methylene blue (NMB), dimethyl methylene blue (DMMB), thionine (TH), methylene green (MG), methyl violet (MV), Nile blue (NB), neutral red (NR), acridine orange (AO) and resorufin (RS) dyes over 480 minutes electrolysis time at 2.0 A and ambient temperature and natural pH with 50 mg/l of each dye and in the presence of NaCl (5 g/l).

During the electro-oxidation process the degradation or destruction of dye is responsible for colour removal from aqueous dye solutions. The data obtained suggest that a treatment of 60 minutes was found to be the optimum value for the complete removal of dyes from aqueous solutions. The UV-Visible spectra showed that the electro-oxidation of dyes process proceeds through the formation of different intermediate species before mineralization. Most of these intermediate species are also destroyed during the electro-oxidation process. However, there are some evidences that the use of the electrolytic

process is unable to remove some of the organic degradation products from the aqueous synthetic dye solutions.

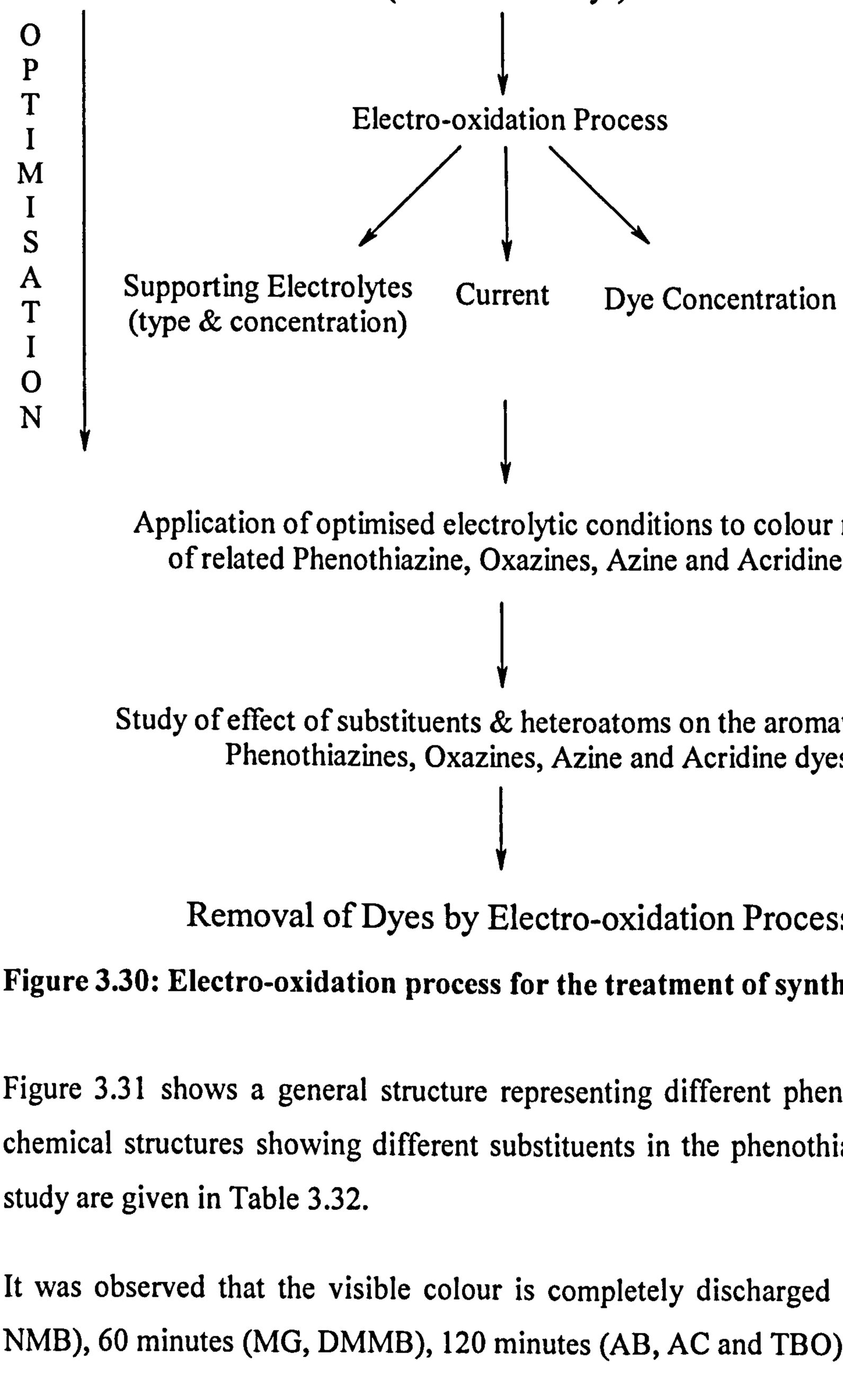


Figure 3.30: Electro-oxidation process for the treatment of synthetic textile dyes

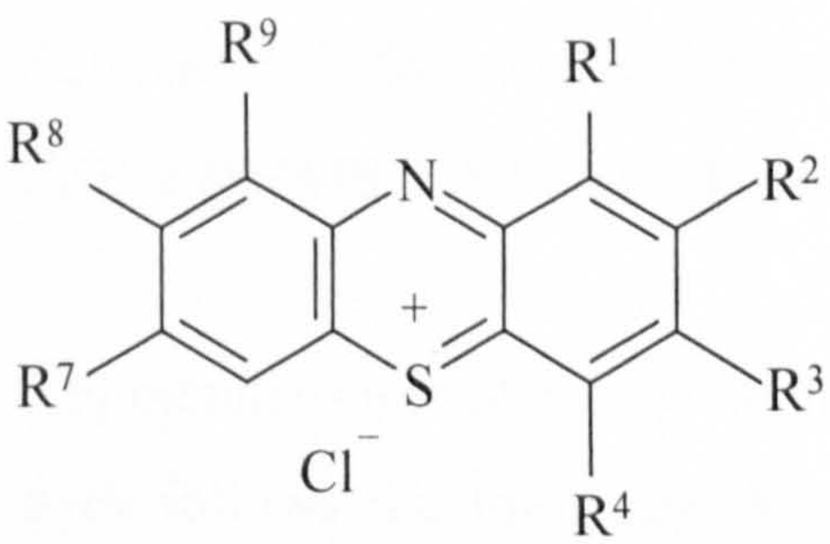
Figure 3.31 shows a general structure representing different phenothiazine dyes and the chemical structures showing different substituents in the phenothiazine dyes used in this study are given in Table 3.32.

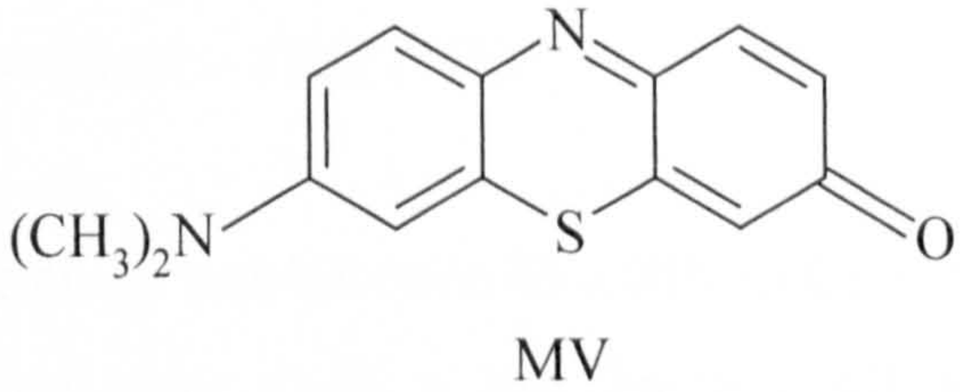
It was observed that the visible colour is completely discharged after 30 minutes (MV, NMB), 60 minutes (MG, DMMB), 120 minutes (AB, AC and TBO) and 180 minutes (AA).

No complete discharge of the original visual colour occurred in the cases of TH even after 480 minutes of electrolysis.

The results indicated that the intensities of all the peaks in the visible region of all the investigated dyes decreased within 30 minutes, however, a new peak appeared at around 303 nm and its intensity increased as the electrolytic process progressed.

The formation of large amount of precipitate in TH was observed which did not disappear with the progress of the electrolysis process. Smaller quantities of precipitates were observed at some stages of the electrolysis process in the cases of AA, AB, AC, NMB, DMMB and TBO. In contrast, no residue was observed during the electrolysis process of MG and MV.





MV

Figure 3.31 Chemical structures of the phenothiazine dyes used in this study

Table 3.32 Chemical structures showing different substituents in the phenothiazine dyes used in this study

Dye name	R^1	R^2	R^3	R^4	R^7	R^8	R^9
(MB)	H	H	NMe_2	H	NMe_2	H	H
(MB-$ZnCl_2$)	H	H	NMe_2	H	NMe_2	H	H
Azure A (AA)	H	H	NH_2	H	NMe_2	H	H
Azure B (AB)	H	H	NHMe	H	NMe_2	H	H
Azure C (AC)	H	H	NH_2	H	NHMe	H	H
Thionine (TH)	H	H	NH_2	H	NH_2	H	H
Methylene Green (MG)	H	H	NMe_2	NO_2	NMe_2	H	H
Toluidine (TBO)	H	Me	NH_2	H	NMe_2	H	H
New Methlene Blue (NMB)	H	Me	NHEt	H	NHEt	Me	H
Dimethyl Methylene Blue (DMMB)	Me	H	NMe_2	H	NMe_2	H	Me
Methylene Violet (MV)	H	H	O	H	NMe_2	H	H

Table 3.33 Comparison summary of percentage colour removal of phenothiazine dyes

Time (min)	Colour removal %										
	MB	MB $ZnCl_2$	AA	AB	AC	NMB	DMMB	TBO	TH	MG	MV
30	97	98	91	96	94	93	95	91	83	99	98
60	98	99	98	97	97	96	98	95	84	100	99
120	98	100	99	100	100	98	100	97	85	100	99

The data in Table 3.33 show the percentage removal of different dyes achieved after 30, 60 and 120 minutes. These results indicated that after:

- 30 minutes electrolysis the colour removal was between 83 to 99% and for different dyes follows the following decreasing order: MG > (MV ≅ MB $ZnCl_2$) > MB > AB > DMMB > AC > NMB > (AA ≅ TBO) > TH

- 60 minutes electrolysis the colour removal was between 84 to 100% and for different dyes follows the following decreasing order: MG > (MV ≅ MB $ZnCl_2$) > (MB ≅ DMMB ≅ AA) > (AB ≅ AC) > NMB > TBO > TH

- 120 minutes electrolysis the colour removal was between 85-100% and for different dyes follows the following decreasing order: (MG ≅ MB $ZnCl_2$ ≅ AB ≅ AC ≅ DMMB) > (AA ≅ MV) > (MB ≅ NMB) > TBO > TH

The lowest decolourisation was achieved in the case of thionine (85% after 120 minutes). A large amount of black residue and the solution remained grey brown colour over 480 minutes electrolysis. Table 3.33 shows that TH has two primary amino ($-NH_2$) groups at positions 3 and 7. These strongly activating electron donating groups (EDG) makes TH more susceptible to attack by the free radical and form substituted intermediates in the first stage of electrolysis before the destruction of the chromophore. The presence of strongly activating primary amino groups ($-NH_2$) substituent probably favours the attack of oxidizing agents, and the production of polymeric products.

During 30 minutes electrolysis AA and TBO showed 91% colour removal. Both AA and TBO have one NH_2 group at position 3 and one $-N(CH_3)_2$ group at position 7. In addition

TBO has a $-CH_3$ group at position 2. These groups are electron donating groups (EDG) - they activate the aromatic ring to attack by radicals and radical ions by increasing the electron density on the ring through inductive effect ($-CH_3$) and a resonance donating effect ($-NH_2$, $-N(CH_3)_2$). They have fewer positions available for polymerisation than TH.

The data in Tables 3.32 and 3.33 show that AC reached 94%, 97% and 100% degradation after 30, 60 and 120 minutes. AC has two EDG: one NH_2 group at position 3 and one $-NHCH_3$ group at position 7.

During 30 and 60 minutes electrolysis both AB and NMB showed 96% and 97% (AB) and 93% and 96% (NMB) colour removal. AB has one $-NHCH_3$ group at position 3 and one $-N(CH_3)_2$ group at position 7. NMB has two $-CH_3$ groups at positions 2 and 8, and two $-NHCH_2CH_3$ groups at positions 3 and 7 (Tables 3.32 and 3.33).

The results in Table 3.33 showed that the colour removal obtained during 30, 60 and 120 minutes are 99%, 100% and 100% for MG, 98%, 99% and 99% for MV and 95%, 98% and 100% for DMMB.

It appears that the presence of EDG makes the dye molecule more susceptible to the attack by the oxidising species ultimately causing degradation.

DMMB has two $-N(CH_3)_2$ groups at positions 3 and 7, and 2 CH_3 groups at positions 1 and 9, whereas methylene green (MG) is formally the 4-nitro derivative of MB. A related molecular type here is methylene violet (MV). This is a neutral species having a quinoid nucleus in place of the phenothiazine cation. Indeed, alkaline hydrolysis of MB yields MV as reported in literature [75].

From the discussion above it could be concluded that the presence of electron withdrawing (EWG) nitro group, ($-NO_2$) at position 4 in MG and carbonyl group (–C=O) in MV increases the degradation of the phenothiazine chromophore. This behaviour could be explained by these dyes having substituents with pi bonds to electronegative atoms (*e.g.* -

C=O in MV and $-NO_2$ in MG). They deactivate the aromatic ring to attack by radicals and electrophiles but increase the susceptibility to attack by nucleophiles, eg OH^- by decreasing the electron density on the ring through a resonance withdrawing effect.

It was observed that dyes with more ($-CH_3$) substituents on the arylamino groups are easy to degrade (i.e. tertiary amino > secondary amino > primary amino) as can be seen in Table 3.35 that each of MB, MG, and DMMB has 4 ($-CH_3$) substituents on the arylamino groups > NMB with 2 ($-CH_2CH_3$) > AB with 3 ($-CH_3$) > TBO, AA with 2 ($-CH_3$) > none in case of TH (with the exception of MV and AC).

The results in Tables 3.32 and 3.33 also showed that the presence/and positions of alkyl substituent (*e.g.* $-CH_3$). Two $-CH_3$ substituents at positions 1 & 9 in DMMB, two at positions 2 & 8 in NMB and one at position 2 in TBO has also influenced the rate of degradation of these three phenothiazines compared to the parent MB, as DMMB is easier to degrade than NMB and TBO. This behaviour could be attributed to the electronic effect (EDG) of ($-CH_3$) which activates the aromatic ring by increasing the electron density on the ring through an inductive donating effect. This effect allows alkyl groups to stabilise the phenothiazine chromophoric carbocations probably more when the ($-CH_3$) groups are in positions 2 & 8 as in NMB making it difficult to degrade compared to positions 1 & 9 in case of DMMB which may allow susceptible sites for easy degradation of the DMMB chromophore. In addition the steric hindrance effect of the two ($-CH_2CH_3$) groups on the arylamine at positions 3 & 7 which are on *ortho* positions with the two auxo ($-CH_3$) groups at positions 2 & 8 may also affect the degradation rate.

During the electrolysis process, it was observed that in general the pH value goes up to a value of 9-10 at the beginning of electrolysis, then decreases slightly near the end of electrolysis process. It was reported in literature that during the course of electrolysis pH is influenced by cathodic and anodic process and by the sequence of the reactions of chlorine in water. For example, the elementary chlorine produced on the anode lowers the pH value.

On the contrary, an increase in pH is caused by reduction of hydrogen ion on the cathode according to the reaction:

$$2\,H_2O + 2\,é \rightarrow H_2 + 2\,OH^-$$

The substitution reaction of chlorine with organic compounds results in pH increase.

$$2\,H_2O \Leftrightarrow O_2 + 4\,H^+ + 4\,e^-$$

$$\text{or } 2\,Cl^- \Leftrightarrow Cl_2 + 2\,e^-$$

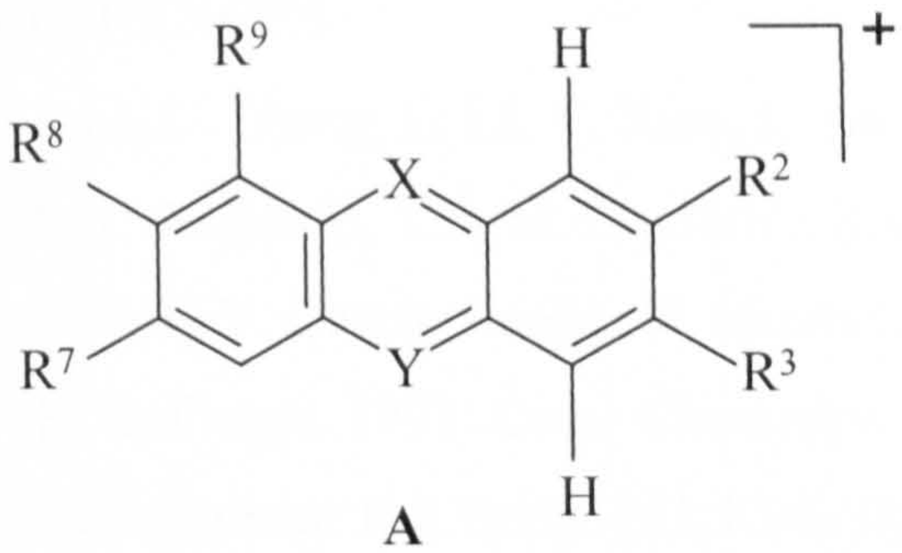
The UV region showed the appearance of absorbance with different intensity at around 303 nm which coincide respectively with the relevant absorptions of the MV and phenothiazinium compounds used. The results show that altering the structure of the phenothiazinium chromophore can lead to improved electrochemical degradation considering the time of electrolysis duration.

A similar effect was found for the azine, acridine and oxazine dyes as can be seen from Table 3.34 and 3.35.

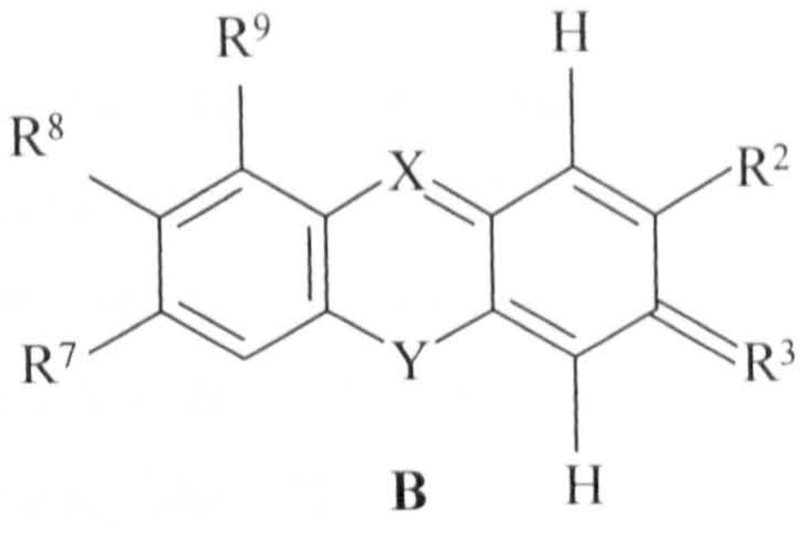
Substituents with C=C (-aryl) are also electron donating groups - they activate the aromatic ring by a resonance donating effect. This is a similar effect to that for ($-NH_2$) substituent except that the electrons are from a bonded pair not a lone pair.

The data in Table 3.34 show that the colour removal achieved within:

- 30 minutes electrolysis ranges from 65-98% and follows the following decreasing order: (AO ≅ MB $ZnCl_2$) > (NB ≅ MB) > NR > RS
- 60 minutes electrolysis ranges from 98-99% and follows the following decreasing order: (NB ≅ NR) > (AO ≅ RS) > MB
- 120 minutes electrolysis ranges from 98-100% and follows the following decreasing order: (MB $ZnCl_2$ ≅ NR ≅ NB) > (RS ≅ AO) > MB



A



B

Table 3.34 Chemical structure showing different substituents and heteroatoms in the azine, acridine and oxazine dyes used in this study

Dye name	Formula	X	Y	R^3	R^7	R^8	R^9
Methylene Blue (MB)	A	N	S	NMe_2	NMe_2	H	H
Acridine Orange (AO)	A	C	N	NMe_2	NMe_2	H	H
Neutral Red (NR)	B	N	NH	$^+NMe_2$	NH_2	Me	H
Nile Blue (NB)	B	N	O	$^+NEt_2$	NH_2	C_4H_4	
Resorufin (Re)	B	N	O	O	NaO	H	H

Table 3.35 Comparison summary of percentage colour removal of azine, acridine and oxazine dyes using NaCl

Time (min)	Colour removal %					
	MB	MB $ZnCl_2$	AO	NR	RS	NB
30	97	98	98	96	65	97
60	98	99	99	99	99	99
120	98	100	99	100	99	100

3.5 REFERENCES

1. J. Li, L. Zheng, L. Li, Y. Xian, L. Jin, *J. Hazard. Mater.*, 2007, **B139**, 72-78.
2. L.S. Andrade, L.A.M. Ruotolo, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, J. Iniesta, V. García-Garcia, V. Montiel, *Chemosphere*, 2007, **66**, 2035-2043.
3. H. Zollinger, 1991. Color Chemistry, 2nd ed. V.C.H. Publisher, New York.
4. D. Rajkumar, B.J. Song, J.G. Kim, *Dyes Pigm.*, 2007, **72**, 1-7.
5. D. Rajkumar and J.G. Kim, *J. Hazard. Mater.*, 2006, **136**, 203-212.
6. E. Chatzisymeon, N.P. Xekoukoulotakis, A. Coz, N. Kalogerakis, D. Mantzavinos, *J. Hazard. Mater.*, 2006, **137**, 998-1007.
7. C. Namasivayam and S. Sumithra, *J. Environ. Manage.*, 2005, **74**, 207-215
8. D.P. Oliveira, P.A. Carneiro, M.K. Sakagami, M.V.B. Zanoni, G.A. Umbuzeiro, *Mut. Res.*, 2007, **626**, 135-142.
9. D.P. Das, N. Baliarsingh, K.M. Parida, *J. Molecular Catal. A: Chem.*, 2007, **261**, 254-261.
10. M.P.E. González, V. Hernández-Montoya, *Biochem. Eng. J.*, 2007, **36**, 230-238.
11. E.A. El-Sharkawy, A. M. Soliman, K.M. Al-Amer, *J. Colloid Interface Sci.*, 2007, **310**, 498-508
12. F.A. Pavan, Y. Gushikem, A.C. Mazzocato, S.L.P. Dias, E.C. Lima, *Dyes Pigm.*, 2007, **72**, 256-266.
13. R. Gong, Y. Jin, J. Chen, Y. Hu, J. Sun, *Dyes Pigm.*, 2007, **73**, 332-337.
14. S.B. Bukallah, M.A. Rauf, S.S. AlAli, *Dyes Pigm.*, 2007, **74**, 85-87.
15. V.S. Ferreira-Leitão, M.E.A. de Carvalho, E.P.S. Bon, *Dyes Pigm.*, 2007, **74**, 230-236.
16. M.C. Ncibi, B. Mahjoub, M. Seffen, *J. Hazard. Mater.*, 2007, **B139**, 280-285.
17. Y. Nacèra, B. Aicha, *Chem. Eng. J.*, 2006, **119**, 121-125.
18. A. Aguiar, A. Ferraz, *Chemosphere*, 2007, **66**, 947-954.
19. K. Dutta, S. Mukhopadhyay, S. Bhattacharjee, B. Chaudhuri, *J. Hazard. Mater.*, 2001, **B84**, 57-71.
20. W. Zhang, Z. Yang, X. Wang, Y. Zhang, X. Wen, S. Yang, *Catal. Commun.*, 2006, **7**, 408-412.

21. S. Mozia, M. Toyoda, M. Inagaki, B. Tryba, A.W. Morawski, *J. Hazard. Mater.*, 2007, **140**, 369-375.
22. X. Lin, F. Huang, W. Wang, J. Shi, *Scripta Materialia*, 2007, **56**, 189-192.
23. W.K. Chang, K.K. Rao, H.C. Kuo, J.F. Cai, M.S. Wong, *Appl. Catal. A: General*, 2007, **321**, 1-6.
24. L.L. Garza-Tovar, L.M. Torres-Martínez, D. Bernal Rodríguez, R. Gómez, G. del Angel, *J. Mol. Catal. A: Chem.*, 2006, **247**, 283-290
25. M.M. Mohamed, M.M. Al-Esaimi, *J. Mol. Catal. A: Chem.*, 2006, **25**, 53-61.
26. G. Sivalingam, K. Nagaveni, M.S. Hegde, G. Madras, *Appl. Catal. B: Environ.*, 2003, **45**, 23-38.
27. T. Zhang, T. Oyama, A. Aoshima, H. Hidaka, J. Zhao, N. Serpone, *J. Photochem. Photobiol. A: Chem.*, 2001, **140**, 163-172.
28. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Hermann, *Appl. Catal. B: Environmental*, 2001, **31**,145-157.
29. X. Zhao, Y. Wua, W. Yao, Y. Zhu, *Thin Solid Films*, 2007, **515**, 4753-4757.
30. N. Shimizu, C. Ogino, M.F. Dadjour, T. Murata, *Ultrason. Sonochem.*, 2007, **14**, 184-190.
31. P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Sáez, *Chemosphere*, 2007, **67**, 832-838.
32. B.K. Körbahti, N. Aktas, A. Tanyolac, *J. Hazard. Mater.*, 2007, **148**, 83-90.
33. M.A.Q. Alfaro, S. Ferro, C.A. Martínez-Huitle, Y.M. Vong, *J. Braz. Chem. Soc.*, 2006, **17**, 227-236.
34. A. Kraft M. Stadelmann, M. Blaschke, *J. Hazard. Mater.*, 2003, **B103**, 247-261.
35. E. Brillas, E. Mur, R. Sauleda, L. Sànchez, J. Peral, X. Domènech, J. Casado, *Appl. Catal. B: Environ.*, 1998, **16**, 31-42.
36. N. Mohan, N. Balasubramanian, C.A. Basha, *J. Hazard. Mater.*, 2007, **147**, 644-651.
37. J.P. Lorimer, T.J. Mason, M. Plattes, S.S. Phull, D.J. Walton, *Pure Appl. Chem.*, 2001, **73**, 1957-1968.
38. T.-C. An, X.-H. Zhu, Y. Xiong, *Chemosphere*, 2002, **46**, 897-903.
39. M. Muthukumar, M.T. Karuppiah, G.B. Raju, *Sep. Purif. Technol.*, 2007, **55**, 198-205.

40. C. Cameselle, M. Pazos, M. A. Sanromán, *Chemosphere*, 2005, **60**, 1080-1086.
41. H.S. Awad, N. Abo Galwa, *Chemosphere*, 2005, **61**, 1327-1335.
42. A. Fernandes, A. Morao, M. Magrinho, A. Lopes, I. Goncalves, *Dyes Pigm.*, 2004, **61**, 287-296.
43. S.B. Jonnalagadda, S. Nadupalli, *Talanta*, 2004, **64**, 18-22.
44. G. Marconi, M. Vilela, R. Quintana, M. Diradourián, E. Young, C. Sueldo, *Fertility and Sterility*, 2004, **82**, 1700-1704.
45. M. Wainwright, *Dyes Pigm.*, ., 2008, **76**, 582-589.
46. M. Wainwright, *Dyes Pigm.*, 2007, **73**, 7-12.
47. M. Wainwright, H. Mohr, W.H. Walker, *J. Photochem. Photobiol. B: Biol.*, 2007, **86**, 45-58.
48. M. Wainwright, M.N. Byrne, M.A. Gattrell, *J. Photochem. Photobiol. B: Biol.*, 2006, **84**, 227-230.
49. M. Wainwright, *Photodiagnosis and Photodynamic Therapy*, 2005, **2**, 263-272.
50. R.A. Floyd, J.E. Schneider, Jr., D.P. Dittmer, *Antiviral Research*, 2004, **61**, 141-151.
51. E.N. Abrahart, Dyes and their Intermediates, 1977, Edward Arnold Publishers Ltd., London, UK.
52. T.S. Ahmed, *The J. Laryngology and Otology*, 2006, **120**, 708-709.
53. K.K. Bach, F.W. Lindsay, L.S. Berg, R.S. Howard, *Anesth. Analg.*, 2004, **99**, 1573-1574.
54. A. M. Faouzi, B. Nasr, G. Abdellatif, *Dyes Pigm.*, 2007, **73**, 86-89.
55. V. López-Grimau, M.C. Gutiérrez, *Chemosphere*, 2006, **62**, 106-112.
56. T. Bechtold, A. Turcanu, W. Schrott, *Diamond & Related Materials*, 2006, **15**, 1513–1519.
57. D. Dogan and H. Türkdemir, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 916-923.
58. M. Panizza, A. Barbucci, R. Ricotti, G. Cerisola, *Sep. Purif. Technol.*, 2007, **54**, 382–387.
59. J.D. Donaldson, S.M. Grimes, N.G. Yasri, B. Wheals, J. Parrick and W.E. Errington, *J. Chem. Technol. Biotechnol.*, 2002, **77**, 756-760.
60. M. Wainwright, R.M. Giddens, *Dyes Pigm.*, 2003, **57**, 245-257.

61. D.R. Waring and G. Hallas, The Chemistry and Application of Dyes, 1990, Plenum Press, New York, USA.
62. Sigma Aldrich Material Safety Data Sheet, Dorset, UK.
63. L.T. Wang-Bennett, D.J. Liebl, G.N. Bennett, Brain Res., 1990, **534**, 122-128.
64. www.hoslink.com, Hazardous dyes (04/08/2003).
65. www.promega.com/msds/us%5Cf212.htm, F212 methylene blue stain (18/10/2002).
66. L. J. Hardie, J. R. Olliver, C. P. Wild, S. Dexter, P. Sahay, *Gastroenterology*, 2004, **126**, 623–634.
67. Sigma Aldrich Material Safety Data Sheet, Gillingham, UK.
68. http://physchem.ox.ac.uk/MSDS/NE/neutral_red.html, safety data for neutral red (04/08/2003).
69. www.hawaii.edu/ehso/bio/BSM_part01.htm.
70. M. Balabanova, L. Popova, R. Tchipeva, *Clinics in Dermatology*, 2003, **21**, 2-6.
71. N. Yasri, PhD Thesis, 2000, Centre for Environmental Research, Brunel University, UK.
72. N. Goswami, PhD Thesis, 2002, Centre for Environmental Research, Brunel University, UK.
73. K. Scott, Electrochemical Processes for Clean Technology, 1995, Royal Society of Chemistry, London, UK.
74. A. Reife and C.M. Freeman, Environmental Chemistry of Dyes and Pigments; 1996, Wiley-Interscience, John Wiley & Sons, New York, USA.
75. K. Fukatsu and S. Kokot, *Textile Res. J.*, 2000, **70**, 340-346.

CHAPTER 4

DECOLOURIZATION AND DEGRADATION OF SYNTHETIC FOOD DYES

4.1 INTRODUCTION

4.1.1 Food Colours in History

Food additives are substances added intentionally to food to preserve flavour or improve its taste and appearance and to promote sale [1-3]. The addition of colourants to foods is thought to have occurred in Egyptian cities, where candy makers around 1500 BC added natural extracts and wine to improve the products appearance. Up to the middle of the 19th century ingredients, such as the spice, saffron, from the area local to the production units were added for decorative effects to certain foodstuffs [4-6].

Following the industrial revolution both the food industry and 'processed food' developed rapidly. The addition of colour, via mineral and metal based compounds, was used to disguise low quality and adulterated foods [1], some more lurid examples being the use of red lead (Pb_3O_4) and vermillion (HgS) to colour cheese and confectionery and the application of copper arsenate to recolour used tea leaves for resale. Copper arsenate also caused two deaths when used to colour a dessert in 1860 [4].

Toxic chemicals were used to tint certain candies and pickles. Historical records show that injuries, even deaths, resulted from tainted colourants. In 1856 the first synthetic colour (mauvine), was developed by Sir William Henry Perkin and, by the turn of the century, unmonitored colour additives had spread through the USA and Europe in all sorts of popular foods, including ketchup, mustard, jellies, and wine [4, 7]. Sellers at the time offered more than 80 artificial colouring agents, some intended for dyeing textiles, not foods. Many colour additives had never been tested for toxicity or other adverse effects [4].

As the 1900s began, the bulk of chemically synthesised colours were derived from aniline, which is toxic. Originally, these colours were dubbed 'coal-tar' colours because the starting materials were obtained from bituminous coal [4].

Although colours from plant, animal and mineral sources, had been used in earlier times, because they were the only colouring agents available, which remained in use until early in 20th century, manufacturers had strong economic incentives to phase them out. Chemically

synthesised colours simply were easier to produce, less expensive, superior in colouring properties [3] and only tiny amounts were needed [4, 7]. They blended easily and didn't impart unwanted flavours to foods. But as their use grew, so did safety concerns [8].

This led to numerous regulations [5] throughout the world. For example, the USA reduced the permitted list of synthetic colours to seven from the 700 being used! [4]. However 'adulteration' continued for many years and this, together with more recent adverse press comments on food colours and health, has continued to contribute to the consumers concern about colour addition to our foodstuffs [1, 4].

4.1.2 Purpose of Food Colouring

Colour variation in foods throughout season and the effects of processing and storage often make colour addition commercially advantageous to maintain the colour expected or preferred by the consumer [6, 9]. Some of the primary reasons include:

- Offsetting colour loss due to the effect of light, air, extremes of temperature, moisture, and storage conditions.
- Masking natural variations in colour.
- Enhancing naturally occurring colours.
- Providing identity to foods.
- Protecting flavours and vitamins from damage by light.
- Decorating purposes such as in cake icing.

Synthetic colours in food products are predominantly azo and triarylmethane dyes. These are mostly acidic or anionic dyes containing carboxylic acids, sulphonic acid or hydroxyl groups [10].

4.2 AZO DYES

Azo compounds are by far the most widely used synthetic organic colourants (60–70%) [11-13] and more than 2000 of such substances are listed in the colour index (CI) [14]. Their chromophoric system consists of azo groups (Ar–N=N–) in association with auxochromes (amino, chloro, hydroxy, methyl, nitro and sulphonate groups). Azo groups do not occur naturally [13]. In theory, azo dyes can supply a complete rainbow of colours,

but yellow/red dyes are more common than blue/brown dyes [13]. It has been estimated that about 50,000 tons of dye are discharged from dyeing and colouration industries every year [11].

4.2.1 Uses of Aromatic Azo Compounds

4.2.1.1 Azo Compounds as Dyes and Pigments

Aromatic azo compounds have intense colours due to the extension of the delocalised aromatic π-electron system made possible by the presence of the azo group. Azo compounds are widely used as dyes and pigments [15-18]. Today more than 2000 different azo dyes are currently being used in the industries such as textiles, leather, plastics, cosmetics and food for the dyeing of various materials [19].

4.2.1.2 Application in Analytical Chemistry

Another area of application of aromatic azo compounds is analytical chemistry where some of these compounds are used as indicators in pH, redox or complexometric titrations [20]. In addition to titrations, direct and indirect determinations of transition metal ions in different matrices have also been presented utilising electroanalytical techniques such as polarography [21] and voltammetry [20, 22-24].

4.2.1.3 Pharmaceuticals

Azo compounds are also used in the pharmaceutical industry [20] as antibacterial medicine in treatment of colon infections [20], and in treatment of rheumatoid arthrithtis and ulcerative colitis [20]. Other uses of azo compound includes preparations of medicinal capsules [25, 26], and many other medications including Berocca, Polaramine, Ventolin syrup [25, 27].

4.3 TRIPHENYLMETHANE DYES

Triphenylmethane dyes form a very important class of commercial dyes. They are among the first of the synthetic dyes to be developed and still find applications in many fields. These dyes are renowned for their outstanding intensity of colour, their brilliant shades of red, blue, and green, and low light fastness on many substrates. These features enable the

uses of triphenylmethane dyes to be divided into two categories: namely (i) where low light fastness is not a problem and intensity of colour is advantageous and (ii) where low light fastness is of interest [28].

Triphenylmethane dyes are used chiefly in copying paper, in hectography and printing inks, and in textile applications [29], and in medicine, histology and cytology as a stain [30]. Tables 4.4 and 4.5 show some applications of azo and triphenylmethane dyes.

4.4 REGULATION

Food colourings are tested for safety by various bodies around the world. For each of them, an acceptable daily intake (ADI) [21] values in food has been established by the Food and Agricultural Organization (FAO) and World Health Organization (WHO) [2, 10, 31, 32]. In the United States, the Federal Food, Drug, and Cosmetic Act (FD&C) requires that numbers be given to approved dyes while, in the European Union, E numbers are used which are usually found on food labels throughout the European Union. The numbering scheme follows that of the International Numbering System (INS) as determined by the Codex Alimentarius Committee (CAC). Only a subset of the INS additives is approved for use in the European Union, giving rise to the 'E' prefix [33-35]. The E- stands for EU (European Union) and these numbers have been tested for safety and been passed for use in the EU. Food dyes without an E in front are allowed in the UK but may have not been passed for use in all EU countries [36]. This numbering scheme has now been adopted and extended to internationally identify all additives, regardless of whether they are approved for use [5, 36].

There are 304 food additives approved for the use across the European Union: 46 colours, 15 sweeteners, and 234 in the other categories. Table 4.1 lists the synthetic food colourant additives with their E numbers.

Currently, the seven permitted synthetic pigments in the USA compares with the 17 permitted synthetic dyes within the EU. The list of permitted food colourants varies from country to country [37].

Tables 4.1: E numbers of synthetic colour food additives

E no.	Colour additives	E no.	Colour additives
E102	Tartrazine*	E128	Red 2G *
E103	Chrysoine Resorcinol	E129	Allura Red AC *
E104	Qinoline Yellow*	E130	Indanthrene blue RS
E105	Fast Yellow AB	E131	Patent Blue V *
E107	Yellow 2G*	E132	Indigo carmine, Indigotine *
E110	Sunset yellow FCF*	E133	Brilliant Blue FCF *
E111	Orange GGN	E142	Greens S *
E122	Carmoisine, Azorubine *	E151	Black PN, Brilliant Black BN *
E123	Amaranth	E152	Black 7984 *
E124	Pnceau 4R, Cochineal Red A, Brilliant Scarlet 4R *	E154	Brown FK, Kipper Brown *
E125	Scarlet GN	E155	Brown HT, Chocolate brown HT *
E126	Ponceau 6R	E172	Iron oxides and hydroxides
E127	Erythrosine*	E180	Pigment Rubine, Lithol Rubine BK

*The E numbers of additives that the Hyper Active Children Support Group (HACSG) recommend should be avoid.

4.5 HAZARDS AND HEALTH PROBLEMS OF FOOD COLOUR ADDITIVES

4.5.1 Toxicity of Azo Dyes

The current environmental concern with azo dyes revolves around the potential carcinogenic health risk that they or their intermediate biodegradation products present to humans [38-41]. As dyes are designed to colour various substances and solutions, there is great potential for these dyes to build up in the environment since many of them pass through wastewater treatment plants virtually untreated.

The genetic toxicity of the major dyestuffs used in foods has been confirmed [42] and structure-activity relationships have been assessed [43, 44]. Weber and Wolfe demonstrated that azo- and nitro-compounds are reduced in sediments [45], and similarly Chung et al. [46] illustrated their reduction in the intestinal environment [43, 47, 48], resulting in the formation of toxic amines [49].

4.5.2 Food Scare of Sudan Dyes

Sudan dyes are non ionic fat-soluble dyes and belong to the azo-dye class. Sudan I (also commonly known as CI Solvent Yellow 14 and Solvent Orange R), is an orange-red [50]

and has a chemical name of 1-phenylazo-2-naphthol [12, 51] (Figure 4.1). Sudan I has also been adopted for colouring various foodstuffs, including particular brands of curry powder and chili powder [52]. Sudan I is also present as an impurity in sunset yellow, which is its disulfonated water-soluble derivative [50] (Figure 4.2). Sudan II (Figure 4.1) is the dimethyl derivative of Sudan I and it has been tested in mice by bladder implantation, resulting in a high incidence of bladder carcinomas [12]. Sudan I has been declared a possible carcinogen. Laboratory tests on mice showed growth of cancerous tumours in the liver. Tumours also developed in the bladder, following a direct injection into the urinary bladder. Tests via oral administration have so far proved negative [50]. However, the additive is banned from use in foods throughout the EU even though the amount of Sudan I used in popular foods is small [50].

Sudan I is not a permitted colour in the UK under the Colours in Food Regulations 1995. It is considered to be a genotoxic carcinogen and its presence is not permitted in foodstuffs for any purpose at any level [3, 51, 53].

In February 2005, Sudan I became a prominent news topic, particularly in the United Kingdom [53, 54]. A Worcester sauce produced by Premier Foods was found to be contaminated by the carcinogenic dye. The origin was traced to adulterated chili powder. The sauce was used in hundreds of supermarket products such as pizzas and ready-made meals, and the contamination has led to over 400 products being taken off the shelves [53].

The Regulation (EC) No. 178/2002 of the European Parliament and of the Council of 28 January 2002 laid down the general principles and requirements of food law [55], suspending the placing on the market or use of a food or feed that is likely to constitute a serious risk to human health. In particular, discovery of the azo dye Sudan I in hot chilli and hot chilli products originating from India and marketed in the EU does not comply with the EU food safety requirements. As a consequence of this discovery, in June 2003, the EC Commission has adopted a decision on emergency measures concerning hot chilli and hot chilli products intended for human consumption [56]. The Food Standards Agency also alerts for the contamination with Sudan I dye of various meat preparations on the market in

UK and issues warnings about frozen meat products, spice mix and chips containing contaminated chili powder [57].

On January 2004, the EU Food Regulations 2003 amended the conditions for the import of chilli and chili products and the EC decided to extend the Commission Decision 2003/460/EC requirement to cover Sudan II, Sudan III and Scarlet Red or Sudan IV [58].

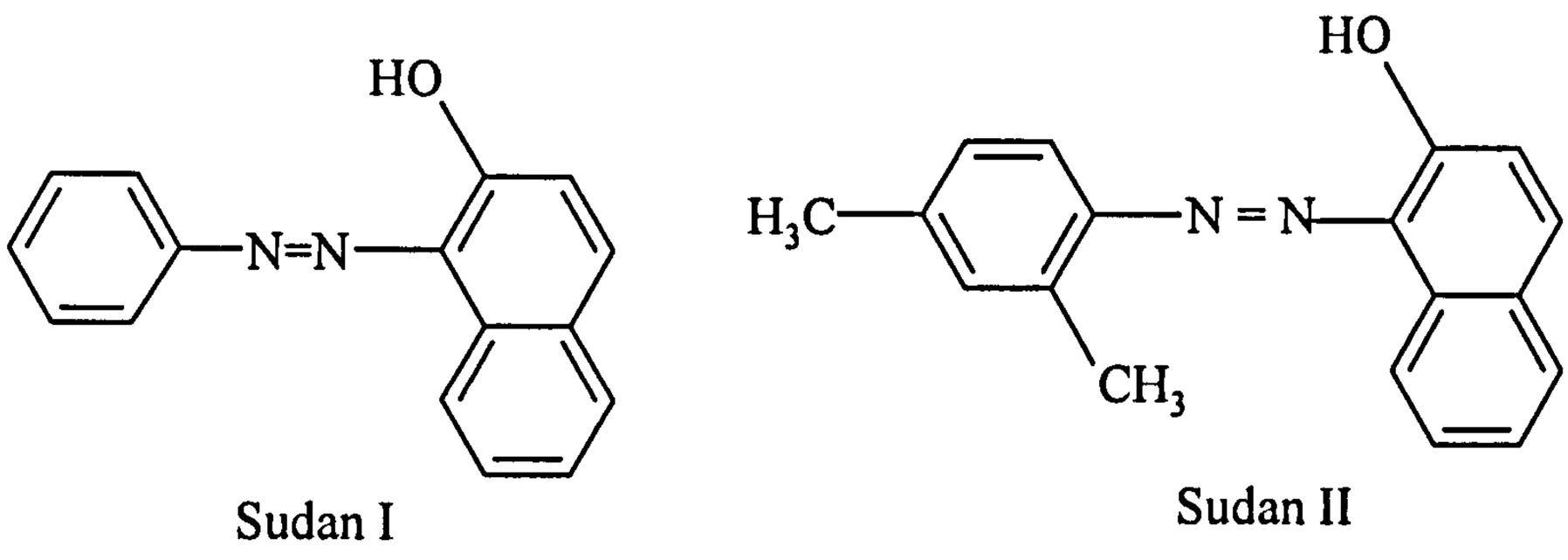


Figure 4.1: Chemical structures of Sudan I and Sudan II dyes

Due to the scare, the government of Sudan has requested that the name of the dye be changed to avoid negative connotations being associated with the country and its food exports [50]. The origins of the "Sudan I" name are uncertain, but one chemist has suggested it "probably got the name as a result of interest in the British Empire at the time it was developed in the late 19th Century."

4.5.3 Blue *Smarties* and triarylmethane dyes

Blue *Smarties* are to be taken off the market and will be replaced by white ones. This was headline news in some of the UK's national newspapers in early May 2006 [59, 60]. Evidently, Nestlé Rowntree is responding to concerns about possible risks to children's health from excessive consumption of certain synthetic food colourants and the company has decided to cease producing confectionery containing brilliant blue (E133), quinoline yellow (E104), sunset yellow (E110), ponceau 4R (E124), and carmoisine red (E122). In excessive quantities, all these colourants are said to exacerbate problems such as hyperactivity [33] and attention deficit syndrome. E133, also known in the US as FD&C Blue-1, erioglaucine or alphazurine, is in the triarylmethane category of colourants. The

International Agency for Research on Carcinogens (IARC) assigns it *Class 3* status – mixed or limited evidence on potential to contribute to human cancers. From June 2006 onwards, red, green and yellow *Smarties* will contain natural instead of synthetic food colourants. Tubes of *Smarties* will also continue to contain the orange, mauve, pink and dark brown varieties. But, according to Nestlé Rowntree, there is no suitable natural blue food colourant, so blue *Smarties* will be replaced by white *Smarties*. Clearly, there is a market opening for a food colour chemist to discover or invent a natural blue.

4.5.4 Allergic Reactions to Food additives

There is some evidence that certain additives can trigger allergic reactions in susceptible people. Additives are often viewed as harmful chemicals added to food without good reason [61]. Despite their safety pass by the EC a few people suffer from allergic reactions to some of them. If these colourants are eaten when certain drugs are being taken (e.g. aspirin, benzoic acid) they can induce allergic and asthmatic reactions in sensitive people [36, 41, 62]. The E numbers are helpful to these people because they can easily see whether the food contains an additive to which they are allergic [63]. Table 4.4 shows side effects of the azo dyes investigated in this study.

4.6 AIM OF THIS WORK

An attractive methodology to remove/degrade colours from aqueous solutions is the use of electrochemical technique, which is considered as a powerful mean of pollution control. This technology offers the possibility of *in situ* destruction or modification of various pollutants to less deleterious structures by anodic oxidation on high area electrodes [64-73].

Several researchers have studied the feasibility of electrochemical degradation of azo dyes used in the textile industry [74-79], however, very little research work has been done on the removal/degradation of synthetic food colours [80, 81].

The main aim of the work described in this chapter is to investigate the electrochemical degradation of eight food colours in aqueous solutions amaranth, carmoisine, ponceau 4R, sunset yellow FCF, tartrazine, blue food colour, green food colour and yellow food colour.

Since the real industry effluents contains dissolved sodium, chloride, and sulphate ions, electrolysis experiments were conducted in a chloride and sulphate medium and compared with the electrochemical degradation in aqueous solution. The Pt/Ti anode was selected in the present study because of its stability, long life, [72, 81], low cost and commercial availability [79]. Brillas et al. mentioned that Pt anode is environmentally preferred since it releases much lower amounts of toxic metallic ions [82].

4.7 EXPERIMENTAL

4.7.1 Dyes and Reagents

The dyes:

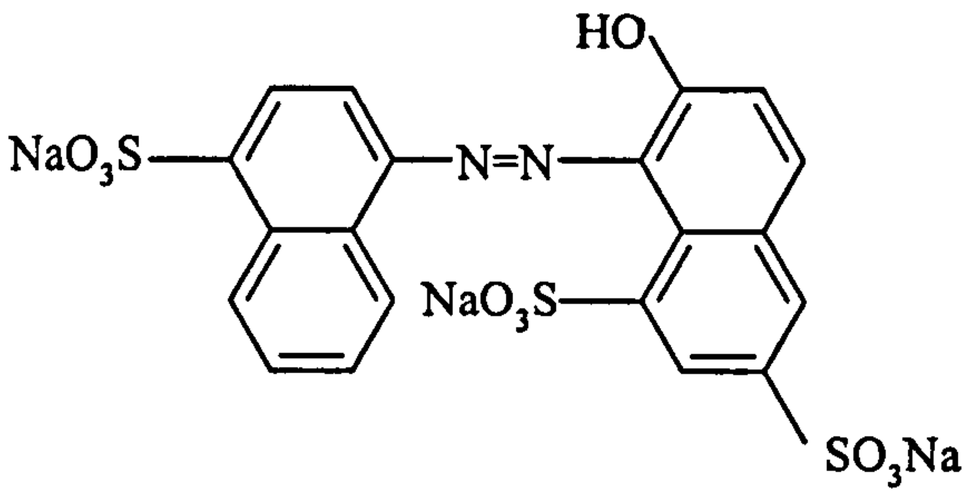
Ponceau 4R (paste) was purchased from local market in Tripoli, Libya. Carmoisine (synthetic cochineal), green food colour, blue food colour and yellow food colour, were synthesised by Supercook, Sherburn-in-Elmet-Leeds and were purchased from Tesco market. Deep orange food colour (sunset yellow FCF) was supplied by KTC (Edible) Ltd, JS House–Moorcroft Dr, Moorcroft Park, Wednesbury, UK. Tartrazine (powder) was supplied by The British Drug House Ltd, (B.D.H.) Poole, England, and amaranth was obtained from Aldrich Chemicals (Plates 4.1 and 4.2). All dyes were used without any further purification.

Sodium chloride and sodium sulphate were employed as electrolytes. All other chemicals used were analytical reagent grade and were used as supplied. Distilled water was used to prepare all solutions, and deionised water was used in TOC analysis.

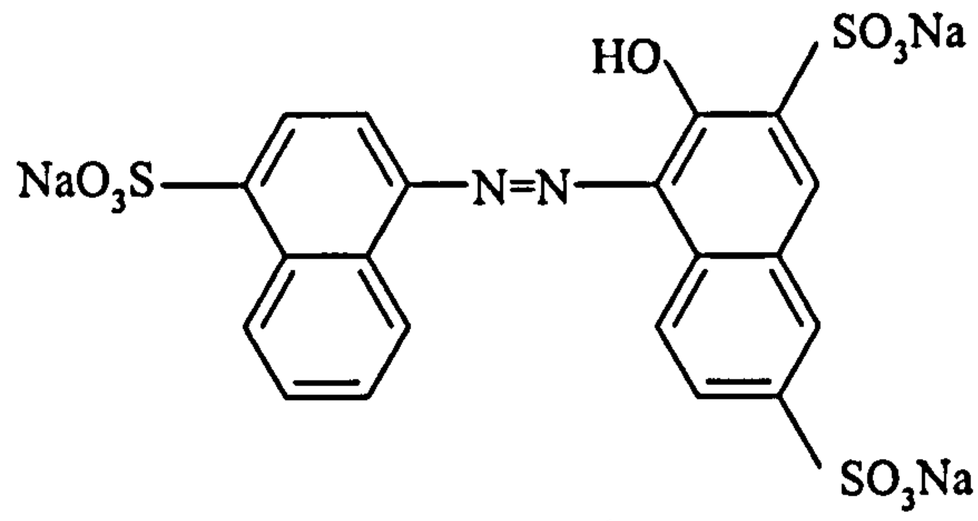
Each dye solution (2L) was prepared by dissolving 0.1 g of the dye in distilled water to make 50 ppm (50 mg/l) of dye concentration. At the beginning of each batch experiment the electrolytic cell was filled with 2 litres of dye solution and the required amount of the electrolyte was added to the solution (5 g/l). Table 4.2 summarises the food colourants and their commercial components used in this investigation.

Figures 4.2 and 4.3 illustrate the chemical structures of the azo and triarylmethane dyes investigated, and Tables 4.3 and 4.4 summarise the key features and names of the food

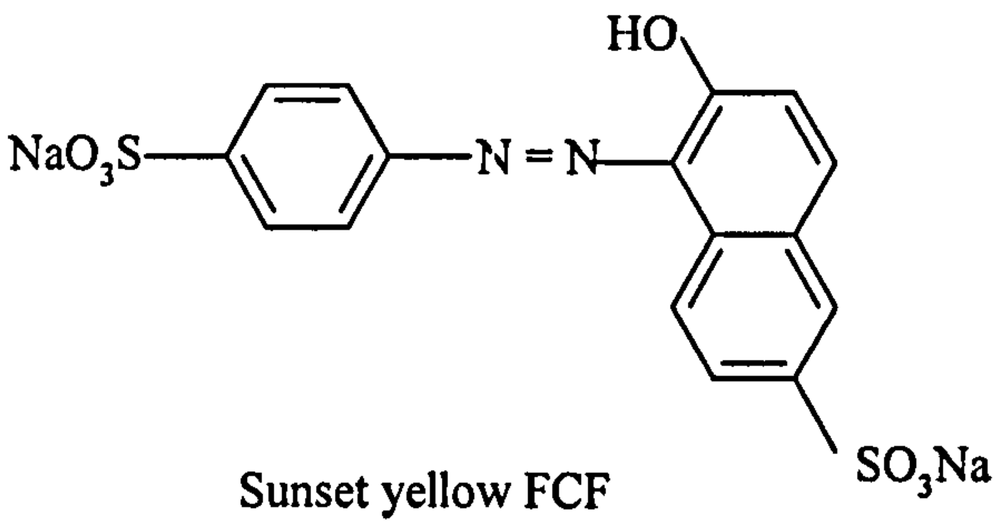
colourants investigated in this study. Tables 4.5 and 4.6 show some of the uses, toxicity and side effects of these colours.



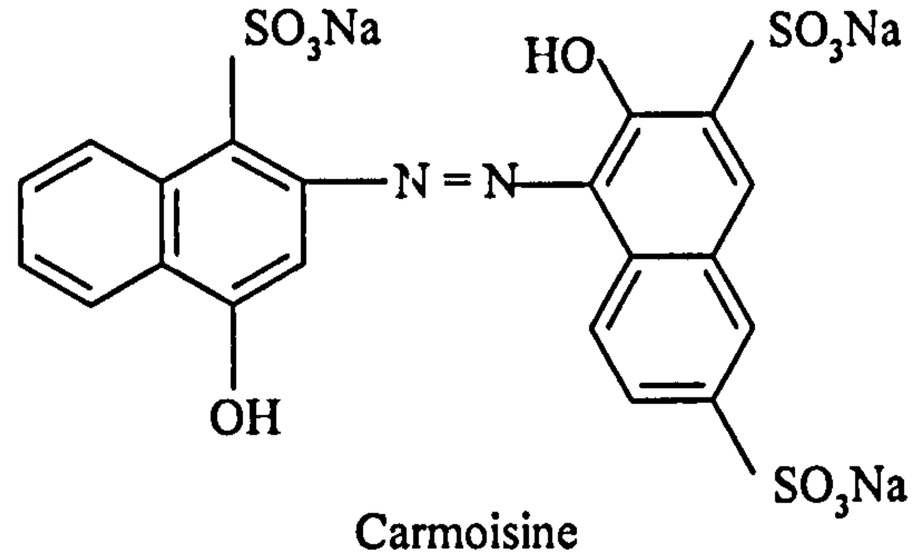
Ponceau 4R



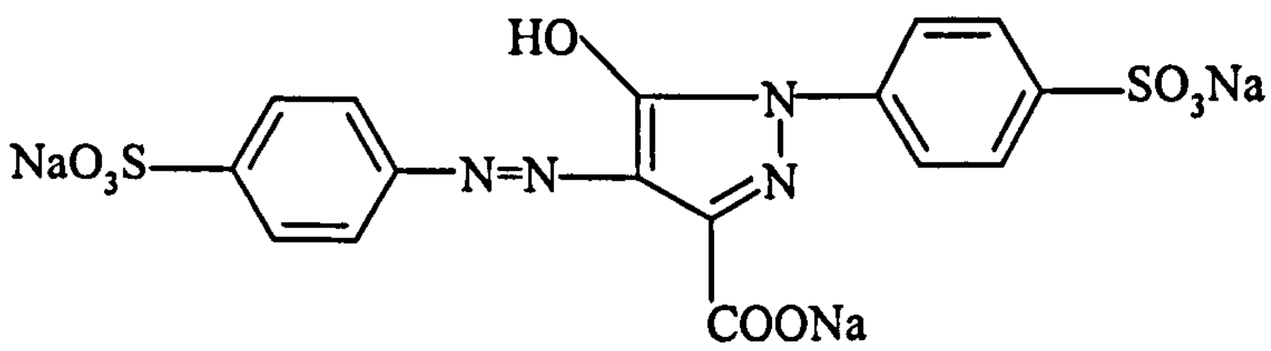
Amaranth



Sunset yellow FCF

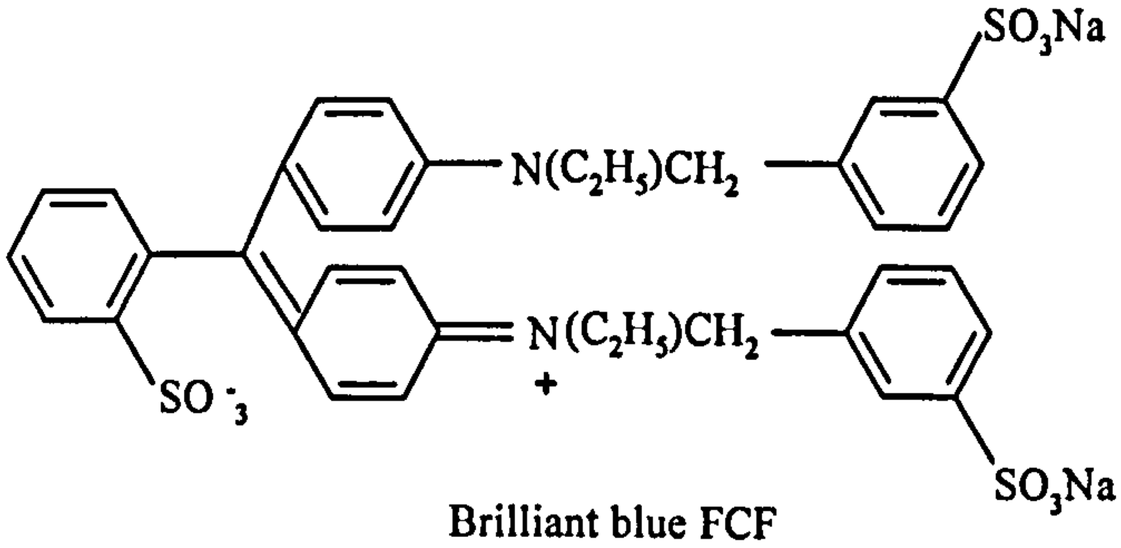


Carmoisine

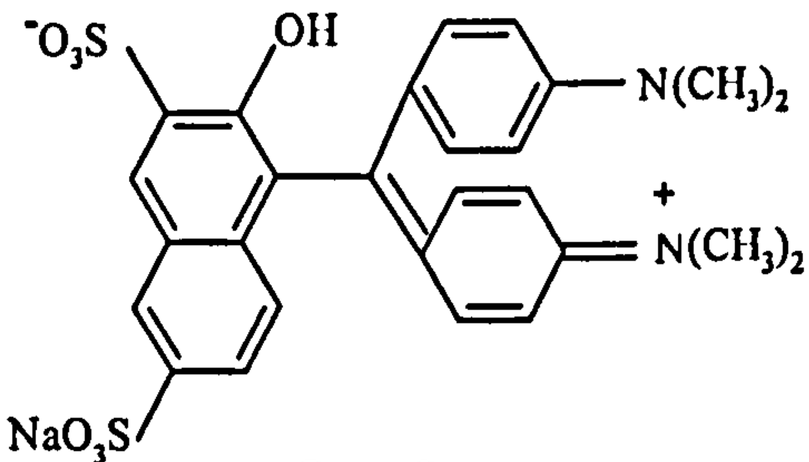


Tartrazine

Figure 4.2: Chemical structures of azo dyes under this study



Brilliant blue FCF



Green S

Figure 4.3: Chemical structures of triphenyl methane dyes used in this study

Plate 4.1: The commercial food colourant solutions used in this study

Plate 4.2: The commercial food colourant powders used in this study

Table 4.2: The food colourants and their commercial components used in this investigation

Food Colour	Comments
Amaranth	Powder
Deep orange food Colour	Sunset yellow FCF, sodium chloride, (Powder)
Tartrazine	Chloride free
Red food colour	Ponceau 4R, glycerine, propylene glycol, thickener, preservatives: E219 (sodium methyl para-hydroxybenzoate), E217 (sodium propyl para-hydroxybenzoate), (the colour is a paste)
Cochineal food colouring	Carmoisine (gluten free), water, glycerine, citric acid, preservative: (E211, sodium benzoate)
Blue Food colouring	Brilliant Blue FCF (0.24%), carmoisine (0.043%) (gluten free), water, glycerine, citric acid, preservative: (E211, sodium benzoate)
Green food colouring	Tartrazine (0.16%), green S (0.05%), water, glycerine, citric acid, preservative (E211, sodium benzoate)
Yellow food colour	Tartrazine (0.13%), sunset yellow FCF (0.011%), ponceau 4R (0.76%), sodium chloride, preservative: (E211, sodium benzoate), citric acid, water

Table 4.3: Key features of the food colourants investigated in this study

E No.	Common name	FDA name (USA name)	Japanese name	C.I. name	C.I. no.	CAS
E102	Tartrazine	FD&C yellow 5	Yellow no.4	Acid yellow 23 (Food yellow 4)	19140	1934-21-0
E110	Sunset yellow FCF	FD&C yellow 6	Yellow no.5	Acid yellow 6 (Food yellow 3)	15985	2783-94-0
E122	Carmoisine (azorubin)	FD&C red10	----	Acid red 14 (Food red 3)	14720	53026-69-9
E123	Amaranth	D&C red 2	Red no.2	Acid red 27 (Food red 9)	16185	915-67-3
E124	Ponceau 4R (New coccine)	FD&C red 8	Red no.102	Acid red 18 (Food red 7)	16255	2611-82-7
E133	Brilliant blue FCF	FD&C blue 1	Blue no.1	Acid blue 9 (Food blue 2)	42090	3844-45-9
E142	Green S	FD&C green 4	----	Acid green 50 (Food green 4)	44090	3087-16-9

CAS; Chem Abstract registry.

Table 4.4: Common and IUPAC names of synthetic food colourants [37]

Common name	IUPAC names
Amaranth	Trisodium 3-hydroxy-4-(4-sulphonato-1-naphthylazo) naphthalene-2,7-disulphonate
Brilliant blue FCF	Disodium [4-(N-ethyl-3-sulphonato benzylamino) phenyl]-[4-(N-ethyl-3 sulphonatobenzyl-imino) cyclohexa-2,5-dienylidene] toluene-2-sulphonate
Carmoisine	Disodium 4-hydroxy-3-(4-sulphonato-1-naphthylazo) naphthalene-1-sulphonate
Green S	Sodium-5-[4-dimethylamino-alpha-(4-dimethyliminocyclohexa-2,5-diethylidene) benzyl]-6-hydroxy-7-sulphonato-naphthalene-2-sulphonate
Ponceau 4R	Trisodium 7-hydroxy-8-(4-sulphonato-1-naphthylazo) naphthalene-1,3-disulphonate
Sunset yellow FCF	Disodium 6-hydroxy-5-(4-sulphonato-phenylazo) napthalene-2-sulphonate
Tartrazine	Trisodium 5-hydroxy-1-(4-sulphonatophenyl)-4-(4-sulphonatophenylazo)pyrazole-3 carboxylate

Table 4.5: Uses, side effects and toxicity of the azo food colourants used in this study

Dye	Uses Food Industry	Other Application Area	Side Effects and Toxicity
Amaranth	Cake mixes, fruit-flavoured fillings, jelly, ice creams, confectionary, soft drinks, gravy granules, soups and prawns [7, 25, 32, 83, 84].	It can be applied to natural and synthetic fibres, leather, paper, and phenol-formaldehyde resins. In cosmetics. For making red ink in Iraq and Central Africa. Thickener in textile printing. In colouring crystals of KDP* [85-88]	Provoke asthma, eczema, hyperactivity, caused birth defects, foetal deaths, and cancer [33]. Banned in USA, Russia, Austria, Japan, Norway, with a very restricted use in France and Italy (caviar only) [25, 27].
Carmoisine	Confectionary, marzipan, jelly crystals, yogurt, puddings, cakes, jams, sauces, sweets, soups, beverages, cheesecake mixes [21, 25, 31, 32, 89].	n.a.	Can produce bad reactions in asthmatic people allergic to aspirin. Banned in Sweden, USA, Austria, Norway [25, 27].
Ponceau 4R	Gelatines, puddings, dairy products, confections, beverages, condiments and salami [3, 7, 21, 25, 31, 32, 90].	In decorative liquids [91].	Carcinogen in animals can produce bad reactions in asthmatics and people allergic to aspirin, banned in USA & Norway, Finland [25, 27].
Sunset yellow FCF	Cereals, backery, snack foods, ice creams, beverages, confectionary, soft drinks, canned fish [3, 7, 25, 27, 31, 84, 90, 92].	Textile dyeing [18] In many medications including Berocca, Polaramine, Ventolin syrup [25, 27]. In colouring crystals of KDP [87]. In decorative liquids [91].	Urticaria, rhinitis, nasal congestion, allergies, hyperactivity, kidney tumours, chromosomal damage, abdominal pain, nausea, vomiting, ingestion, distaste of food. Banned in Norway, Finland [25, 27].
Tartrazine	Fruit squash, fizzy drinks, jams, canned fish, custards, beverages, ice creams, confections, preserves, cereals, soups, cake mixes, sauces, marzipan, mustard, yogurt and many convenience foods together with glycerin, lemon and honey products [3, 7, 25, 26, 83, 84, 90, 92]	In decorative liquids [91]. In medicinal capsules [25, 26]	Cause allergies in some people. It provokes asthma (though the US FDA do not recognize this), urticaria (hives) in children, linked to thyroid tumours, chromosomal damage, hyperactivity, aspirin sensitivity [33, 93]. Other reactions can include migraine, blurred vision, itching, rhinitis and purple skin patches [25, 26, 27].

*KDP: Potassium dihydrogen phosphate, n.a.; not available.

Table 4.6: Uses, side effects & toxicity of the triarylmethane food colourants used in this study

Colour	Uses Food Industry	Other Application Area	Side Effects and Toxicity
Brilliant blue FCF	Beverages, dairy products powders, jellies, confections, condiments, icings, syrups, extracts [7, 25, 27, 84, 92, 94].	In drugs, soaps, shampoos, and other hygiene, cosmetics preparation and as hydrolytic tracer [95]. In inks, as a fabric and wool dye, and to stain proteins [25, 96].	It has previously been banned in Belgium, Germany, Switzerland, Sweden, Austria, Norway, Denmark, France, Greece, Italy and Spain but has been certified as a safe food additive in the EU and is today allowed in most of the countries [25, 96].
Green S	Canned peas, mint jelly and sauce, packed bread crumbs and cake mixes, preserved fruits and vegetables [25, 27]	Used to stain living cells. It is used in ophthalmology, to diagnose various disorders of the eye's surface [97].	It may cause allergic reactions. Banned in Sweden, USA Canada, Finland, Japan and Norway [25, 27, 97].

4.7.2 Experimental Set-up for Electrolysis of Artificial Food Colourants

The electrolytic cell (Plate 4.3) used in the present work for electrolysis of artificial food colourants was made of Perspex sheets. The thickness of the Perspex sheet was 5 mm. The internal size of the cell was 14.0 cm × 25.5 cm × 22.0 cm (width × length × depth) with effective volume of 2 litres. Three holders for placing three electrodes were made at the top edges of two opposite walls of the cell. The distance between these electrodes was fixed at 1.5 cm. Experiments were conducted using two mesh anodes and one plate cathode. The size of the cathode was 0.15 cm × 10.5 cm × 14.5 cm (thickness × width × length). The size of each mesh anode was 12 cm × 10.2 cm (width × length). A power pack having an input of 230 V and variable output of 0-15 V with maximum current of 4.0 A was used as a direct current source. All experiments were conducted at ambient temperature. Each experiment was run for 8 hours or otherwise specified depending on the nature of the experiment and the solution was kept agitated constantly by a magnetic stirrer. About 20 ml of the solution was sampled in predetermined intervals from the middle part of the electrolytic cell by a glass pipette. The samples were analysed to monitor the percentage removal of dyes by using UV/visible spectrometer and TOC analyser. Experiments were performed in duplicate and found to be reproducible.

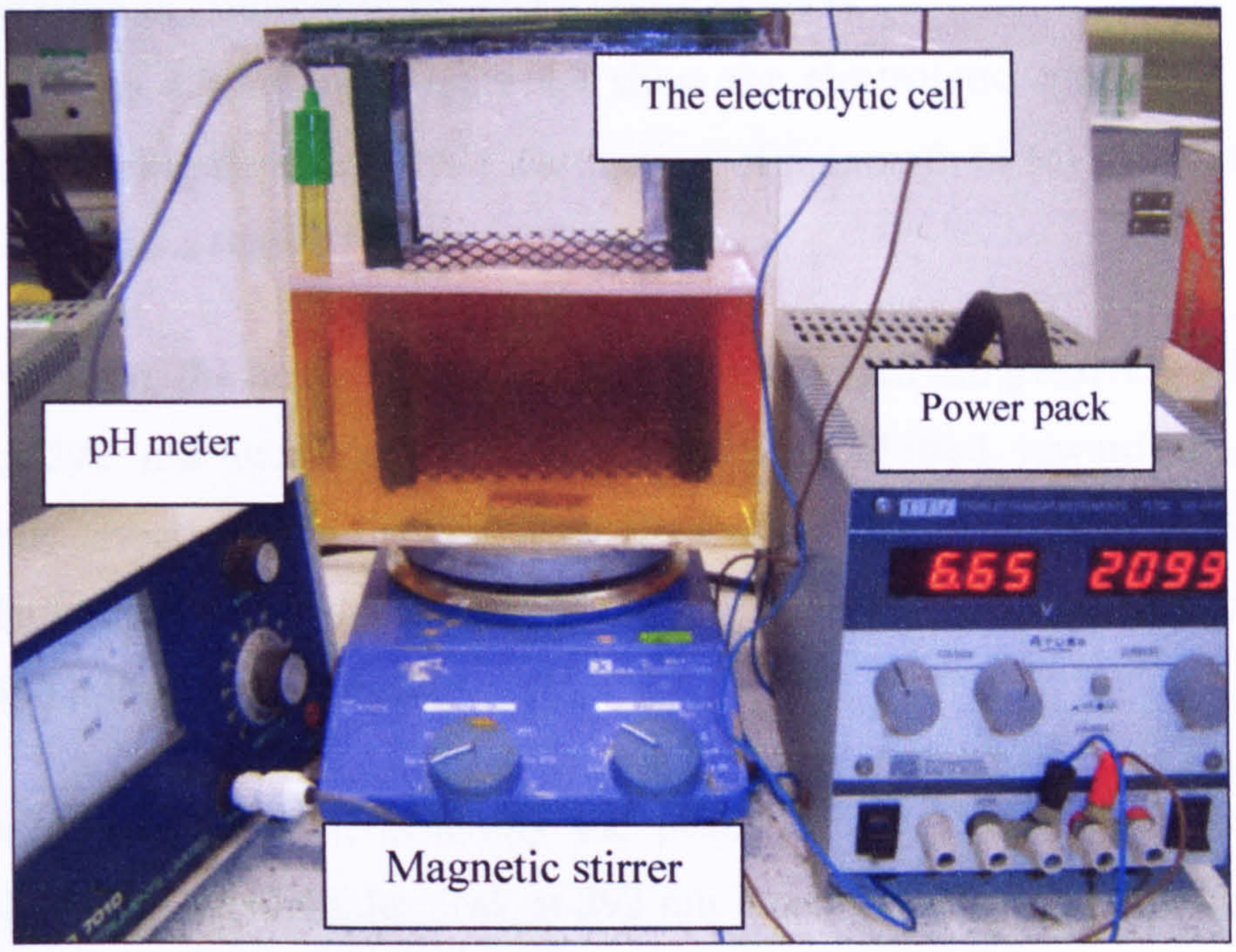


Plate 4.3: The experimental setup used for the electrochemical degradation of synthetic food colourants

4.7.3 Apparatus and Analysis

The pH meter was Mettler delta (Toledo) 320 Model pH–meter, calibrated with buffer solution (pH 4 and pH 7 ± 0.05). A Perkin-Elmer Lambda 9 UV-visible Spectrophotometer was used in this work for the determination of dye concentrations at the maximum absorbance in the range of 250-700 nm or otherwise specified on the spectra. Total organic carbon (TOC) was determined by using a model 700 (O.I. Corporation) TOC analyzer. All solutions were prepared in deionised water for TOC analysis.

4.8 RESULTS AND DISCUSSION

Three solutions were made in distilled water for each colour: (i) water only, (ii) water and sodium sulphate (5 g/l) and (iii) water and sodium chloride (5 g/l). Samples were withdrawn at intervals during the course of the electrolysis and analyzed using UV-visible absorption spectroscopy. Decrease in the intensity of absorbance was taken as an indication of decolourisation due to transformation of dyes. The pH of the each sample was measured before each analysis.

4.8.1 Degradation of Amaranth by Electrolytic Process

The data in Tables 4.7-4.9 and Figure 4.4 show the electrolytic conditions and the UV-Visible spectra during the electrolytic destruction of amaranth in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions respectively.

In aqueous solution, the peaks at 346 and 533 nm decreased progressively while the peaks at 275 and 292 nm increased with the later peak shifted toward the blue region (hypsochromic effect) during the course of electrolysis. Although 52% colour removal is achieved, the colour of the solution faded slightly, and the pH dropped from 8.2 to 6.00 during the 480 minutes electrolysis.

In aqueous Na_2SO_4 solution, generally the peaks at 275, 346 and 533 nm decreased progressively, while the shoulder peak at 292 nm increased slightly. Although 91% colour removal was reached during the course of electrolysis only a slight change of the original colour and the UV region of the dye remained at pH (5.3-7.3).

In aqueous NaCl solution generally all the peaks at 292, 346 and 533 nm declined after 5 minutes electrolysis, while the peak around 275 nm decreased and shifted progressively toward the blue region. The original colour of the amaranth in aqueous NaCl solution discharged completely after 5 minutes and 99% of colour removal is achieved after 15 minutes electrolysis. An increase in the pH (4.5-8.7) was observed which indicate the formation of basic organic residues. The TOC data showed that 41% reduction in organic carbon was achieved in the presence of NaCl (Table 4.10).

Hattori et al. [81] reported that a portion of amaranth is decomposed on the cathode surface while the other portion is decomposed to lower molecular weight components on the anode surface during the electrolytic process. Acetic acid and oxalic acid are detected as intermediate substances, and CO_2 gas is generated as a final product corresponding to the decrease in the oxalic acid concentration.

Comparison between our study of electrochemical degradation of amaranth with other literature studies of amaranth are summarised in Table 4.11.

Table 4.7: Electrochemical decolourisation of amaranth in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	8.2	14.80	Scarlet red	0
5	7.7	15.60	Scarlet red	09
15	7.6	15.01	Scarlet red	11
30	7.4	15.20	Scarlet red	12
60	7.4	15.60	Scarlet red	20
120	7.3	15.63	Light Scarlet red	28
240	7.3	14.80	Light Scarlet red	39
360	7.2	14.80	Light Scarlet red	48
480	6.0	14.80	Light Scarlet red	52

Conditions: current, 0.051 A; temperature, ambient; concentration (amaranth, 50 mg/l)

Table 4.8: Electrochemical decolourisation of amaranth in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.3	9.65	Scarlet red	0
5	7.5	9.67	Scarlet red	29
15	7.4	9.70	Scarlet red	46
30	7.4	9.60	Scarlet red	47
60	7.4	9.40	Scarlet red	58
120	7.4	9.32	Light Scarlet	79
240	7.2	9.00	Light purple	82
360	7.1	8.95	Light purple	88
480	7.3	9.24	Light pink	91

Conditions: current, 2.0 A; temperature, ambient; concentration (amaranth, 50 mg/l; Na_2SO_4, 5 g/l)

Table 4.9: Electrochemical decolourisation of amaranth in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.5	5.75	Scarlet red	0
5	7.3	5.80	Colourless	95
15	7.7	5.88	Colourless	99
30	8.3	5.89	Colourless	99
60	8.3	5.85	Colourless	99
120	8.4	5.76	Colourless	99
240	8.7	5.74	Colourless	99
360	8.7	5.71	Colourless	99
480	8.7	5.70	Colourless	99

Conditions: current, 2.0 A; temperature, ambient; concentration (amaranth, 50 mg/l; NaCl, 5 g/l)

Table 4.10: TOC data of electrochemical degradation amaranth in aqueous sodium chloride

Time (min)	TOC	% Removal
0	1179	0
30	1000	15
60	976	17
120	840	29
240	813	31
360	764	35
480	700	41

Table 4.11: Comparison of electrochemical studies of amaranth with literature reports

Dye conc.	Electrodes	Electrolytes	Duration time (min)	Degradation products	References
50 mg/l	Platinised titanium mesh	NaCl, Na_2SO_4	480 480	Not investigated	This study
80 mg/l	Activated carbon fibre (ACF)	Na_2SO_4	480	n.i.	[80]
100 mg/l	Diamond and platinum	Na_2SO_4	120	1-aminonaphthalene -4-sulfonateacetic, oxalic and maleic acids	[81]

n.i. not indicated or not available

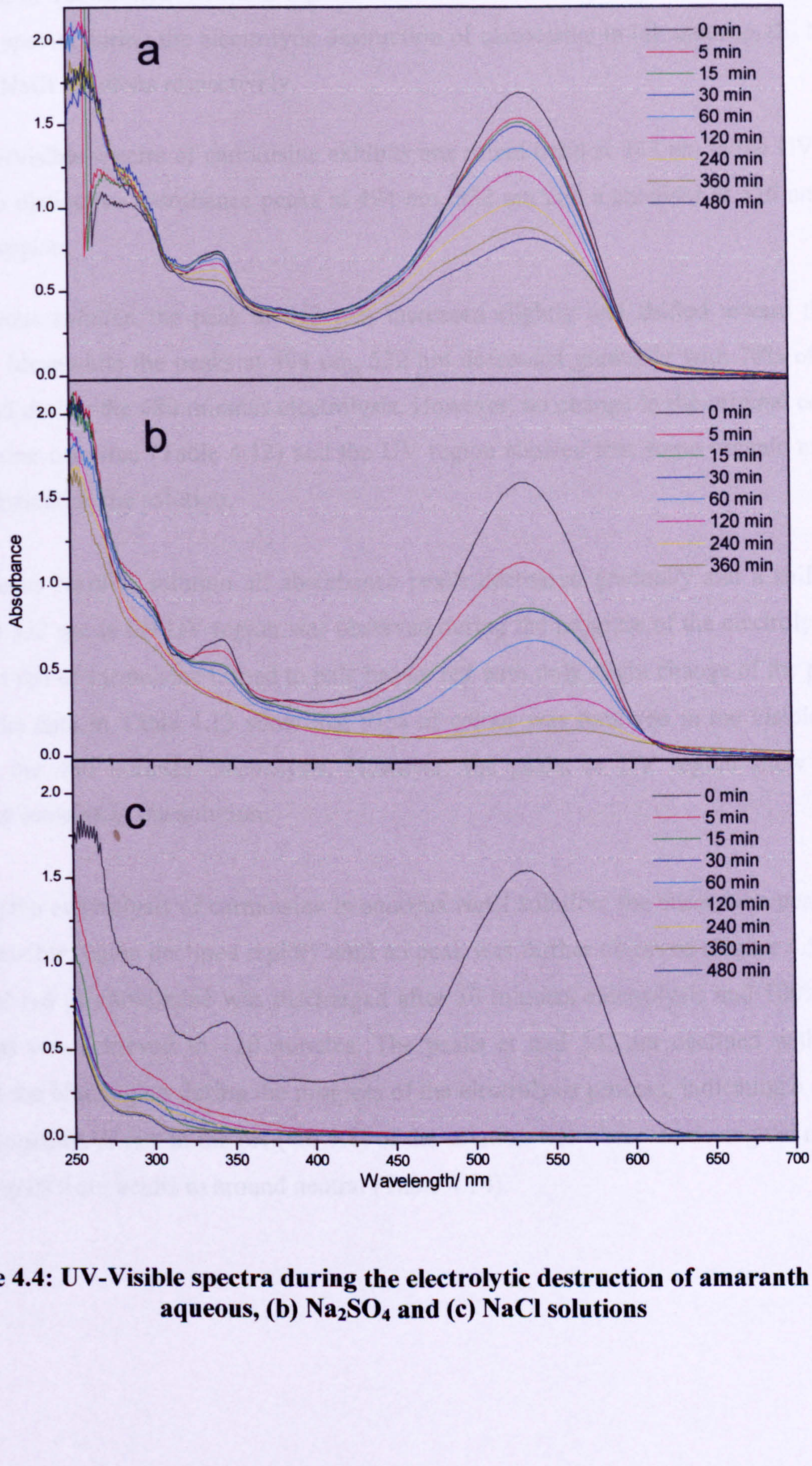


Figure 4.4: UV-Visible spectra during the electrolytic destruction of amaranth in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions

4.8.2 Degradation of Carmoisine by Electrolytic Process

The data in Tables 4.12-4.14 and Figure 4.5 show the electrolytic conditions and the UV-Visible spectra during the electrolytic destruction of carmoisine in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions respectively.

The UV/visible spectra of carmoisine exhibits one round band at 343 nm in the UV region and two distinctive absorbance peaks at 494 nm, 532 nm and a shoulder at 576 nm in the visible region.

In aqueous solution the peak at 343 nm, increased slightly and shifted toward the blue region. Meanwhile the peaks at 494 nm, 532 nm decreased gradually with 70% of colour removed during the 480 minutes electrolysis. However, no change in the original colour of carmoisine occurred (Table 4.12) and the UV region showed that some organic materials still remained in the solution.

In aqueous Na_2SO_4 solution all absorbance peaks decreased gradually and a shift of the peak at 532 nm to the UV region was observed during the progress of the electrolysis. The original red of carmoisine turned to pale brown red with only slight change of the pH (4.2-4.0). The data in Table 4.13 show that 91% of colour was removed in the visible region during the 480 minutes electrolysis. However, the peaks in UV region show organic material remains in the solution.

During the electrolysis of carmoisine in aqueous NaCl solution, the absorption peak at 538 nm in visible region declined rapidly until no peak was further observed (Figure 4.5 c). The original red of carmoisine was discharged after 30 minutes electrolysis and 100% colour removal was achieved in 120 minutes. The peaks at and 343 nm declined with a shift toward the blue region during the progress of the electrolysis process, indicating a decrease in conjugation. A rise in the pH (4.0-7.8) of the solution was observed during the course of electrolysis from acidic to around neutral (Table 4.14).

Table 4.12: Electrochemical decolourisation of carmoisine in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.4	14.90	Red	0
5	4.5	14.30	Red	22
15	4.9	14.70	Red	39
30	5.3	14.65	Red	42
60	5.5	14.90	Red	44
120	4.7	15.15	Red	47
240	5.8	15.30	Red	58
360	4.4	15.62	Red	66
480	4.2	15.63	Red	70

Conditions: current, 0.138 A; temperature, ambient; concentration (carmoisine, 5 ml/l)

Table 4.13: Electrochemical decolourisation of carmoisine extract in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.2	9.36	Red	0
5	4.2	9.40	Red	29
15	4.2	9.40	Red	31
30	4.3	9.30	Red	41
60	6.8	8.95	Red	57
120	4.4	8.70	Red	62
240	3.8	8.46	Light red	77
360	4.2	8.50	Pale red	86
480	4.0	8.45	Pale brown red	91

Conditions: current, 2.0 A; temperature, ambient; concentration (carmoisine, 5 ml/l; Na_2SO_4, 5 g/l)

Table 4.14: Electrochemical decolourisation of carmoisine in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.0	5.40	Red	0
5	4.2	5.42	Light yellow	95
15	4.6	5.45	Pale yellow	96
30	5.4	5.46	Colourless	98
60	6.4	5.43	Colourless	99
120	7.3	5.38	Colourless	100
240	7.7	5.35	Colourless	100
360	7.7	5.50	Colourless	100
480	7.8	5.60	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (carmoisine, 5 ml/l; NaCl, 5 g/l)

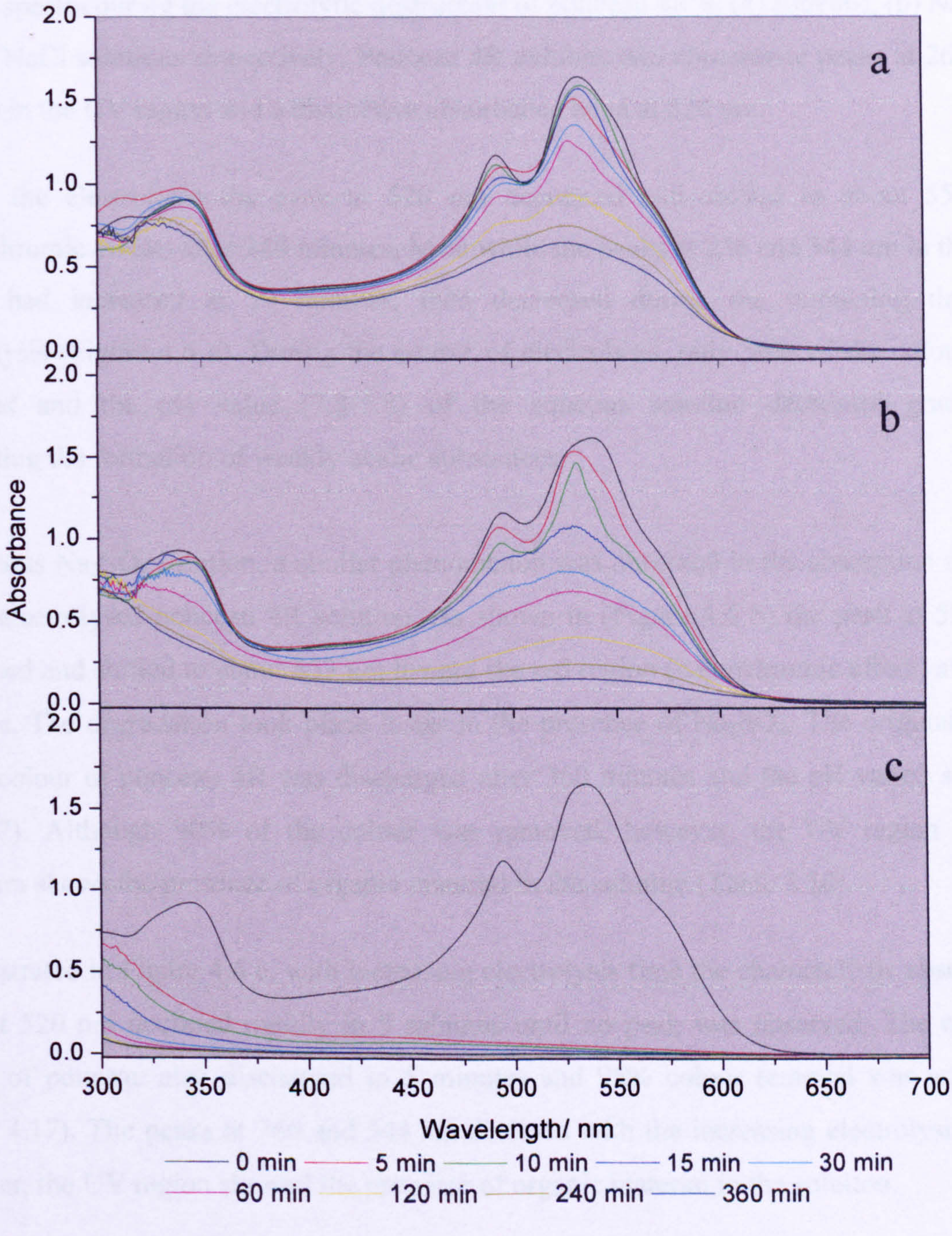


Figure 4.5: UV-Visible spectra during the electrolytic destruction of carmoisine in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions

4.8.3 Degradation of Ponceau 4R by Electrolytic Process

The data in Tables 4.15-4.17 and Figure 4.6 show the electrolytic conditions and the UV-Visible spectra during the electrolytic destruction of ponceau 4R in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions respectively. Ponceau 4R exhibits two absorbance peaks at 260 and 344 nm in the UV region and a distinctive absorbance band at 520 nm.

During the electrolysis the peak at 520 nm decreased and shifted to about 553 nm (bathochromic effect) after 240 minutes. Meanwhile the peaks at 256 and 344 nm in the UV region had increased at 30 minutes, then decreased during the remaining time of electrolysis (Figure 4.6 a). During the course of electrolysis, only 56% of the colour was removed and the pH value (7.8-5.8) of the aqueous solution decreased gradually, suggesting the formation of weakly acidic substances.

In aqueous Na_2SO_4 solution, a similar phenomenon was observed in the absorption spectra of the electrolysed ponceau 4R solution. As shown in (Figure 4.6 b) the peak at 520 nm decreased and shifted to about 553 nm toward the red region (bathochromic effect) after 60 minutes. The degradation took place faster in the presence of Na_2SO_4. The original pink-peach colour of ponceau 4R was discharged after 360 minutes and the pH varied slightly (5.8-6.7). Although 90% of the colour was removed, however, the UV region of the spectrum shows the presence of organic material in the solution (Table 4.16).

As illustrated in Figure 4.6 c, with increasing electrolysis time the characteristic absorption peak at 520 nm declined rapidly in 5 minutes until no peak was observed. The original colour of ponceau also discharged in 5 minutes and 95% colour removal was achieved (Table 4.17). The peaks at 260 and 344 nm declined with the increasing electrolysis time, however, the UV region showed the presence of organic material in the solution.

Table 4.15: Electrochemical decolourisation of ponceau 4R in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.8	14.73	Pink peach	0
5	7.1	14.76	Pink peach	06
15	6.8	14.80	Pink peach	15
30	6.2	14.67	Pink peach	16
60	6.0	14.30	Pink peach	18
120	5.9	13.30	Pale peach	38
240	5.9	11.94	Pale peach	43
360	5.8	11.12	Pale peach	46
480	5.8	10.70	Pale peach	56

Conditions: current, 0.008 A; temperature, ambient; concentration (ponceau 4R, 100 mg/l)

Table 4.16: Electrochemical decolourisation of ponceau 4R in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.8	11.28	Pink peach	0
5	6.0	11.50	Pale peach	27
15	6.0	11.25	Pale pink	47
30	6.0	11.00	Pale pink	50
60	6.2	10.95	Pale pink	52
120	6.4	10.70	Pale pink	58
240	6.4	10.60	Pale pink	68
360	6.6	10.40	Colourless	74
480	6.7	10.36	Colourless	90

Conditions: current, 2.0 A; temperature, ambient; concentration (ponceau 4R, 100 mg/l; Na_2SO_4, 5 g/l)

Table 4.17: Electrochemical decolourisation of ponceau 4R in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.7	5.90	Pink peach	0
5	7.7	5.96	Colourless	95
15	7.8	6.00	Colourless	97
30	8.0	6.03	Colourless	97
60	8.2	5.97	Colourless	97
120	8.3	5.88	Colourless	98
240	8.6	5.80	Colourless	99
360	8.6	5.90	Colourless	100
480	8.8	5.80	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (ponceau 4R, 100 mg/l; NaCl, 5 g/l)

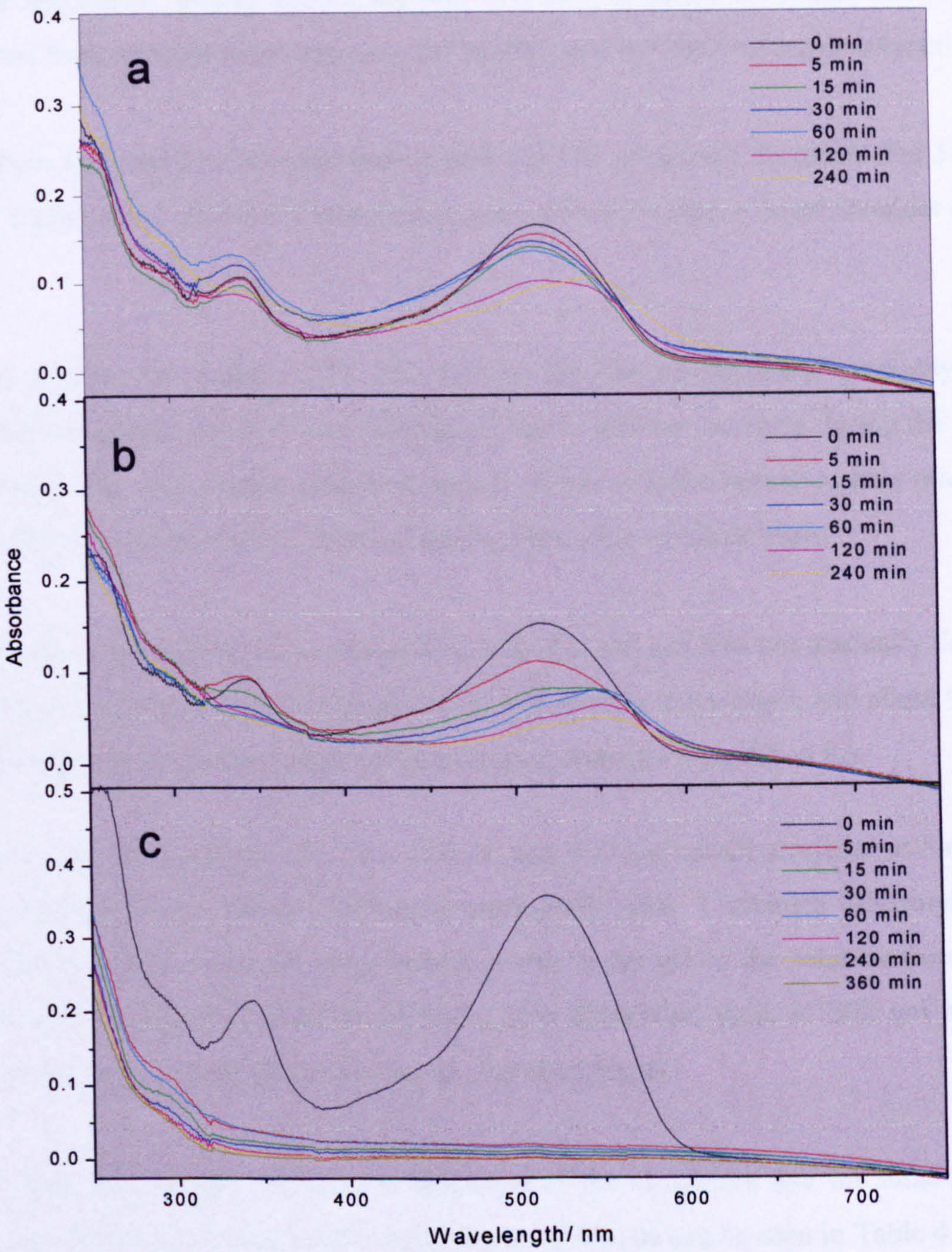


Figure 4.6: UV-Visible spectra during the electrolytic destruction of ponceau 4 R in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions

4.8.4 Degradation of Sunset Yellow FCF by Electrolytic Process

The data in Tables 4.18-4.20 and Figure 4.7 show the electrolytic conditions and the UV/visible absorption spectra during the electrolytic destruction of sunset yellow FCF solutions and their residues in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions respectively.

Sunset yellow FCF exhibits two absorbance peaks at 274 nm (small shoulder) and 328 nm in the UV region and a distinctive absorbance band at 490 nm and a broad shoulder at 420 nm.

In aqueous solution, the peaks at 274, 328, 420 nm and 490 nm decreased gradually and a red shift (bathochromic effect) of the absorption peak at 490 nm occurred during the course of electrolysis. The oily orange colour of sunset yellow solution turned to pale pink with more than 73% of colour removal attained during the course of electrolysis.

In aqueous Na_2SO_4 solution, the peaks at 274, 328, 420 nm and 490 nm gradually declined and the original orange colour discharged after 240 minutes electrolysis and about 98% of colour removal was achieved. The pH of the solution changed from 7.5 to 9.3.

In NaCl solution, the peaks at 274, 328, 420 nm and 490 nm rapidly declined in 5 minutes and the original orange colour discharged completely after 5 minutes electrolysis and almost 100% of colour removal was reached. A rise in the pH of the solution from 5.5 to 8.6 also occurred. The UV spectra showed a new absorption peak at 302 nm after 15 minutes which enhanced progressively during the electrolysis.

The TOC data showed the residual concentration of the remaining dye for sunset yellow FCF was less than half of their initial concentration (54%) as can be seen in Table 4.21.

Table 4.18: Electrochemical decolourisation of sunset yellow FCF in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.7	14.80	Oily orange	0
5	7.5	15.65	Yellow	09
15	7.4	15.32	Light peach	15
30	7.3	15.50	Light peach	22
60	7.2	15.55	Peach	40
120	7.2	15.63	Peach	59
240	7.0	15.63	Light pink	73
360	7.1	14.93	Baby pink	74
480	7.1	14.84	Pale pink	78

Conditions: current, 0.154 A; temperature, ambient; concentration (sunset yellow FCF, 5 ml/l)

Table 4.19: Electrochemical decolourisation of sunset yellow FCF in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.5	9.90	Oily orange	0
5	7.8	9.82	Oily orange	09
15	7.7	9.75	Oily orange	27
30	7.6	9.80	Pale orange	36
60	7.5	9.79	Light peach	57
120	7.6	9.57	Pale peach	80
240	7.7	9.65	Colourless	92
360	8.7	9.50	Colourless	96
480	9.3	9.47	Colourless	98

Conditions: current, 2.0 A; temperature, ambient; concentration (sunset yellow FCF, 5 ml/l; Na_2SO_4, 5 g/l)

Table 4.20: Electrochemical decolourisation of sunset yellow FCF in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.5	5.85	Oily orange	0
5	5.6	5.96	Colourless	90
15	8.3	5.92	Colourless	98
30	8.6	5.95	Colourless	99
60	8.2	5.79	Colourless	99
120	8.6	5.60	Colourless	99
240	8.6	5.63	Colourless	99
360	8.6	5.65	Colourless	100
480	8.6	5.75	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (sunset yellow FCF, 5 ml/l; NaCl, 5 g/l)

Table 4.21: TOC data of electrochemical degradation sunset yellow FCF in aqueous sodium chloride

Time (min)	TOC (ppm)	% Removal
0	2.73	0
5	2.39	12
10	2.17	20
15	2.07	24
30	2.06	25
60	1.39	49
75	1.26	54

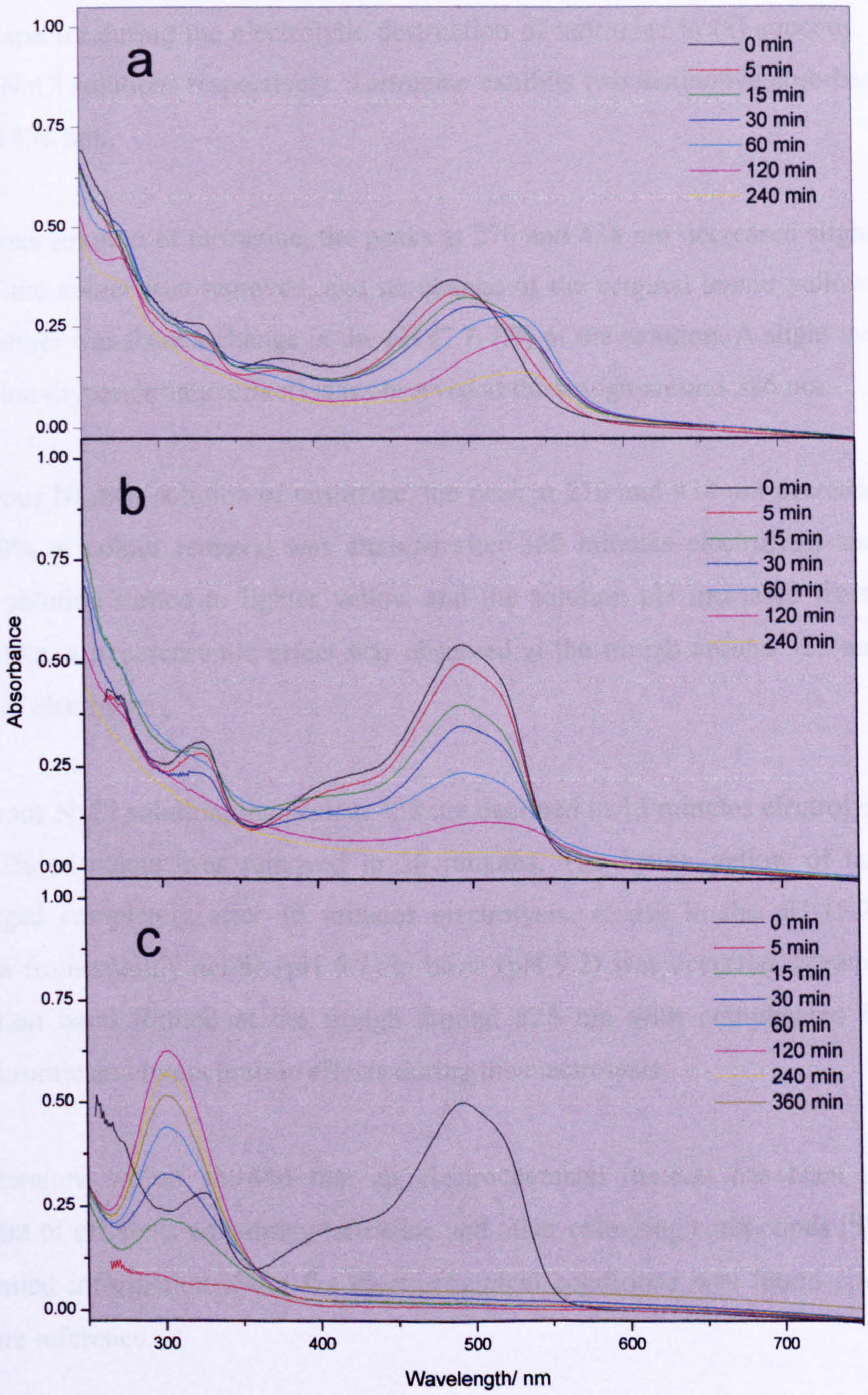


Figure 4.7: UV-Visible spectra during the electrolytic destruction of sunset yellow FCF in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions

4.8.5 Degradation of Tartrazine by Electrolytic Process

The data in Tables 4.22-4.24 and Figure 4.8 show the electrolytic conditions and the UV-Visible spectra during the electrolytic destruction of tartrazine in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions respectively. Tartrazine exhibits two distinctive absorbance peaks at 270 and 438 nm.

In aqueous solution of tartrazine, the peaks at 270 and 438 nm decreased slightly and only 22% of the colour was removed, and no change of the original lemon yellow colour was seen, neither was there a change in the pH (7.7-7.3) of the solution. A slight increase in the absorption (hyperchromic effect) was observed at the trough around 326 nm.

In aqueous Na_2SO_4 solution of tartrazine, the peak at 270 and 438 nm decreased gradually until 89% of colour removal was attained after 360 minutes electrolysis and the lemon yellow solution turned to lighter yellow and the solution pH increased from 5.7 to 8.5. Meanwhile, a hyperchromic effect was observed at the trough around 325 nm during the course of electrolysis.

In aqueous NaCl solution, the peak at 438 nm declined in 15 minutes electrolysis and more than 97% of colour was removed in 30 minutes. The lemon yellow of tartrazine was discharged completely after 15 minutes electrolysis. A rise in the pH (5.7-9.2) of the solution from slightly acidic (pH 5.7) to basic (pH 9.2) was occurred. Meanwhile, a new absorption band formed at the trough around 328 nm with complicated behaviour of hyperchromic and hypochromic effects during the electrolysis.

The literature search showed that an electrochemical method has been used for the treatment of effluents containing tartrazine and other colouring compounds [98]. However, no detailed information about the electrochemical conditions was found concerning this literature reference.

Table 4.22: Electrochemical decolourisation of tartrazine from aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.7	14.80	Lemon yellow	0
15	7.7	15.20	Lemon yellow	03
30	7.8	15.60	Lemon yellow	06
120	7.3	15.80	Lemon yellow	11
180	7.5	15.60	Lemon yellow	12
240	7.5	15.60	Lemon yellow	17
300	7.3	14.80	Lemon yellow	22

Conditions: current, 0.044 A; temperature, ambient; concentration (tartrazine, 1 g/l)

Table 4.23: Electrochemical decolourisation of tartrazine in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.7	8.25	Lemon yellow	0
5	6.2	8.80	Lemon yellow	06
15	6.2	9.16	Lemon yellow	11
30	6.1	9.35	Lemon yellow	19
60	6.1	9.04	Lemon yellow	33
120	6.5	8.70	Lemon yellow	51
240	6.3	8.96	Lemon yellow	69
360	8.2	9.06	Light yellow	83
480	8.5	9.15	Pale yellow	89

Conditions: current, 2.0 A; temperature, ambient; concentration (tartrazine, 1 g/l; Na_2SO_4, 5 g/l)

Table 4.24: Electrochemical decolourisation of tartrazine in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.7	5.75	Lemon yellow	0
15	8.4	5.60	Colourless	96
30	8.6	5.71	Colourless	96
60	8.7	5.25	Colourless	97
120	8.2	5.40	Colourless	97
240	9.1	5.45	Colourless	97
300	9.1	5.52	Colourless	97
480	9.2	5.56	Colourless	97

Conditions: current, 2.0 A; temperature, ambient; concentration (tartrazine, 1 g/l; NaCl, 5 g/l)

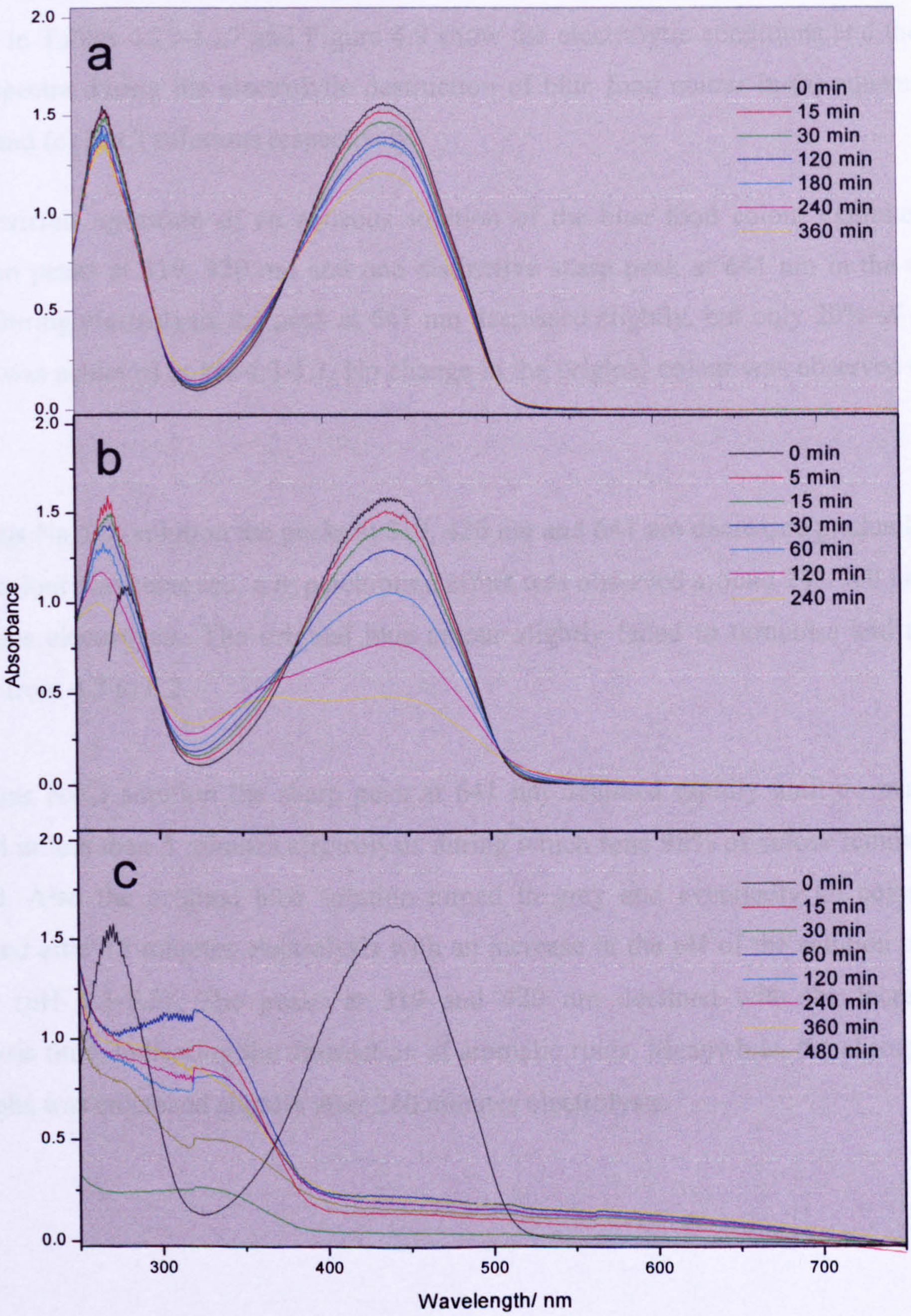


Figure 4.8: UV-Visible spectra during the electrolytic destruction of tartrazine in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions

4.8.6 Degradation of Blue Food Colour (Brilliant Blue FCF & Carmoisine) by Electrolytic Process

The data in Tables 4.25-4.27 and Figure 4.9 show the electrolytic conditions and the UV-Visible spectra during the electrolytic destruction of blue food colour in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions respectively.

The UV/visible spectrum of an aqueous solution of the blue food colour exhibited two absorption peaks at 319, 420 nm and one distinctive sharp peak at 641 nm in the visible region. During electrolysis the peak at 641 nm decreased slightly, but only 20% of colour removal was achieved at pH 4.3-3.7. No change in the original colour was observed (Table 4.25).

In aqueous Na_2SO_4 solution the peaks at 319, 420 nm and 641 nm decreased gradually until 68% of colour was removed, a hyperchromic effect was observed around 245-300 nm after 30 minutes electrolysis. The original blue colour slightly faded to turquoise and the pH changed from 4.7 to 6.2.

In aqueous NaCl solution the sharp peak at 641 nm declined rapidly until no peak was observed in less than 5 minutes electrolysis during which time 99% of colour removal was achieved. Also the original blue solution turned to grey and eventually all colour was discharged after 15 minutes electrolysis with an increase in the pH of the solution to basic medium (pH 5.5-8.5). The peaks at 319 and 420 nm declined with the increase of electrolysis time, indicating the destruction of aromatic rings. Meanwhile, the absorption at the troughs was enhanced slightly after 240 minutes electrolysis.

Table 4.25: Electrochemical decolourisation of blue food colour (brilliant blue FCF & carmoisine) in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.3	14.30	Blue	0
5	3.7	15.10	Blue	07
15	4.2	15.00	Blue	08
30	4.2	15.22	Blue	09
60	4.0	15.25	Blue	09
120	4.1	14.45	Blue	10
240	3.6	13.15	Blue	11
360	3.5	11.50	Blue	16
480	3.7	10.63	Blue	20

Conditions: current, 0.032 A; temperature, ambient; concentration (blue food colour, 5 ml/l)

Table 4.26: Electrochemical decolourisation of blue food colour (brilliant blue FCF & carmoisine) in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.7	10.60	Blue	0
5	4.6	10.50	Blue	05
15	5.0	10.38	Blue	07
30	4.9	10.30	Blue	09
60	4.8	10.05	Blue	22
120	5.0	9.82	Light blue	22
240	5.2	9.67	Light blue	37
360	5.5	9.76	Turquoise	64
480	6.2	9.80	Turquoise	68

Conditions: current, 2.0 A; temperature, ambient; concentration (blue food colour, 5 ml/l, Na_2SO_4, 5 g/l)

Table 4.27: Electrochemical decolourisation of blue food colour (brilliant blue FCF & carmoisine) in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.5	5.87	Blue	0
5	5.2	5.90	Grey	99
15	8.0	5.96	Colourless	100
30	8.6	5.95	Colourless	100
60	9.0	5.93	Colourless	100
120	9.6	5.83	Colourless	100
240	8.5	5.85	Colourless	100
360	8.4	5.90	Colourless	100
480	8.5	5.93	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (blue food colour, 5 ml/l, NaCl, 5 g/l)

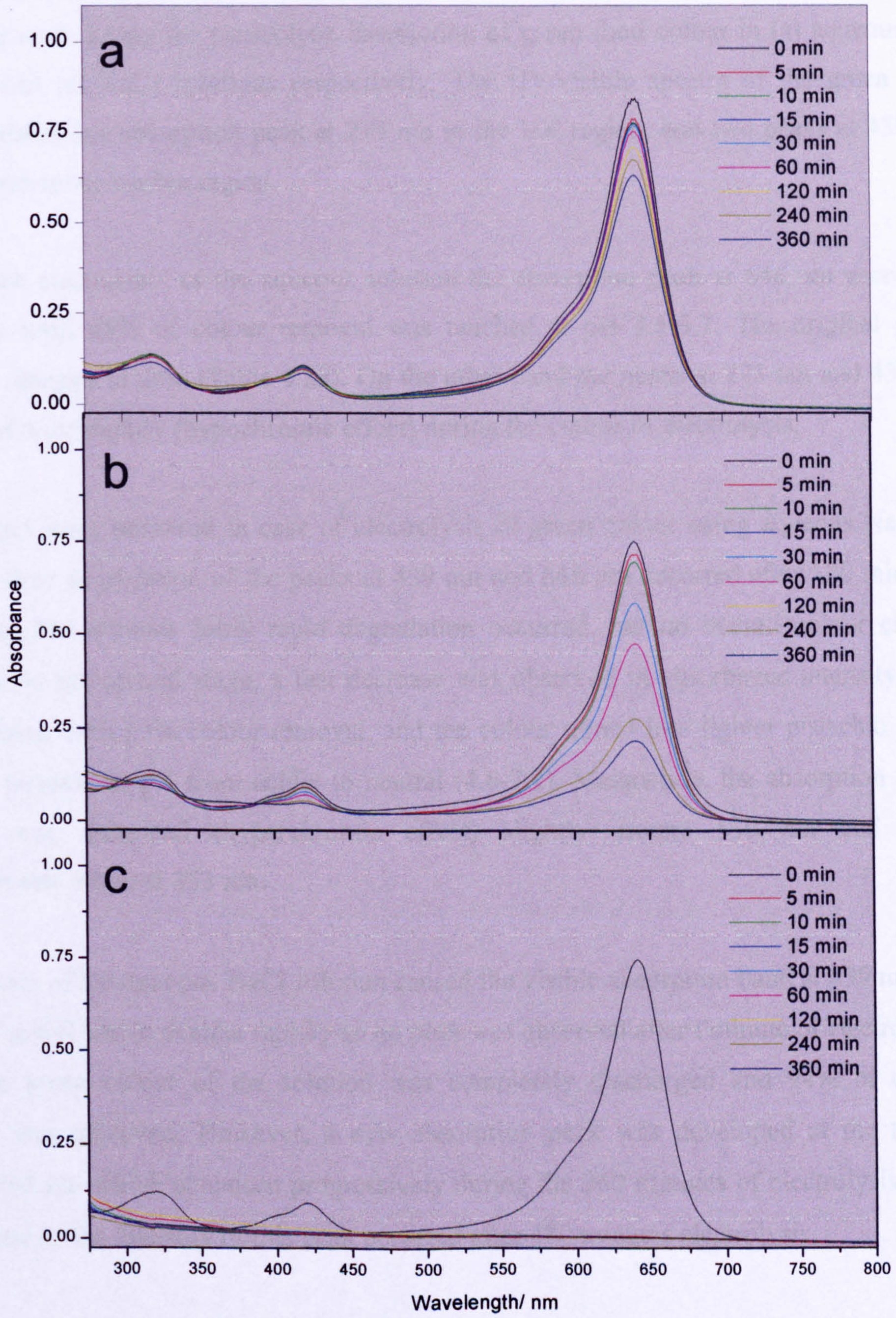


Figure 4.9: UV-Visible spectra during the electrolytic destruction of blue food colour in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions

4.8.7 Degradation of Green Food Colour (Tartrazine, Green S) by Electrolytic Process

The data in Tables 4.28-4.30 and Figure 4.10 show the electrolytic conditions and the UV-Visible spectra during the electrolytic destruction of green food colour in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions respectively. The UV/visible spectra of the green food colour exhibit one absorption peak at 275 nm in the UV region, and two peaks at 439 nm and 646 nm in the visible region.

During the electrolysis of the aqueous solution the absorption peak at 646 nm decreased gradually until 85% of colour removal was reached at pH 3.5-3.7. The original green solution changed to lime (Table 4.28). On the other hand the peaks at 275 nm and 439 nm decreased only slightly (hypochromic effect) during the course of electrolysis.

Two stages were observed in case of electrolysis of green colour using aqueous Na_2SO_4. Initially slow degradation of the peaks at 439 nm and 646 nm occurred after 120 minutes, then after 240 minutes fairly rapid degradation occurred, but no overall colour change occurred. In the second stage, a fast decrease was observed in absorbance intensity after 360 minutes, with 85% colour removal, and the colour turned into lighter pistachio green with an increase in pH from acidic to neutral (4.6-7.2). Meanwhile, the absorption at the troughs was enhanced (hyperchromic effect) slightly around 530 nm and more hyperchromic effect at 353 nm.

Electrolysis of the aqueous NaCl solution caused the visible absorption band at 439 nm and the peak at 641 nm to decline rapidly so no peak was observed after l minute of electrolysis. Also the green colour of the solution was completely discharged and 94% of colour removal was achieved. However, a new absorption peak was developed at the trough around 308 nm which enhanced progressively during the 360 minutes of electrolysis time. A decrease of the intensity of this peak occurred after 480 minutes electrolysis.

Table 4.28: Electrochemical decolourisation of green food colour in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	3.5	15.71	Green	0
15	3.7	15.69	Green	07
30	3.5	15.63	Green	11
60	3.5	15.25	Green	24
120	3.5	15.62	Green	39
240	3.5	15.31	Light green	62
360	3.7	15.02	Lime	76
480	3.7	15.62	Lime	85

Conditions: current, 0.071 A; temperature, ambient; concentration (green food colour, 5 ml/l)

Table 4.29: Electrochemical decolourisation of green food colour in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.6	10.20	Green	0
15	4.6	10.02	Green	02
30	4.7	9.80	Green	04
60	4.6	9.60	Green	07
120	4.6	9.45	Green	12
240	4.7	9.38	Green	26
360	7.0	9.34	Light green	83
480	7.2	9.28	Pistachio green	85

Conditions: current, 2.0 A; temperature, ambient; concentration (green food colour, 5 ml/l; Na_2SO_4, 5 g/l)

Table 4.30: Electrochemical decolourisation of green food Colour in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.3	7.71	Green	0
1	4.5	7.59	Colourless	94
15	6.5	7.55	Colourless	98
30	5.3	7.47	Colourless	98
60	5.4	7.50	Colourless	98
120	5.2	7.53	Colourless	98
240	5.5	7.57	Colourless	99
360	5.7	7.59	Colourless	100
480	5.7	7.65	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (green food colour, 5 ml/l; NaCl, 5 g/l)

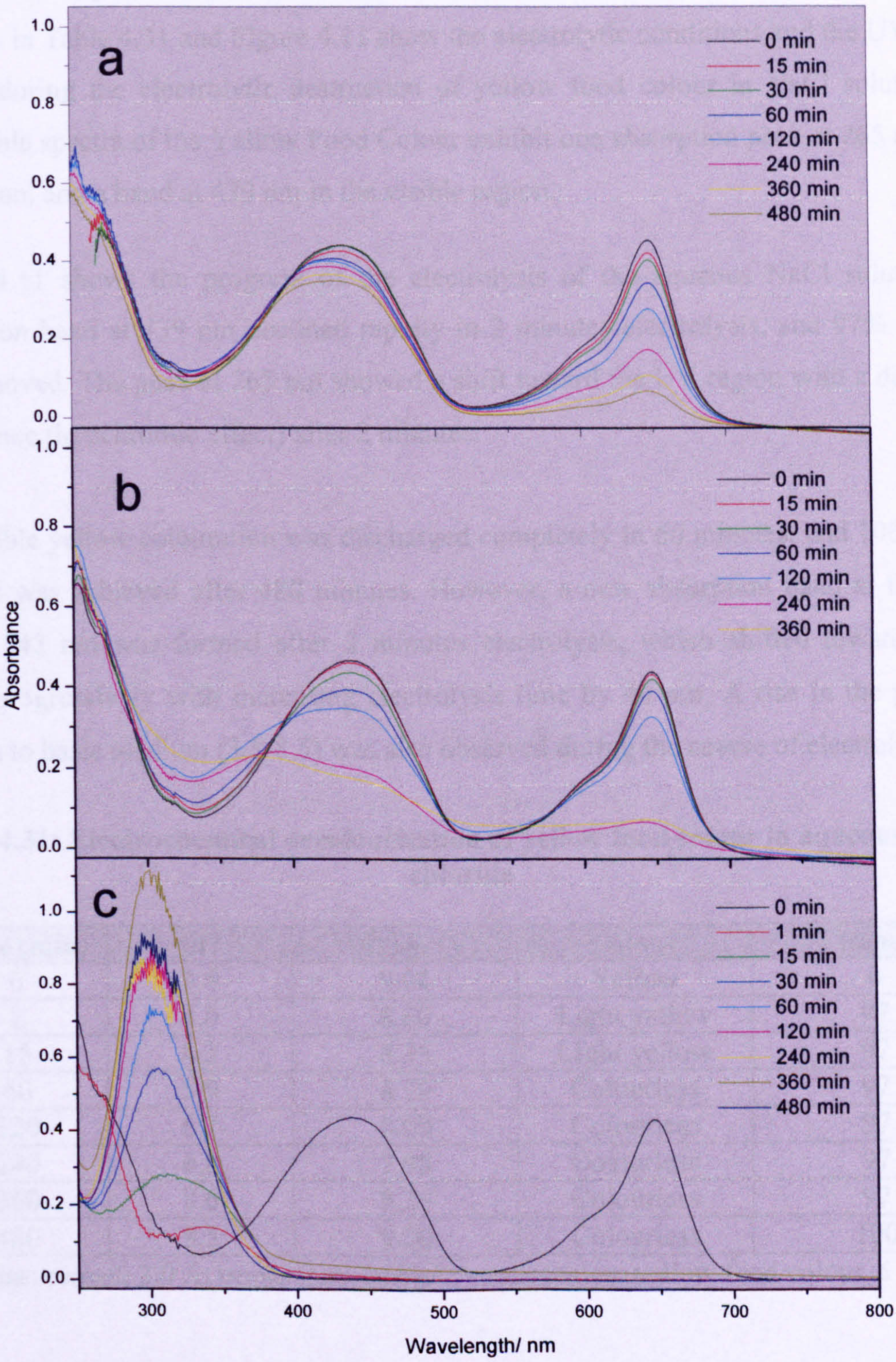


Figure 4.10: UV-Visible spectra during the electrolytic destruction of green food colour in (a) aqueous, (b) Na_2SO_4 and (c) NaCl solutions

4.8.8 Degradation of Yellow Food Colour (Tartrazine, Sunset Yellow FCF, Ponceau 4R) by Electrolytic Process

The data in Table 4.31 and Figure 4.11 show the electrolytic conditions and the UV-Visible spectra during the electrolytic destruction of yellow food colour in NaCl solution. The UV/visible spectra of the Yellow Food Colour exhibit one absorption peak at 265 nm in the UV region, and a band at 439 nm in the visible region.

Figure 4.11 shows the progress of the electrolysis of the aqueous NaCl solution. The absorption band at 439 nm declined rapidly in 2 minutes electrolysis, and 97% of colour was removed. The peak at 265 nm showed a shift toward the UV region with a decrease in absorbance (hyochromic effect) after 2 minutes.

The visible yellow colouration was discharged completely in 60 minutes, and 100% colour removal was achieved after 480 minutes. However, a new absorption band at the trough around 342 nm was formed after 2 minutes electrolysis, which shifted toward the UV region progressively with increasing electrolysis time by 40 nm. A rise in the pH of the solution to basic medium (3.8-8.5) was also observed during the course of electrolysis.

Table 4.31: Electrochemical decolourisation of yellow food colour in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	3.8	9.04	Yellow	0
2	4.0	8.60	Light yellow	97
15	4.2	8.35	Light yellow	97
60	5.9	8.20	Colourless	97
120	6.7	8.00	Colourless	97
240	6.8	7.98	Colourless	97
360	8.6	8.20	Colourless	97
480	8.5	9.00	Colourless	100

Conditions: current, 2.0 A; temperature, ambient; concentration (yellow food colour, 5 ml/l; NaCl, 5 g/l)

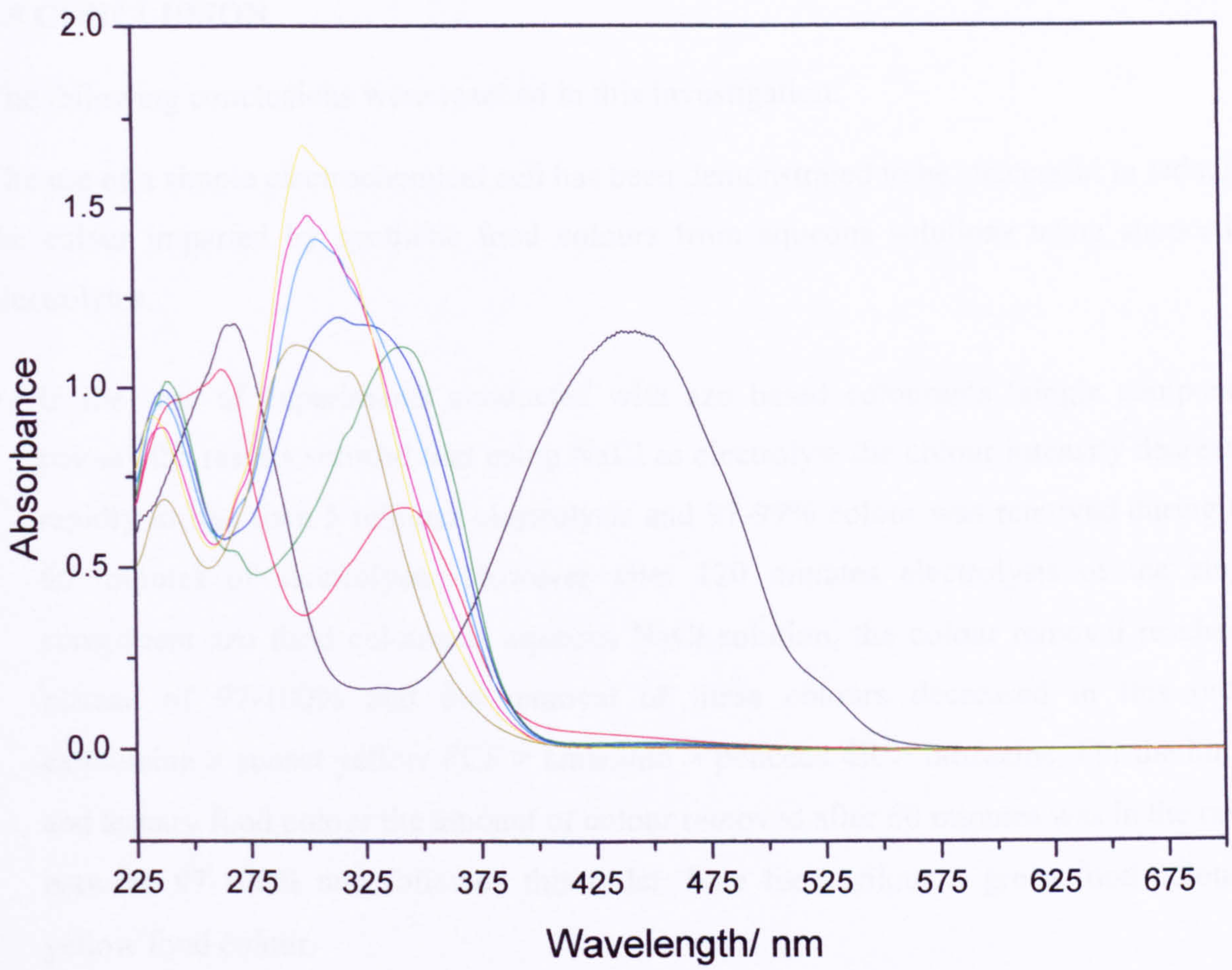


Figure 4.11: UV-Visible spectra during the electrolytic destruction of yellow food colour in NaCl solutions.

Electrolysis time: 0 min____, 2 min____, 15 min____, 60 min____, 120 min____, 240 min____, 300 min____ and 480 min____.

4.9 CONCLUSION

The following conclusions were reached in this investigation:

The use of a simple electrochemical cell has been demonstrated to be successful in reducing the colour imparted by synthetic food colours from aqueous solutions using supporting electrolytes.

- In the case of experiments conducted with azo based colourants (single component colour) the results showed that using NaCl as electrolyte the colour intensity decreased rapidly in less than 5 minutes electrolysis and 97-99% colour was removed during the 60 minutes of electrolysis. However after 120 minutes electrolysis of the single component azo food colours in aqueous NaCl solution, the colour removal reached a plateau of 97-100% and the removal of these colours decreased in this order: carmoisine > sunset yellow FCF > amaranth > ponceau 4R > tartrazine. For the binary and ternary food colour the amount of colour removed after 60 minutes was in the range between 97-100% and followed this order: blue food colour > green food colour > yellow food colour.

- The addition of Na_2SO_4 as a supporting electrolyte also increased the colour removal efficiency slowly. About 51-80% and 89-98% of colour destruction was achieved during the 120 and 480 minutes of electrolysis and the decolourisation rate increased in the order: sunset yellow FCF > amaranth > carmoisine > ponceau 4R > tartrazine for single component azo colour. However, electrochemical degradation conducted on binary mixtures of blue and green colours using Na_2SO_4 as electrolyte over 480 minutes showed only 68-85% colour removal and the rate of removal was green > blue food colour.

- The electrolytic process in the absence of added electrolyte was less effective in removing the colour of the single component azo food colours from aqueous solution. For example, after 120 minutes electrolysis the colour removal achieved ranged from 11 to 59% and followed this decreasing order: sunset yellow FCF > carmoisine >

ponceau 4R > amaranth > tartrazine. In case of the binary food colours, the range of decolourisation was from 10 to 39% following this order: green > blue food colour.

- Except for tartrazine, all other dyes (amaranth, carmoisine, ponceau 4R, sunset yellow FCF) are naphthol-based dyes with two or three sulphonic groups. The above results showed that tartrazine was the least decolourised and this could be due to the presence of the pyrazole ring and carboxylate group. This suggested that there is some selectivity for substrate structure in the destruction of azo dyes during the electrolytic process.

- The result also showed that prolonging the time of electrolysis of the food colours from 60 minutes to 480 minutes has no significant effect on the colour removal when NaCl was used as a supporting electrolyte. Meanwhile extending the electrolysis process to remove food colours from aqueous and Na_2SO_4 solutions from 60 minutes to 480 minutes showed a significant and gradual increase. For example, the percentage removal of amaranth from aqueous Na_2SO_4 solution was 58, 79 and 91% after 60, 120 and 480 minutes, respectively.

- The UV spectra indicate that intermediate products were formed during the 480 minutes electrolysis in the cases of sunset yellow FCF, tartrazine, green colour and yellow colour in aqueous NaCl. For example, in the cases of amaranth and sunset yellow FCF, 41 and 54% TOC reduction was achieved. Meanwhile the UV-visible spectra of carmoisine and blue food colour showed no peaks in the UV region indicating that no significant amounts of organic compounds remain as intermediate compounds in the electrolytic solutions.

The data in Tables 4.32-4.34 and Figures 4.12-4.14 showed the percentage removal of the synthetic food colours after 60, 120 and 480 minutes electrolysis.

Table 4.32: The colour removal percentage at 60 minutes electrolysis

Dye	% Colour removal		
	Aqueous	Na_2SO_4	NaCl
Amaranth	20	58	99
Carmoisine	44	57	99
Ponceau 4R	18	52	97
Sunset yellow FCF	40	57	99
Tartrazine	–	33	97
Blue food colour	09	22	100
Green food colour	24	07	98
Yellow food colour	–	–	97

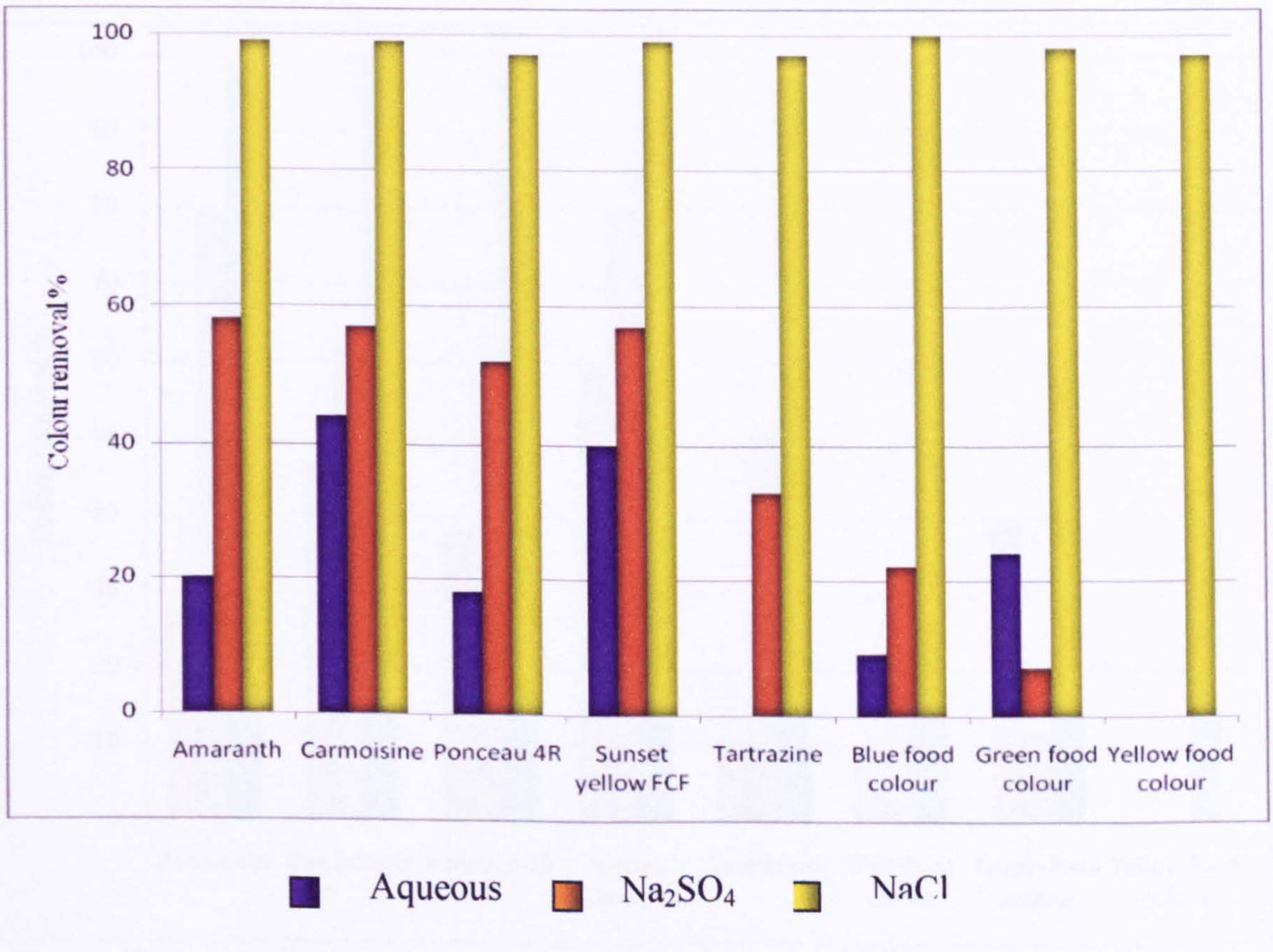


Figure 4.12: The colour removal percentage of the synthetic food colours after 60 minutes electrolysis

Table 4.33: The colour removal percentage at 120 minutes electrolysis

Dye	% Colour removal		
	Aqueous	Na_2SO_4	NaCl
Amaranth	28	79	99
Carmoisine	47	62	100
Ponceau 4R	38	58	98
Sunset yellow FCF	59	80	99
Tartrazine	11	51	97
Blue food colour	10	22	100
Green food colour	39	12	98
Yellow food colour	–	–	97

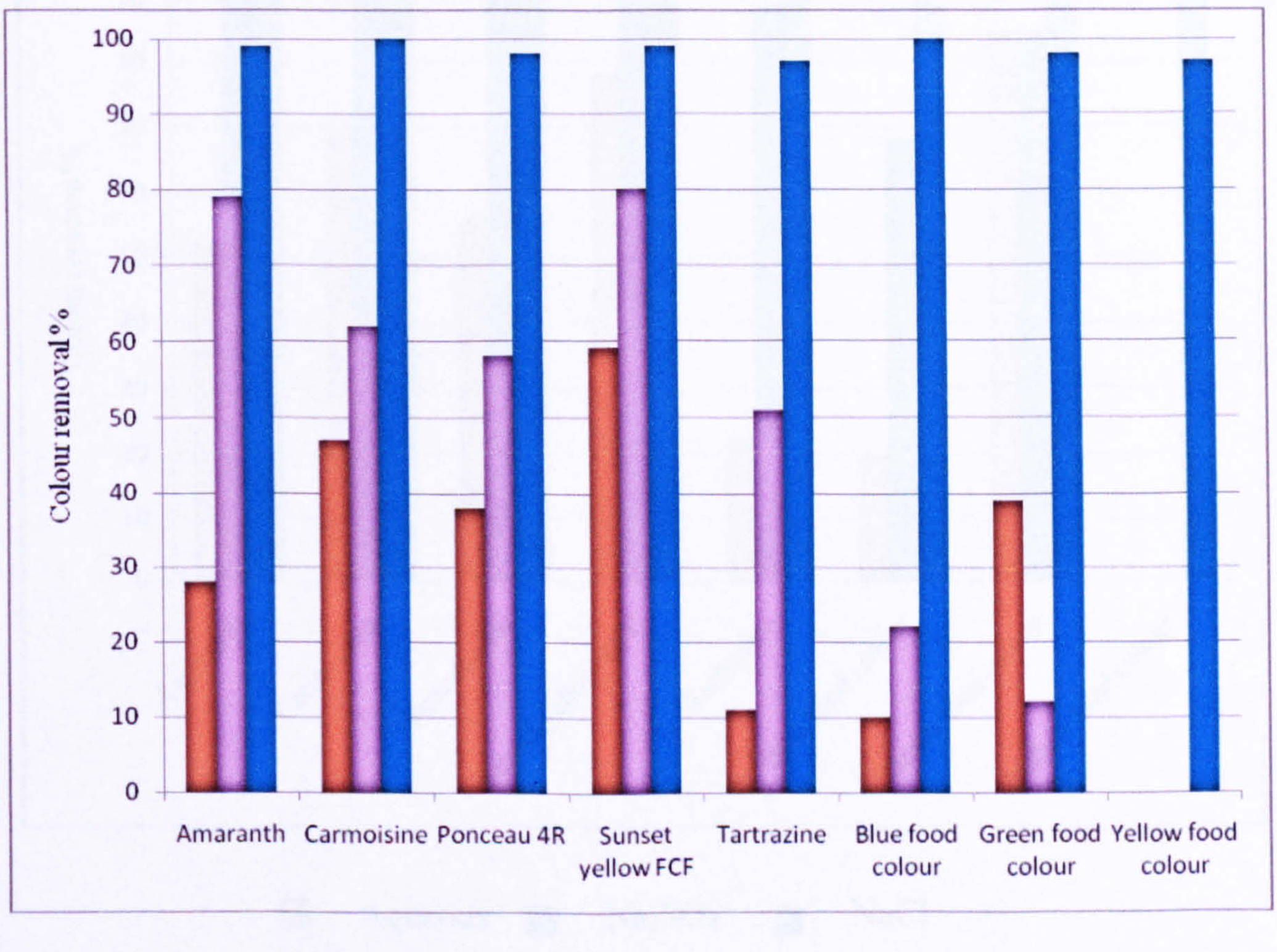


Figure 4.13: The colour removal percentage of the synthetic food colours after 120 minutes electrolysis

Table 4.34: The colour removal percentage at 480 minutes electrolysis

Dye	% Colour removal		
	Aqueous	Na_2SO_4	NaCl
Amaranth	52	91	99
Carmoisine	70	91	100
Ponceau 4R	56	90	100
Sunset yellow FCF	78	98	100
Tartrazine	22	89	97
Blue food colour	20	68	100
Green food colour	85	85	100
Yellow food colour	–	–	100

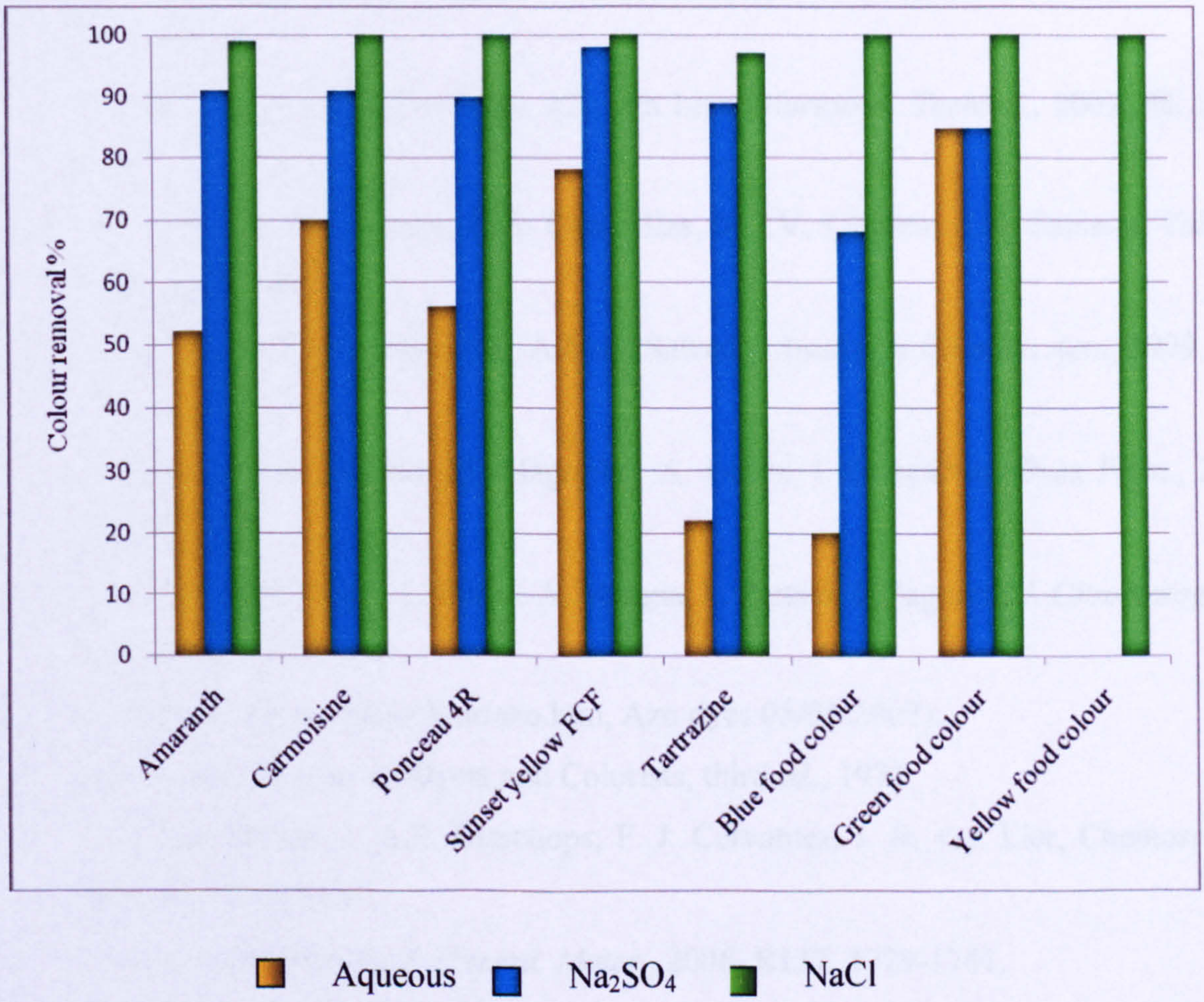


Figure 4.14: The colour removal percentage of the synthetic food colours after 480 minutes electrolysis

4.10 REFERENCES

1. M. Tripathi, S.K. Khanna, M. Das, *Food Control*, 2007, **18**, 211-219.
2. K.S. Minioti, C.F. Sakellariou, N.S. Thomaidis, *Analytica Chimica Acta*, 2007, **583**, 103-110.
3. M. Ma, X. Luo, B. Chen, S. Su, S. Yao, *J. Chromatogr. A*, 2006, **1103**, 170-176.
4. A. Downham and P. Collins, *Int. J. Food Sci. Technol.*, 2000, **35**, 5-22.
5. http://ec.europa.eu/food/fs/sfp/flav_indexen.html, food additives (28/06/2006).
6. http://en.wikipedia.org/wiki/Food_coloring, food coloring (04/01/2007).
7. Q.-C. Chen, S.-F. Mou, X.-P. Hou, J.M. Riviello, Z.-M. Ni, *J. Chromatogr. A*, 1998, **827**, 73-81.
8. A.B. dos Santos, F.J. Cervantes, J.B. van Lier, *Bioresour. Technol.*, 2007, **98**, 2369-2385.
9. J.J.B. Nevado, J.R. Flores, C.G. Cabanillas, M.J.V. Llerena, A.C. Salcedo, *Talanta*, 1998, **46**, 933-942.
10. J.J.B. Nevado, C.G. Cabanillas, A.M.C. Salcedo, *Analytica Chimica Acta*, 1999, **378**, 63-71.
11. A. Fernandes, A. Morão, M. Magrinho, A. Lopes, I. Gonçalves, *Dyes Pigm.*, 2004, **61**, 287-296.
12. F. Calbiani, M. Careri, L. Elviri, A. Mangia, L. Pistarà, I. Zagnoni, *J. Chromatogr. A*, 2004, **1042**, 123-130.
13. www.food-info.net/uk/colour/azo.htm, Azo dyes 05/01/2007).
14. Color Index, Society of Dyers and Colorists, third ed., 1971.
15. A. B. dos Santos, I. A.E. Bisschops, F. J. Cervantes, J. B. van Lier, Chemosphere, 2004, **55**, 1149–1157.
16. R. Patel and S. Suresh, *J. Hazard. Mater.*, 2006, **B137**, 1729-1741.
17. T. Kurbus, Y.M. Slokar, A.M. Le Marechal, D.B. Vončina, *Dyes Pigm.*, 2003, **58**, 171-178.
18. J. Gooding, R.G. Compton, C.M. Brennan, J.H. Atherton, *J. Colloid Interface Sci.*, 1996, **180**, 605-613.

19. M.H. Vijaykumar, P.A. Vaishampayan, Y.S. Shouche, T.B. Karegoudar, *Enzyme Microb. Technol.*, 2007, **40**, 204-211.
20. A. Eriksson, Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 638, 2001, Acta Universitatis Upsaliensis Uppsala.
21. S. Combeau, M. Chatelut, O. Vittori, *Talanta*, 2002, **56**, 115-122.
22. Y. Ni, J. Bai, L. Jin, *Analytica Chimica Acta*, 1996, **329**, 65-72.
23. Y. Ni and J. Bai, *Talanta*, 1997, **44**, 105-109.
24. S. Mo, J. Na, H. Mo, *Talanta*, 1992, **39**, 1255-1258.
25. www.bryngollie.freeserve.co.uk/Enumbers.htm#E122.
26. http://en.wikipedia.org/wiki/Tartrazine, Tartrazine (28/06/2006).
27. www.yourtruehealth.com, what foods are safe to eat? (20/11/2003).
28. D.F. Duxbury, *Chem. Rev.*, 1993, **93**, 381-433.
29. www.britannica.com/eb/article-9073407/triphenylmethane-dye, triphenylmethane (05/01/2007).
30. www.drugs.com/dict/triphenylmethane_dyes.html, triphenylmethane (05/01/2007).
31. L.D. Giovine and A.P. Bocca, *Food Control*, 2003, **14**, 131-135.
32. M.C. Gennaro, E. Gioannini, S. Angelino, R. Aigotti, D. Giacosa, *J. Chromatogr. A*, 1997, **767**, 87-92.
33. M. Hanssen, J. Marsden, E for Additives, (The Complete Number Guide), 1985, Thornson Publishers Limited, Wellingborough, Northamptonshire.
34. www.eurunion.org/legislat/Foodstuffs/ENumbers.htm, E numbers (06/11/2006).
35. http://en.wikipedia.org/wiki/E_number, E number (06/11/2006).
36. www.foodreactions.org/allergy/additives/, food colours (4/01/2007).
37. M. Masár, D. Kaniansky, V. Madajová, *J. Chromatogr. A*, 1996, **724**, 327-336.
38. J. Bell, J.J. Plumb, C.A. Buckley, D.C. Stuckey, *J. Environ. Eng. (ASCE)*, 2000, **126**, 1026-1032.
39. Y. Ni and X. Gong, *Analytica Chimica Acta*, 1997, **354**, 163-171.
40. M.J. Prival, M.D. Periperl, S.J. Bell, *Fd Chem. Toxic.*, 1993, **31**, 751-758.
41. R.D. Combes and R.B. Haveland-Smith, *Mutat. Res. /Genetic Toxicol.*, 1982, **98**, 101-243.

42. J.P. Brown, G.W. Roem, R.J. Brown, *Mutat. Res. / Fundamental and Molecular Mechanisms of Mutagenesis*, 1978, **56**, 249-271.
43. S.A. Marathe, H.R. Adhikari, M.S. Netrawali, P.M. Nair, *Fd Chem. Toxic.*, 1993, **31**, 739-744.
44. M.J. Prival, V.M. Davis, M.D. Periperl, S.J. Bell, *Mutat. Res. / Genetic Toxicol.*, 1988, **206**, 247-259.
45. E. Weber N.L. Wolfe, *Environ. Toxicol. Chem*, 1987, **6**, 911-920.
46. K.T. Chung, G.E. Fulk, M. Egan, *Appl. Environ. Microbiol.*, 1978, **35**, 558-562.
47. M. Yamada, T. Morimoto, M. Nakamura, H. Nakazawa, *J. Chromatogr. B*, 2001, **754**, 411-417.
48. M.D. Peiperl, M.J. Prival, S.J. Bell, *Fd Chem. Toxic.*, 1995, **33**, 829-839.
49. T. Robinson, G. McMullan, R. Marchant, P. Nigam, *Bioresour. Technol.*, 2001, **77**, 247-255.
50. http://en.wikipedia.org/wiki/Sudan_I, Sudan I (09/01/2007).
51. D. Meiju, H. Xiaogang, Z. Zihao, W. Shouguo, *Food Chem.*, 2007, **105**, 883-888.
52. Daily Mail (London), 22 February 2005. www.dailymail.co.uk, Dye in ready meals.
53. The Colours in Food Regulations 1995, ISBN 0110537319, www.hmso.gov.uk.
54. file://C:\data\sudan2.htm, Sudan I product list 18 February 2005 (04/01/2007).
55. EC Regulation No 178/2002, OJ L. 31 (01/02/2002).
56. Commission Decision of 20 June 2003 on emergency measures regarding hot chilli and hot chilli products, notified under document number C (2003) 1970, (2003/460/EC), OJ No L. 154/114 (21-6-2003).
57. Food Standards Agency, www.food.gov.uk.
58. Implementation of Commision Decision 2003/460/EC of the 21st January 2004.
59. Daily Mail (London), 8 May 2006. www.dailymail.co.uk.
60. R. Adams, *Focus on Pigments*, May 2006, **5**, 1-2.
61. www.pnp.co.za/kitchen/additives.html (28/05/2003).
62. J.J.B. Nevado, C.G. Cabanillas, A.M.C. Salcedo, *Talanta*, 1995, **42**, 2043-2051.
63. www.lactose.co.uk/milkallergy/foodadditives100.html, food additive (24/11/2002).
64. M.A.Q. Alfaro, S. Ferro, C.A. Martínez-Huitle, Y.M. Vong, *J. Braz. Chem. Soc.*, 2006, **17**, 227-236.

65. V. López-Grima and M.C. Gutiérrez, *Chemosphere*, 2006, **62**, 106-112.
66. D. Rajkumar, B.J. Song, J.G. Kim, *Dyes Pigm.*, 2007, **72**, 1-7.
67. D. Dogan and H. Türkdemir, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 916-923.
68. S.B. Jonnalagadda and S. Nadupalli, *Talanta*, 2004, **64**, 18-22.
69. A. Kraft, M. Stadelmann, M. Blaschke, *J Hazard. Mater.*, 2003, **B103**, 247-261.
70. G. Lissens, J. Pieters, M. Verhaege, L. Pinoy, W. Verstraete, *Electrochimica Acta*, 2003, **48**, 1655-1663.
71. J.D. Donaldson, S.M. Grimes, N.G. Yasri, B. Wheals, J. Parrick, W.E. Errington, *J. Chem. Technol. Biotechnol.*, 2002, **77**, 756-760.
72. L. Szpyrkowicz, G.H. Kelsall, S.N. Kaul, M. De Faveri, *Chemical Engineering Science*, 2001, **56**, 1579-1586.
73. J. Naumczyk, L. Szpyrkowicz, F. Zilio-Grandi, *Wat. Sci. Tech.*, 1996, **34**, 17-24.
74. M. Muthukumar, M.T. Karuppiah, G.B. Raju, *Sep. Purif. Technol.*, 2007, **55**, 198-205.
75. H.S. Awad and N. Abo Galwa, *Chemosphere,* 2005, **61**, 1327-1335.
76. R. Podsiadly, J. Sokolowska, A. Mrcinek, J. Zielonka, A. Socha, M. Kazmierska, *J. Photochem. Photobiol. A*: *Chem.*, 2005, **171**, 69-76.
77. A. Wang, J. Qu, J. Ru, H. Liu, J. Ge, *Dyes Pigm.*, 2005, **65**, 227-233.
78. J.P. Lorimer T.J. Mason, M. Plattes, S.S. Phull, *Ultrasonics Sonochemistry*, 2000, **7**, 237-242.
79. N. Goswami, Ph. D Thesis, 2002, Centre for Environmental Research, Brunel University, UK.
80. L. Fan, Y. Zhou, W. Yang, G. Chen, F. Yang, *J. Hazard. Mater*, 2006, **B137**, 1182–1188.
81. S. Hattori, M. Doi, E. Takahashi, T. Kurosu, M. Nara, S. Nakamatsu, Y. Nishiki, T. Furuta, M. Iida, *J. Appl. Electrochem.*, 2003, **33**, 85-91.
82. E. Brillas, E. Mur, R. Sauleda, L. Sànchez, J. Peral, X. Domènech, J. Casado, *Appl. Catal. B: Environ.*, 1998, **16**, 31-42.
83. C.C. Blanco, A.M.G. Campaña, F.A. Barrero, *Talanta*, 1996, **43**, 1019-1027.
84. P.L. López-de-Alba, K. Wróbel-Kaczmarczyk, K. Wróbel, L. López-Martínez, J.A. Hernández, *Analytica Chimica Acta*, 1996, **330**, 19-29.

85. F. Kotb, Medicinal Plants in Libya, 1985, Arab Encyclopedia House, Beirut, Lebanon.
86. M.D. Teli, V. Shanbag, P.R. Kulkarni, R.S. Singhal, *Carbohydrate Polymers*, 1996, **31**, 119-122.
87. J.S. Hirota, H. Miki, K. Fukui, K. Maeda, *J. Crystal Growth*, 2002, **235**, 541-546.
88. http://en.wikipedia.org/wiki/Amaranth, Amaranth (28/06/2006).
89. http://en.wikipedia.org/wiki/Carmisine, Carmisine (28/06/2006).
90. S. Sayar and Y. Özdemir, *Food Chem.*, 1998, **61**, 367-372.
91. B. Lundskov, A.D. Pedersen, E. Andersen, Danish Environmental Protection Agency, Danish Ministry of the Environment, Survey of Chemical Substances in Consumer Products, Survey no.**20**, 2003.
92. H.-Y. Huang, Y.-C. Shih, Y.-C. Chen, *J. Chromatogr. A*, 2002, **959**, 317-325.
93. A. Mittal, J. Mittal, L. Kurup, *J. Hazardous Materials B*, 2006, **136**, 567-578.
94. F. Gosetti, V. Gianotti, E. Mazzucco, S. Polati, M.C. Gennaro, *Dyes Pigm.*, 2007, **74**, 424-432.
95. J. Mon, M. Flur, J.B. Harsh, *Geoderma*, 2006, **133**, 217-224.
96. http://en.wikipedia.org/wiki/ Brilliant blue FCF, brilliant blue FCF (28/06/2006).
97. http://en.wikipedia.org/wiki/Green S, Green S (28/06/2006).
98. http://envfor.nic.in/report/0102/chap07.html, MoEF ANNUAL REPORT 2001-2002 (21/12/2003).

CHAPTER 5

APPLICATION OF NATURAL DYES ON TEXTILE FABRICS

5.1 INTRODUCTION

Plants producing pigments which have current or potential uses in textile dyeing industries represent possible alternative crops having high value and quality. Textiles are articles of prime necessity with a greater degree of 'skin proximity' and regulations have been legislated which seek to avoid risks to the textile end-user [1]. On the other hand, textile dyeing is characterized by high environmental pollution and by high health risk to personnel handling harmful substances. Many colourants from synthetic sources can be harmful and cause allergies in humans, therefore, interest in natural dyes has increased considerably during the last few years [2, 3-11].

Natural dyes have a long and rich history-all the beauty and finery of past age were dyed naturally [12-14], because before 1856 all colours were naturally dyed. Since textile fibres are very fragile, few survive. The oldest known dyed fabrics date only to around 6000 BC. Seeds of the weld plant were found in several Neolithic excavations. There are dyed textiles from lacustrine settlements in Switzerland, Provençal pastel dyed fabrics, and cotton fabrics found in Mohenjo-Daro, in the Indus Valley (2500-1500 BC) [15]. In Crete, murex purple dyes dating to 1600 BC have been found. Ancient textiles have survived best in the dry climate of the eastern Mediterranean, particularly Egypt [14, 15].

In the last decade, investigations about possible use of natural dyes in textile dyeing processes have been performed by various research groups. The dyeing of cotton and jute with tea as a natural dye using alum, copper sulphate, or ferrous sulphate mordants has been studied by Deo and Desai [16]. Bhattacharya et al. [17] investigated the properties of selected natural dyes on jute [17-19]. Chan et al. utilized Chinese tea waste materials in dyeing wool fabric [20]. Brückner et al. investigated the colour depth and fastness properties of selected natural dyes on wool and on synthetic fibres, e.g., polyester, polyamide, and polyacylonitrile [21]. Lokhande and Dorugade presented results with selected natural dyes on polyamide using various mordants, e.g., alum, ferrous sulphate, stannous chloride and tannic acid [22]. In general, the authors described encouraging results with regard to colour depth, shade, and fastness properties. The dyeing procedures are mainly two-bath dyeings including a separated mordanting step, so such processes are

rather difficult to handle in a modern dyehouse. In the study of Brückner [21], the final conclusion focuses on the unsatisfying fastness properties of the natural dyes, which must be understood as an indicator for a distinct need for research to overcome these problems [11].

In the application of the dyes, different techniques of mordanting and post-treatment were used to improve colour fastness properties [3, 23-26]. As a result, a broad set of variations in the dyeing recipes is given in the literature [7, 27-32] and an optimization of the dyeing conditions with regard to the type of natural dye is quite common [8, 33-38].

The numerous variations of plant sources and dyeing processes proposed in the literature make an introduction of natural dyeing into full-scale technical dyeing processes rather difficult. The rapid changes in trends and fashion and the demand for good fastness properties on different substrates requires a basic database describing possible applications of natural dyes, otherwise too much parallel optimisation work has to be done by each dyehouse [7].

This situation has led to a rather controversial discussion of expected advantages resulting from future use of natural dyes. While some experts focus on numerous difficulties which could hinder the successful introduction of natural dyes into regular dyeing processes [39-42], others concentrate more on expected advantages of technologies which are based upon sustainable sources [4, 9, 37]. The introduction of natural dyes into modern dyeing procedures e.g., ultrasonic dyeing [3, 30, 43, 44] that can be seen as one step of a continuous development of textile dyeing and finishing processes towards increased sustainability with regard, for example, to water, chemicals, and energy consumption. As a result of the use of natural products with low toxicity, a decrease in the overall reduction of exposure to harmful chemicals is expected for both textile workers and wearers of the cloths. As long as the natural dyes remain chemically unchanged, the released dyebaths will fit into the natural pathways of biodegradation.

Application of natural antimicrobial agents on textiles dates back to antiquity, when the ancient Egyptians used spices and herbs to preserve mummy wraps. Natural antimicrobials

were used to inhibit the growth of bacteria and mould in the fabric [45]. The prevention of microbial attack on textiles has become increasingly important to consumers and textile producers; therefore, interests in antimicrobial fabric finishing have steadily increased over the last few years [45, 46].

Many of the plants used for dye extraction are classified as medicinal, and some of these have recently been shown to possess remarkable antimicrobial activity. Pomegranate [47] and many other common natural dyes e.g., cutch [46], sumac [48], are reported as potent antimicrobial agents owing to the presence of a large amount of tannins [49-52]. Several other sources of plant dyes rich in naphthoquinones such as lawsone from henna, juglone from walnut, and lapachol from alkannet are reported to exhibit antibacterial and antifungal activity [47, 53]. Pharmacological studies have demonstrated that curcumin used in traditional medicine results in antifungal activities [45].

Due to the fact that natural dyes can often inhibit the growth of microorganisms without toxicity, the study and application of these dyes on fabrics have gained attention [45, 46]. These textiles dyed with these natural dyes can be very useful in developing clothing for infants, elderly and infirm people to protect them against common infections. They will be equally useful in bed linen, carpets and other home textiles, which are major propagators of common infections.

In this research work, results from a study to evaluate sources for natural dyes are presented. Starting with about 53 different types of plants (and one dye of animal origin), which could be used as raw materials for dyestuff extraction, a selection was performed with regard to the following requirements:

- Production of the plant material in sufficient amounts with modern agricultural methods including simple and environmentally clean extraction methods to obtain the dyestuffs.
- Formation of a suitable class of dyes which is, in its applicability, comparable to the classes of synthetic dyes in use at the present.

In literature, this is the second study of natural plant colours to investigate such a large number of dye plants using objective colour descriptors based on sun light analysis and normalised fastness tests to determine colour stability. The first study was carried out by Guinot et al., [54]. In their study, 43 different plant species were investigated for dyeing properties using wool and cotton fabrics. The screening in their study involved a preliminary phytochemical characterisation of dyeing molecules present in the dyeing bath by thin layer chromatography, followed by a dyeing procedure, which included different fabric supports, a colourimetric analysis and a study of the fastness to light and to water of the dyed samples [54].

Objectives:

The objectives of the work described in this chapter are:

- To use natural pigments in dye applications (e.g., textile fabrics)
- To identify major pigments occurring naturally in fruits, vegetables and spices from literature.
- To assess the colour fastness to wash and both natural and artificial sun light.

The aims of the work described in this chapter are to dye three different fabric textiles, paj silk (animal fibre), brushed cotton (plant cellulose fibre) and crystallized shimmering satin (synthetic fibre) with eco-friendly natural dyes, and to investigate the effect of mordants type and mordanting techniques on the dyeing process. The major pigments occurring naturally in each dye are also discussed.

5.2 CLASSIFICATION OF DYES BASED ON COLOUR

Various natural dyes could present all the colours of the visible spectrum. The natural colour and hue of a dye can be altered by treatment with metal salts [44]. If the dye is of plant origin, the colour may vary depending on the part used and its age, the locality and conditions for growth, and season of harvesting [44, 55].

5.2.1 Red Colour Dyes

Most red dyes are found in roots or bark of plants or camouflaged in the bodies of dull grey insects (e.g. cochineal). Unlike the wide abundance of yellow, the sources of red colour are limited.

Cochineal is an important red dye and it is the brightest of all the available natural red dyes. Manjith (munjeet), alizarin and madder among the vegetable sources, lac and kermes among the animal sources give red colours [44] (Table 5.3). Usually the red dyes are of anthraquinone and naphthoquinone type (lawsone from henna) [55], and anthocyanins pigments are also responsible for the red colour of some fruits (e.g., red skin of ripe apple) [56]. Betanin is the major red pigments in the betacyanins (betalains) family (e.g., red beet and prickly pear) [57]. Red colour can also be found in flavonoids (e.g., red clover, madder) (Table 5.4) [1, 55].

5.2.2 Yellow and Orange Dyes

Many of the yellow and orange hues of nature are due to carotenoids [58]. Yellow is the liveliest and perhaps the most abundant colour in nature. The plants, which yield yellow dyes, outnumber those yielding other colours [44]. Carotenes (carotenoids) are responsible for the yellow and orange e.g., lycopene in tomatoes and capsicum. β-carotene is also partly responsible for the colour of mango (Table 5.12) [55, 58]. Xanthophylls (zeaxanthin) are the oxygenated carotenes and are responsible for the yellow colour of *cis*-bixin (annatto), crocin (saffron) and orange colour from norbixin (annatto) [55]. Lutein, a molecule which differs from zeaxanthin only in the location of the last double bond (Figure 5.2) is also responsible for yellow colour. Both kinds of molecules are present in deeply coloured vegetables such as spinach [58]. Both zeaxanthin and lutein collect in the macula region of the retina (the *macula lutea*, or 'yellow spot'), where their two-fold function is to filter out some of the blue light and ultraviolet radiation, to protect the retina against its constant exposure to light, and to scavenge free radicals. Macular degeneration is the most common form of blindness in the elderly, and zeaxanthin is nature's version of internal sun-glasses [58].

Yellow pigments can also be obtained from flavonoids family, flavonols and flavones, e.g. quercetin (onion skins, tea and sumac), kaempferol (tea, indigo) [59], myricetin and fisetin (e.g., sumac), neoflavonoid berberine from barberry [55, 60]. Most natural yellows in the plants occur as glycosides or esters of tannic acid. Gallotannins and ellagitannins are the hydrolysable form of tannins (e.g., sumac, aljedari (debagh), dates, tea and pomegranate) [52, 55] (Table 5.12).

5.2.3 Blue Dyes

Indigo and woad, both contained the same principal colouring matter, indigo can be found in the leaves of indigo plant, *Indegofera inctoria*. Flavonoids, with their principal subclass the anthocyanins give flowers and fruits their red to blue colours (e.g., delphinidin) [55].

5.2.4 Purple Dyes

Originally, purple dye was made from huge numbers of the 'murex' shellfish, and used in Imperial Rome [61]. Only important and wealthy people were allowed to wear this colour and it became known as Imperial Purple. The anthocyanin malvidin can also produce purple colour.

5.2.5 Green Dyes

Chlorophyll is the green pigment used by plants for capturing light energy. Natural sources of chlorophyll are usually spinach, peas, stinging nettle, alfalfa or corn [55].

5.2.6 Black Dyes

No colouring agent yields a perfect black; like white, black is a colour that does not exist in a pure form, except in imagination. Black absorbs all possible light and no paint or dye can quite achieve perfect absorption. Black pigments and dyes are made from very dark browns and blues [15]. In the 18^{th} century black dyes were made based on indigo and the tinctorial woods logwood and sumac.

5.3 CHEMISTRY OF NATURAL COLOURANTS

The plant dye groups considered to be most important are indicated below (with examples of dyes and sources) [55, 62, 63].

A plant species will often contain several dyes and a particular dye may well be present in other plant species than those used as the traditional source. This naturally occurring combination of dyes may be used or a particular dye may be extracted for use alone. Table 5.1 shows the main categories of natural dyes.

Table 5.1: Classification of natural dyes [62]

Dyes classes	Compound type	Colours
Anthracenes	Anthraquinone Naphthoquinone	Red Brown, purple-grey
Carotenoids	Carotene, lycopene Xanthophyll	Yellow, orange, red Yellow
Flavonoids	Flavone Flavonol Anthocyanin	Yellow Yellow Red, blue, purple, magenta
Indigoids	Indigo	Blue
Porphyrins	Chlorophylls	Green
Neoflavonoids	Isoquinoline	Yellow
Tannins	Gallotannin, ellagitannin	Yellow, brown
Benzopyrones	Dihydropyran	Purple, black

5.3.1 Anthracenes

The two major groups of the anthracenes are anthraquinones and napthoquinones [55].

5.3.1.1 α-Hydroxynaphthoquinones

The most prominent members of this class of dyes are lawsone and juglone, which are shown in Figure 5.1. Table 5.2 shows some examples of natural α-hydroxynaphthoquinone dyes with their CI number, CI names and plant sources.

Table 5.2: Examples of natural alpha-hydroxynaphthoquinone dyes [55]

Dye name	CI[a] number	CI name	Natural source
Lawsone	75480	Natural Orange 6	*Lawsonia inermis*
Lapachol	75490	Natural Yellow 16	Taigu or lapachol wood
Juglone	75500	Natural Brown 7	Walnut shells
Deoxysantalin	75510	Natural Red 22, 23	Sandelswood, barwood
Alkannan	75520	Natural Red 20	*Anchusa tinctoria*
Alkanin or anchusin	75530	Natural Red 20	*Anchusa tinctoria*
Shikonin	75535	n.a.	*Lithospermum erythrorhizon*

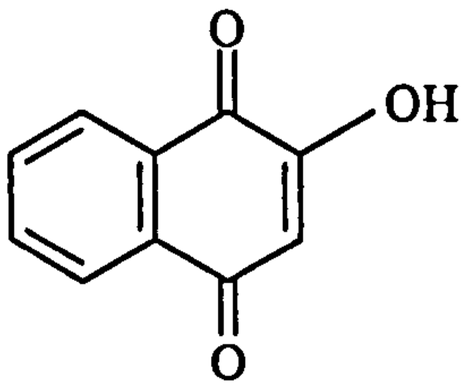
[a] Colour index, n.a.; not available

5.3.1.2 Anthraquinones

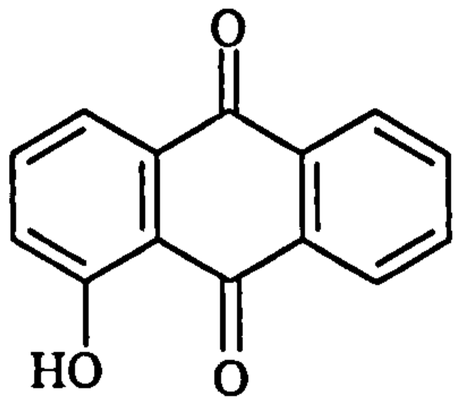
Some of the most important red dyes are based on the anthraquinone structure. They are obtained both from plants and insects [55]. Table 5.3 lists some examples of the key features of natural anthraquinone dyes. The chemical structures of some anthraquinones are shown in Figure 5.1.

Table 5.3: Examples of natural anthraquinone dyes [55]

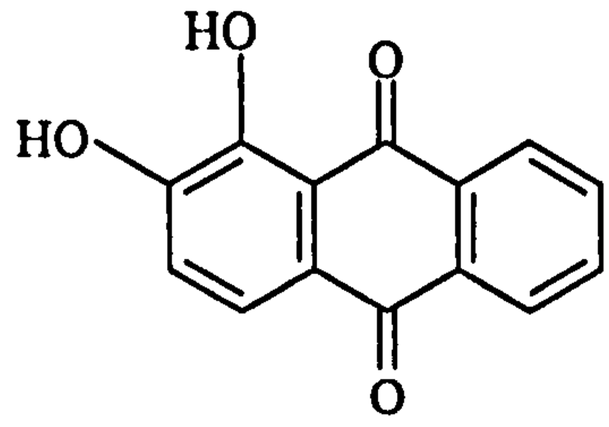
Dye name	CI number	CI name	Natural source
Alizarin	75330	Natural Red 6,8,9,10,11,12	Madder, chayroot
Purpuroxanthin	75340	Natural Red 8, 16	Madder, munjeet
Rubuadin	75350	Natural Red 8,16	Madder, *Gallium*
Morindanigrin	75360	Natural Red 19	*Morinda umbellata*
Munjistin or purpurin-xanthin-carboxylic acid	75370	Natural Red 16,8	Madder, munjeet
Morindadiol	75380	Natural Red 18	Morinda root
Sorajidiol	75390	Natural Red 18	Morinda root
Chrysophanic acid	75400	Natural Red 23	Turkey rhubarb
Purpurin	75410	Natural Red 16,8	Munjeet, madder
Pseudopurpurin	75420	Natural Red 14,9,8	*Gallium*, madder
Morindon	75430	Natural Red 19	Oungkouda
Emodin	75440	Natural Green 2	Persian berries
Laccaic acid	75450	Natural Red 25	*Coccus laccae*
Kermesic acid	75460	Natural Red 3	*Coccus ilici*
Carminic acid (cochineal)	75470	Natural Red 4	*Coccus cacti*



Lawsone

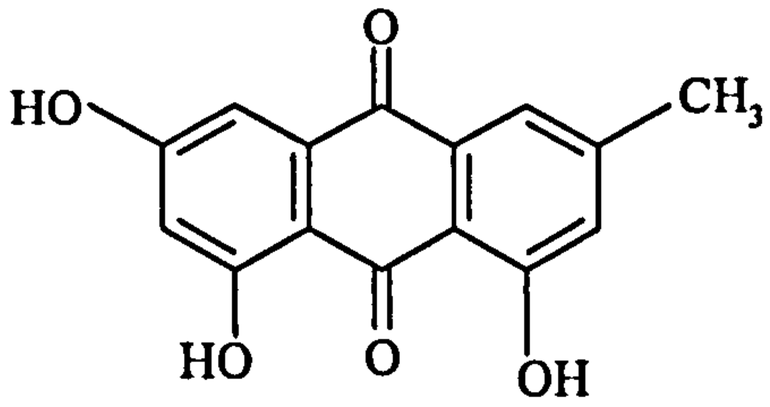


Juglone



Alizarin

Carminic acid



Emodin

Figure 5.1: Chemical Structures of α- hydroxy naphthoquinones and anthraquinones

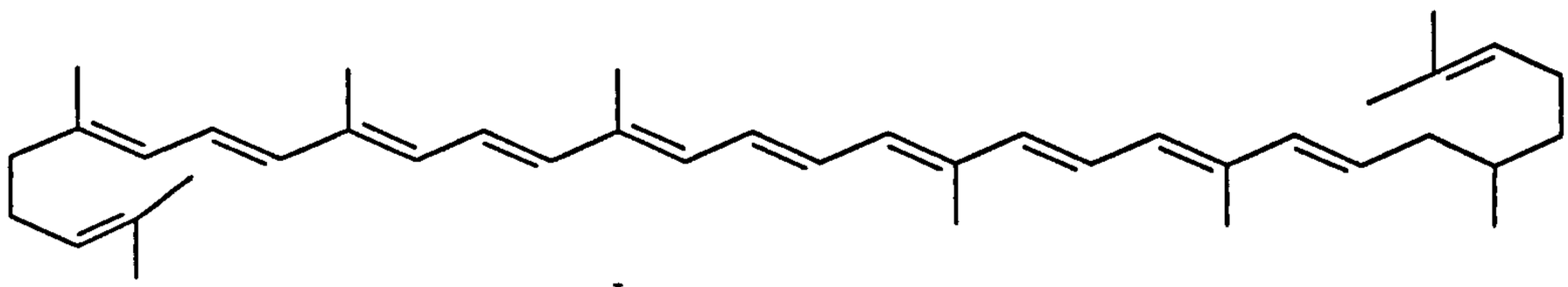
5.3.2 Carotenoids (Isoprenoids)

These are a family of yellow and orange pigments found in most photosynthesising organisms. The colour is due to the presence of an extended conjugated system of double bonds. Over 200 naturally occurring carotenoids have been identified but only a few are commercially available, including β-carotene, β-apo-8'-carotenal and canthaxanthin.

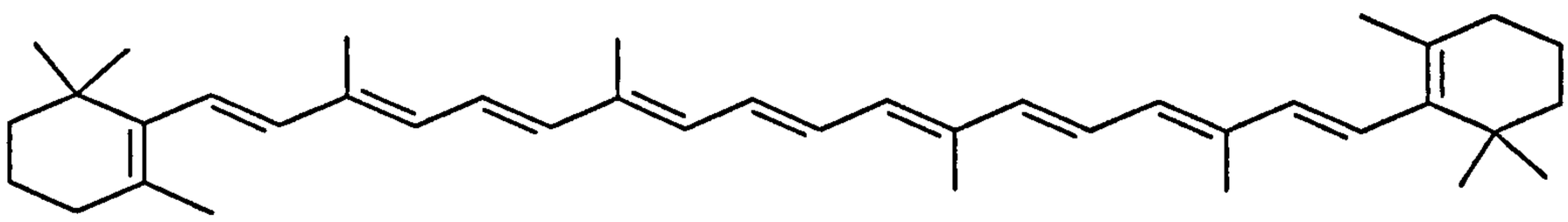
The carotenoid pigments are terpenoids based on a structure of 40 carbon atoms, and sometimes one or both ends of the carbon chain and an alicyclic group. Carotenoids are lipid soluble and, water insoluble except when very strong polar groups, such as polysaccharides, esterify the carotenoid backbone. A good example is crocetin glycosyl esters, dyes that give the colour to saffron stigmas [64]. The two major groups in the family are the **carotenes** (orange or red-orange) and the **xanthophylls** (yellow) [55].

5.3.2.1 Carotenes

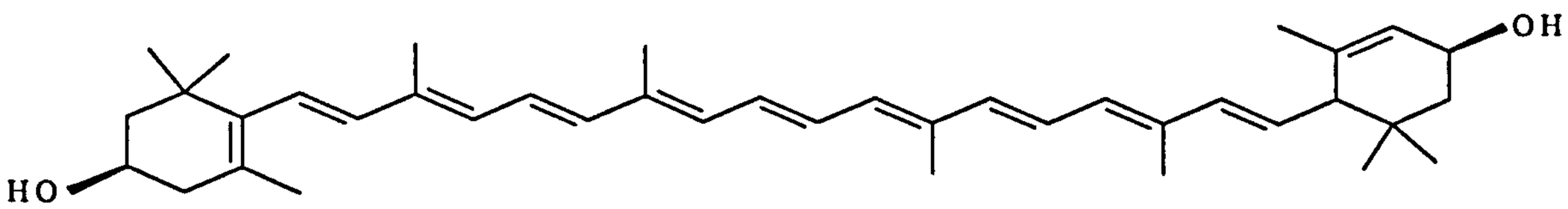
Carotene was first isolated as red crystals from carrots in 1831. It is closely related to vitamin A and generally occurs as a mixture of α-, β- and γ-carotene in the ratio 15:85:0.1. Carotenes can also be isolated from tomatoes in the form of lycopene [55].



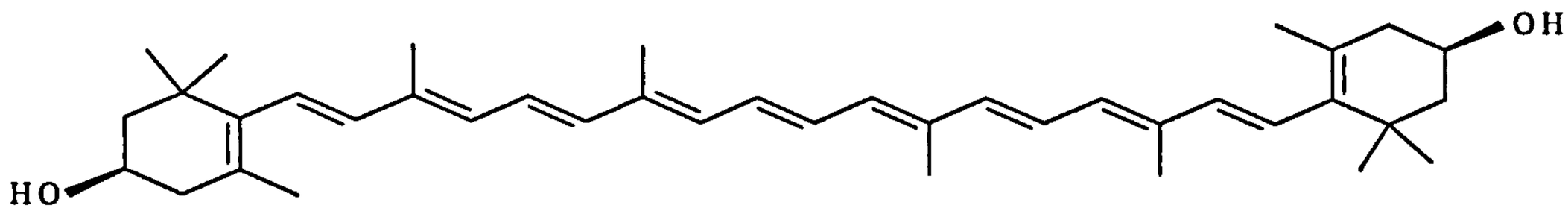
Lycopene



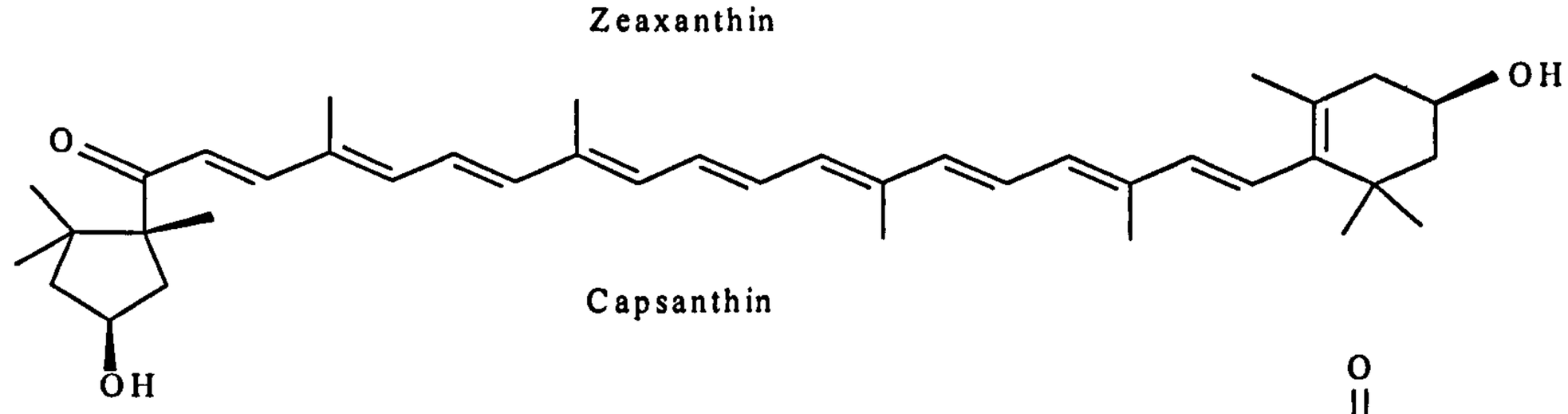
Beta-carotene



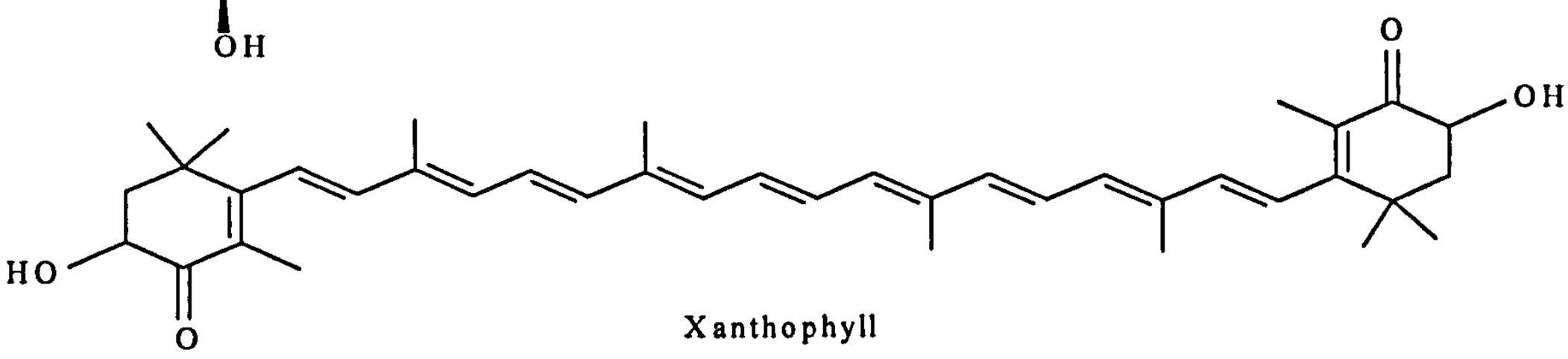
Lutein



Zeaxanthin



Capsanthin

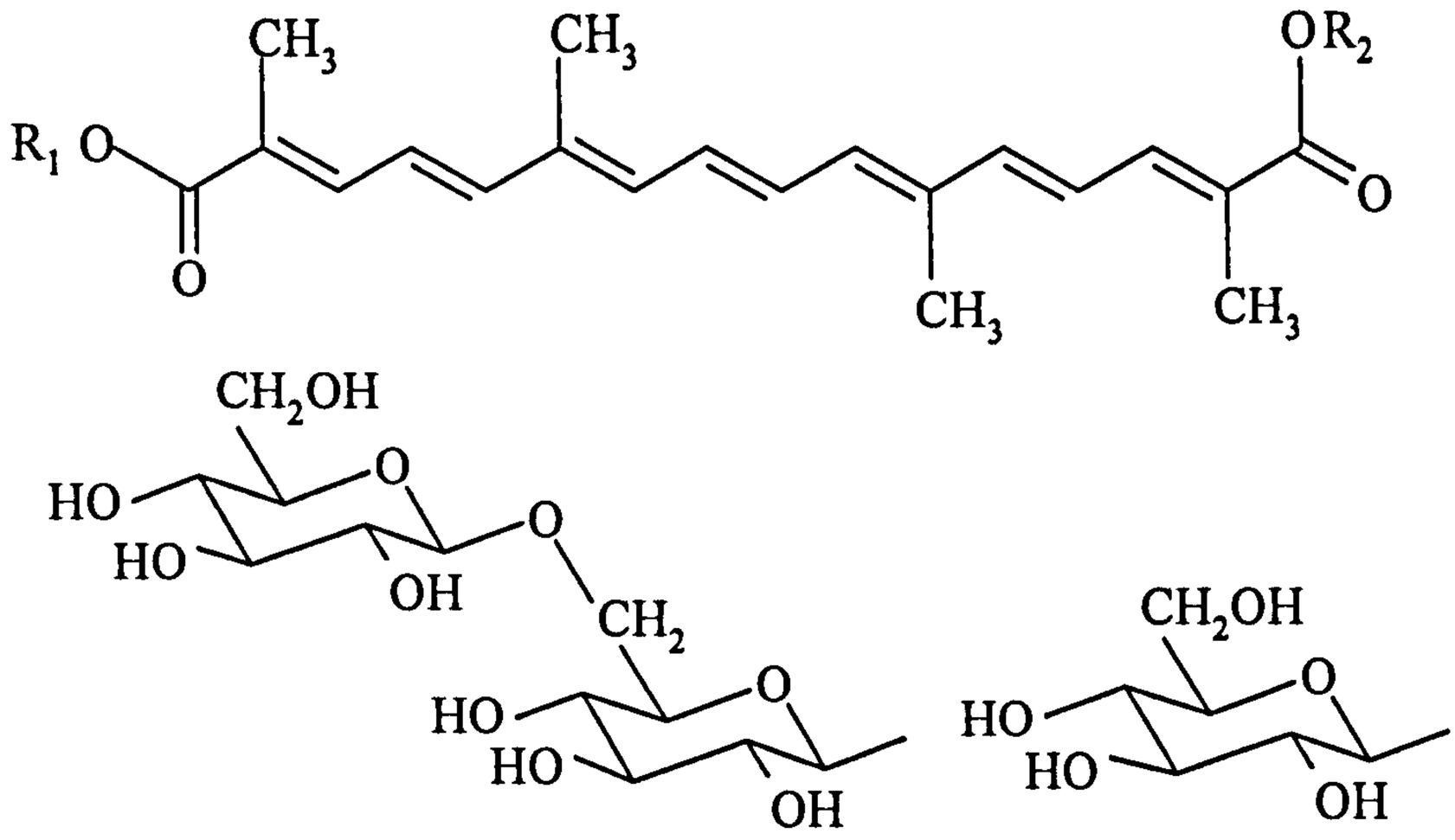


Xanthophyll

Figure 5.2: Chemical structures of carotenoids

5.3.2.2 Xanthophylls

These are oxygenated carotenes. Examples are - lutein (nettles, French marigolds), *cis*-bixin (annatto), crocin (saffron), capsicum (peppers) [55, 64]. Figures 5.2 and 5.3 show the chemical structures of some of the carotenoids found in plants.



X = ß-D-gentiobiosyl

Y= ß-D-glucosyl

Crocins (1: R_1=R_2=X; 2: R_1=X, R_2=Y, 3: R_1=X, R_2=H, 4: R_1=Y, R_2=H) and crocetin (R_1=R_2=H)

Figure 5.3: Chemical structures of some crocin and crocetin carotenoids found in saffron stigmas

5.3.3 Flavonoids

The structure of the flavonoids is based on the flavonoid nucleus, which consists of three phenolic rings referred to as the A, B, and C rings (Figure 5.4). The benzene ring A is fused with a six-member ring (C), which in the 2-position carries a phenyl substituent. Ring C may be a heterocyclic pyran, which yields flavanols (catechins) (Figure 5.4) and anthocyanidins (Figure 5.5), or pyrone, which yields flavonols, flavones, and flavanones (Figure 5.4) [65].

The oxidation state of the pyrone ring and the hydroxylation or methoxylation of ring (A) distinguish the various groups of flavonoids [66]. The three major groups are the flavones, flavonols and anthocyanidins; others include the anthocyanins, isoflavonoids, chalcones and aurones.

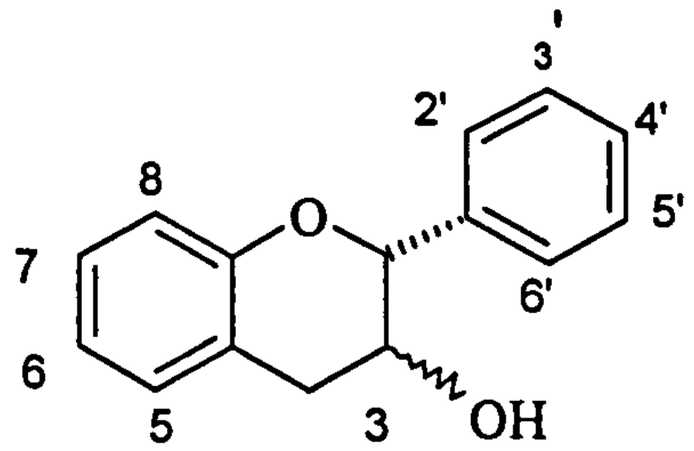
In plants, they are relatively resistant to heat, oxygen, dryness, and moderate degrees of acidity but can be modified by light. Photostability of the flavonoid molecule depends on

the nature of the hydroxyl group attached to C-3 of ring C (Figure 5.4). The absence or glycosylation of this hydroxyl group results in high photostability of the molecule [65].

Table 5.4: Examples of natural flavonoid dyes

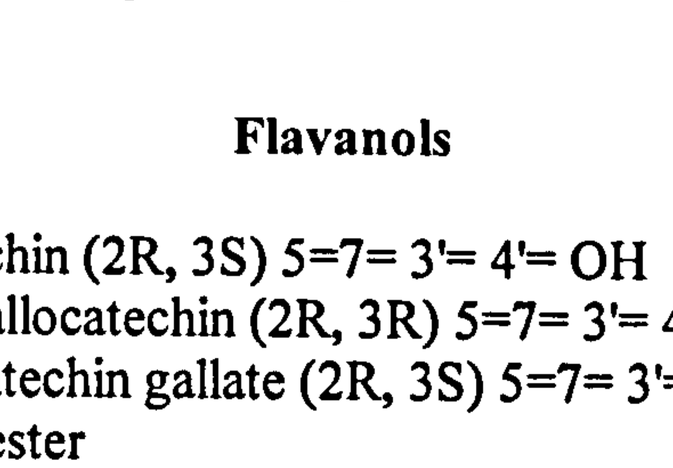
Dye name	CI number	CI name	Natural source
Pratol	75570	Natural Yellow 10	Red clover
Apigenin	75590	Natural Yellow 1, 2	Greek chamomiles, weld
Luteolin	75590	Natural Yellow 2	Dyers rocket, dyers wood
Fulsugetin	75600	–	Garcinia spicata
Genistein or prunetol	75610	–	Dyers broom, greenweed
Fisetin	75620	Natural Brown 1	Venetian sumac
Datiscetin	75630	Natural Yellow 12	Hemp
Kaempferol, trifolitin or indigo yellow	75640	Natural Yellow 13,10	Natal indigo, dyers knotgrass
Kaempferol-7-methyl ether	75650	Natural Green 2	Sap green, Hungarian berries
Morin	75660	Natural Yellow 8,11	Dyers mulberry, osage orange
Quercetin, meletin or sophoretin	75670	Natural Yellow 10, Natural Red 1	Persian, berries, Indian mahogany tree
Isorhamnetin	75680	Natural Yellow 10	Red clover
Rhamnetin	75690	Natural Yellow 13	Buckthorn
Xanthorhamnin	75700	Natural Green 2, Natural Yellow 13	Sap green, Hungarian berries
Rhamnazin	75710	Natural Yellow 13	Persian berries, dyers buckthorn
Quercimeritrin	75720	Natural Yellow 10	Indian cotton
Quercitron	75730	Natural Yellow 10	Quercitron bark
Rutin	75740	Natural Yellow 10	Chinese berries
Gossypetin	75750	Natural Brown 5, Natural Yellow 10	Indian cotton

Flavonoids tend to absorb UV-B light very strongly and it is thought that they may play a role in preventing damage to leaf tissues by ultraviolet radiation. They also attract insects such as pollinators sensitive to UV light by causing UV-reflecting patterns on flowers [55]. Figure 5.4 and 5.5 show the chemical structures of the main flavonoid subclasses.



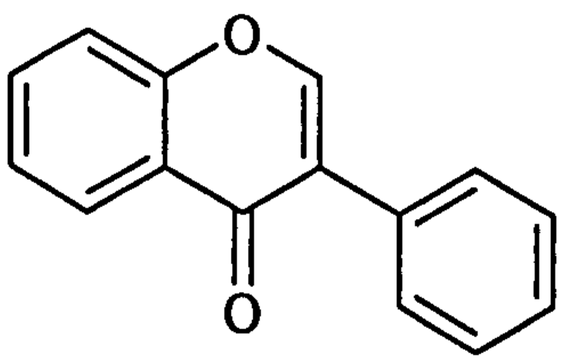
Flavanols

Catechin (2R, 3S) 5=7= 3'= 4'= OH
Epigallocatechin (2R, 3R) 5=7= 3'= 4'= OH
Epicatechin gallate (2R, 3S) 5=7= 3'= 4'= OH, 3-gallic acid ester
Epigallocatechin gallate (2R, 3R) 5=7=3'=4'=5'= OH, 3-gallic acid ester

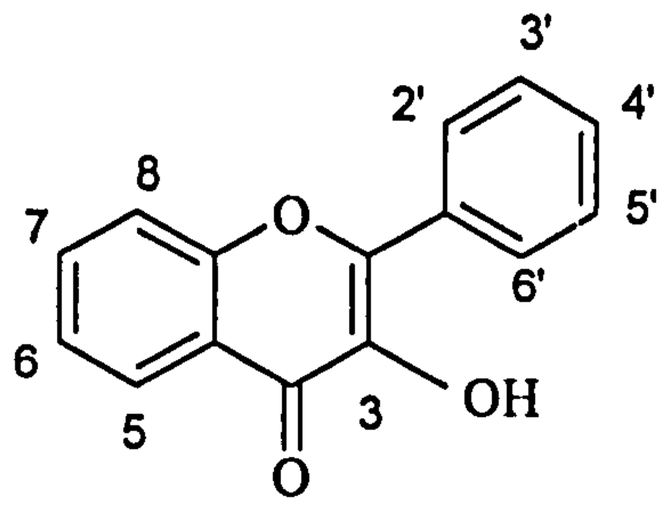


Flavones

Apigenin 5=7=4'=OH
Luteolin 5=7=3'=4'=OH



Isoflavones

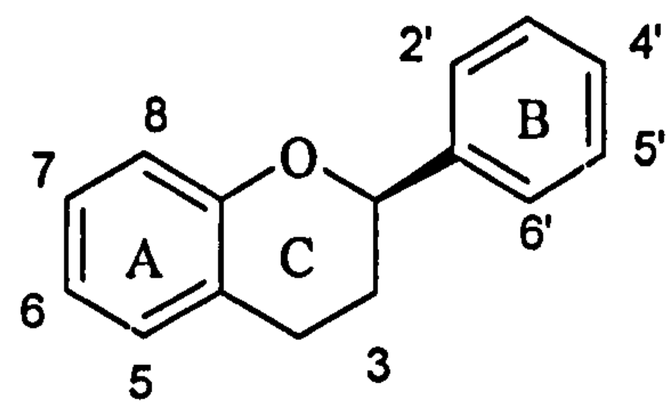


Flavonols

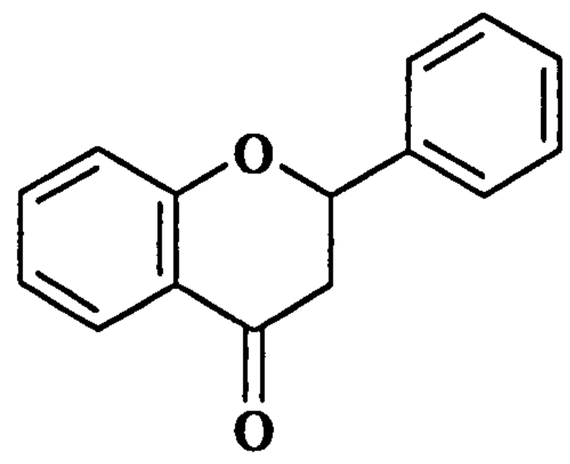
Fisetin 7= 3' = 4' = OH
Kaempferol 5 = 7 = 4' = OH
Morin 5 = 7 = 2' = 4' = OH
Quercetin 5 = 7 = 3' = 4' = OH
Myricetin 5 = 7 = 3' = 4' = 5'= OH
Gossypetin 5 = 7 = 8 =3' = 4' = OH
Isorhamnetin 5 = 7 = 4' = OH, 3' = OCH3

Flavonol glycosides

Rutin quercetin 3-*O*-glucoside



Flavan



Flavanones (dihydroflavone)

Figure 5.4: Chemical structures of the main flavonoid subclasses

5.3.3.1 Flavonols

Flavonols tend to fade in strong light, flavones tend to be more permanent but paler in colour - quercetin, kaempferol and myricetin (many families); fisetin (fustic, nettles). Morin (fustic, osage-orange) can be used on leather, silk, wool and nylon when mordanted with chrome [55]. The major exploited source of quercitron is the inner bark of quercitron tree (*Quercus tinctoria*) but it is present also in horse chestnuts, onion skins, tea and sumac, and several other plants [55].

5.3.3.2 Flavones most of the natural yellow colours are hydroxy and methoxy derivatives of flavones and isoflavones. Luteolin was an important yellow dye and weld was cultivated for this use in much of northern Europe. A major use was the dyeing of gold braid. With the appropriate mordant (alum) on silk it is the most light-fast natural yellow. It is reputedly still used in parts of Europe for dyeing leather [55].

5.3.3.3 Flavanols

Flavanols are polyphenolic compounds known as catechins, which constitute the main components of green tea. The six major catechins present in green tea and known to possess biological properties are (+)-catechin (C), (−)-epicatechin (EC), (−)-epigallocatechin (EGC), (−)-epicatechin gallate (ECG), (−)-epigallocatechin gallate (EGCG), and (−)-gallocatechin gallate (GCG) [67]. Figure 5.4 shows some of the polyphenolic catechins.

5.3.3.4 Anthocyanins

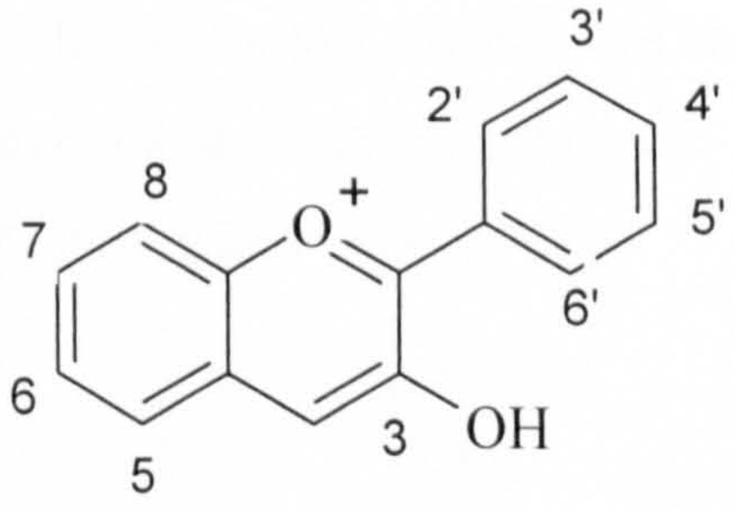
They are all red, blue or violet dyes, which present in the cell sap of many flowers, fruits, stems and leaves (Table 5.5). The class, "Anthocyanins", consists of some 200 or more compounds [55]. The anthocyanins normally exist as glycosides; the aglycone component alone is extremely unstable [55].

The anthocyanins are water-soluble and are easily extracted into weakly acidic solution. However, anthocyanidins and anthocyanins are both sensitive to pH and this can restrict their use as colourants in certain situations, eg, in foods [55]. Table 5.5 lists the key features

of the common anthocyanins. Figure 5.4 shows the chemical structures of the common anthocyanins.

Table 5.5: Key features of the common anthocyanins

Anthocyanins	CAS number	E number	Colour
Pelargonidin	8466-51-8	E163 (d)	Red brown
Cyanidin	28905-48-8	E163 (a)	Red
Delphinidin	26984-07-6	E163 (b)	Blue
Peonidin	26838-13-1	E163 (e)	Dark red
Petunidin	26984-08-7	E163 (f)	Dark red
Malvidin	1329-33-5	E163 (c)	Purple



Anthocyanidins

Pelargonium 5 = 7= 4' = OH
Cyanidin 5 = 7 = 3' = 4' = OH
Peonidin 5 = 7 = 4' = OH, 3' = OCH_3
Delphinidin 5 = 7 = 3' = 4' = OH
Petunidin 5 = 7 = 4' = 5'= OH, 3' = OCH_3
Malvidin 5 = 7 = 4' = OH, 3' = 5' = OCH_3

Anthocyanins

Cyanidin 3-glucoside
Cyanidin 3-rutinoside

Figure 5.5: Chemical Structures of anthocyanidins and anthocyanins

5.3.3.5 Minor Flavonoids

Chalcones – examples are coreopsidoside and mareoside (daisy family) [55].

Aurones – an example is sulphuroside (fustic, daisy family).

Isoflavones- tend to produce strong, permanent colours [55]- genistein (pea family), osajin and pomiferin from osage-orange (*Maclura pomifera*)

Figure 5.6 shows the chemical structures of chalcones and aurones.

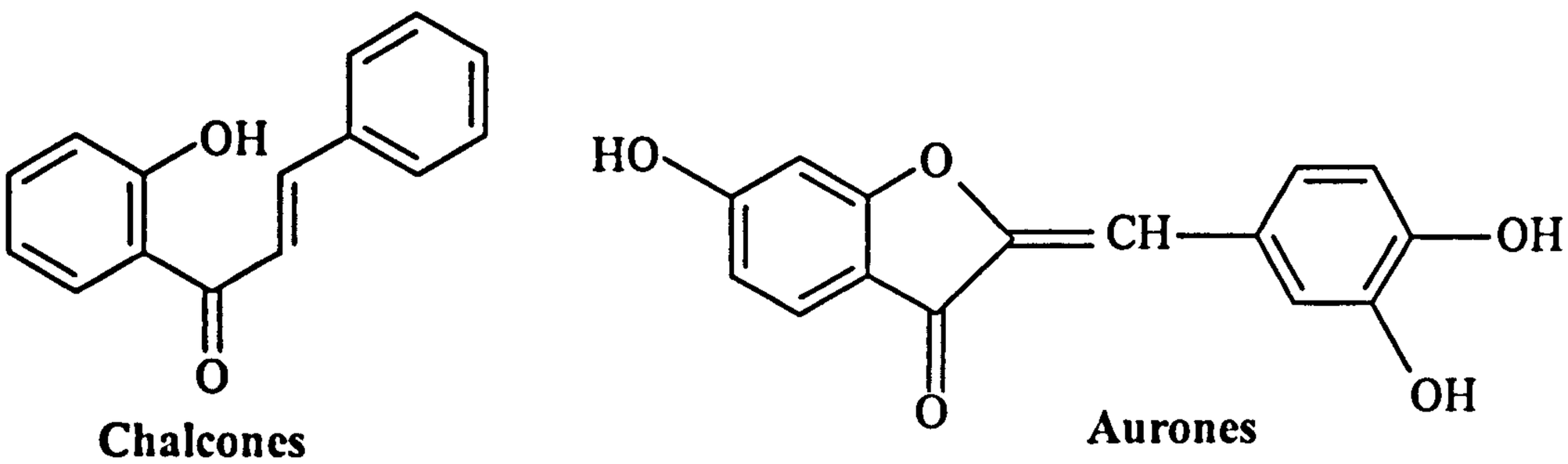


Figure 5.6: Chemical structures of chalcones and aurones

5.3.4 Dihyropyrans

These are closely related to flavones (Figure 5.7). The most important dyes are haematin and haemotoxylin, which are the principal dyes found in logwood, used traditionally in Mexico and Central America to dye textiles blue. Logwood is used in the leather industry for tanning and dyeing [55].

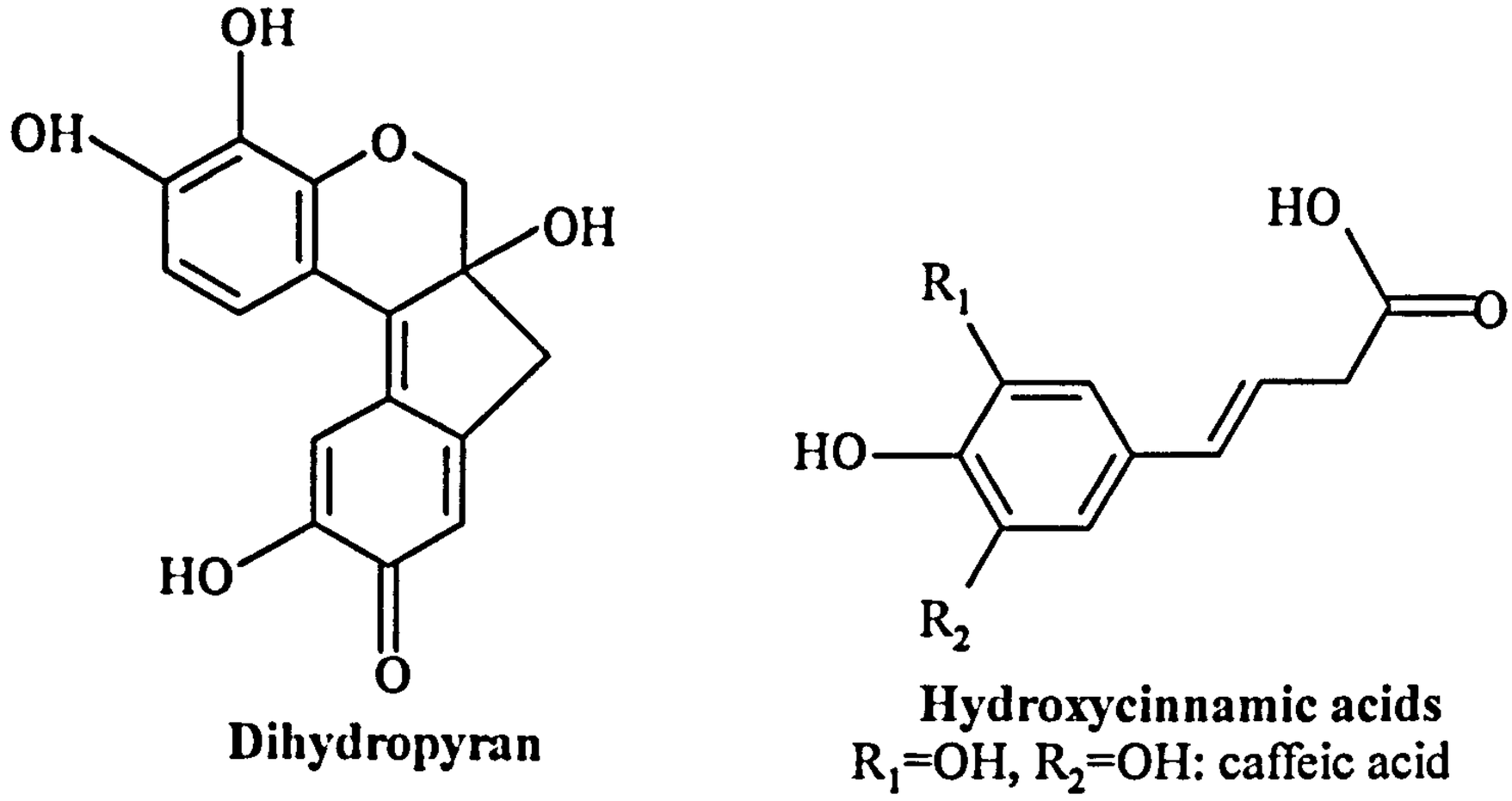


Figure 5.7: Chemical structures of dihydropyran and hydroxycinnamic acids

5.3.5 Betacyanins (betalains)

These red dyes and the related group the betaxanthins (yellows) were thought to be flavonoids but differ in that they contain nitrogen and do not change colour reversibly in the same way as anthocyanins do to pH. They are glycosylated as are the anthocyanins [55].

Apparently they are only present in a few families of the *Chenopodiacae*, such as the beet and prickly pear. Betanin is an extract from the red beet (*Beta vulgaris*) (Figure 5.8) that is used mainly as a food colouring [55].

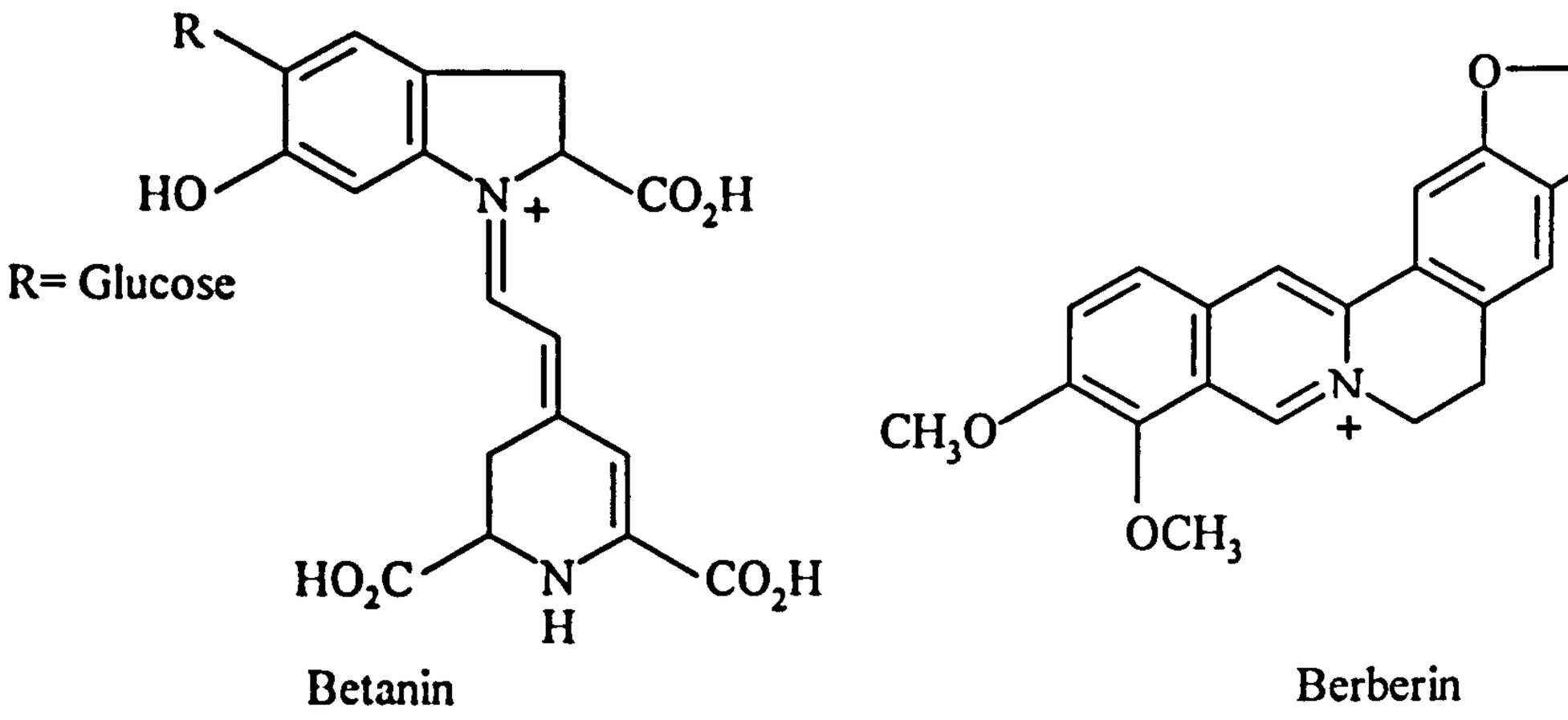


Figure 5.8: Chemical structures of betanin (beetroots) and berberin (barberry)

5.3.6 Flavins

Flavins are very common in living organisms, riboflavin and two of its derivatives being the three most common. Riboflavin (e.g., in banana) is a yellow dye closely related to vitamin B2 and used for colouring food [55]. The chemical structure of riboflavin is shown in Figure 5.11.

5.3.7 Tannins

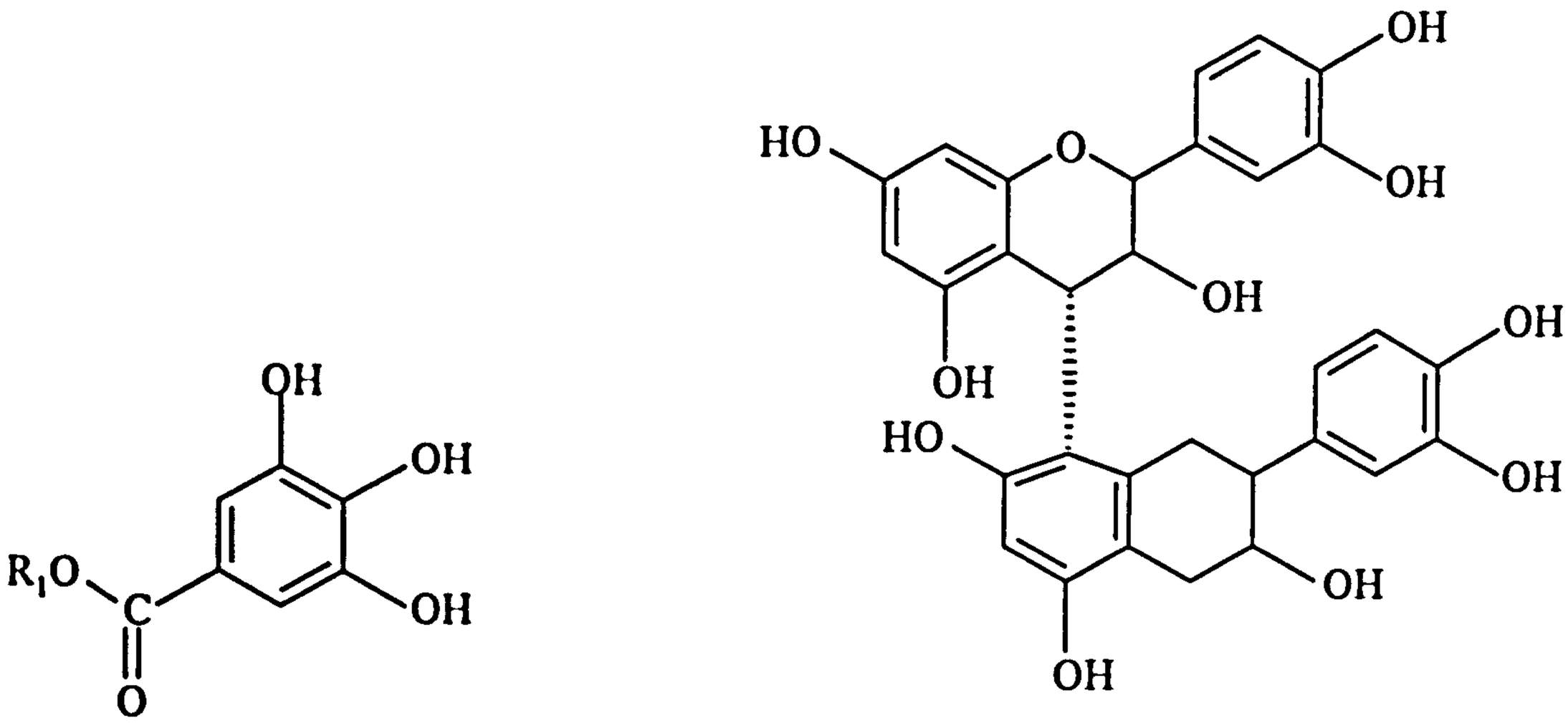
Tannins are present in most plant tissues but are especially associated with damaged tissues and with bark. They are produced from the flavonoids, especially the anthocyanins, when tissues break down. Most natural yellows occur in the plant as glycosides or esters of tannic acid [55].

Tannins are astringent, bitter-tasting plant polyphenols that bind and precipitate proteins [68]. The term tannin refers to the source of tannins used in tanning animal hides into leather; however, the term is applied to any large polyphenolic compound containing sufficient hydroxyls and other suitable groups (such as carboxyls) to form strong

complexes with proteins and other macromolecules. Tannins have molecular weights ranging from 500 to over 20,000 [69]. Tannins are usually divided into hydrolysable tannins and condensed tannins [69].

5.3.7.1 Hydrolysed tannins

At the centre of a hydrolysable tannin molecule, there is a polyol carbohydrate (usually D-glucose). The hydroxyl groups of the carbohydrate are partially or totally esterified with phenolic groups such as gallic acid (in gallotannins) or ellagic acid (in ellagitannins e.g., sumac, *Rhus tripartita*) [69]. Hydrolysable tannins (yellowish colours) are hydrolysed by weak acids or weak bases to produce carbohydrate and phenolic acids. Hydrolysable tannins are water soluble. Punicalagins is the major component of hydrolysable tannins in pomegranate [69].



Hydrolysable tannins (e.g. gallic acid derivatives)
R_1=glucose: monogalloyl-glucose

Condensed tannins
(e.g. procyanidin B3)

Figure 5.9: Chemical structures of hydrolysable and condensed tannins

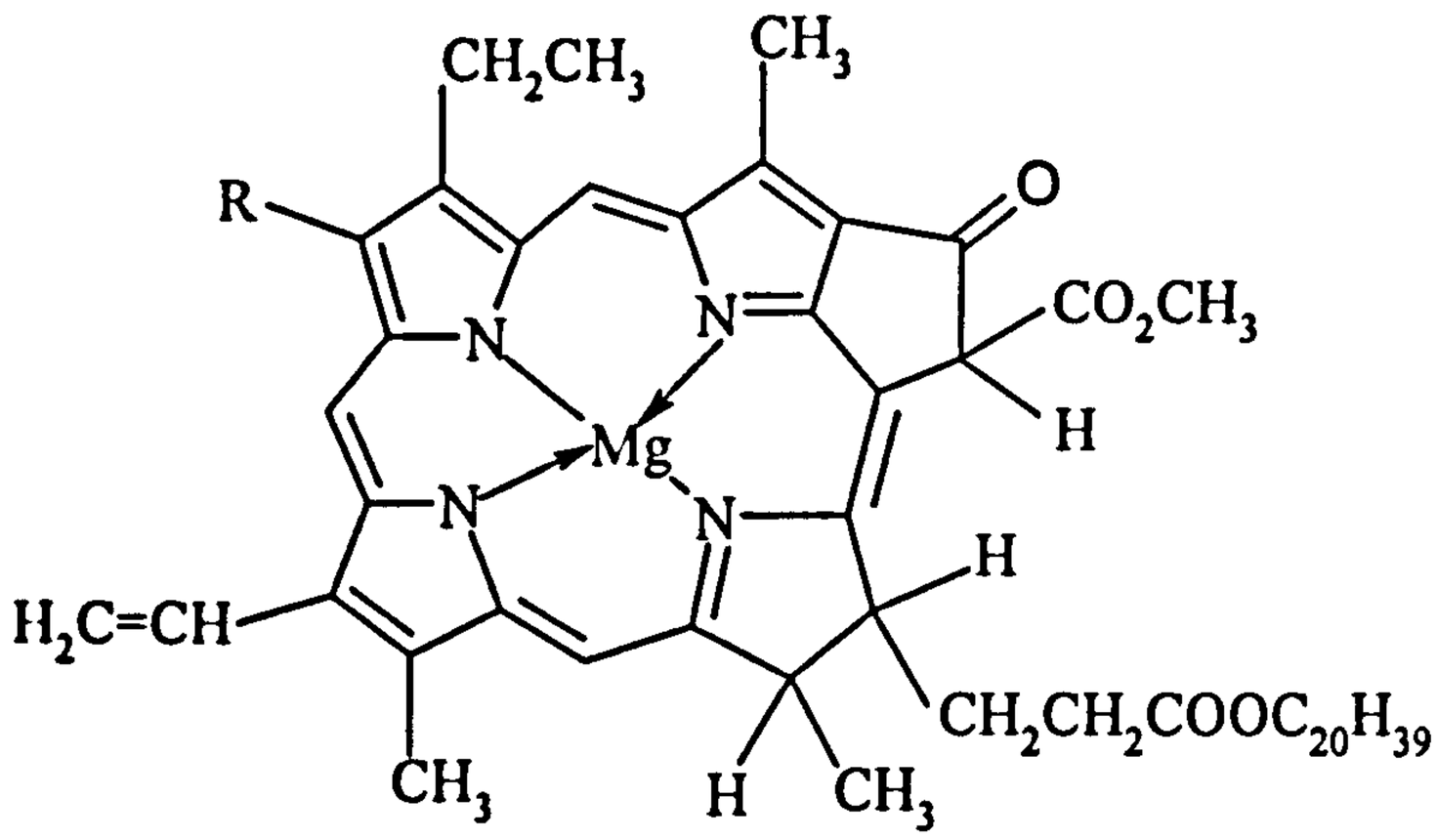
5.3.7.2 Condensed tannins

Condensed tannins, also known as proanthocyanidins, are polymers of 2 to 50 (or more) flavonoid units that are joined by carbon-carbon bonds, which are not susceptible to being cleaved by hydrolysis [69]. Several studies reported that condensed tannins are responsible for the anti-herbviore defence of plants [68]. Most condensed tannins (reddish colours) are

water soluble; some very large condensed tannins are insoluble. Prodelphinidin is a type of proanthocyanidins which present in tea leaves as a condensed tannins [69]. Examples of condensed and hydrolysable tannins are shown in Figure 5.9. The phenolic compound caffeic acid derivative of hydroxycinnamic acid is shown in Figure 5.7.

5.3.8 Tetrapyrroles (Porphyrins)

Chlorophylls from green leafy vegetables and hemes in meats [55, 64] are examples of porphyrins. Chlorophylls a and b (Figure 5.10) is the major pigment used by plants for capturing light energy.



Chlorophyll a R = CH_3
Chlorophyll b R = CHO

Figure 5.10: Chemical structures of Chlorophylls from Spinach

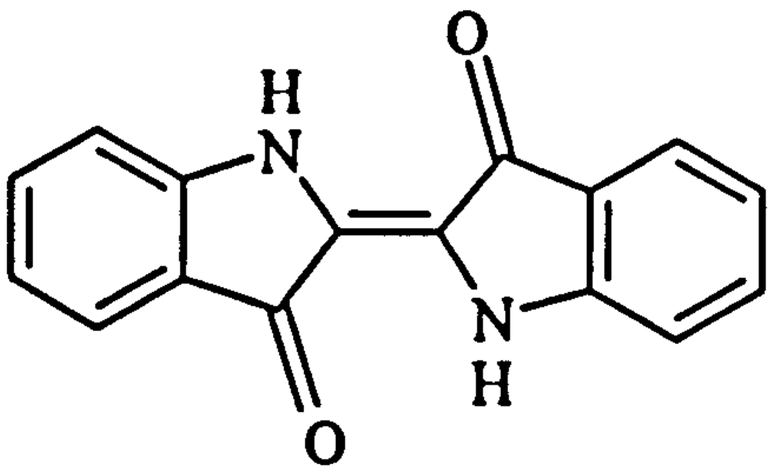
5.3.9 Phycobilins

These are accessory pigments used in capturing light energy by red algae and cyanobacteria. Three of the four known phycobilins are involved in photosynthesis-phycoerythrin (phycoerythrobilin), phycocyanin (phycocyanobilin) and allophycocyanin (allophycocyanobilin). In structure they are similar to the chlorophylls but are linked to a protein. Phycobiliproteins appear as red or blue pigments and are being investigated as possible colourants for foods and cosmetics. The fourth phycobiliprotein is phytochrome, which also is very important in higher plants as a light receptor, especially in plant development [55].

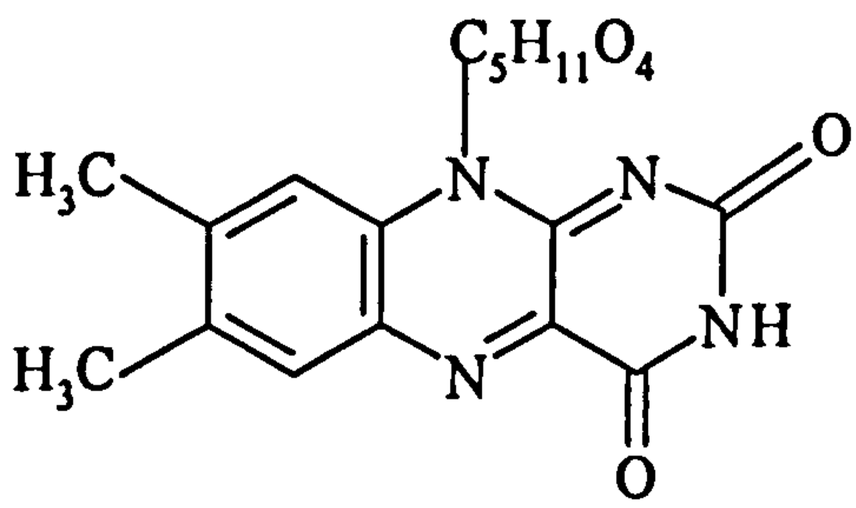
5.3.10 Indigoid

The two most important dyes in this group are Tyrian purple, derived from the molluscs *Murex trunculus*, *M. brandaris* and *Purpura lapillus*, and indigo. The main dye chemical in Tyrian purple is 6, 6'-dibromoindigo; the natural source is not used now because of the large number of shellfish needed to produce even a small amount of the dye and because of the relative scarcity of the shellfish [55].

Indigo is known to be present in a small number of plants; indigo (*Indigofera tictoria*), woad (*Isatis tinctoria*) and other species. The synthetic product is known as CI Vat Blue, CI number 73000, the natural product as CI Natural Blue 1, CI number 75780. The colour produced by the two products differs slightly because natural indigo also contains other dye chemicals (such as indirubin, indigo brown, indigo gluten and indigo yellow) [55]. Figure 5.11 shows the chemical structures of indigo.



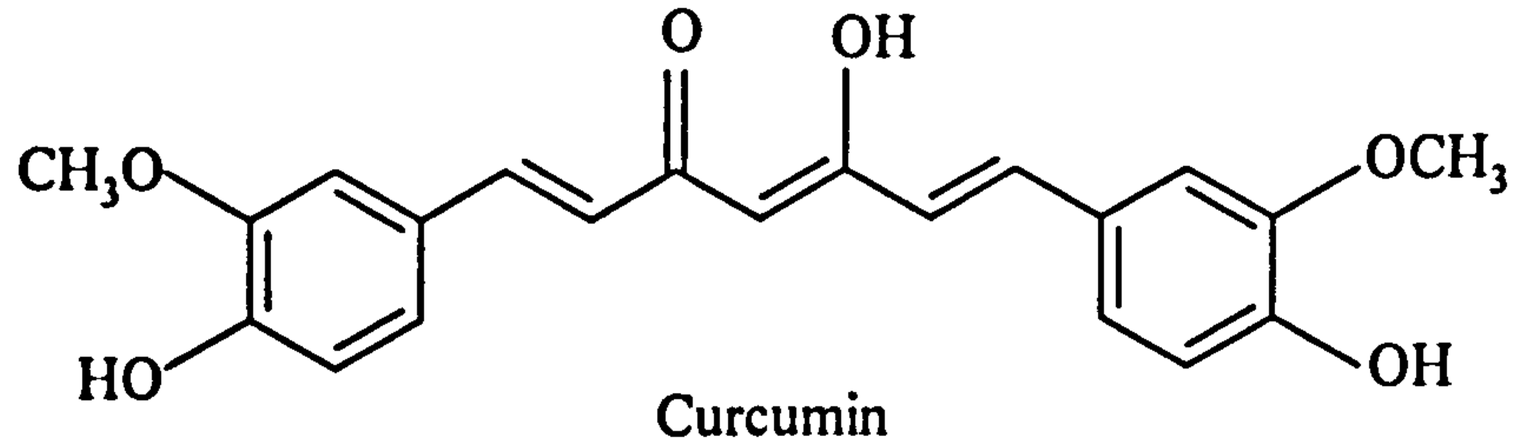
Indigo



Riboflavin

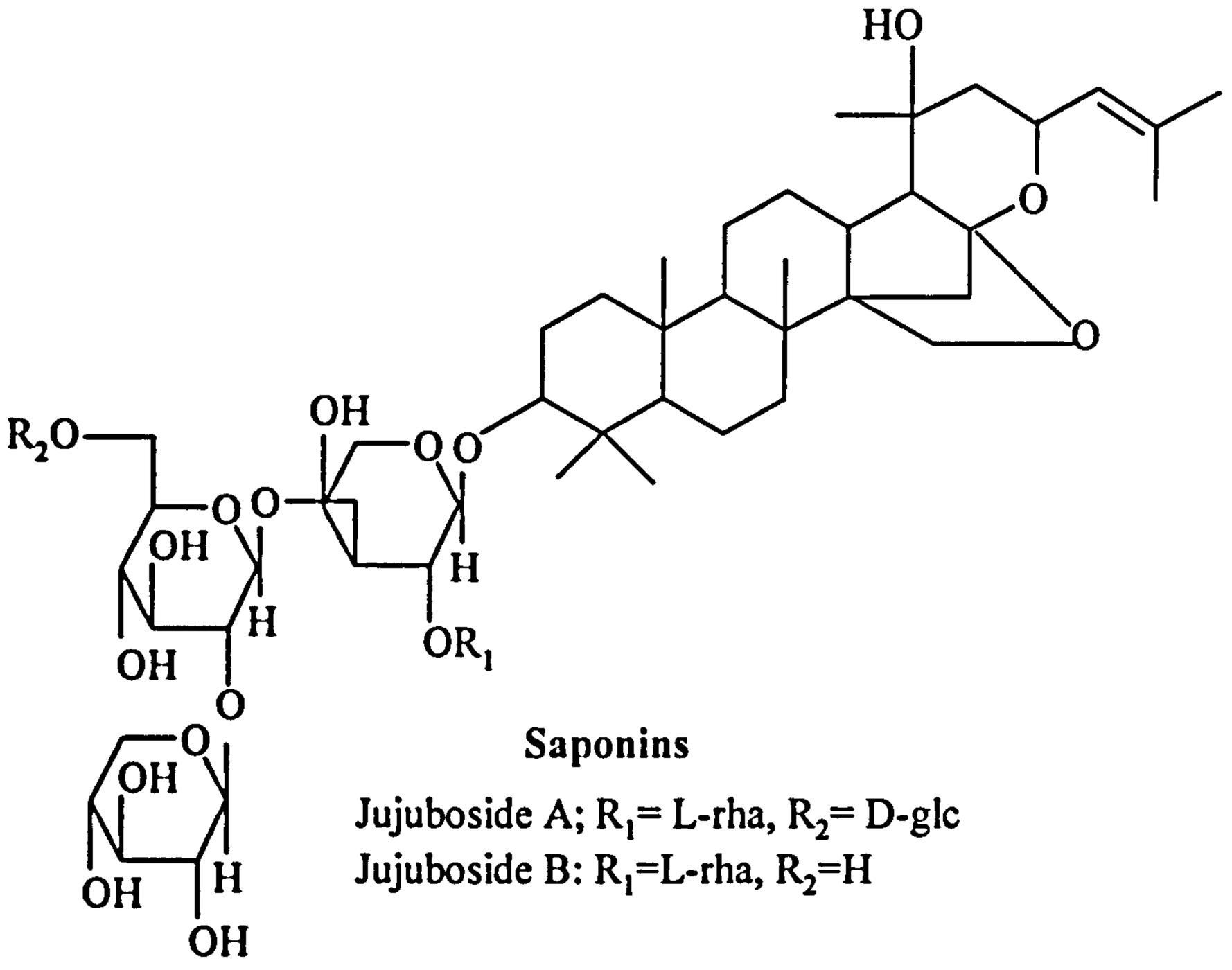
Figure 5.11: Chemical structures of indigo and riboflavin

5.3.11 Other dyes include the **diaroylmethane** curcumin (from turmeric) (Figure 5.12), the **saponins** (from fenugreek and zizyphus) (Figure 5.13) and the **neoflavonoid** berberine (from barberry) (Figure 5.8) [55].



Curcumin

Figure 5.12: Chemical structure of turmeric (*Curcuma longa*)



Saponins

Jujuboside A; R_1= L-rha, R_2= D-glc

Jujuboside B: R_1=L-rha, R_2=H

Figure 5.13: Chemical structure of some saponins found in *zizyphus jujube*

5.3.12 Lichens and fungi

Lichens are composite organisms of fungi and algae, and have long been used for dyeing textiles [55]. The colour obtained from the dye-bearing lichens range from oranges, yellows and browns to reds, pinks and purples. They tend to grow slowly and only in unpolluted conditions, so their use on a large-scale for dyes would not seem to be ecologically desirable or sustainable. However, their dyes are substantive, extremely fast to light, washing and salt water, and generally requires short, simple extraction processes [55]. Little seems to be known about the dyes present in or produced by lichens and fungi [55].

5.4 METHODS OF ANALYSIS AND IDENTIFICATION OF NATURAL DYES IN ARCHEOLOGICAL AND PRESENT TEXTILES

Various methods have been applied in identification and analysis of natural dyes on archeological textiles [12-14, 70-72]. The principle techniques used were electronic absorption spectroscopy, cyclic voltammetry (CV), thin layer chromatography (TLC) and reversed-phase HPLC with diode-array UV–Vis spectrophotometric detection [70]. In

addition, the type of metals present as mordants to the dyes were identified by energy dispersive analysis by X-ray (EDAX).

5.5 METHODS OF COLOUR ASSESSMENTS

Reflectance spectrophotometer and tristumulus colorimeter [73, 74] were used in assessment of colour difference of values of natural dyed fabrics were also determined [3, 16, 43, 45, 54, 75]. The fastness properties of cotton and wool fabrics dyed with natural dyes were determined [1, 31, 76, 77].

Other methods available for the assessment of colour change are the Standard Blue Scale, the Standard Gray Scale and the Sun Test (solar light) [3, 8, 27].

5.6 TYPES OF TEXTILE FABRIC

Most fabrics are constructed from yarns which, in turn, are made from fibres. Over thousands of years humans have learnt to twist fibres together to form yarns. Natural fibres come in various lengths, and this is often referred to as staple length. Synthetic fibres are manufactured in continuous lengths, known as filaments [78]. The filaments can then be cut up as required into shorter lengths- this is also known as staple length. The flow chart in Figure 5.14 shows the origin of some fibres.

5.6.1 Types of Dyes According to Application to Textile Dyeing

Natural dyes fall into three main categories according to application [27]:

Substantive dyes are those that do not need a mordant to bind the dye to the fibre, such as cutch. There are relatively few substantive dyes.

Additive dyes, or mordant dyes, need a mordant in order for the dye to bond with fibre, such as madder, cochineal and weld. This is the most common type of dye.

Vat dyes form the third category and include indigo and woad. These dyes are insoluble in water, and need to be dissolved in a vat with alkalis. Oxygen is removed by a chemical process called reduction. On contact with air (oxidation), the dyes become stable soluble compounds.

5.6.2 Textile Fabrics

Cotton, linen, flax, sisal and ramie are vegetable cellulose fibres. Wool, leather, and silk are, of course, animal fibres. Figure 5.14 shows classification and sources of synthetic and natural fibres with some examples.

5.6.2.1 Animal Fibres

SILK – silk is a natural protein fibre (Figure 5.15) made from the cocoons of silk worm caterpillar *Bombyx mori*, which only feeds on the white mulberry tree, *Morus alba* [78]. It consists of the solidified viscous fluid excreted from special glands in the silk worm.

It is only made on one occasion by the worm during its life-cycle for the purpose of protection whilst it is in the chrysalis state [79]. The long fibres of the cocoons are unwound and spun into threads.

Silk posses nearly all the desirable properties of a textile fibre: strength, elasticity, softness, and affinity [79]. Silk is the strongest natural fibre. A steel filament of the same diameter as silk will break before a filament of silk [80]. Silk absorbs colour well, but needs to be treated with care [27].

Silks can be cultivated or wild [27]. Wild silks are produced by a number of undomesticated silkworms. The term wild implies that these silkworms are not capable of being domesticated and artificially cultivated like the mulberry worms [81]. Aside from differences in colours and textures, they all differ in one major respect from the domesticated varieties. The cocoons, which are gathered in the wild, have usually already been chewed through by the pupa or silkworm before the cocoons are gathered and thus the single thread, which makes up the cocoon, has been cut into shorter lengths [81].

The shimmering appearance, for which silk is prized, comes from the fibres' triangular prism-like structure, which allows silk cloth to refract incoming light at different angles [81].

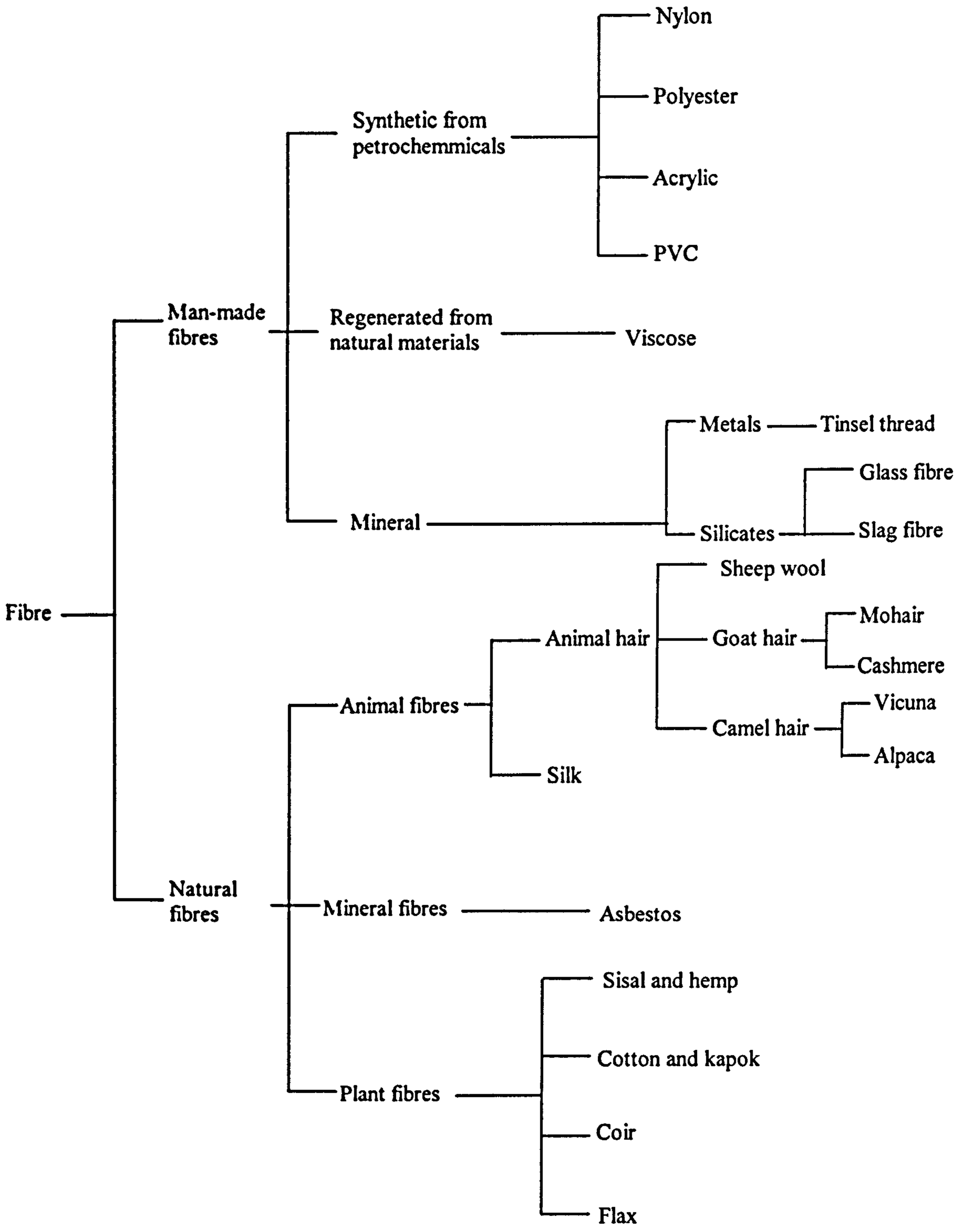
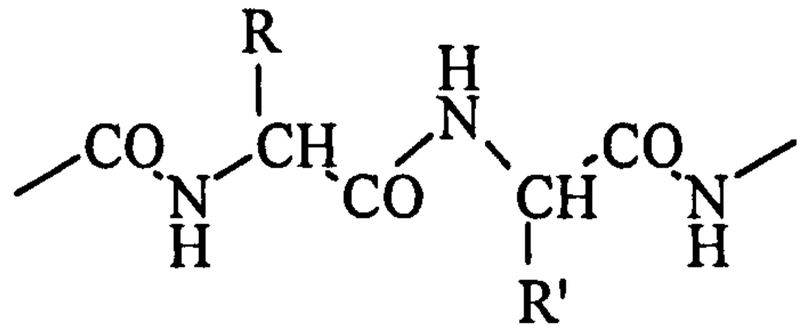


Figure 5.14: Synthetic and natural sources of fibres [78]



Protein fibres

Figure 5.15: Chemical structure of protein fibre

Silk fabric types vary in weight and different textures, from rough wild silks such as tussah, to strong hard-wearing twills, which recognized by the tiny diagonal rib in the weave. Smooth high shine satin has a luxurious quality. Pongee silk has a nice smooth finish with a soft sheen. This silk can also be called habutai or Japanese silk. Other variety are also available, e.g. paj silk [82], silk georgette, organza silk, eri silk [33], wild silk, mulberry silk [6], crêpe de shine silk and velvet silk [81, 83].

Terms and weight of silk fabrics

The standard Chinese term for the weight of silk is a mommi, which is abbreviated to mm and refers to the number of silk threads per millimetre. A silk referred to as a 5 mm has been woven with 5 threads per millimetre, whereas a silk with a weight of 12 mm has 12 threads per millimetre and is a much heavier fabric [82].

Guide to weights and types of silk fabrics

3.5 mm = a very light silk like a chiffon or mousseline silk.

5 mm = a lightweight silk like a paj or pongee silk.

8 mm = medium weight silk like a habotai, crepe de chine or georgette silk.

12 mm and over = heavyweight silk like a satin, dupion, or taffeta.

5.6.2.2 Cellulosic Fibres

Vegetable fibres are made up of cellulose, the most abundant of all organic polymers, natural or otherwise; cellulose is a linear polymer of glucose molecules (Figure 5.16). The main plant fibres that are used in the textile industry are cotton, linen, jute, hemp and ramie.

All have their particular characteristics [27]. Vegetable fibres take longer than animal fibres to prepare and dye because of the cellular structure of the fibre. The presence of –OH groups, the size and configuration of the glucose units, are of great importance in the physics and chemistry of cotton dyeing, since the three hydroxyl groups of each hexose unit can be acetylated to produce cellulose triacetate [84].

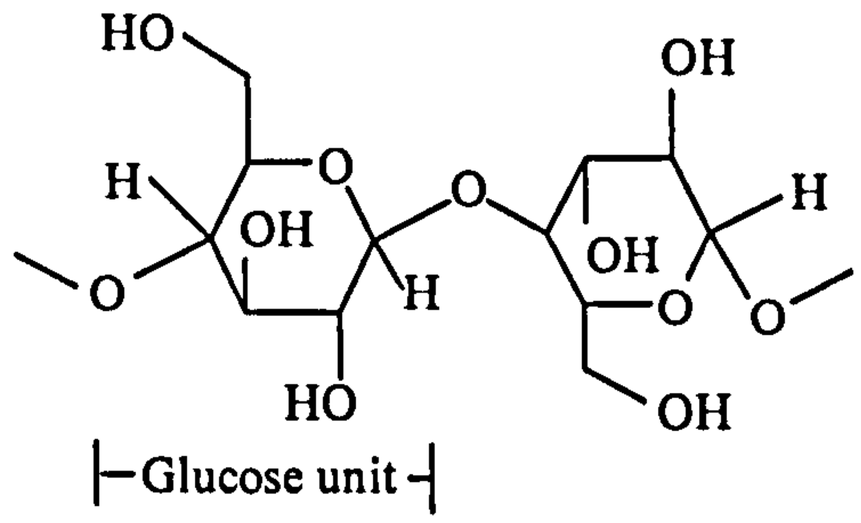


Figure 5.16: The structure of cellulosic fibres

Cotton — The principal clothing fibre of the world [80]. A cellulose fibre consisting of unicellular hairs attached to the seed of the cotton plant *Gossypium* spp. The normal colour of cotton is light to dark cream, and its chemical composition is almost pure cellulose. A distinct feature of the mature fibre is its spirality or twist. In fabrics, cotton makes for strong, versatile, cool-wearing, soft and comfortable garments [27, 84]. Brushed cotton twill [85] was used in this study. Brushed cotton is knit or woven fabrics cotton. The result is a flannel-like texture. Cotton twill is a family of fabrics with a twill weave, including denim, gabardine, drill and chino. Distinguished by its diagonal stripes, it has a moderately stiff drape. It is strong and does not tear easily, which makes it an ideal choice for uniforms and work wear. Sews easily (although it is a bit bulky), but won't hold a crease very well

5.6.2. 3 Man-Made Fibres

- Synthetic from petrochemicals (nylon, polyester, acrylic, PVC)
- Regenerated from natural materials (viscose)
- Minerals
    1. Metals (tinsel & thread)
    2. Silicates (glass fibre & slag fibre)

Synthetic Fibres

The three important synthetic fibres are polyamide, polyester and poly acrylic [84].

Satin- a weave with wide and regularly spaced threads, resulting in a smooth, shiny side and a dull back. A satin-woven fabric tends to have a high lustre due to the high number of floats on the fabric. Floats are missed interlacings, where, the wrap yarn lays on top of the weft yarn, or vice versa. The floats tend to make the fabric look glossier as well as give it a 'smoother hand' in most cases.

(terephthalic acid/ethyleneglycol polymer)

Figure 5.17: The structure of polyester fibre

If a fabric is formed with a satin weave using filament fibres such as silk, nylon, or polyester, the corresponding fabric is termed a satin. If the yarns used are short-staple yarns such as cotton, the fabric is considered sateen [86].

Table 5.6: Textile fibres affinity [87]

Hydrophilic Fibres	Hydrophobic Fibres
Cellulosic fibres a) Natural-cotton, linen b) Regenerated-viscose rayon	Regenerated- fibres Cellulose acetate, cellulose triacetate
Protein fibres a) Natural-wool, cashmere b) Regenerated-casein	Synthetic fibres Polyamide, polyester, polyacrylonitrile

Shimmer Satin (75% rayon, 25% polyester) [86] was used in this study. Rayon is a manufactured fibre composed of regenerated cellulose, derived from wood pulp, cotton linters, or other vegetable matter. Today, various names for rayon fibres are taken from different manufacturing processes. Viscose is most common type of rayon. It is produced in much greater quantity than cuprammonium rayon, the other commercial type. An

example of polyester fibre is shown in Figure 5.17. The affinity of textile fibres toward water is classified in Table 5.6.

5.7 MORDANTS

Natural dyes are not substantive, requiring a mordant to fix to the fabric, and prevent the colour from either fading with exposure to light or washing out. These compounds bind the natural dyes to the fabric. Mordants can also determine how the dye reacts to the fibre, resulting in several colours [27]. Mordants can be applied before dyeing (pre-mordanting), during the dyeing process (one-bath method) or after dyeing (post- mordant).

Mordants help binding dyes to fabric by forming a chemical bridge from dye to fibre, thus improving the staining ability of a dye along with increasing its fastness properties. Mordants form insoluble compounds of the dye within the fibre.

Table 5.7: Mordant metal types

Common name	Chemical name	Colour effect	Colour of crystals	Type
Alum	Potassium aluminium sulphate/or potash alum	Keeps colour pure	White	Pre-mordant
Chrome	Potassium dichromate	Gives golden yellow/orange shades	Orange	Pre-mordant/ one-bath
Copper	Copper sulphate	Sadden the colour but softer, duller, less intense	Turquoise	Pre-mordant/ after-mordant
Iron	Ferrous sulphate	Sadden colour (dark shades)	Green	After mordant
Tin	Stannous chloride	Brighten colour	White	Pre-mordant/ after-mordant
Tannic acid	Gallic acid derivatives	Tanning	Yellow	Pre-mordant

5.7.1 Metallic Mordants

Metal salts of aluminium, chromium, iron, copper and tin are used. Two of the best are aluminum and iron. Aluminum brightens dyes, while fixing the colour. Iron fixes the colour and darkens it. Iron has a tendency to turn many yellow dyes green. Grey-black colour can be produced from plant dyes mordanted with iron [44]. The types of metal mordants and their characters are shown in Table 5.7.

5.7.2 Plant Mordants

Plants are a useful source of natural mordants [27, 69]. Oxalic acid is found naturally in rhubarb leaves (*Rheum species*), alum is found in clubmoss (*Lycopodium selago*) and tannin is found in many plant species e.g., oak galls (from the Quercus species), punicalagins from pomegranate, tea, cutch and sumac [27, 44, 69]. *Rhus tripartita* (aljedary or debagh) is used as mordant tannin in leather industry in Libya.

5.7.3 Oil Mordants

Oil mordants are used mainly in the dyeing of Turkey red colour from madder. The main function of the oil mordant is to form a complex with alum used as the main mordant. The sulphonated oil, which possesses better metal binding capacity than the natural oils due to the presence of sulphonic acid groups, binds to metal ions forming a complex with the dye to give superior fastness and hue [44].

5.7.4 Mordant Assistants

Assistants combine with the mordant and help the dye to attach itself to the fibre in a more permanent state, as well as allowing for less mordant to be used. Table 5.8 shows some of the mordant assistants with their colour effects [27].

Table 5.8: Mordant assistants

Common name	Colour effect
Acetic acid	Used with copper to improve its absorption and efficiency, and allows smaller amounts of copper to be used with better results
Cream of tartar	Brighten colours and improves the absorption of the alum mordant on animal fibres and helps keep wool soft
Formic acid	Used in conjunction with chrome, helps chrome bond with wool and enables a more efficient take up of the mordant
Oxalic acid	Used in conjunction with tin to give better results, it ensures an efficient take up and prevents superficial fixing of mordant
Sodium carbonate	Combined with alum to increase the alkalinity and facilitate absorption
Sodium hydrosulphite	Used to remove the oxygen from indigo and woad vats
Sodium phosphate	Used with vegetable fibres treated with alum. It clears the fibre of surplus, unattached alum

5.8 BONDING

Natural dyes work best with natural fibres such as cotton, linen, wool, silk, jute, ramie and sisal. Among these, wool takes up dyes most easily followed by cotton, linen, silk and then the coarse fibres such as sisal and jute. Nearly all of them require some sort of a mordant [44].

5.8.1 Mechanism of Bonding

Dyeing is in general carried out in aqueous solution. The chemistry of bonding of dyes to fibres is complex. The process of attachment of the dye molecule to the fibre is one of adsorption [84]. It involves direct bonding, by ionic forces (hydrophobic interactions), H-bonds, covalent linkages and 'Van der Waal' forces. The presence of certain functional groups in suitable positions in the dye molecule causes its coordination [88]. Figure 5.18 shows the coordination complex between the fibre mordant and dye, as when alizarin binds to cotton.

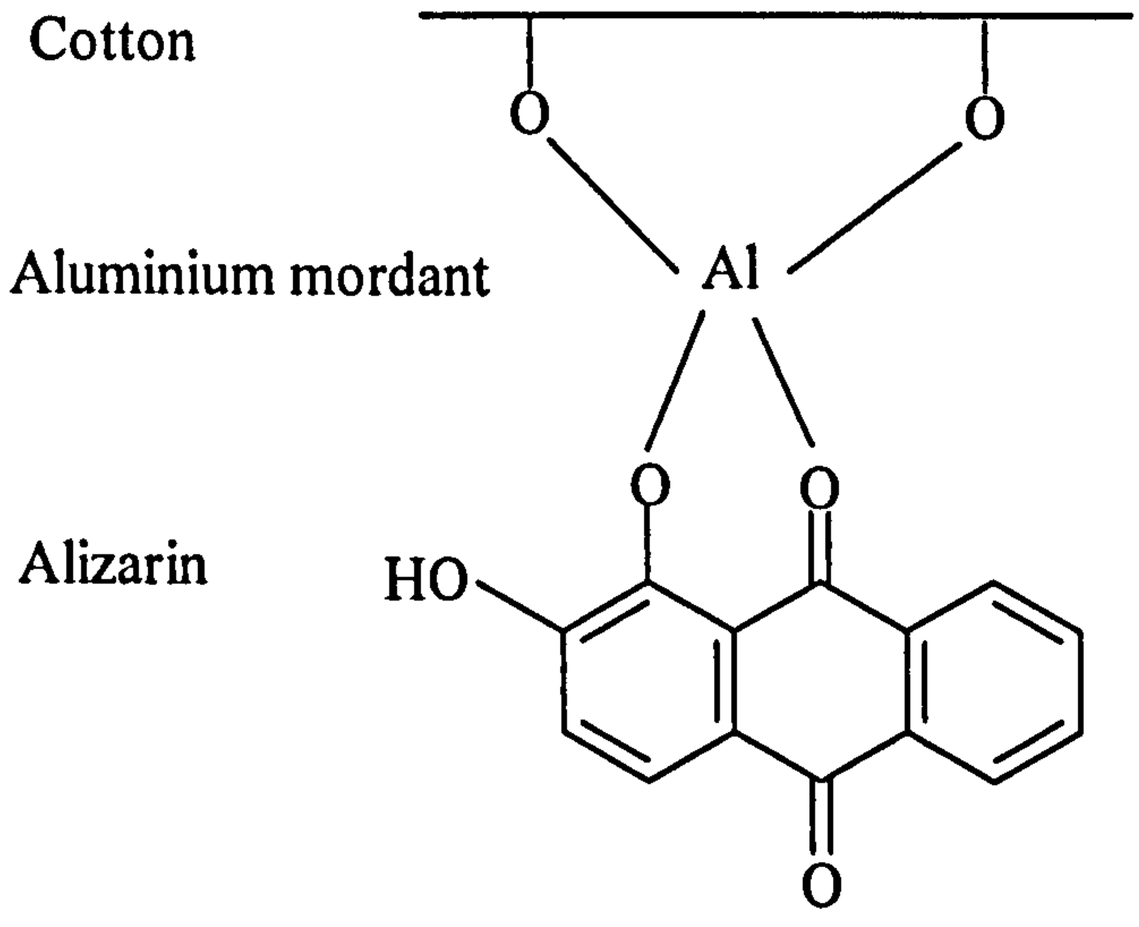


Figure 5.18: Formation of a coordinate complex between the cotton fibre and alizarin

5.8.1.1 Ionic Forces

As the name implies, ionic forces are the mutual interactions between positive centres in a fibre and negative centres in a dye molecule and between negative fibre sites and positive centres in a dye molecule [84]. A free amino group and a free carboxyl group in silk may be represented (Figure 5.19) thus:

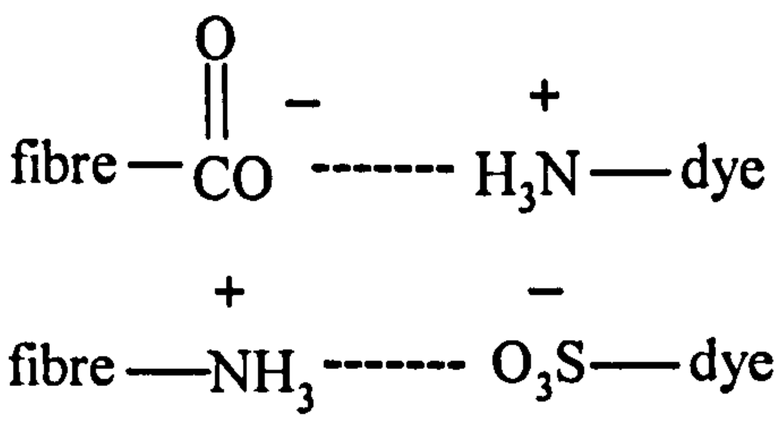


Figure 5.19: Formation of ionic attraction between the dye and fibre

5.8.1.2 Hydrogen Bonding

Result from the acceptance by a covalently bound hydrogen atom of a lone pair of electrons from an electron donor atom. The fibres made of proteins, such as wool, silk, and man-made fibres retain the dye through hydrogen bonding between the polypeptide linkages and the dye [84]. An example of alizarin is given in Figure 5.20 to show the nature of bonding with synthetic fibre, which also has peptide linkages [44].

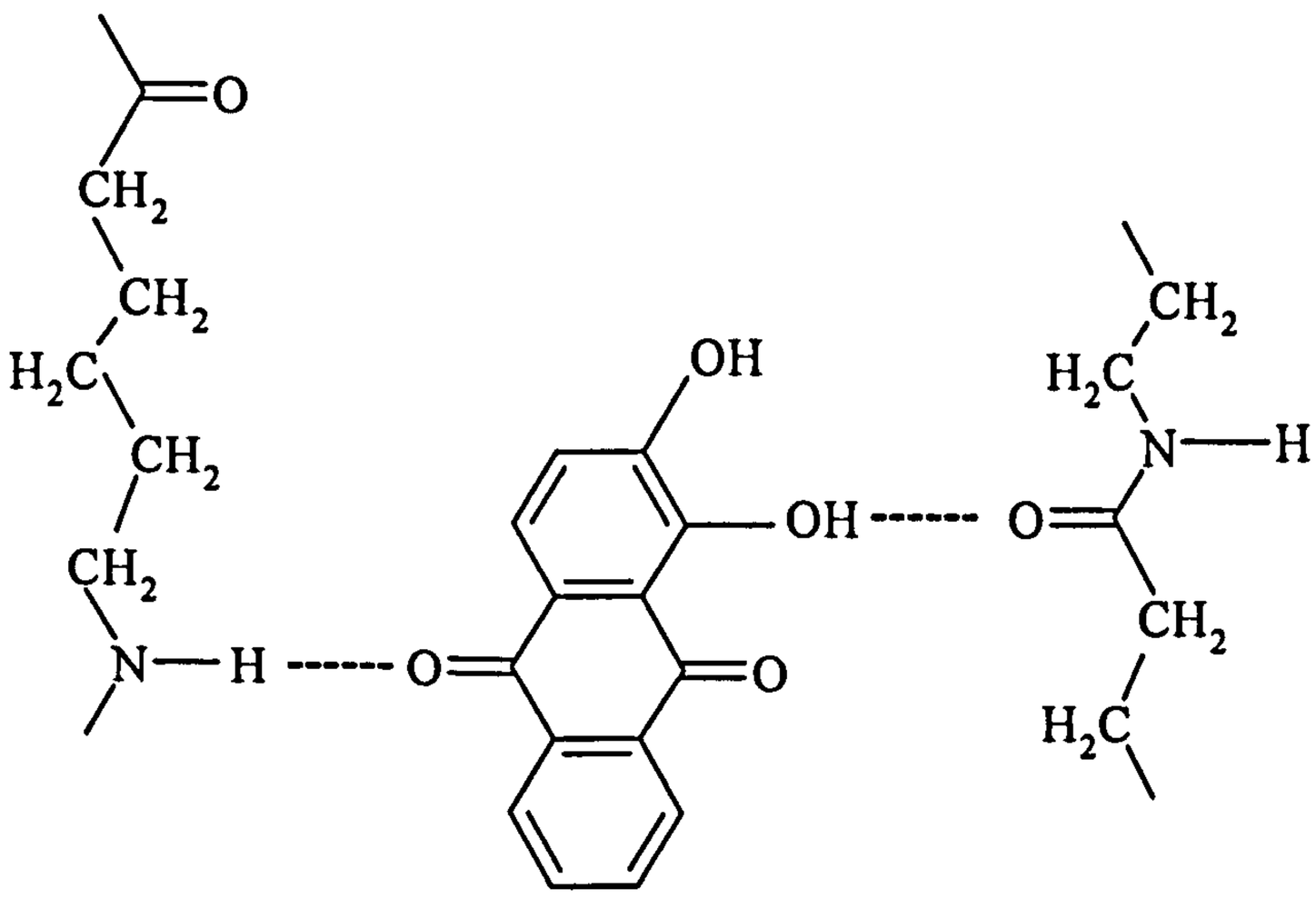


Figure 5.20: Hydrogen bonded dye interaction with the fibre [44]

This is not thought probable with cellulose, since the attachment through hydrogen bonding of water molecules of the amorphous areas of the fibre is such that the dye molecule is not able to displace these water molecules [84].

5.8.1.3 Van der Waals

Van der Waals is weak intermolecular attractions between nonpolar molecules. They are especially effective if the dye molecule is linear and if it has a large surface area to interact with the surface to be dyed, especially, when dye and fibre both contain alkyl or aryl groups as is the case with certain wool dyes and with the majority of polyester dyes [84].

5.8.1.4 Covalent Linkages

Covalent linkages are actual chemical bonds between dye and substrate molecules. They are brought about by chemical reaction between a reactive dye molecule and, for example, a hydroxyl group of a cotton fibre [84] as shown in Figure 5.21.

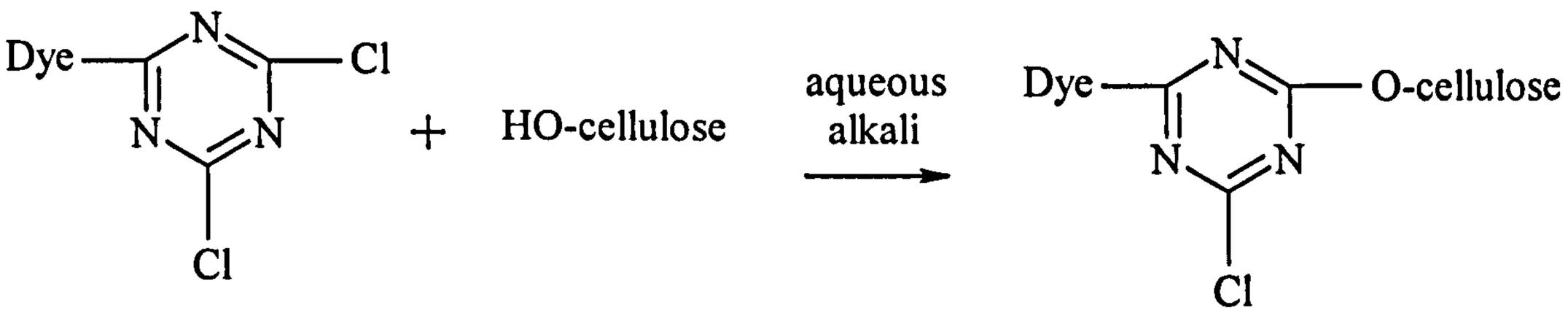


Figure 5.21: Formation of covalent bonding between the dye and the fibre

5.9 SELECTION OF PLANT SOURCES

In this work, to keep transportation to a minimum, a study of plant sources available in the moderate climate of England and Libya was undertaken. The number of possible plant sources was reduced by rigorous selection considering the main aspects given in Table 5.9. A general overview of the dyestuff production and dyeing step is given in Figure 5.22.

The extraction of the dyestuffs had to be performed by a simple aqueous extraction. The use of chemicals or non-aqueous solvents for improvement of the dyestuff extraction was excluded to maintain the possibility for further use of the extracted residue, e.g., as fertilizer or as animal feed.

Relatively simple equipments were used and simple experimental procedures were applied to permit a primary extraction with inexpensive apparatus near the site of harvesting to avoid long-distance transportation of the bulk of the plant materials.

For the first selection, literature information was used to generate a basic set of dyes containing a yellow, green, brown, red, blue and black shade [Table 5.10 and Tables 5.14-5.18]. The dyes had to be applicable with iron or alum mordants. Dyeing with the use of mordants such as Co, Sn or Cr salts will cause problems with the effluents released from the dyeing process because of the wastewater limits defined for the concentrations of heavy metals. Such mordants were, therefore, not used in this research. In this study only ecofriendly mordants such as alum and iron were used as mordants.

Table 5.9: The main requirements for a basic set of natural dyes [7]

Agricultural demands
Reasonable requirements for production and harvesting of the plant materials
Easy handling and storage of raw materials
High dyestuff content
Easy extraction with water
Requirements defined by a technical dyehouse
Simple and rapid dyeing process, no intermediate drying steps.
Broad range of shades formed by a basic set of brilliant dyes, including dark shades (black)
Easy correction of deviations in colour depth and shades
Acceptable fastness properties
Applicability in dyeing machines in use today
Observance of existing waste water limits, e.g., heavy metals
No use of mordants based upon Co, Sn, or Cr salts
Bio-degradability of dyes and non-allergic potential of dyed material
Non-toxic properties of dyes and non-allergic potential of dyed material
Consumption of chemicals and energy comparable or lower than the current state of the art systems based upon synthetic dyestuffs

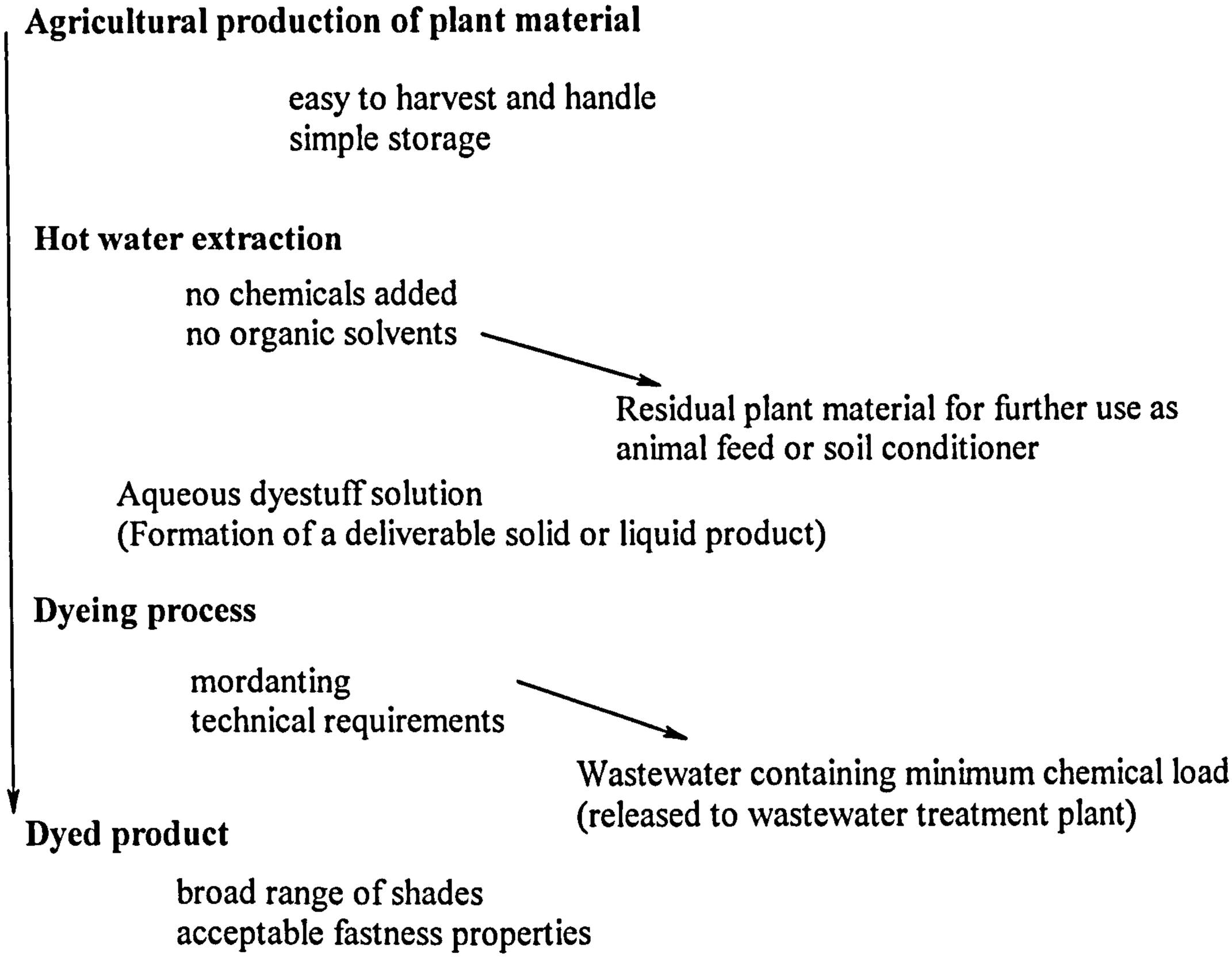


Figure 5.22: Dyestuff extraction and dyeing step [7]

The natural source and identified main colouring components of the plants used in dyeing the textile fabrics in this study were compiled in Table 5.10 and 5.11. Table 5.12 summarises some literature studies of the natural dyes used for textile dyeing in this investigation.

Table 5.10: Natural source and identified main colouring components of the plants used in dyeing the textile fabrics in this study

Common name	Colouring matter	Class	References
Apple	Quercetin, cyanidin, procyanidin, rutin, catechin, hydroxycinnamic acid, phloretin glycosides	Flavonoids	[56, 65, 66, 89, 90]
Banana	Riboflavin, anthocyanin, xanthophyll	Flavins Flavonoids Carotenoids	[90]
Barberry	Berberin	Isoquinolines	[7]
Beetroot	Betanin-betacyanin, betaxanthin	Betalains	[91, 90, 92, 55,93]
Blackberry	Cyanidin, malvidin	Flavonoids	[56, 94]
Blackcurrant	Cyanidin, deliphinidin, quercetin	Flavonoids	[65, 95, 96, 97, 94]
Black tea	Theaflavin, thearubigin, quercetin , kaempferol, catechins	Flavonoids Tannins	[59, 65, 66, 89]
Blueberry	Cyanidin, malvidin	Flavonoids	[55, 56, 93, 98]
Cabbage (red)	Cyanidin-3-rutinoside, cyanidin-3-glucoside, quercetin	Flavonoids	[55, 56, 96, 99]
Capsicum	Capsanthin, capsorubin, luteolin	Carotenoids	[89, 91, 92, 99, 100]
Cherry	Cyanidin, peonidin, quercetin	Flavonoids	[65, 89, 93, 101]
Cloves	Gallotannic acid	Tannins	[102, 103]
Coffee	Theobromine, parazanthin	Methylxanthines	[104]
Cutch	Flavone, condensed tannins	Flavonoids Tannins	[46]
Date fruit	Betanin-betacyanin, anthocyanin, santalin, carotene, lutein, cinnamic acid, xantoxylin	Betalains Flavonoids	[75, 105, 106]
Eggplant	Anthocyanins	Flavonoids	[107]
Elderflower	Quercetin, sambucin, chrysanthemin	Flavonoids	[55, 65]
Grapes	Enocionia, peonidin, cyanidin, rutin, quercetin, quercitrin, flavan-3-ol, catechins	Flavonoids Tannins	[55, 56, 66, 92, 96, 93, 108]
Green tea	Catechins, quercitrin	Flavonoids	[66, 67,89]
Henna	Lawsone	Naphthoquinones	[14, 55, 60]
Indigo	Indigotin, indirubin, natal indigo, kaempferol, trifolitin or indigo yellow	Flavonoids	[3, 13, 14, 55]

Table 5.10: Natural source and identified main colouring components of the plants used in dyeing the textile fabrics in this study (*continued*)

Common name	Colouring matter	Class	References
Kiwi	Carotenes, flavanol	Carotenoids Flavonoids	[90]
Kumquats	Riboflavin, carotene, lycopene, lutein, zeaxanthin	Flavins	[109, 110]
Lemon	Eriodictyol, diosmin, hesperidin, naringin, quercetin	Flavonoids	[66, 89, 90]
Lychee	Cyanidin, malvidin	Flavonoids	[111, 112, 113]
Madder	Alizarin, rubuadin, purpuroxanthin, munjistin, purpurin, lucidin pseudopurpurin	Anthraquinones	[3, 7, 13, 114]
Mango	β-Carotene	Carotenoids	[58, 90]
Mulberry	Morin, cyaniding	Flavonoids	[55, 100, 115]
Onion	Quercetin, luteolin, kaempferol	Flavonoids	[65, 90, 116, 100, 89]
Pomegranate	Gallotannins, ellagitannins, catechol tannins, puniclagins	Tannins Flavonoids	[47, 49, 52, 117]
Prickly pears	Betanin, isobetanin, indicaxanthin	Betalains	[57]
Raspberry	Pelargonidin, cyanidin, riboflavin	Flavonoids	[65,89,94]
Roselle	Cyanidin, hibiscin, gossypicyanin, gossypetin, bibiscin, protocatechuic acid	Flavonoids	[55, 118,119, 60]
Rhus tripartita	Gallotannins, ellagitannins and catechol tannins	Tannins	[120]
Saffron	Crocin, crocetin, zeaxanthin, carotene, kaempferol	Carotenoids	[121, 122, 123, 92]
Senjed (jujube)	Jujuboside A, jujuboside B, polysaccharides	Saponins	[124, 125]
Spinach	Chlorophyll, lutein, zeaxanthin	Porphyrins	[55, 58,100, 126]
Strawberry	Pelargonidin, cyanidin, quercetin	Flavonoids	[56, 66, 93, 97]
Sumac	Gallotannins, ellagitannins, catechol tannins Fisetin, myrecetin, anthocyanin	Tannins Flavonoids	[55, 56, 60, 127, 128]
Tomato	Lycopene, quercetin, rutin	Carotenoids Flavonoids	[65, 90, 89, 91]
Turmeric	Curcumin	Phenalones	[45, 91, 92, 99, 129]
Weld	Apigenin, luteolin	Flavonoids	[3, 13, 14, 55]

Table 5.11: A summary of molecular groups of the studied natural dyes

Molecular groups	Plants
Flavonoids	Apple, banana, blackberry, blackcurrant, black tea, blueberry, cabbage (red), cherry, cutch, dates, eggplant, elderflower, grapes, green tea, kiwi, kumquats, lemon, lychee, orange, mulberry, onion (brown), onion (red), pepper, pomegranate, raspberry, roselle, spinach, strawberry, sumac, tomato, weld
Carotenoids	Banana, kiwi, kumquats, mango, orange, pepper, saffron, tomato
Anthraquinones and naphthoquinones	Henna, madder, cochineal
Betalains	Beetroot, dates, prickly pears
Hydrolysable and condensed tannins	Al-jedari, black tea, cloves, cutch, grapes, pomegranate, sumac
Isoquinolines	Barberry
Flavins	Banana, kumquats, raspberry
Diferuloylmethanes	Turmeric
Indigoids	Indigo
Porphyrins	Spinach, geranium, vine leaves
Methylxanthines	Coffee
Hydroxycinnamic acids	Apple, dates
Saponins	Fenugreek, zizyphus

5.10 EXPERIMENTAL

5.10.1 Plant Material and Extraction

Classification of the plants used in dyeing the textile fabrics in this study is given in Table 5.13, with their common and botanical names and the part of the plant used in dyeing the fabric materials. While part of the plants will be produced by farming, others, for example, barks are by-products from the wood processing where bark is removed prior to sawing.

In many cases, several components of the plant were used, including leaves and fruits (e.g. grapes), seed fruit and rinds (e.g. pomegranate), and different kinds of plant species (e.g. onion, coffee, tea). The dyes used in this study can be classified as:

Fruits: apple, banana, barberry, blackberry, blackcurrant, blueberry, cherry, dates, grapes, kiwi, kumquats, passion fruits, plum, pomegranate, prickly pears, lychee, mango, mulberry, orange, raspberry, strawberry, zizyphus.

Table 5.12: Some literature studies of the natural colourants used for textile dyeing

Natural colourants	Textile fabric	Mordant	References
Barberry	n.i.	Alum, $FeSO_4$	[7]
	Wool	$FeSO_4$, $CuSO_4$, $K_2Cr_2O_7$, alum	[23]
	Acrylic fibre	n.i.	[130]
Chlorophyll	Wool, cotton	Alum, $FeSO_4$, $KNaC_4H_4O_6.4H_2O$	[76]
Cochineal (carmine)	Wool	Alum, $CaCl_2$	[12]
	Wool	Alum, $FeSO_4$	[14]
	Wool, cotton	$KNaC_4H_4O_6.4H_2O$	[76]
	Wool, nylon 6	n.i.	[131]
Curcumin	Wool	Alum	[8]
	Wool	n.i.	[45]
	Wool	Alum, $FeSO_4$	[77]
	Silk (mulberry)	n.i.	[132]
	Silk	n.i.	[133]
Cutch	Jute fibres	Alum, $CuSO_4$, $K_2Cr_2O_7$	[19]
	Wool, cotton	Metal salts	[27]
	Wool	Tannin based	[46]
Henna	Wool	Alum, $FeSO_4$	[14]
	Nylon 6,6 fabrics, cotton, wool, viscose rayon, silk	Organic/inorganic mordants	[29]
	Nylon 6.6	Inorganic mordants	[38]
	Silk (mulberry)	n.i.	[132]
	Wool, nylon 6.6	$K_2Cr_2O_7$	[134]
Indigo (woad)	Cotton yarn	Alum, ($Na_2S_2O_4$/ NaOH)*	[3]
	Wool	Alum, $FeSO_4$	[14]
	Jute fibres	Alum, $CuSO_4$, $K_2Cr_2O_7$	[19]
	Silk (mulberry)	n.i.	[132]
Madder (alizarin)	Cotton, wool, silk	n.i.	[1]
	Cotton yarn	Alum	[3, 54]
	Wool	Alum	[8, 54]
	Wool	Alum, $CaCl_2$	[12]
	Wool	Alum, $FeSO_4$	[14]
	Wool, nylon 6	n.i.	[131]
Pomegranate	Silk		[135]
Roselle	n.i.	n.i.	[136]
Saffron	Wool	Alum, $FeSO_4$	[77]
Tannins	Wool	Alum, $FeSO_4$	[14]
Tea (Lung Chinese tea waste)	Cotton and jute	Alum, $FeSO_4$, $CuSO_4$,	[16]
	Wool	n.i.	[20]
Weld	Cotton yarn	Alum	[3, 54]
	Wool	Alum	[8, 54]
	Wool	Alum, $FeSO_4$	[14]

n.i., not indicated or not informed, alum: Al (NH_3) (SO_4)$_3$; potassium sodium tartarate, $KNaC_4H_4O_6.4H_2O$; * as vat bath for indigo

Vegetables: beetroot, cabbage (red), carrot, eggplant, lemon, onion (brown), onion (red), pepper, spinach, and tomato.

Spices: cloves, fenugreek, saffron, sumac, and turmeric

Herbal teas and coffee: black tea, green tea, coffee (Arabic), coffee (espresso), coffee (green beans), and roselle (karkade).

Herbal plants: aljedari, cutch, elderflower, geranium, henna, indigo, madder, weld, vine leaves.

Insect: cochineal beetles (dried)

Before extraction of the dyestuffs, the plant materials were crushed and ground to pieces of about 1-5 mm. The dyestuff was then extracted with boiling water by applying a bath liquor ratio of plant pigment as indicated in Table 5.13. The duration of the extraction was fixed at 60 minutes. The insoluble residue was separated by sedimentation and filtration through a stainless steel filter fabric (0.3 mm mesh). The resulting extract was used for the dyeing experiments. Plates 5.1-5.3 show the extraction process of some samples of the plant materials.

5.10.2 Chemicals and Reagents

Aluminum ammonium sulphate (alum) [Al (NH_4) $(SO_4)_2$ .12 H_2O] and iron (II) sulphate [$FeSO_4$ .7 H_2O] were used as mordants. Soap powder Ariel Gold Plus (15-30 % phosphates, 5-15 % anionic surfactants, oxygen based bleaching agents, < 5% cationic surfactants, nonionic surfactants, polycarboxylates, enzymes) was used as a soap detergent. Distilled water was used in extraction and for preparation of all chemical solutions. Deionised water was used for the dyeing process.

5.10.3 Fabric Materials

Fabric samples 15 × 12 cm of paj silk, crystallized shimmering satin and brushed cotton twill were used for each dyeing experiment. For display, fabric samples were cut into 4.5 × 2 cm strips. The paj silk fabric was purchased from a local fabric store at Uxbridge, while cotton and satin were obtained from a commercial source in Tripoli, Libya.

Table 5.13: Classification of the plants used in dyeing the textile fabrics in this study

Common name/ (part used)	Latin name	Family name	Bath ratio (g/100ml)
Aljedari (barks)	*Rhus tripartita*	*Anacardiaceae*	06
Apple (skins)	*Pyrus malus*	*Rosaceae*	04
Banana (Skins)	*Musa paradisiaca*	*Musaceae*	08
Barberry (berries)	*Berberis vulgaris*	*Berberidaceae*	10
Beetroot (roots)	*Beta vulgaris*	*Chenopodiaceae*	30
Blackberry (berries)	*Rubus fructicosus*	*Rosaceae*	10
Blackcurrant (berries)	*Ribes nigrum*	*Grossulariaceae*	10
Black tea (leaves)	*Camellia sinensis*	*Theaceae*	04
Blueberry (berries)	*Vaccinium myrtillis*	*Ericaceae*	60
Cabbage (leaves)	*Brassica oleracea*	*Brassicaceae*	23
Cherry (berries)	*Prunes avium*	*Rosaceae*	10
Cloves (flower buds)	*Eugenia caryphyllus*	*Myrtaceae*	04
Coffee (beans)	*Coffee arabica*	*Rubiaceae*	04
Cutch (heartwood)	*Acacia catechu*	*Mimoseae*	03
Dates (fruits)	*Phoenix dactylifera*	*Palmae*	12
Eggplant (skins)	*Solanum melongena*	*Solanaceae*	25
Geranium (leaves)	*Pelargonium sp.*	*Geranaceae*	04
Grapes (fruits)	*Vitis vinfera*	*Vitaceae*	54
Green tea (leaves)	*Camellia sinensis*	*Theaceae*	04
Henna (leaves)	*Lawsonia inermis*	*Lythraceae*	02
Indigo (whole plant)	*Indigofera tinctoria*	*Leguminoseae*	01
Kiwi (fruits)	*Actinidia chinensis*	*Actinidiaceae*	04
Kumquats (fruits)	*Fortunella margarita*	*Rutaceae*	10
Lemon (peel)	*Citrus limon*	*Rutaceae*	20
Lychee (pericap)	*Litchi chinensis*	*Sapindaceae*	07
Madder (roots)	*Rubia tinctorum*	*Rubiaceae*	03
Mango (fruits)	*Mangifera indica*	*Anacardiaceae*	25
Mulberry (berries)	*Morus nigra*	*Moraceae*	10
Onion (Skins)	*Allium cepa*	*Liliaceae*	04
Passion fruit (skins)	*Passiflora edulis*	*Passifloraceae*	63
Pepper (fruits)	*Capsicum annum*	*Solanaceae*	15
Plum (fruits)	*Prunus domistica*	*Rosaceae*	60
Pomegranate (rinds)	*Punica granatum*	*Punicaceae*	10
Prickly pears (skins)	*Opuntia ficus indica*	*Moraceae*	40
Raspberry (berries)	*Rubus idaeus*	*Rosaceae*	60
Roselle (calyces)	*Hibiscus sabdariffa*	*Malvaceae*	04
Saffron (stigma)	*Crocus sativus*	*Iridaceae*	03
Spinach (leaves)	*Spinacia oleraceae*	*Chenopodiaceae*	38
Strawberry (berries)	*Fragaria vesca*	*Rosaceae*	38
Sumac (seeds, leaves)	*Rhus coriaria*	*Anacardiaceae*	10
Tomato (fruits)	*Lycopersicun esculentum*	*Solanaceae*	25
Turmeric (roots)	*Turmeric longa*	*Zingiberaceae*	04
Weld (leaves)	*Reseda luteola*	*Resedaceae*	03
Zizyphus (berries)	*Ziziphus zizyphus*	*Rhamnaceae*	10

5.10.4 Dyeing Procedures

1. Dyeing without mordant: Fabric samples (silk, cotton and satin), were placed in a glass beaker of 1L capacity containing 500 ml of dyestuff and boiled for 60 minutes. The fabric samples were rinsed with distilled water and air dried.
2. Dyeing after treatment with a mordant: silk, cotton and satin fabric samples were boiled with alum mordant in distilled water (5 g/l) for 20 minutes. Then, the mordanted fabrics and the dyeing bath solution were put together in the dyeing beaker for 60 minutes. The dye bath ratio for each plant is recorded in Table 5.13. After dyeing, the unfixed dyestuff was removed by rinsing with cold water, and then air-dried as shown in Plate 5.4. The same procedure was followed for iron mordant dyeing.
3. Dyeing after treatment with alum/tartaric acid: the same dyeing procedure was followed except with addition of tartaric acid in a 1:1 w/w ratio with alum. Only eggplant dye extract was used in dyeing silk, cotton and satin fabrics to see the effect of changing pH on anthocyanins by using acid medium mordant.

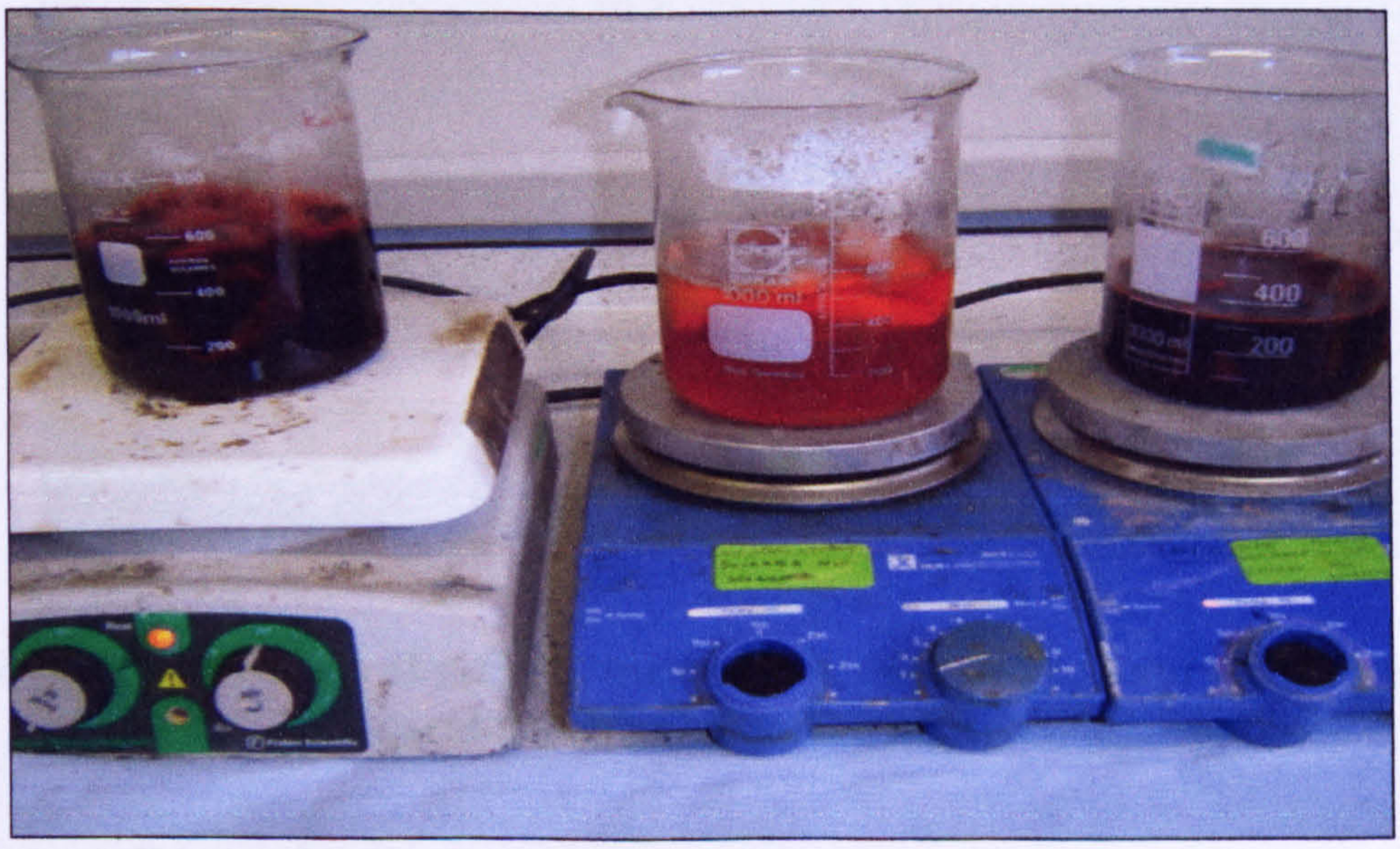


Plate 5.1: Extraction of the natural dyes

Plate 5.2: Dye extracts of cherry, grapes and strawberry which contain anthocyanins as colouring matter

Plate 5.3: Dye extracts of saffron, turmeric, pepper and tomato which contain carotenoids as colouring matter

5.10.5 Fastness Properties

5.10.5.1 Hand Washing:

Dyed and undyed fabric samples in contact were agitated in a soap solution (Ariel, Egypt) (0.5 g/l) for 20 minutes at 40°C. After rinsing and drying, the change in colour of the dyed

samples and the bleeding to the white fabric (cotton, silk, satin) was determined visually (Plate 5.7). The changes were graded with marks 1–5, 1 = poor, 5 = excellent.

Plate 5.4: Dyed fabrics are air-dried after dyeing

5.10.5.2 Light fastness to sun daylight

The test is used to determine if a textile changes colour or if the colour is destroyed by the action of daylight. The samples of the dyed textiles are exposed to daylight under standard conditions, including protection from rain, along with eight dyed wool standards according to **BS EN ISO 105 B02**. Change in colour of the dyed samples related to standard scale of blue dyeing were assessed in the normal way visually by giving grade marks 1–8, 1 = poor, 8 = excellent).

5.10.5.3 Colour Fastness to Artificial Light

The light fastness was also determined using artificial illumination with a xenon arc light according to **BS EN ISO 105 B02** Precision Processes Textiles (PPT) in Ambergate (Derbyshire) and was related to the standard scale of blue dyeings (marks 1–8, 1 = poor, 8 = excellent).

5.11 RESULTS AND DISCUSSION

5.11.1 Colour Characterisation

Dyes were extracted from the original dyestuff using a heated water bath as can be seen in Plates 5.1-5.3. However, not all coloured extract could function as a dye; for example, beetroot extract was found to be a poor textile dye. Although the beetroot, eggplant and prickly pear produce an intense purple, blue and red colour respectively, the colourants did not bind with the fibre even with using alum or iron as mordants, and thus, were not considered viable textile dyes.

More than 32 plants produced noticeable colour and had fair to good fastness performance indicating potential marketability as dyestuffs. Among them were blackberry, blueberry, pomegranate (rind and fruit seeds), aljedari, black tea, banana, barberry, cabbage, cloves, coffee (Arabic and espresso), cutch, dates, green tea, fenugreek, henna, indigo, lychee, madder, mulberry, onion (brown and red), plum, raspberry, roselle, saffron, strawberry, sumac, turmeric, weld and cochineal.

The range of colours achieved, and a verbal description of the shades are given in Tables 5.14-5.18. As can be seen from the data, the use of an iron mordant result in a distinct shift of colour depth and shade compared to the shade of the dyeings without mordanting, while the use of an alum mordant does not change the shade to such an extent. The iron-mordanted dyeings are generally darker compared to the other methods; this is of particular interest for dark shades, e.g., dark grey/ and black which are obtained with pomegranate, henna, lychee, clove and cochineal.

For all samples, it appeared that colours were darker on silk and satin than on cotton, although darker colours on cotton were observed for aljedari, green tea, roselle, indigo, dates, lemon and banana. These plants have different molecular groups, as has previously been described in the literature (Tables 5.10 and 5.11). On silk, the darkest samples were obtained with tannin containing species (aljedari, black tea, cutch), anthocyanins containing species (blackberry, blueberry, plum, roselle and sumac), and anthraquinones (cochineal). Obviously, darker colours are better for dyeing as they may be lightened to produce a lighter shade if so required.

On the other hand, silk and satin gave the brightest shades on dyed samples. The brightest colours were obtained from madder, saffron, sumac, strawberry, pomegranate (seed), and weld. Plants that contain anthocyanins gave less saturated colours on cotton, as for samples dyed with strawberry, pomegranate (seed).

Higher degrees of saturation were found on silk and satin for madder, weld, saffron, turmeric and cutch, cochineal (insect extract). It is interesting to note that these species were extensively used for dyeing and colouring in previous centuries because of the quality of the orange (madder), yellow (weld, saffron, turmeric), brown (cutch), reddish brown (cochineal) shades they provided. This could be explained by the presence of flavones in their phytochemical patterns, such as luteolin or apigenin for weld, crocins carotenoid for saffron, tannin for cutch, anthraquinones for madder and cochineal (Table 5.11).

Unexpected results were obtained with madder which produced orange colour shades on all fabrics instead of red as reported in literature [1]. This behaviour could be attributed to the level of dyeing bath ratio and also to the age of used roots. In fact, it was demonstrated by Angelini et al. [1] that optimum anthraquinones content was observed for 30-month aged roots.

The weak uptake of the plants containing carotenes, e.g., banana, kiwi, kumquats, lemon, pepper, prickly pears, mango, and tomato was probably attributed to the insolubility of carotenes in aqueous solution. Spinach gave only yellow or pale green colour due to the low affinity of chlorophyll towards water. The yellow shades provides by spinach was probably due to the presence of lutein in spinach.

The weak adsorption of barberry and zizyphus is probably due to the poor preservation of anthocyanins in dried berries. Low anthocyanin content in apple skin also contributed to the failure to produce red colour on silk mordanted with alum and iron.

It should be noted that although indigo is a vat dye, needs an alkali ($Na_2S_2O_4$/ NaOH) present in order to bond to the fabric. Nevertheless, dark grey blue shades were produced

on satin and cotton in the absence of alkali, though this procedure with silk failed to produce any noticeable colour.

These results underline the fact that the nature of the fabric plays an important role in the affinity between dye molecules and the supporting material. Moreover, it is important to remark that protein-based fibres (silk) are more basic than cellulose-based fibres (cotton) and those anthocyanins are well known to turn blue in basic conditions [54].

5.11.2 Fastness Properties

Tables 5.14- 5.17 illustrate the rating of colour fastness to light of each sample. It may be seen that some samples presented unexpected behaviours following the test: twelve of the 54 samples on silk and fourteen of the 54 samples on cotton and sixteen of the 54 samples on satin returned to the original colour of the fabric after the test (score 0); 4 of the 54 samples on silk and nine of the 54 on cotton and thirteen of the 54 on satin showed a darker colour after the test (score 10).

Those dyestuffs that provided sufficient colour were further evaluated for fastness or resistance to fading upon (i) exposure to daylight (Plate 5.5 and Plate 5.6) and artificial light and (ii) hand washing using the test methods standardized for the textile industry. Best results of colour fastness were obtained with sumac, pomegranate (rind and fruit seeds), aljedari, cutch, madder, henna, onion (brown), banana, barberry, black tea, dates, lychee, mulberry, cloves, coffee (Arabic and espresso), fenugreek, indigo, weld and cochineal (insect origin). These were given grades 4-5 as can be seen from Table 5.14- 5.17. Plants that produced fair to medium colour fastness were given 3-4 grades. These are blackberry, cherry, raspberry, green tea, onion (red), saffron, turmeric.

Some other plants produced noticeable colour, but when evaluated for colour fastness to light and washing did not meet minimal consumer standards. These are blackcurrant, blueberry, grapes, passion fruits, plum, roselle, strawberry and cabbage. These plants which showed low resistance to light contain anthocyanins in their molecular groups as can be seen from Tables 5.14-5.16. These results confirm the low stability of anthocyanins as previously described in the literature [54].

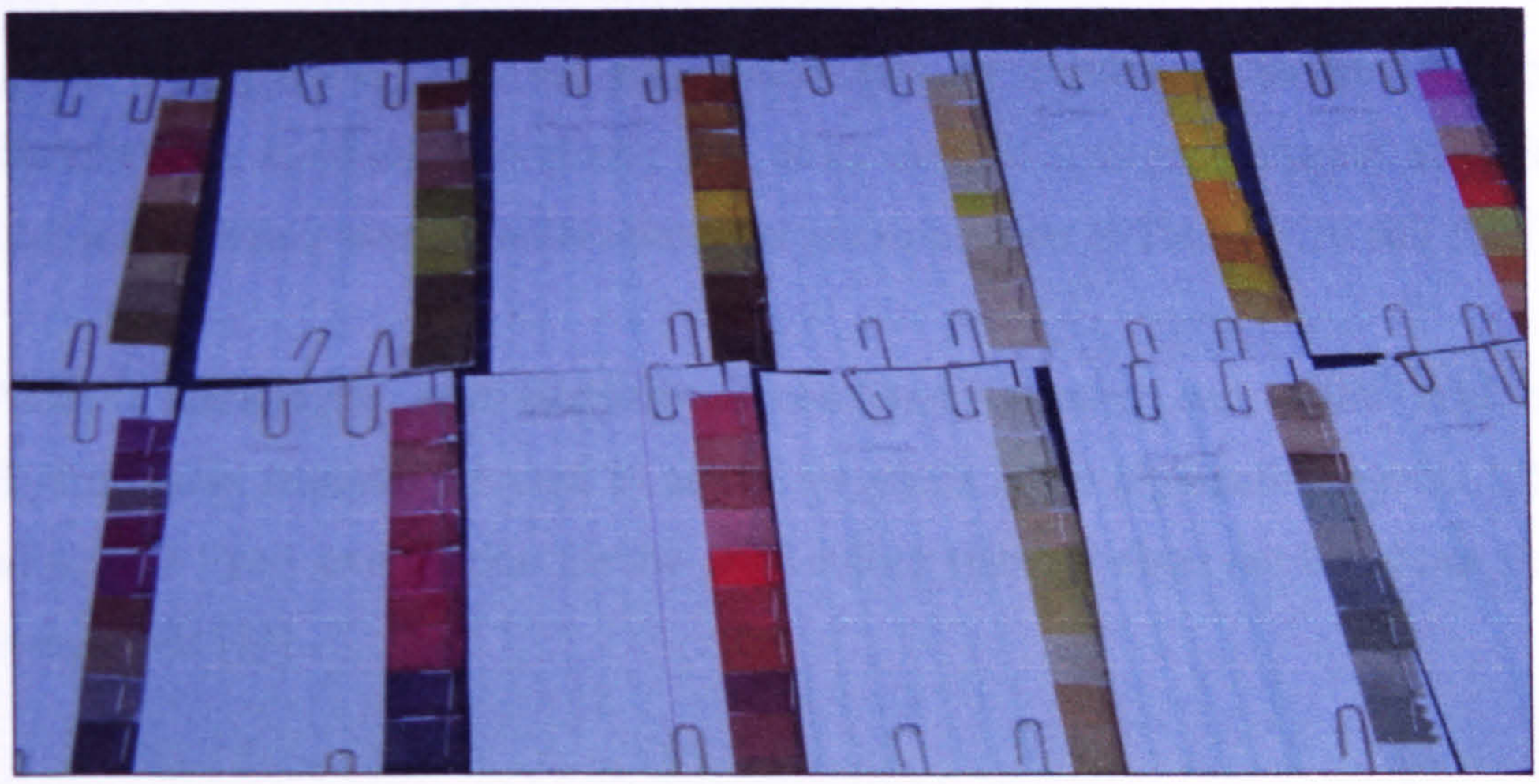


Plate 5.5: Samples exposed to natural sunlight for lightfastness tests

The 16 dyestuffs and components that produced only a faint tinge was not evaluated for colour fastness since they offered only minimal value as dyes (score 0). These are apple, carrot, coffee (green), kiwi, kumquats, lemon, macadamia hull, mango, orange, prickly pear, pepper, tomato, spinach, geranium leaves, vine leaves and zyziphus.

Plate 5.6: Some dyed samples against Blue Wool Standards after exposed to natural daylight

Light fastness is also influenced by the chemical structure of dyes, nature of mordants, mordanting methods and fibres used. Concerning chemical structures, it is interesting to

note that some common points can be identified: aljedari, black tea, cloves, cutch, coffee, henna, pomegranate rinds are particularly rich in condensed tannins and gallic acid (hydrolysable tannins) derivatives, and dates contain hydroxycinnamic acid derivatives. Madder and henna contain anthraquinones as can be seen in Tables 5.10 and 5.11.

Phenolic carboxylic acid derivatives, condensed tannins and gallic acid derivatives (hydrolysable tannins) are said to act as mordants or co-pigmenting agents [27, 44, 69], which is a likely explanation for the good colour stability observed for plants rich in these compounds [54].

5.11.2.1 Effect of Fibres Nature on Fastness Properties

Moreover, the nature of fibres used [137] could bring another explanation: in fact, cotton is a cellulosic fibre, and fading of dyed cotton is attributed to an oxidative process [54]. The presence of gallic and hydroxycinnamic acid derivatives, well known for their anti-oxidative properties [54, 138], could act as protective agents and provide light stability.

As well, fading of dyed silk, a proteinaceous fibre is attributed to a reductive mechanism [54] but this might be inhibited by the protective action of the proteins towards oxidable polyphenolics [54].

The results were better in relation to water stability. Most samples on the three fibres presented good stability: i.e. scored 3-5 (on a scale of 5) except for the colouring by beetroot, blackberry, blueberry, cabbage, cherry, grapes, passion fruit, plum, raspberry, strawberry on all fabrics and saffron on silk and cotton that scored 1-2 (Tables 5.14-5.17). As has been previously stated, all these plant species are rich in anthocyanins excluding saffron which has crocin carotenoids (water soluble) as colouring material (Table 5.11). Once again these results confirm the low stability of anthocyanins involved.

Most species also presented good stability in relation to colour discharge: 20 samples (no mordant), 26 samples (alum) and 33 samples (iron) of 54 samples dyed on silk, 9 samples (no mordant), 28 samples (alum) and 19 samples (iron) of 54 samples dyed cotton and 14

samples (no mordant), 32 samples (alum) and 26 samples (iron) of 54 samples dyed with satin scored 3-5.

The lowest score (1-2) was obtained with only a few samples, namely beetroot, blackberry, blueberry, blackcurrant, cabbage, cherry, eggplant, grapes, fenugreek, henna, lychee, passion fruit, pomegranate (fruit seeds), plum, raspberry, roselle, strawberry, saffron, turmeric, weld and cochineal

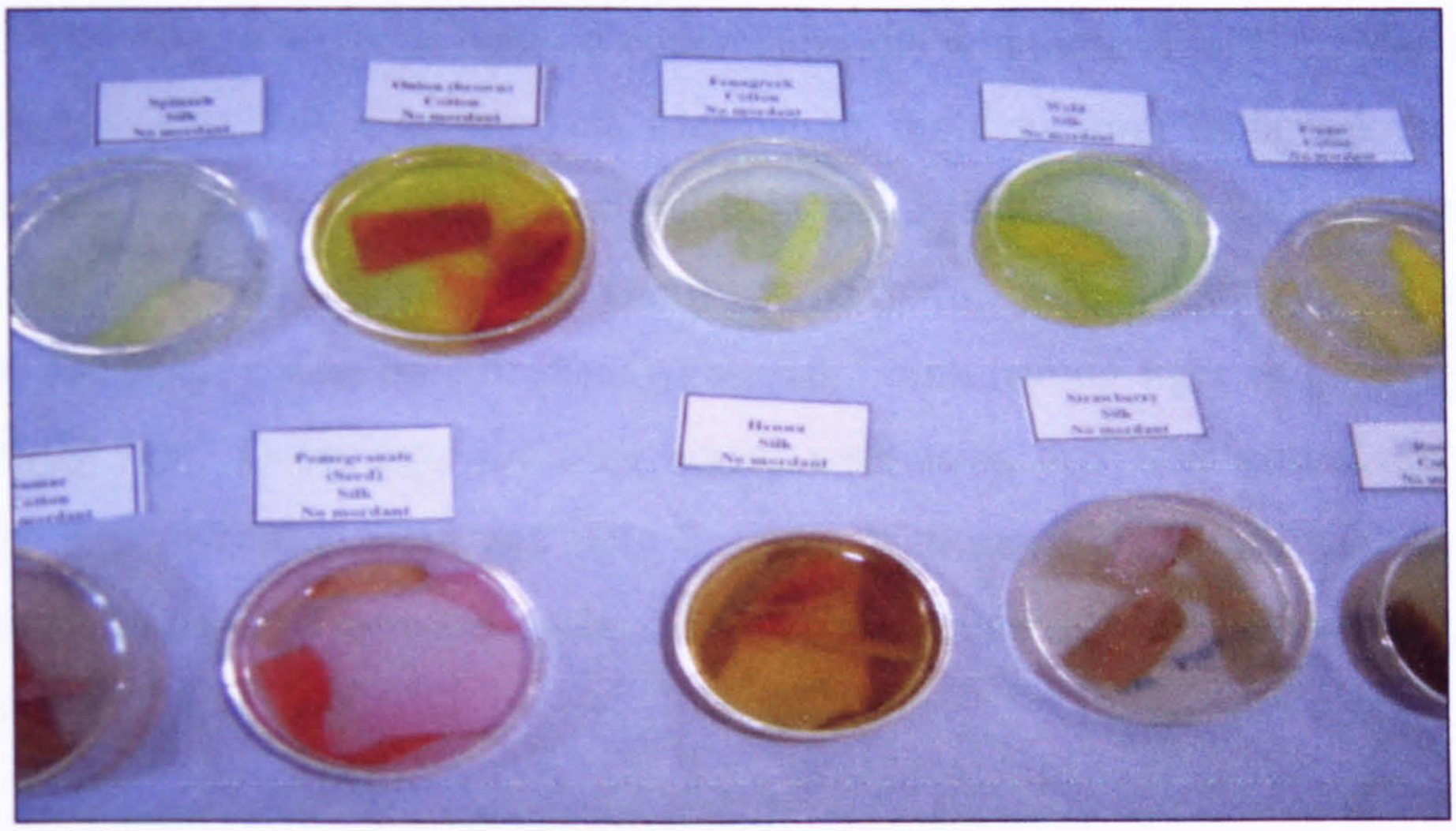


Plate 5.7: Hand washing of dyed samples

It is apparent from the above discussion that silk gave the best results in relation to colour discharge stability and cotton was the poorest.

5.11.2.2 Effect of mordants on Fastness Properties

Using iron and alum mordants generally increases the fastness properties. Improvement of the light fastness after application of iron mordant is of particular interest. However, the use of alum mordants did not affect the light fastness to such an extent in some cases (blackberry, cherry, green tea, raspberry and turmeric on silk) and (blackberry, banana, henna, indigo on cotton) and (blackberry, black tea and Arabic coffee on satin).

Aljedari, madder, cloves, cutch, pomegranate rind, black tea, coffee, henna, onion, weld and sumac give dyeings with generally higher levels of fastness properties without and with mordants. However the use of mordants, namely iron will increase the level of the fastness properties achieved.

Table 5.18 compiles the colour characterization yielded by natural dyes, while Table 5.19 presents comparison study of lightfastness of some samples tested with natural and artificial light. The results showed that aljedari scored (4-5) (max 8) with natural light, and (3-4) with exposing to artificial light on cotton substrate without and with mordants and on silk and satin using $FeSO_4$ as mordant. Meanwhile, the dyes from fenugreek on cotton (both alum and $FeSO_4$) scored 4 with natural light and 3 with artificial light, both henna on silk (alum) and pomegranate on silk (alum) scored 5 with natural light and 3-4 with artificial light and prickly pear on silk ($FeSO_4$) scored 5 with natural light and 4 when exposed to artificial light. Dates gave different results with using $FeSO_4$ on cotton and satin scored grade 5 with natural light and only 2 grades with exposing to artificial light. Plate 5.8 presents some dyed samples against Blue Wool Standards after exposed to artificial light source PPT.

Total scores of colour fastness properties of each species used in dyeing the textile fabrics in this study were summarised in Table 5.20. The natural dyes which scored total of (60-81) are: tannins containing (aljedari, black tea, sumac, cloves, cutch, green tea, henna, and pomegranate rinds), flavonoids (dates, onions and weld) and anthraquinones (henna, madder and cochineal). These were given grades 4-5 on ISO standard scale. Banana, barberry, blackberry, beetroot, saffron, roselle, raspberry, pomegranate seeds, grapes, indigo, fenugreek, espresso and Arabic coffee, scored a total of (40-59).

Meanwhile, blueberry, cherry, passion fruits, plum, and cabbage scored (30-40) of total scores of colourfastness properties. Natural dyes which gave total scores of < 30 were obtained with blackcurrant, green coffee, eggplant, geranium, kiwi, kumquats, macadamia, mulberry, pepper, prickly pear, senjed, spinach, and vine leaves.

Table 5.14: A listing of plant material used in dyeing paj silk

Plant	Without mordant			Alum mordant			$FeSO_4$ mordant		
	Colour	Fastness		Colour	Fastness		Colour	Fastness	
		Wash	Light		Wash	Light		Wash	Light
Aljidari	Orange brown	4-5	4-5	Umber brown	4	5	Grey black	4	5
Apple	Milky ivory	w.a.	w.a.	Blush pink	w.a.	w.a.	Pearl grey	w.a.	w.a.
Banana	Gold chamois	2-3	4	Pearl cream	w.a.	w.a.	Pearl beige	3	4
Barberry	Cinnamon	4	4	Buff brown	4	4	Luster buff brown	4	4
Beetroot	Peach coral	1	2	Coral	1	2	Brown ochre	2	2
Blackberry	Cerise	1	2	Cerise	1	3	Purple	1	4
Blackcurrant	n.a.	n.a.	n.a.	Pink	1	2-3	Light pink	1	1
Black tea	Camel	4	5	Buff brown	3	5	Gold beige	4	5
Blueberry	Amethyst violet	1	2	Amethyst violet	2-3	3	Amethyst blue	3	2
Cabbage [a]	Amethyst	1-2	2	Blue violet	1	3	Indigo blue	4	3
Carrot	Milk cream	w.a.	w.a.	Cream	w.a.	w.a.	Milk cream	w.a.	w.a.
Cherry	Rosy brown	1	2	Peach pink	2	2	Plum brown	2-3	3
Cloves	Gold	4	5	Gold yellow	4	5	Dim grey	4	5
Coffee [b]	Golden rod	4	5	Honeycomb	5	5	Gold grey	4-5	5
Coffee [c]	Beige	4	4	Beige cream	4	4	Olive grey	3	4
Coffee [d]	Ivory cream	w.a.	w.a.	Cream	w.a.	w.a.	Grey cream	w.a.	w.a.
Cutch	Buff brown	4	4	Buff brown	4	4	Grey brown	4	4
Dates	Chestnut	4	5	Auburn brown	4	4	Antique cream	w.a.	w.a.
Eggplant	Beige khaki	w.a.	w.a.	Silver grey	1	2	Grey	2	2
Fenugreek	Light yellow	3	3	Yellow	4	4	Brown olive	2	3
Grapes	Dusky pink	2	3	Rose pink	1	2-3	Pink	1	3-4
Green tea	Gold yellow	4	3	Light gold	4	3	Grey brown	4	3-4
Henna	Cinnamon	3	5	Gold yellow	3	5	Copper-grey	4	5
Indigo	Pale blue grey	2	1	Silver grey	w.a.	w.a.	Beige	w.a.	w.a.
Kiwi	Beige cream	w.a.	w.a.	Ivory	w.a.	w.a.	Ivory	w.a.	w.a.
Kumquats	Yellow cream	w.a.	w.a.	Cream	w.a.	w.a.	Beige cream	w.a.	w.a.
Lemon	Cream yellow	3	3	Cream yellow	2/3	3	Pale cream yellow	w.a.	w.a.

Table 5.14: A listing of plant material used in dyeing paj silk (*continue*)

Plant	Without mordant			Alum mordant			$FeSO_4$ mordant		
	Colour	Fastness		Colour	Fastness		Colour	Fastness	
		Wash	Light		Wash	Light		Wash	Light
Lychee	Dark salmon	3	4	Pale brown	3	4	Dim grey	3	4
Macadamia	Cream	w.a.	w.a.	Pearl white	w.a.	w.a.	Antique cream	w.a.	w.a.
Madder	Terracotta	3	4	Orange	4-5	5	Buff brown	4-5	5
Mango	Snow cream	w.a.	w.a.	Snow	w.a.	w.a.	Plum grey	3	4
Onion [e]	Brown brick	3	3	Olive green	4	5	Bronze grey	4-5	5
Onion [f]	Brown orange	4-5	5	Yellow	4-5	5	Gold Brown	4	5
Orange	Light yellow	w.a.	w.a.	Yellow	4	3	Beige	4	4
Passion fruit	Garnet	2	2	Peach beige	1	2	Grey beige	3	2
Pepper	Orange yellow	3	1	Ivory cream	w.a.	w.a.	Antique cream	w.a.	w.a.
Plum	Rosy pink	1	2	Cerise	1	3	Purple blue	3	3
Pomegranate rind	Tan yellow	4-5	5	Light yellow	4	5	Bronze grey	4	5
Pomegranate seeds	Dark terracotta	2	3	Terracotta	2	3	Plum brown	3	3
Prickly pears	Pale yellow	w.a.	w.a.	Cream yellow	3	2	Olive green	4	5
Raspberry	Dusty rose	2	3	Pink	1	3	Plum	3	4
Roselle	Siena	1	4	Beige pink	3	4	Siena (burnt umber)	3	2-3
Saffron	Fuchsia	1	2	Orange red	4-5	4	Fiery orange	4-5	3-4
Senjed	Cream	w.a.	w.a.	Antique cream	w.a.	w.a.	Beige	3	3
Spinach	Snow cream	w.a.	w.a.	Ivory cream	w.a.	w.a.	Cream	w.a.	w.a.
Strawberry	India red	1	3-4	Coral	3	3	Beige plum	3	2
Sumac	India red	2	5	Pink	4	5	Indian red (brick)	4	5
Tomatoes	Orange cream	w.a.	w.a.	Ivory	w.a.	w.a.	Cream	w.a.	w.a.
Turmeric	Fiery yellow	3	3	Yellow	4-5	3	Golden yellow	4-5	4
Weld	Pale yellow	4	4	Bright yellow	4-5	5	Chocolate brown	4-5	5

[a] Red cabbage; [b] espresso coffee; [c] Arabic coffee; [d] green coffee, [e] red onion; [f] brown onion
1-very poor, 2-poor, 3-fair, 4-very fair, 5-good, 6-very good; w.a., weak absorption; n.a., not available

Table 5.15: A listing of plant material used in dyeing brushed cotton twill

Plant	Without mordant			Alum mordant			$FeSO_4$ mordant		
	Colour	Fastness		Colour	Fastness		Colour	Fastness	
		Wash	Light		Wash	Light		Wash	Light
Aljidari	Orange brown	3	4-5	Buff brown	4	4-5	Chocolate brown	4	4-5
Apple	Milky ivory	w.a.	w.a.	Milky ivory	w.a.	w.a.	Pearl grey	w.a.	w.a.
Banana	Chamois	2-3	3	Beige brown	2	3	Grey brown	3	4
Barberry	Tan brown	1	3	Camel brown	3	4	Tan brown	2-3	4
Beetroot	Pale cerise	1	3	Chestnut brown	3	3	Plum brown	3	3
Blackberry	Cerise	1	3	Pink English rose	2	3	Dark purple	1	4
Blackcurrant	n.a.	n.a.	n.a.	Cerise pink	2	3	Pale pink	1	1
Black tea	Tan	w.a.	w.a.	Dark brown	4	5	Brown	3	5
Blueberry	Light cerise	1	3	Plum English rose	2	3	Blue violet	1	3
Cabbage [a]	Amethyst	1	1	Amethyst	1	3	Blue green	1	3
Carrot	Yellow cream	w.a.	w.a.	Cream	w.a.	w.a.	Cream	w.a.	w.a.
Cherry	Dusty pink	1	2	Baby pink	1	2-3	Purple brown	3	3
Cloves	Brown yellow	4	5	Brown yellow	4	5	Brown black	4	5
Coffee [b]	Tan brown	w.a.	w.a.	Olive	5	5	Yellow brown	2	4
Coffee [c]	Tan	w.a.	w.a.	Cream	w.a.	w.a.	Greenish grey	1-2	3
Coffee [d]	Ivory cream	w.a.	w.a.	Ivory cream	w.a.	w.a.	Beige grey	2	3
Cutch	Buff brown	3	4	Buff brown	4-5	4	Dark chocolate brown	4-5	4-5
Dates	Cream beige	3	4	Espresso brown	4	5	Grey beige	4	5
Eggplant	Beige brown	w.a.	w.a.	Blue grey	1	2-3	Light cream grey	2	2
Fenugreek	Light yellow	2	4	Bright yellow	3	4	Olive	1-2	4
Geranium	n.a.	n.a.	n.a.	Yellow brown	3	4	n.a.	n.a.	n.a.
Grapes	Old rose	2	3-4	Cerise pink	1	3	Plum pink	1	2
Green tea	Brown yellow	2	3-4	Burnt umber	4	5	Grey brown	4	3-4
Henna	Tan brown	1	4	Khaki brown	3	4	Dark olive	1	3
Indigo	Green blue	4	4-5	Light blue grey	4	4	Green blue	4	3-4
Kiwi	Beige cream	w.a.	w.a.	Sandy khaki	2	3	Ivory white	w.a.	w.a.
Kumquats	Ivory	w.a.	w.a.	Khaki	1	2	Beige khaki	1	2
Lemon	Antique cream	w.a.	w.a.	Khaki yellow	3	4	Pale yellow	3	2

Table 5.15: A listing of plant material used in dyeing brushed cotton twill (*continue*)

Plant	Without mordant			Alum mordant			$FeSO_4$ mordant		
	Colour	Fastness		Colour	Fastness		Colour	Fastness	
		Wash	Light		Wash	Light		Wash	Light
Lychee	Salmon	1	3	Camel	3	4	Brown grey	3	4
Macadamia	Cream	w.a.	w.a.	Milk cream	w.a.	w.a.	Beige	2	3
Madder	Peach orange	2	3	Terracotta	4	5	Violet brown	4	5
Mango	Light yellow	1	1	Sandy khaki	4	4	Grey plum	4	4
Mulberry	n.a.	n.a.	n.a.	Plum violet	1	4	n.a.	n.a.	n.a.
Onion [e]	Dusty pink	2	3	Lime green	3	5	Olive green	4	5
Onion [f]	Orange brown	3	4	Olive green	4	5	Yellow brown	4	5
Orange	Cream	w.a.	w.a.	Light yellow	2	4	Beige	2	3
Passion fruit	Old rose	1	2	Pale pink	3		Grey beige	4	2
Pepper	Orange yellow	3	1	Blush orange cream	w.a.	w.a.	Antique cream	w.a.	w.a.
Plum	Rosy pink	1	3	Cerise	1	3	Bluish violet	2-3	2
Pomegranate rinds	Tan yellow	4	5	Yellow green	4	5	Black	4	5
Pomegranate seeds	Pink beige	1	3	Cream pink	1	3	Khaki	2	2
Prickly pears	Pale yellow	w.a.	w.a.	Milk white	w.a.	w.a.	Olive brown	3	3
Raspberry	Hot pink	2	4	Rosette pink	1	4	Plum purple	3	4
Roselle	Siena ruby	1	3	Ruby	3	3	Deep cerise	1	2
Saffron	Peach	1	2	Deep yellow	4	3	Peach orange	4-5	5
Senjed	Cream	w.a.	w.a.	Cream	w.a.	w.a.	Cream beige	3	4
Spinach	Yellow green	2-3	3	Yellow green	1	3	Olive green	3	2
Strawberry	Dark Salmon pink	1	3-4	Pink	1		Red brick	1	2-3
Sumac	Burly wood	2	5	Sandy khaki	3	5	Pink beige	2	5
Tomatoes	Orange green	w.a.	w.a.	Blush peach	w.a.	w.a.	Cream yellow	w.a.	w.a.
Turmeric	Fiery yellow	2-3	3	Citrine yellow	3-4	3	Yellow brown	4-5	3
Weld	Pale yellow	4	5	Lemon yellow	4-5	4-5	Olive brown	4-5	5
Vine leaves	n.a.	n.a.	n.a.	Yellow	2	4	n.a.	n.a.	n.a.

[a] Red cabbage; [b] espresso coffee; [c] Arabic coffee; [c] green coffee [d], red onion; [e] brown onion

1-very poor, 2-poor, 3-fair, 4-very fair, 5-good, 6-very good; w.a., weak absorption; n.a., not available

Table 5.16: A listing of plant material used in dyeing shimmer satin

Plant	Without mordant			Alum mordant			$FeSO_4$ mordant		
	Colour	Fastness		Colour	Fastness		Colour	Fastness	
		Wash	Light		Wash	Light		Wash	Light
Aljidari	Gold orange	4-5	4-5	Gold khaki	4	5	Golden greyish beige	4	5
Apple	Milky ivory	w.a.	w.a.	Cream	w.a.	w.a.	Cream	w.a.	w.a.
Banana	Chamois	2-3	4	Beige brown	3	4	Beige green	3	4
Barberry	Gold	2	4	Buff brown	4	4	Pale beige	w.a.	w.a.
Beetroot	Gold pink	1	3	Gold Chestnut	3	4	Brilliant beige	1	4
Blackberry	Bronze	1	3	Dusk rose	2	3	Purple	1	4
Blackcurrant	n.a.	n.a.	n.a.	Pink rose	1	1	Pink rose	1	1
Black tea	Gold	3	4	Calcite brown	3	4	Bronze	3	5
Blueberry	Dusk plum	1	2	Dusk rose	3	3	Purple	2	2
Cabbage [a]	Lilac	1-2	2	Dark purple	1	2-3	Indigo grey	1	3
Carrot	Milk cream	w.a.	w.a.	Milk cream	w.a.	w.a.	Milk cream	w.a.	w.a.
Cherry	Peach gold	1	2	Blush pink peach	1	2	Plum	2	3
Cloves	Gold	4	5	Pale yellow	4	5	Beige grey	4	5
Coffee [b]	Gold cappuccino	2	3	Khaki	1	3	Gold olive	1	3
Coffee [c]	Gold	2	3	Gold cream	3	3	Dim silver grey	4	4
Coffee [d]	Ivory cream	w.a.	w.a.	Gold cream	3	3	Gray cream	w.a.	w.a.
Cutch	Chocolate	1	4-5	Cupper brown	4-5	4	Dark brown	4-5	5
Dates	Gold	4	5	Pink brown	4	5	Beige green	4	5
Eggplant	Beige	w.a.	w.a.	Silver grey	2	2	Brilliant silver grey	2	2
Fenugreek	Light yellow	3	3	Yellow	3	3	Olive	1	3
Geranium	n.a.	n.a.	n.a.	Dark gold cream	4	4-5	n.a.	n.a.	n.a.
Grapes	Misty rose	2	3	Pink	3	3	Plum pink	3	2
Green tea	Gold	2	2	Gold brown	4	2-3	Beige brown	4	2-3
Henna	Gold cinnamon	2	4	Gold khaki	3	4	Bronze	3	4
Indigo	Silver blue	4	4-5	Silver grey	4	4	Dim grey	3	4
Kiwi	Ivory cream	w.a.	w.a.	Pearl peach	1	2	Cream	w.a.	w.a.
Kumquats	Ivory	w.a.	w.a.	Yellow cream	w.a.	w.a.	Cream	w.a.	w.a.
Lemon	Gold ivory	1	3	Honey comb	2	3	Cream yellow	1	2

Table 5.16: A listing of plant material used in dyeing shimmer satin (*continue*)

Plant	Without mordant			Alum mordant			$FeSO_4$ mordant		
	Colour	Fastness		Colour	Fastness		Colour	Fastness	
		Wash	Light		Wash	Light		Wash	Light
Lychee	Pink salmon	2	4	Peach	3	3-4	Dim grey	3	4
Macadamia	Cream	w.a.	w.a.	Ivory cream	w.a.	w.a.	Beige cream	2	3
Madder	Fiery orange	4	5	Orange	4-5	5	Cinnamon Brown	4-5	5
Mango	Ivory	w.a.	w.a.	Ivory cream	1	2	Brilliant plum beige	3	3
Mulberry	n.a.	n.a.	n.a.	Grey violet	1	4-5	n.a.	n.a.	n.a.
Onion [e]	Bronze brown	3	3	Pale lime green	4	5	Dark olive green	4	4
Onion [f]	Gold orange	3	4	Bright yellow	4	5	Bronze brown	4	5
Orange	Antique cream	w.a.	w.a.	Pale yellow cream	w.a.	w.a.	Cappuccino Beige	2	
Passion fruit	Rosy pink	1	2	Peach	3	2	Beige	3	2
Pepper	Gold yellow	2	1	Blush peach	1	1	Cream	w.a.	w.a.
Plum	Rosy pink	1	2	Cerise pink	1	2	Purple blue	1	3
Pomegranate rinds	Gold yellow	4-5	5	Cream	3	5	Pale grey green	4	5
Pomegranate seeds	Rose pink	4	4	Rose pink	4	4	Rose pink	4	4
Prickly pears	Cream	w.a.	w.a.	Cream	w.a.	w.a.	Gold beige	w.a.	w.a.
Raspberry	Pink plum	2	4	Rosette pink	3	4	Pale plum	3	2
Roselle	Sienna	2	4	Ruby	3	4	Deep salmon pink	2	2-3
Saffron	Rosy pink	3	1	Yellow lemon	4-5	3-4	Lemon yellow	4-5	4
Senjed	Cream	w.a.	w.a.	Cream	w.a.	w.a.	Pale beige cream	w.a.	w.a.
Spinach	Milky cream	w.a.	w.a.	Light gold yellow	3		Beige cream	3	2
Strawberry	Hot pink	1	2	Copper red magenta	2	2	Beige pink	2	2
Sumac	Gold coral	2	3	Coral	3-4	5	Brilliant pink	3	5
Tomatoes	Ivory	w.a.	w.a.	Antique cream	w.a.	w.a.	Ivory	w.a.	w.a.
Turmeric	Fiery yellow	2-3	3	Marseille yellow	4-5	3	Deep yellow	4-5	3
Weld	Gold yellow	4	4	Lemon yellow	4-5	5	Bright lemon yellow	4-5	5
Vine leaves	n.a.	n.a.	n.a.	Yellow	2	4	n.a.	n.a.	n.a.

[a] Red cabbage; [b] espresso coffee; [c] green coffee; [d] green coffee [e]; red onion; [f] brown onion
1-very poor, 2-poor, 3-fair, 4-very fair, 5-good, 6-very good; w.a., weak absorption; n.a., not available

Table 5.17: Colours and fastness properties of dyed and mordanted silk, cotton and satin fabrics with cochineal extract

Fabric	Without mordant			Alum mordant			$FeSO_4$ mordant		
	Colour	Fastness		Colour	Fastness		Colour	Fastness	
		Wash	Light		Wash	Light		Wash	Light
Silk	Fire brick	2	5	Leaden grey	4	5	Rose purple	4	5
Cotton	Fire brick	1	2	Cream grey	4	4	Amethyst purple	4	4
Satin	Gold brick	2	5	Leaden grey	4	5	Gold rose purple	4	5

Table 5.18: Colour Characterization yielded by natural dyes

Colour	Plants
Red	Roselle, strawberry, pomegranate (seeds), cochineal (insect), sumac
Yellow	Clove, fenugreek, geranium, lemon, pomegranate, prickly pears, onion (brown), orange, saffron, spinach, turmeric, weld
Orange-peach	Beetroot, lychee, madder, passion fruit, saffron, strawberry, onion (brown), aljedari
Pink-Purple	Beetroot, blackberry, blackcurrant, blueberry, cabbage (red), cherry, eggplant, grapes, mango, mulberry, onion (red), passion fruit, plum, pomegranate (seed), raspberry, roselle, saffron, strawberry, sumac, cochineal
Green- Olive	Aljedari, banana, cherry, coffee (espresso), dates, fenugreek, henna, kiwi, mango, onion (red), onion (brown), passion fruits, pomegranate (rind), prickly pears, spinach, sumac
Black-greys	Aljedari, beetroot, black tea, cabbage (red), cloves, coffee (Arabic), clove, dates, eggplant, green tea, indigo, lychee, mango, mulberry, pomegranate, prickly pear, cochineal
Brown	Aljedari, banana, barberry, beetroot, black tea, cherry, coffee (espresso), cutch, dates, green tea, henna, madder, onion (brown), onion (red), lychee, turmeric, weld
Gold-bronze	Aljedari, black tea, cherry, cloves, coffee (Arabic), coffee (espresso), cutch, fenugreek, green tea, henna, kiwi, prickly pear, pomegranate (rind), onion (brown), onion (red), sumac, turmeric
Cream-ivory	Apple, banana, carrot, coffee (Arabic), coffee (green), dates, eggplant, kiwi, kumquats, fenugreek, macadamia, mango, orange, pepper, prickly pears, spinach, tomato, zizyphus
Beige	Barberry, banana, black tea, beetroot, cherry, coffee (green), dates, indigo, kiwi, kumquats, lemon, macadamia, mango, orange, passion fruit, spinach, sumac, weld, vine leaves, zizyphus
Blue	Blueberry, cabbage (red), eggplant, indigo, plum

Table 5.19: Comparison of lightfastness of some samples tested with natural and artificial light

Natural dye	Fabric	Mordant	Natural light	Artificial light
Aljedari	Cotton	No mordant	4-5	3-4
Aljedari	Cotton	Alum	4-5	3-4
Aljedari	Cotton	$FeSO_4$	4-5	3
Aljedari	Silk	$FeSO_4$	5	3-4
Aljedari	Satin	$FeSO_4$	5	3
Dates fruit	Cotton	$FeSO_4$	5	2
Dates fruit	Satin	$FeSO_4$	5	2
Fenugreek	Cotton	Alum	4	3
Fenugreek	Cotton	$FeSO_4$	4	3
Henna	Silk	Alum	5	3-4
Pomegranate rind	Silk	Alum	5	3-4 (sample turned red)
Pomegranate seed	Silk	Alum	3	2
Prickly pear	Silk	$FeSO_4$	5	4

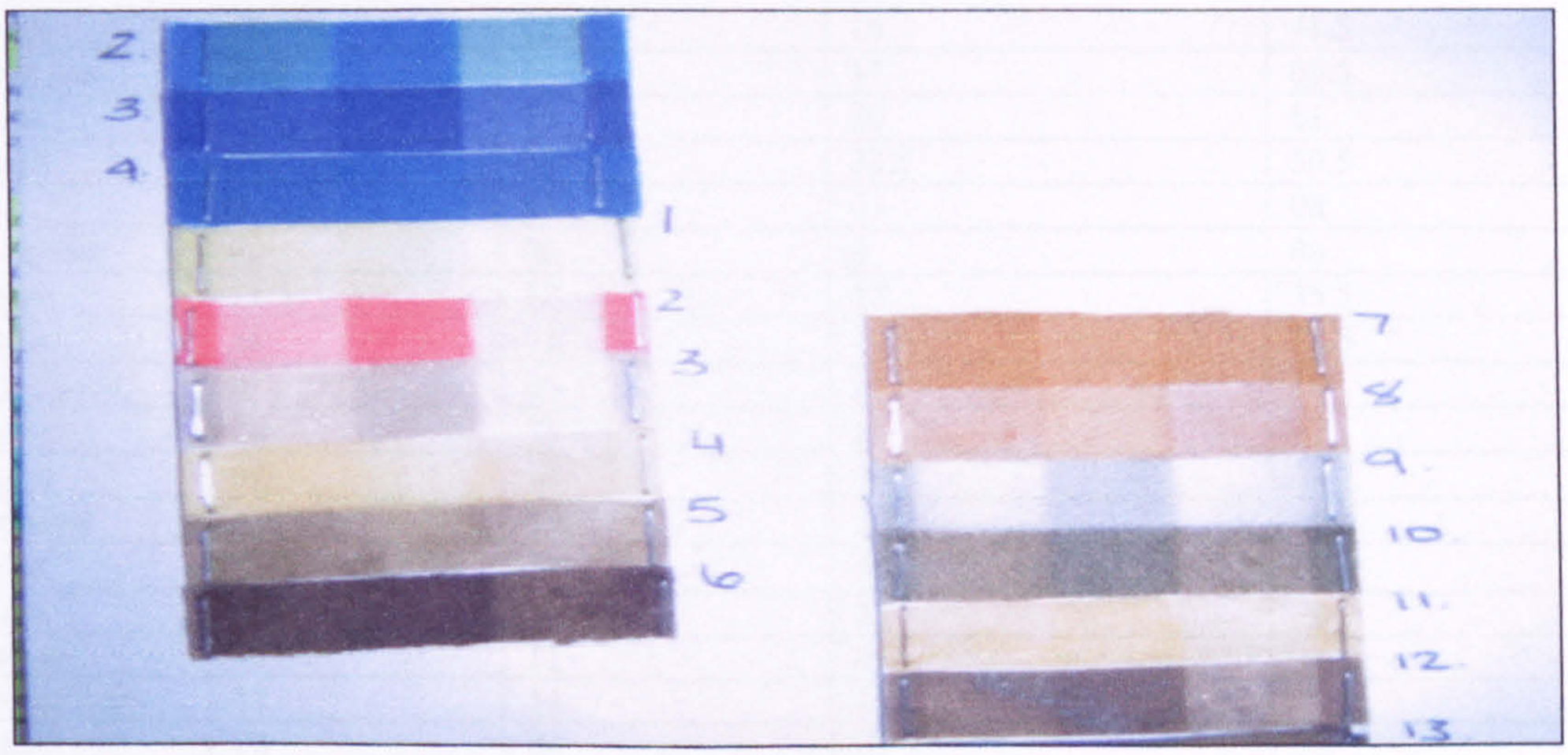


Plate 5.8: Some dyed samples against Blue Wool Standards after exposed to artificial light source PPT

Plates 5.9-5.16 display some selected dyed sample fabrics according to colour yielded.

Table 5.20: Total scores of colour fastness properties of each species used in dyeing the textile fabrics in this study

Species	Scores			Total Scores
	Paj silk	Cotton	Satin	
Aljedari	27	24.5	27	78.5
Banana	13.5	17.5	20.5	51.5
Barberry	24	17.5	14	55.5
Beetroot	10	16	16	42
Blackberry	12	14	14	40
Blackcurrant	05.5	07	04	16.5
Black tea	26	17	22	65
Blueberry	13.5	13	13	39.5
Cabbage [a]	14.5	10	13	37.5
Cherry	12.5	12.5	11	36
Cloves	27	24.5	27	78.5
Cochineal	25	19	25	69
Coffee [b]	28.5	16	13	57.5
Coffee [c]	23	4.5	19	46.5
Coffee [d]	0	05	06	11
Cutch	24	24.5	23.5	72
Dates	17	25	27	69
Eggplant	07	7.5	08	22.5
Fenugreek	19	18.5	16	53.5
Geranium	n.a.	07	8.5	15.5
Grapes	13	12.5	16	41.5
Green tea	21.5	22	17	60.5
Henna	25	16	20	61
Indigo	03	24	23.5	50.5
Kiwi	0	05	03	08
Kumquats	0	06	0	06
Lemon	11.5	12	12	35.5
Lychee	21	18	19.5	58.5
Macadamia	0	05	05	10
Madder	26	23	28	77
Mango	07	18	09	34
Mulberry	n.a.	05	5.5	10.5
Onion [e]	24.5	22	23	69.5
Onion [f]	28	25	25	78
Orange	15	11	06	32
Passion fruit	12	14	13	39
Pepper	04	04	05	13
Plum	13	12.5	10	35.5
Pomegranate [g]	27.5	27	26.5	81
Pomegranate [h]	16	12	24	52
Prickly pears	14	06	0	20
Raspberry	16	18	18	52
Roselle	17.5	13	17.5	48
Saffron	19.5	19.5	20	59
Senjed	06	07	0	13
Spinach	0	14.5	11	25.5
Strawberry	15.5	12	11	38.5
Sumac	25	22	21.5	68.5
Turmeric	22	19.5	20.5	62
Weld	27	27.5	26	80.5
Vine leaves	n.a.	06	06	12

[a] Red cabbage; coffee ([b] espresso [c] Arabic; [d] green), onion ([e] red, [f] brown), Pomegranate ([g] rinds, seeds [h])

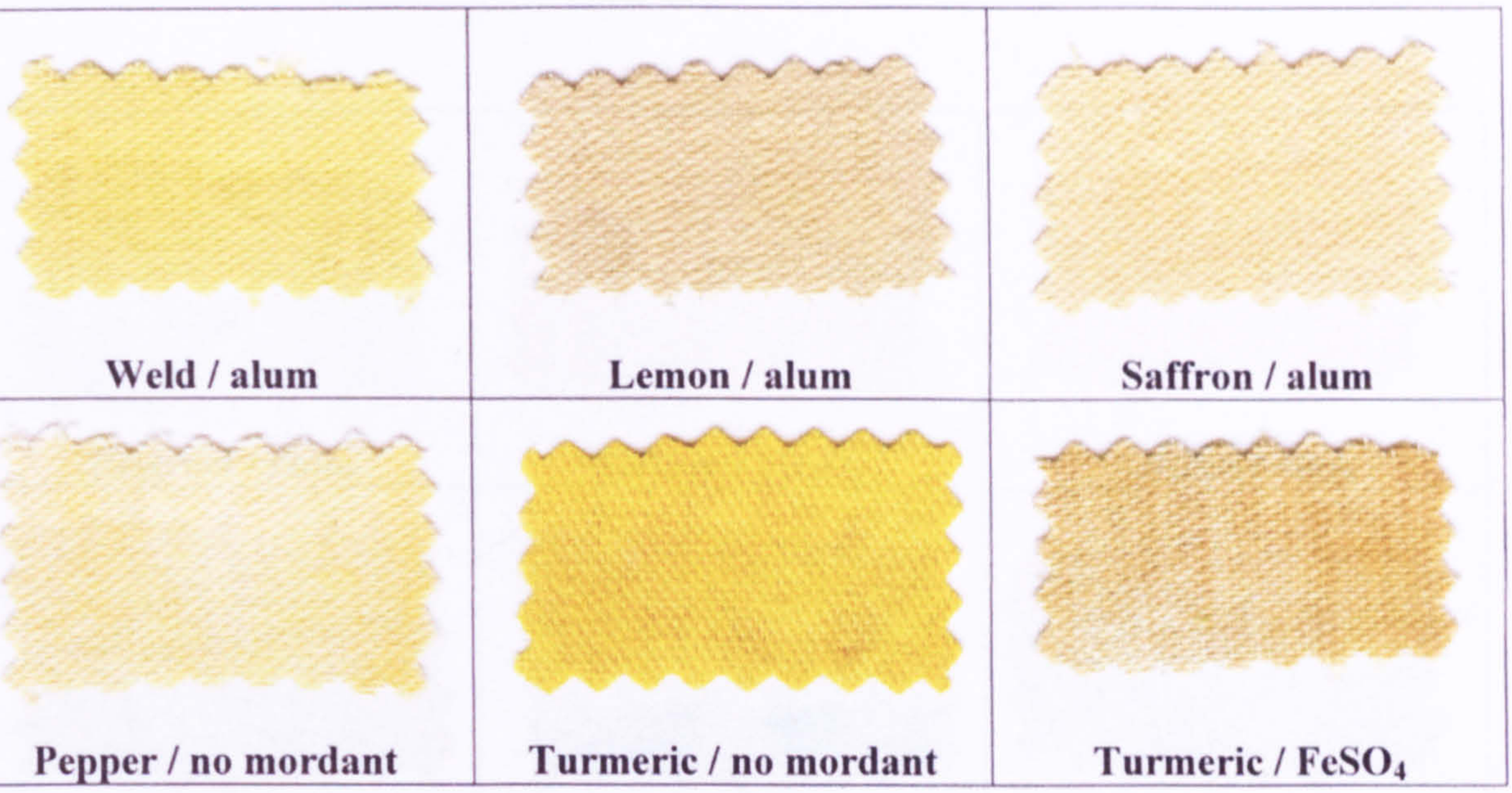


Plate 5.9: Samples of cotton fabric dyed with aqueous extracts of plants yielded yellow shades

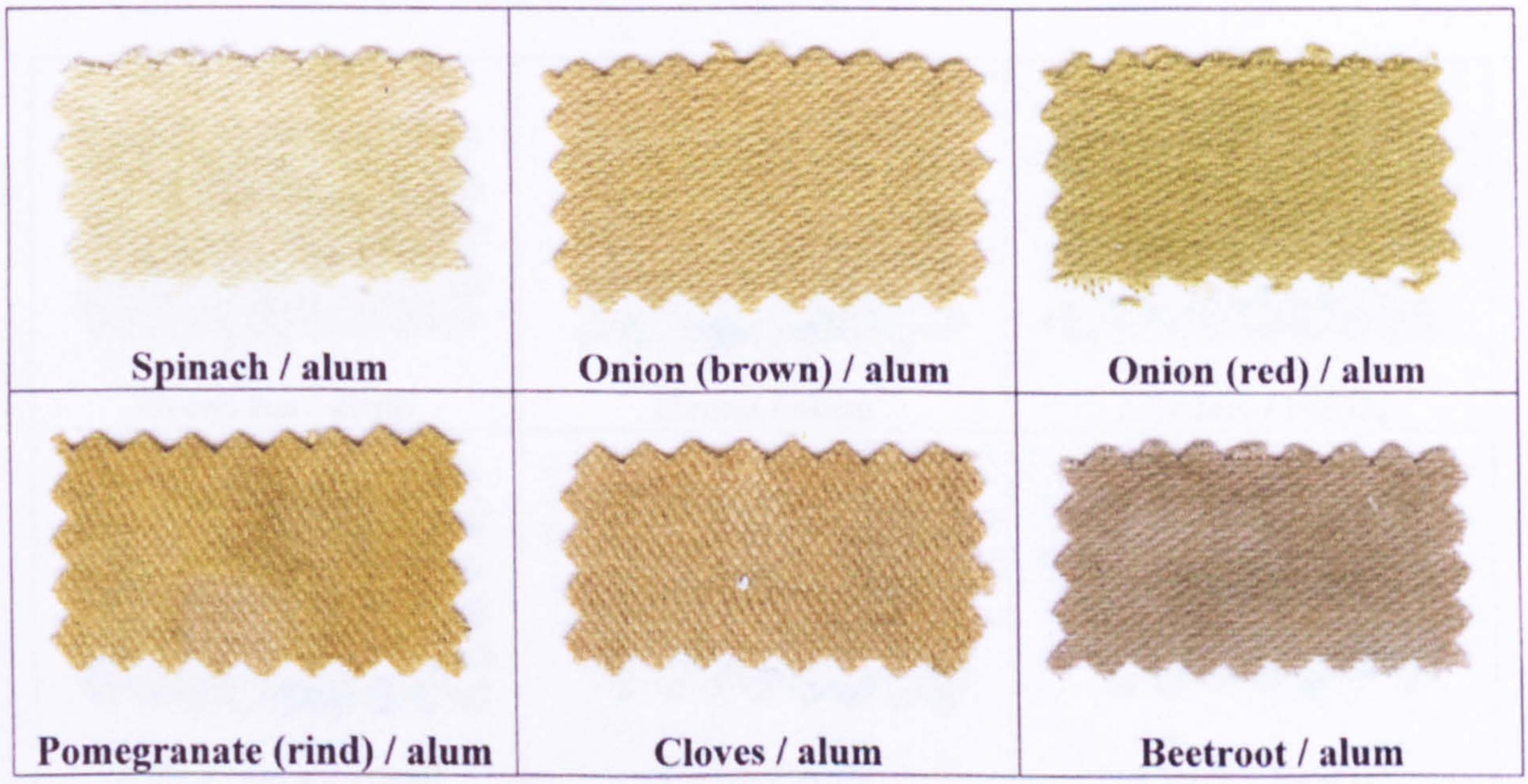


Plate 5.10: Samples of cotton fabric dyed with aqueous extracts of plants yielded green-olive shades

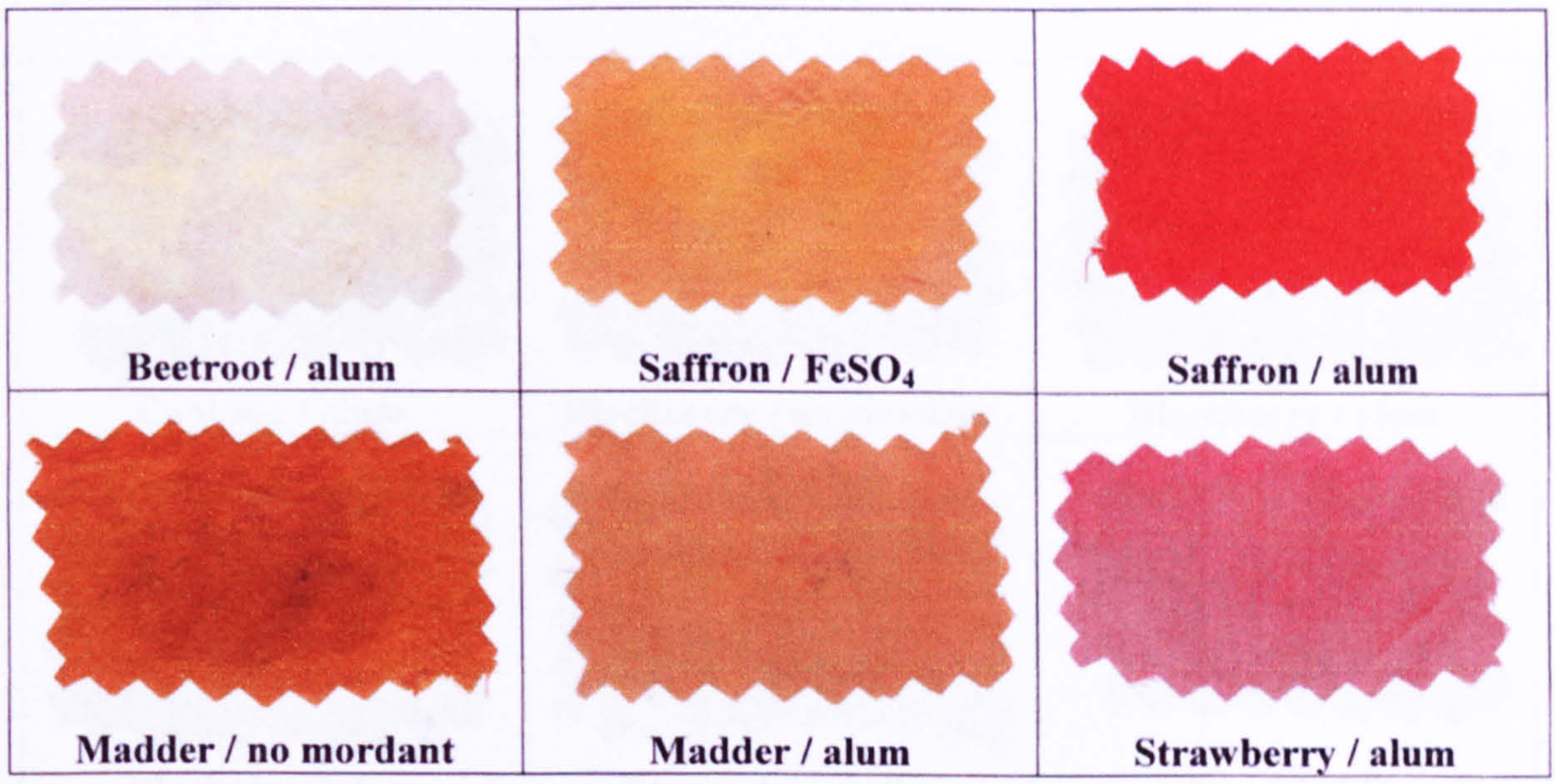


Plate 5.11: Samples of silk fabric dyed with aqueous extracts of plants yielded orange shades

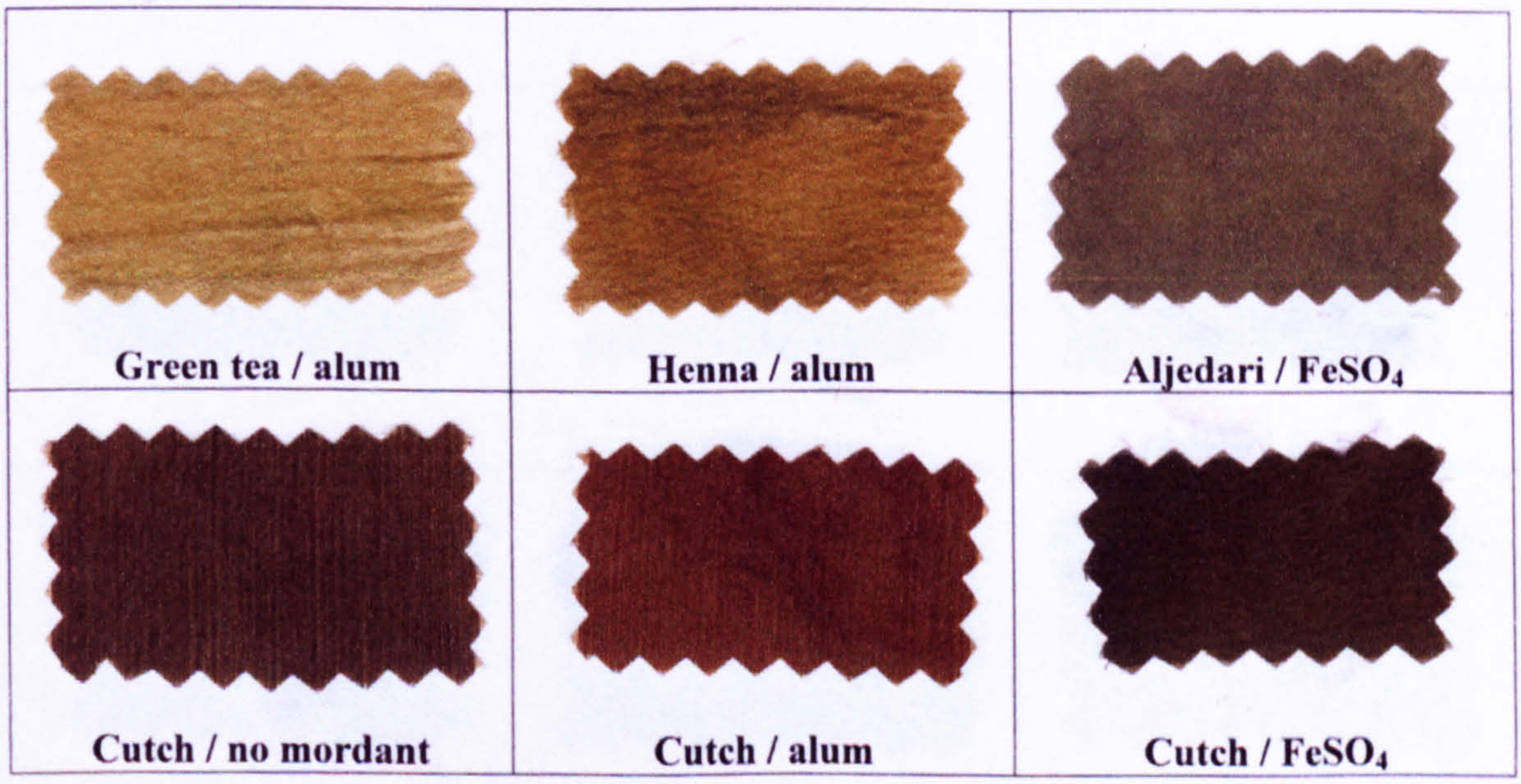


Plate 5.12: Samples of satin fabric dyed with aqueous extracts of plants yielded brown shades

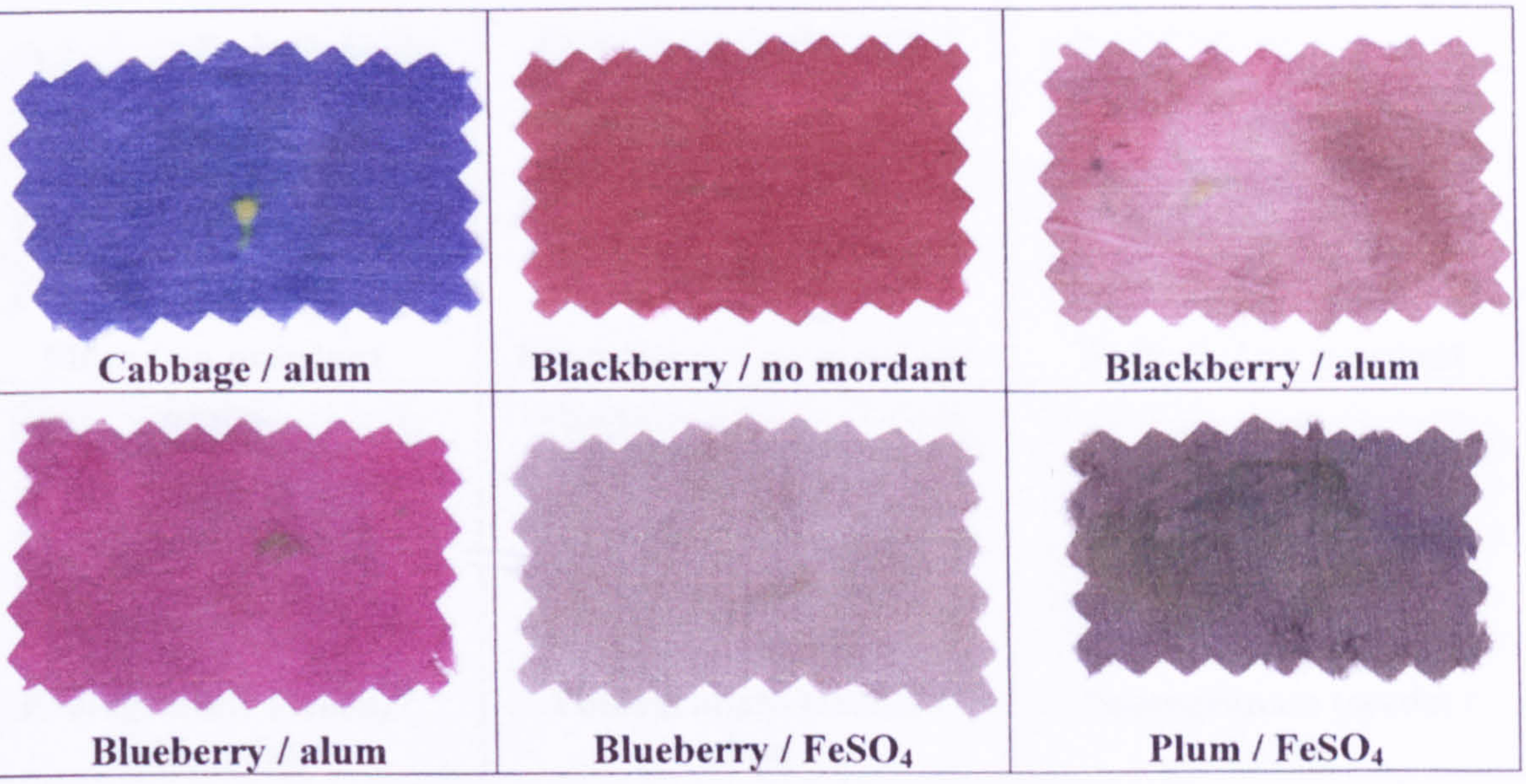


Plate 5.13: Samples of silk fabric dyed with aqueous extracts of plants yielded purple-violet shades

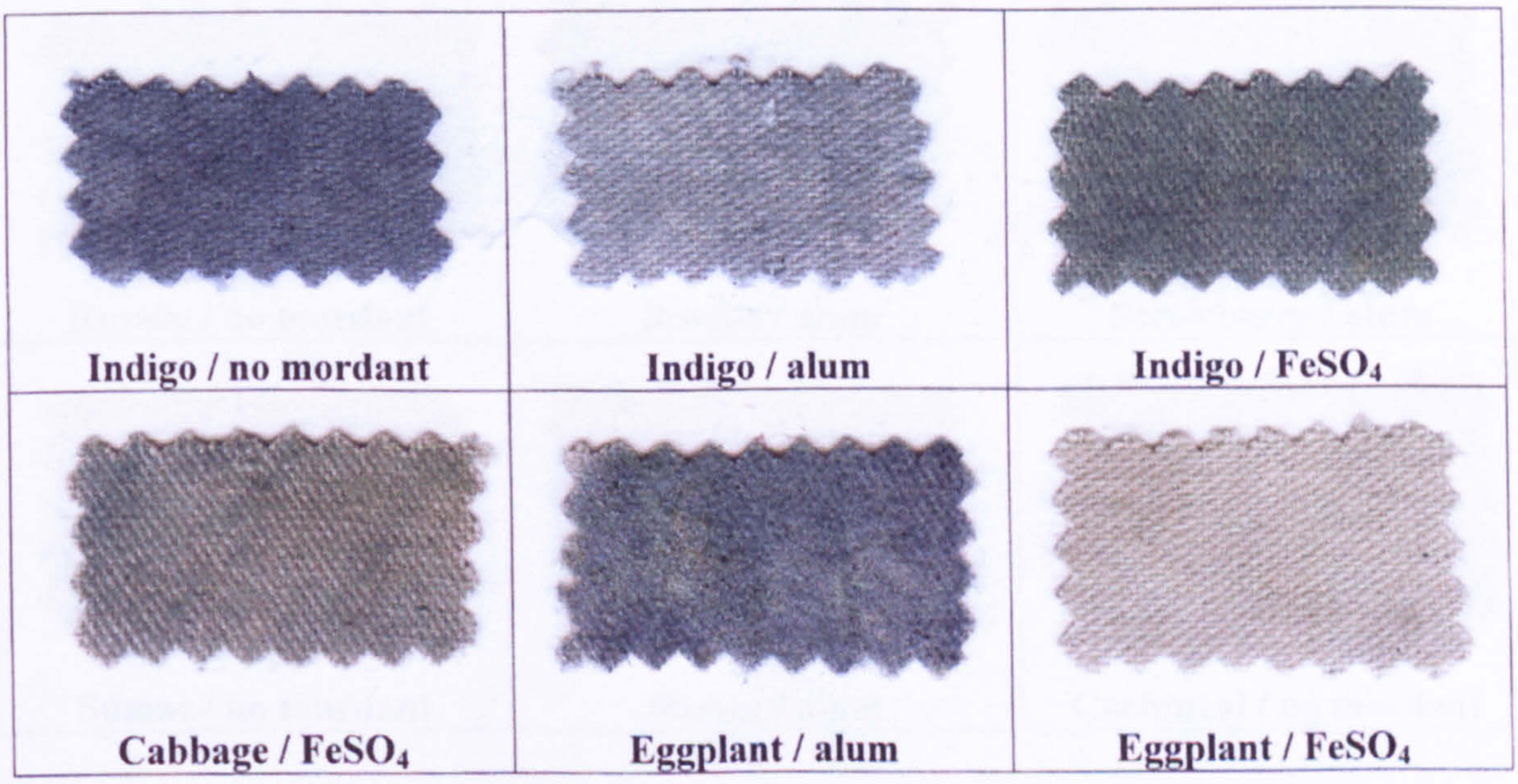


Plate 5.14: Samples of cotton fabric dyed with aqueous extracts of plants yielded blue shades

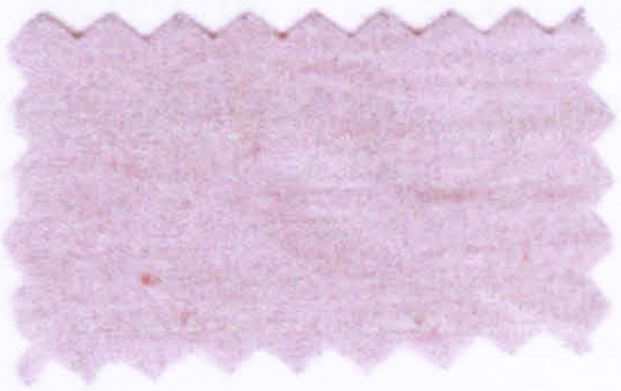
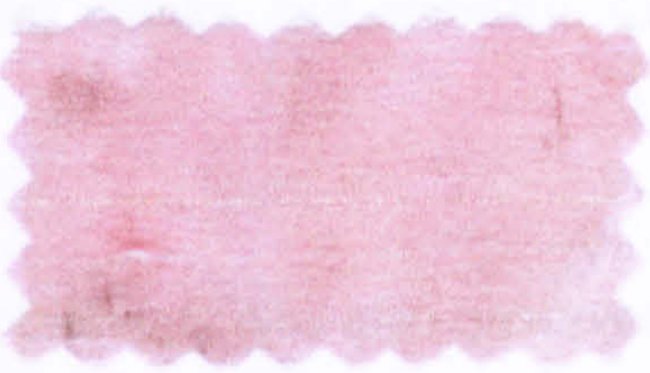
		
Plum / no mordant	**Strawberry / no mordant**	**Saffron / no mordant**
		
Pomegranate (seeds) / no mordant	**Pomegranate (seeds) / alum**	**Pomegranate (seeds) / $FeSO_4$**

Plate 5.15: Samples of satin fabric dyed with aqueous extracts of plants yielded pink shades

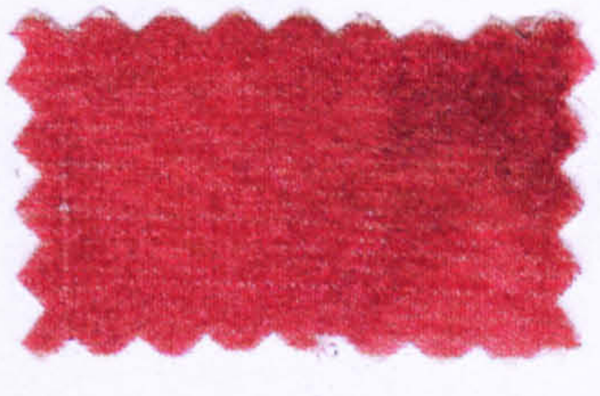
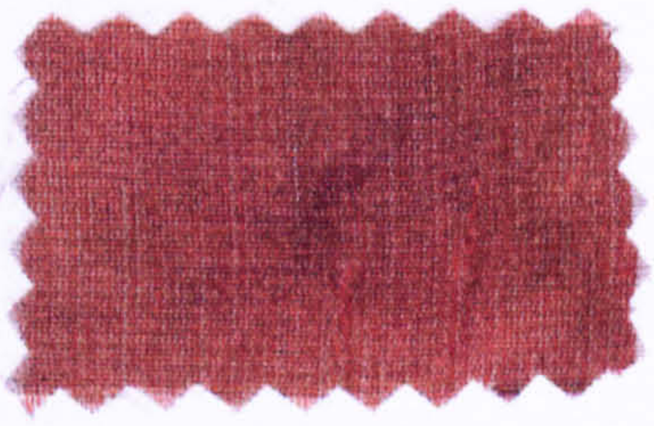
		
Roselle / no mordant	**Roselle / alum**	**Strawberry / alum**
		
Sumac / no mordant	**Sumac / alum**	**Cochineal / no mordant**

Plate 5.16: Samples of satin fabric dyed with aqueous extracts of plants yielded ruby-red shades

5.12 SUMMARY

The following conclusions are drawn from the results presented in this chapter:

Natural dyes are able to produce strong, clear colour that is fast to consumer use. Of the 54 dyestuffs studied, 32 plants are potentially able to produce marketable natural dyes. These dyes produce good colour and met minimal performance standards for colour fastness to light and washing.

Silk, cotton and satin fabrics can be dyed successfully by the natural dyes extracted from different species. Silk gave the best performance of dyeing uptake and stability. Cotton gave the poorest fastness properties.

Iron and alum mordants generally increase the fastness properties. It was also observed that using alum mordant brightens the natural dyes, while fixing the colour. Iron fixes the colour and darkens it. Iron also has a tendency to turn many yellow dyes green. Grey-black colour can be produced from plant dyes mordanted with iron.

Considering molecular associations the fastness properties were of the order:

anthraquinones and tannins > indigoid > flavones > flavonols > flavanols > carotenoids > anthocyanins.

5.13 REFERENCES

1. L.G. Angelini, L. Pistelli, P. Belloni, A. Bertoli, S. Panconesi, *Ind. Crops Prod.*, 1997, **6**, 303-311.
2. R.D. Combes and R.B. Haveland-Smith, *Mutat. Res.*, 1982, **98**, 101-243.
3. D. Cristea and G. Vilarem, *Dyes Pigm.*, 2006, **71**, 39-46.
4. S. Janhom, R. Watanesk, S. Watanesk, P. Griffiths, O.-A. Arquero, W. Naksata, *Dyes Pigm.*, 2006, **71**,163-168.
5. M.M. Kamel, R.M. El-Shishtawy, B.M. Yussef, H. Mashaly, *Dyes Pigm.*, 2005, **65**, 103-110.
6. R. Bhuyan and C.N. Saikia, *Bioresour. Technol.*, 2005, **96**, 363-372.
7. T. Bechtold, A. Turcanu, E. Ganglberger, S. Geissler, *J. Cleaner Prod.*, 2003, **11**, 499-509.
8. K. Yoshizumi and P.C. Crews, *Dyes Pigm.*, 2003, **58**, 197-204.
9. P.M. Chan, C.W.M. Yeun, K.W. Yeung, *Text. Asia*, 1998, **29**, 59-60.
10. K. Ramakrishna, *Colourage*, 1999, **46**, 29-30.
11. B. Ghorpade, M. Darrekar, P.S. Vankar, *Colourage*, 2000, **47**, 27-30.
12. G.G. Balakina, V.G. Vasiliev, E.V. Karpova, V.I. Mamatyuk, *Dyes Pigm.*, 2006, **71**, 192-198.
13. I. Surowiec, A. Quye, M. Trojaowicsz, *J. Chromatogr.A*, 2006, **112**, 209-217.
14. J. Orska-Gawrys, I. Surowiec, J. Kehl, H. Rejniak, K. Urbaniak-Walczak, M. Trojanowicz, *J. Chromatogr. A*, 2003, **989**, 239-248.
15. F. Delamare and B. Guineau, Colour Making Using Dyes and Pigments, 2000, Thames and Hudson Ltd., London, UK.
16. H.T. Deo and B.K. Desai, *J. S. D. C.*, 1999, **115**, 224-227.
17. N. Bhattacharyya and A.S. Sahasrabudhe, *Resume of papers, 38th technological conf.*, Ahmedabad, February 1997, (Published by ATIRA), 185-192.
18. N. Bhattacharya and S. Acharekar, *BTRA Scan*, 1998, **29**, 18-25.
19. N. Bhattacharya; B.A. Doshi; A.S. Sahasrabudhe, *Am. Dyestuff Rep.*, 1998, **87**, 26-29.

20. P.M. Chan, C.W.M. Yuen, K.W. Yeung, *Text. Asia*, 2000, **31**, 28-30.
21. U. Brückner, S. Struckmeier, J.-H. Dittrich, R.-D. Reumann, *Textilvered.*, 1997, **32**, 112-116.
22. H.T. Lockhande and V.A. Dorugade, *Am. Dyestuff Rep.*, 1999, **88**, 29–34.
23. A. Bansal and A. Sood, *Text. Asia*, 2001, **32**, 27-30.
24. P. Khanna and E.M. Dedhia, *Colourage,* 1999, **46**, 25-28.
25. P. Venkidusamy and J. Arunkumar, *Man-made T.*, 1997, **40**, 259-262.
26. D.P. Chattopadhyay, J.K. Sharma, R.B. Chavan, *Man-Made T.*, 1997, **40**, 361-365.
27. G. Fereday, Natural Dyes, 2003, The British Museum Press, London, UK.
28. V. Tiwari, B. Ghorpade, P.S. Vankar, *Asian Text. J.*, 2000, **9**, 28-30.
29. E. M. Dedhia, *Colourage*, 1998, **65**, 45-49.
30. B. Ghorpade, V. Tiwari, P.S. Vankar, *Asian Text. J.*, 2000, **9**, 68-69.
31. M.L. Gulrajani, R.C. Srivastava, M. Goel, *Color. Technol.*, 2001, **117**, 225-228.
32. K.K. Agarwal, *Asian Text. J.*, 2000, **9**, 65-67.
33. A. Gogia, *Indian Silk*, 1999, **38**, 21-24.
34. D. Gupta, *Colourage*, 1999, **46**, 35-38.
35. V. Riganti, E. Gallotti, L. Gallotti, *Tinctoria*, 1998, **95**, 63-71.
36. P.V. Samy, A.S.M. Raja, G. Ramsingh, *Man-Made T.*, 1998, **41**, 132-134.
37. M.L. Gulrajani, *Colourage*, 1999, **46**, 19-28.
38. M.K. Yakubu and A.M. Baba, *Man-Made T.*, 2000, **43**, 293-298.
39. N. Sekar, *Colourage*, 1999, **46**, 33-34.
40. W.B. Achwal, *Colourage*, 1998, **45**, 45-46.
41. I. Doraisamy and K.P. Janakiraman, *Text. Mag.*, 1999, **28**, 8-11.
42. B. Glover, *J. S. D. C.*, 1998, **114**, 4-7.
43. P.S. Vankar, R. Shanker, J. Srivastava, *Dyes Pigm.*, 2006, **71**, 230-234.
44. P.S. Vankar, *Resonance*, October 2000, 73-80.
45. S. Han and Y. Yang, *Dyes Pigm.*, 2005, **64**, 157-161.
46. R. Singh, A. Jain, S. Panwar, D. Gupta, S.K. Khare, *Dyes Pigm.*, 2005, **66**, 99-102.
47. T.B. Machado, A.V. Pinto, M.C.F.R. Pinto, I.C.R. Leal, M.G. Silva, A.C.F. Amaral, R.M. Kuster, K.R. Netto-dosSantos, *Int. J. Antimicrob. Agents*, 2003, **21**, 279-284.

48. G. Saxena, A.R. McCutcheon, S. Farmer, G.H.N. Towers, R.E.W. Hancock, *J. Ethnopharmacol.*, 1994, **42**, 95-99.
49. S.M. Hussein, H.H. Barakat, I. Merfort, M.A.M. Nawwar, *Phytochemistry,* 1997, **45**, 819-823.
50. M. Verzele and P. Delahaya, *J. Chromatogr. A*, 1983, **268**, 469-476.
51. Y. Seino, M. Nagao, T. Yahagi, T. Sugimura, T. Yasuda, S. Nishimura, *Mutat. Res.*, 1978, **58**, 225-229.
52. http://en.wikipedia.org/wiki/Tannin, Tannin (28/06/2006).
53. www.eastonwest.co.uk/scieihenna.html, Henna (06/07/2006).
54. P. Guinot, A. Rogé, A. Gargadennec, M. Garcia, D. Dupont, E. Lecoeur, L. Candelier, C. Andary, *Color. Technol.*, 2006, **122**, 93–101.
55. M. Hancock, Potential for Colourants from Plant Sources in England & Wales, 1997, ST0106, Arable Crops & Horticulture Division, ADAS Boxworth, Cambridge, UK.
56. J. Chandrasekaran, *Resonance*, 2001, 66-75.
57. E. Forni, A. Polesello, D. Montefiori, A. Maestrelli, *J. Chromatogr. A*, 1992, **593**, 177-183.
58. P. Atkins, Atkins' Molecules, 2003, Cambridge University Press, Cambridge, UK.
59. C. Dufresne and E. Farnworth, *J. Nutr. Biochem.*, 2001, **12**, 404-421.
60. J.M. Watt, B. Brandwijk, M. Gerdina, Medicinal and Poisonous Plants of Southern and Eastern Africa, 1962, Livingstone Ltd, Edinburgh, London, UK.
61. P.F. Gordon and P. Gregory, Organic Chemistry in Colour, 1983, Springer-Verlag, Berlin Heidelberg, New York.
62. www.apparelsearch.com/natural_dyes.htm, natural dyes (16/07/2005).
63. N. Sekar, *Colourage*, 1999, **46**, 57-60.
64. B. Schoefs, *Trends Food Sci. Technol.*, 2002, **13**, 361-371.
65. S.A. Aherne and N.M. O'Brien, *Nutrition*, 2002, **18**, 75-81.
66. E. de Rijke, P. Out, W.M.A. Niessen, F. Ariese, C. Gooijer, U.A.T. Brinkman, *J. Chromatogr. A*, 2006, **1112**, 31-63.

67. A. Perva-Uzunalic, M. Škerget, Ž. Knez, B. Weinreich, F. Otto, S. Grüner, *Food Chem.*, 2006, **96**, 597-605.

68. H. Heil, B. Baumann, C. Andary, K.E. Linsenmair, D. McKey, *Naturwissenschaften*, 2002, **89**, 519-524.

69. P. Schofield, D.M. Mbugua, A.N. Pell, *Animal Feed Sci. Technol.*, 2000, **91**, 21-40

70. A.M. Al-Saeed, D.Phil., Sussex University, 39-6490, 1989, D2a, www.theses.com/idx/039/it039006490.htm, (08/10/2001).

71. B. Szostek, J. Orska-Gawrys, I. Surowiec, M. Trojaowicsz, *J. Chromatogr. A*, 2003, **1012**, 179-192.

72. A.R. Hall, *Quaternary Sci. Rev.*, 1996, **15**, 635-640.

73. A. Gilchrist and J. Nobbs, *J. S. D. C.*, 1999, **115**, 4-7.

74. J. Tawil, Colorimetry, International Cinematographic Guild, Edited by Mark Woods. www.cameraguild.com/technology/colorimetry/colorimetry.htm, Colorimetry. (07/09/2005).

75. S.N. Al-Hooti, J.S. Sidhu, J.M. Al-Saqer, A. Al-Othman, *Food Chem.*, 2002, **79**, 215-220.

76. E. Tsatsaroni and M. Liakopoulou-Kyriakides, *Dyes Pigm.*, 1995, **29**, 203-209.

77. E. Tsatsaroni, M. Liakopoulou-Kyriakides, I. Eleftheriadis, *Dyes Pigm.*, 1998, **37**, 307-315.

78. J. Goodwin, A Dyer's Manual, 1982, Pelham Books Ltd., London, UK.

79. E.R. Trotman, Dyeing and Chemical Technology of Textile Fibres, 1964, Griffin and Company Ltd., London, UK.

80. J. Gillow and B. Sentance, 1999, Thames & Hudson, London, UK.

81. http//en.wikipedia.org/wiki/silk, Silk (15/07/2006).

82. C. Earl, An Introduction to Silk Painting, 2002, D & S Book Ltd, Devon, UK.

83. S. Stokoe, Practical Batik, 2000, London, UK: Anness Publishing Ltd.

84. E.N. Abrahart, Dyes and their Intermediates, 1977, Edward Arnold Publishers Ltd., London, UK.

85. www.carrtextile.com/polycottontwill.html, Cotton twill (16/07/2005).

86. www.orioletex.com/6300.html, Shimmer Satin (16/07/2005).

87. D.R. Waring and G. Hallas, The Chemistry and Application of Dyes, 1990, Plenum Press, New York, USA.
88. P.S. Bailey, Jr. and C.A. Bailey, Organic Chemistry, 1989, Allyn and Bacon, Inc., Boston, USA.
89. K.E. Heim, A.R. Tagliaferro, D.J. Bobilya, *J. Nutr. Biochem.*, 2002, **13**, 572-584.
90. A. Schieber, F.C. Stintzing, R. Carle, *Trends Food Sci. Technol.*, 2001, **12**, 401-413.
91. X. Sun, X. Yang, E. Wang, *Anal. Chim. Acta*, 2005, **547**, 153-157.
92. J.B. Hallagan, D.C. Allen, J.F. Borzelleca, *Food Chem. Toxicol.*, 1995, **33**, 515-528.
93. U. Wissgott and K. Bortlik, *Trends Food Sci. Technol.*, 1996, **7**, 298-302.
94. M. Plessi, D. Bertelli, A. Albansini, *Food Chem.*, 2007, **100**, 419-427.
95. H. Matsumoto, Y. Nakamura, H. Iida, K. Ito, H. Ohguro, *Experimental Eye Research*, 2006, **83**, 348-356.
96. M. Dyrby, N. Westergaard, H. Stapelfeldt, *Food Chem.*, 2001, **72**, 431-437.
97. K. Iwasaki-Kurashige, R.Y. Loyaga-Rendon, H. Matsumoto, T. Tokunaga, H. Azuma, *Vascular Pharmacol.*, 2006, **44**, 215-223.
98. M.-S. Su and J.L. Silva, *Food Chem.*, 2006, **97**, 447-451.
99. T. Watanabe and S. Terabe, *J. Chromatogr. A*, 2000, **880**, 311-322.
100. J.-Y. Lin and C.-Y. Tang, *Food Chem.*, 2007, **101**, 140-147.
101. S.-Y. Kang, B.P. Seeram, M.G. Nair, L.D. Bourquin, *Cancer Lett.*, 2003, **194**, 13-19.
102. E. Parziale, Clove, http://earthnotes.tripod.com/clove.htm, Clove-Herb (13/07/2006).
103. http://earthnotes.tripod.com/clove.htm, Clove (13/07/2006).
104. H. Ashihara and A. Crozier, *Trends Plant Sci.*, 2001, **6**, 407-413.
105. A. Mansouri, G. Embarek, E. Kokkalou, P. Kefalas, *Food Chem.*, 2005, **89**, 411-420.
106. H. Boudries, P. Kefalas, D. Hornero- Méndez, *Food Chem.*, 2007, **101**, 1372-1377.
107. K. Matsubara, T. Kaneyuki, T. Miyake, M. Mori, *J. Agric. Food Chem.*, 2005, **53**, 6272-6275.
108. Y. Cadot, M.T.M. Castelló, M. Chevalier, *Anal. Chim. Acta*, 2006, **563**, 65-75.
109. R.C. Pendleton, www.wise2food.com/food09149.html, Kumquat (13/07/2006).

110. www.kumquatgrowers.com/what.html, What is a Kumquat (13/07/2006).
111. Z. Zhang, X. Pang, Z. Ji, Y. Jiang, *Food Chem.*, 2001, **75**, 217-221.
112. J. Rivera-López, C. Ordorica-Falomir, P. Wesche-Ebeling, *Food Chem.*, 1999, **65**, 195-200.
113. X. Zheng and S. Tian, *Food Chem.*, 2006, **96**, 519-523.
114. G.C.H. Derksen, H.A.G. Niederländer, T.A. van Beek, *J. Chromatogr. A*, 2006, **978**, 119-127.
115. P.-N. Chen, S.-C. Chu, H.-L. Chiou, W.-H. Kuo, C.-L. Chiang, Y.-S. Hsieh, *Cancer Lett.*, 2006, **235**, 248-259.
116. V. Lanzotti, *J. Chromatogr. A*, 2006, **1112**, 3-22.
117. L.J. Ignarro, R.E. Byrns, D. Sumi, F. de Nigris, C. Napoli, *Nitric Oxide*, 2006, **15**, 93-102.
118. G. Gradinaru, C.G. Biliaderis, S. Kallithraka, P. Kefales, C. Garcia-Viguera, *Food Chem.*, 2003, **83**, 423-436.
119. Y.-C. Chang, K.-X. Huang, A.-C. Huang, Y.-C. Ho, C.-J. Wang, *Food Chem. Toxicol.*, 2006, **44**, 1015-1023
120. http://www.answers.com/topic/sumac, sumac (15/07/2006).
121. A. Ortega-Regules, I. Romero-Cascales, J.M. Ros-García, J.M. López-Roca, E.G. Plaza, *Anal. Chim. Acta*, 2006, **563**, 26-32.
122. P. Lozano, M.R. Castellar, M.J. Simancas, J.L. Iborra, *J. Chromatogr. A*, 1999, **830**, 477-483.
123. N. Li, G. Lin, Y.-W. Kwan, Z.-D. Min, *J. Chromatogr. A*, 1999, **849**, 349-355.
124. J. Zhao, S.P. Li, F.Q. Yang, P. Li, Y.T. Wang, *J. Chromatogr. A*, 2006, **1108**, 188-194.
125. J.W. Li, S.-D. Ding, X.-L., Ding, *J. Food Eng.*, ., 2007, **80**, 176-183.
126. S.S. Teng and B.H. Chen, *Food Chem.*, 1999, **65**, 367-373.
127. A. Zalacain, M. Prodanov, M. Carmona, G.L. Alonso, *Biosystem Eng.*, 2003, **84**, 211-216.
128. R. Niemetz and G.G. Gross, *Phytochemistry*, 1998, **49**, 327-332.
129. E. Pfeiffer, S. Höle, A.M. Solyom, M. Metzler, *J. food Eng.*, 2003, **56**, 257-259.

130. D. Gupta, *Colourage*, 2000, **47**, 23-26.

131. T. Wakida, S. Choi, S. Tokino, M. Lee, *Text. Res. J.*, 1998, **68**, 848-853.

132. S.S. Ahmed, A. Gogi, R. Phukon, N. Gogi, *Indian Silk,* 1997, **36**, 17-19.

133. S.P. Mishra, M. Pattanaik, P. Mohapatra, N. Das, *Asian Text. J.*, 2001, **10**, 32-34.

134. B.M. Badri and S.M. Burkinshaw, *Dyes Pigm.*, 1993, **22**, 15-25.

135. P.S. Vankar, R. Shanker, A. Verma, *J. Cleaner Prod.*, 2007, **15**, 1441-1450.

136. Dyeing properties of *Hibiscus sabdariffa*, *The Colourists*, Summer 2004, issue 2 (Technical SDC Grant Scheme).

137. A. Imaizumi and K. Yoshizumi, *Color. Technol.*, 2006, **122**, 86-92.

138. D. Cristea and G. Vilarem, *Dyes Pigm.*, 2006, **70**, 238-245

CHAPTER 6

DECOLOURIZATION AND DEGRADATION OF NATURAL DYES

6.1 INTRODUCTION

Materials of natural origin have been used to provide colour in foods, drugs and cosmetics for thousands of years. Ash from fires, mineral compounds and plants were probably among the first materials used for cosmetic purposes. Later, it was discovered that certain materials, mostly plant derived, could be used to enhance the taste and appearance of foods and thus turmeric, paprika and saffron were used for more than just their flavouring properties. By the early 1990s, natural and synthetic colour additives were used extensively to colour foods, drugs and cosmetics [1]. In the later part of the nineteenth century, synthetic organic dyes were developed to provide a more economical and extensive array of colourants. Colour is important for cosmetic purposes among many populations, and also for safety purposes such as the identification of pharmaceuticals.

Colour is an important characteristic and selection criterion for food choice. Many studies have highlighted this importance and have shown how selection may change among certain populations, and over time. Colour additives exempt from certification are used for a wide variety of purposes in foods, drugs and cosmetics [1-5]. Based on the origin of food colours can be classified as natural, nature identical and synthetic. There is an increasing demand for the use of natural colours as they are preferred in foods over the synthetic colours. The usage of dyes and pigments in foods and the level of incorporation are governed by the regulatory requirements of the individual countries [2, 6].

Significant developments have occurred with natural dyes since their wider commercialisation around 25 years ago. The growth in use of natural dyes comes from increasing consumer pressure for 'natural' products in light of their distrust for the food industry, based on unsubstantiated health scares related to additives in general, but especially related to hyperactivity and its perceived association with many azo dyes such as tartrazine [3].

Colour is spread widely throughout nature in fruit, vegetables, seeds and roots. In our daily diets we consume large quantities of many pigments, especially anthocyanins, carotenoids and chlorophylls [3].

Dyes from nature vary widely in their physical and chemical properties. Many are sensitive to oxidation, pH change and light and their inherent solubility varies widely [3].

There are currently 13 permitted naturally derived colours for use in the EU and 26 colours exempt from certification in the USA. Table 6.1 lists food additives permitted in UK and Table 6.2 details the colour shade and key characteristics of the most commonly used permitted naturally derived colours [3].

Table 6.1: Name and type of natural-derived dyes permitted for use of food in the UK [5]

Name/Type	E number	Name	E number
Alkanet extract (P)		Curcumin (P)	E100
Amaranth (P/S)	E123	Flavoxanthin (P/S)	E160a
Annatto & extract (P)	E160b	Gold (M)	E175
Anthocyanins (P)	E163	Grape colour & skin extract (P)	
Barley extract (P)		Malt (P)	
Beetroot powder (P)	E162	Red beet extract (P)	E162
Canthxanthin (P/S)	E161g	Riboflavin, vitamin B2 (P/S)	E101
Caramel (S)	E150	Riboflavin tetrabutyrate (P/S)	
Vegetable carbon, Carbon black (P/S)	E153	Saffron (P)	
Carmines (A)	E120	Terpene resin (S)	
Carotenes (P/S)	E160a	Titanium oxide (M)	E171
Chichory extract (P)		Turmeric (P)	E100
Chlorophylls (P)	E140	Xanthophylls (P/S)	
Citraxanthin (P/S)		Paprika (P)	E160c
Cochineal (A)	E120	Shellac (A)	
Cottonseed flour (P)		-------	

A - Animal; M - Mineral; P - plant; S – Synthesized

Table 6.2: Key features of naturally derived colours [3]

Pigment	Sources	Colour shade	Comments
Curcumin	Turmeric rhizome	Bright lemon yellow	A non soluble pigment that is light sensitive.
Lutein	Marigold and alfalfa	Golden yellow	Oil soluble carotenoid pigment naturally present in many foods. Used in deserts, soft drinks and bakery products. Only permitted in the USA in chicken feed.
Natural mixed carotenes	Palm oil, D. salina (algae)	Golden yellow to orange	Oil soluble, naturally sensitive to oxidation.
Bixin/norbixin	Bixa Orellana bush seeds	Orange	Bixin is oil soluble and norbixin water soluble.
Capsanthin/ capsorubin	Paprika (*Capsicum annum* L.)	Reddy orange	Oil soluble carotenoid from the red pepper. The flavour level (capsaicin) must be lower than 250ppm in the EU.
Lycopene	Tomatoes	Orangy red	Oil soluble carotenoid pigment, has found little commercialisation as a colour owing to high cost, poor stability. Not listed in the USA as a colour additive.
Carminic acid	Cochineal insect (female)	Orange to red	Water dispersible pigment
Carmine	Cochineal insect (female)	Pink to red	The aluminium lake of carminic acid
Betanin	Red table beetroot	Pink to red	Water soluble pigments that are degraded by prolonged heating
Anthocyanin	Black grape skin, elderberries, black carrots, red cabbage	Pink/red to mauve/blue depending on pH	Natural pigment of many red fruits, flowers and vegetables.
Chlorophyll	Grass, Lucerne, spinach and nettle	Olive green	Oil dispersible
Copper chlorophyll	Grass, Lucerne, and nettle	Bluish green	Exchange of Mg^{2+}
Crocins	Saffron/Gardenia fruit	Yellow	Water soluble carotenoid pigment. No longer listed in EU. Saffron listed in USA
Titanium dioxide	Anatase (mineral)	White	Insoluble white colour derived from nature by various processes

Natural dyes were initially considered much less stable, more difficult to use and more expensive than the synthetic colours they aimed to replace. It was always thought the colour shades achieved would be less vibrant and appealing [3]. Indeed, this was one reason why synthetic dyes replaced natural dyes in the 19-20 centuries.

It is estimated that worldwide up to 70% of all plants have not been investigated fully and that only 0.5% have been exhaustively studied [4]. From this it could be concluded that we have only just begun our search for sources of natural food colour sources. Any totally new pigment source would require assessment, which would be costly and time consuming, prior to any Food and Drug Administration (FDA) petitioning and EU approval for use as a food colourant. The final drawback is that many 'undiscovered pigments' will be in unprospected land or the sea and commercialization could be an uneconomic prospect.

With these drawbacks in mind suppliers of natural colours have focused on the development currently permitted pigments in three main areas: i) formulation technology, ii) processing technology and iii) alternative sources of pigments. These approaches have proved very successful and have contributed to the increase in usage of natural colours throughout the food and drink industry. Food manufacturers are now confident that a colour supplier can produce most colour shades in a natural form giving the vibrancy, stability and usage characteristics they require [3].

6.2 USES OF NATURAL DYES

The dye molecules may function in the plant as colourants and/or in other roles, e.g., in photosynthesis [5]. Wissgott and Bortlik classified plant dyes according to five main functions [4].

i) Conversion of light energy during photosynthesis (chlorophylls, phycobilins and carotenoids)
ii) Communication between plants and animals (carotenoids and flavonoids)
iii) Detoxification of reactive oxygen species (carotenoids)
iv) Response to stress (flavonoids)
v) Unknown functions (flavonoids)

The following subsections details some areas in which natural dyes can be used as colouring material.

6.2.1 Food and Drink

The dyes that occur naturally in a food plant have, of course, been the source of the traditional colour of the prepared food, after the processing needed to produce the edible food. Such dyes could be viewed as accidental dyes in that they are present only because they or their precursors are present in the food source.

Deliberately introduced dyes have become much more important as the manufacture of processed foods has grown. The reasons for their use include the replacement of colour lost during processing, storage or cooking by the consumer intensification of pale natural colours; correction of seasonal variations of natural colour so that a consistent product is presented to the consumer [5].

6.2.2 Textiles

The use of dyes to colour textiles is generally considered to be about 2000 years old. The dyes used were derived from natural sources and some, such as Tyrian purple, were particularly prized and an important part of the local economy and world trade at the time. Dyes were obtained from flowering plants, fungi, lichens (eg, crottle), insects (eg, kermes, cochineal and lac), shellfish (eg, Tyrian purple) and earths (eg, ochre). The social history associated with dyes is extensive but not covered in this section (see chapter 5). Most plant species will produce a dye but relatively few produce strong, bright colours, especially in the primary colours. Those that did were highly prized [5] (see chapter 5 for examples).

6.2.3 Cosmetics

Many of dyes and pigments have been used for cosmetic for centuries. A common name of annatto (*Bixus orellana*) is the lipstick plant. Natural indigo from *Indigofera tinctoria* was used by the Romans and Greeks in a blue crayon for eye shadow while the powdered form had other cosmetic applications, such as body painting [5].

6.2.4 Hair Colouring

Rosemary, chamomile and henna [5, 7] are still used in hair colouring preparations and there has been a move towards the development of more natural hair colourants by some of the major cosmetic manufacturers. For example, Wella (a German-based company) has produced a series of natural herbal colour granules containing henna (*L. inermis*), chamomile (*Chamaemelum nobile*), cutch (*Acacia catechu*), sedre (*Phus latus rhamnaceae*), indigo (*Indigofera tinctoria*) and sage (*Salvia officinales*) in various proportions to achieve a wide range of hair colours [5]. Chamomile and sage grow widely in Europe, especially in the Mediterranean region. The other plants are not native to Europe and not generally cultivated in the UK. In Venice in the late 1500s, saffron was used as a hair dye and applied in a mixture with sulphur to hair pre-treated with dried caul, egg yolk and honey. The hair was gradually dyed yellow with the action of the sun. The Ladies' Dictionary of 1694 provided recipes for dyeing hair. Concoctions used in that period included a mixture of elderberries and wine for turning hair black, the use of radish extract to achieve an auburn shade, and a blend of ceruse (lead derivative), lime, and saffron or turmeric for those with blond ambitions [8].

Other miscellaneous uses includes fur dyeing, leather dyeing, colouring paper, shoe polish, plastics, paints and in toiletries and detergent preparations [5].

6.2.5 Functional Food Ingredients

There is growing evidence that many food components perform additional beneficial functions in the body [3]. Our instinctive preference for eating naturally coloured fruits and vegetables over pale coloured foods is thought to be natures' way of providing our diet with certain phytochemical compounds along with any micronutrients and vitamins naturally present. Natural antioxidants are now thought to possibly prevent the increasing incidence of many western diseases such as cancers and heart disease, thus these diseases have been linked to a lack of fruit and vegetables in the diet. Although most people know that they are recommended to eat 5 portions of fruit and vegetables every day, less than 10% of the population achieve this target.

Many natural dyes and pigments currently used primarily for colouring purposes are phytochemicals which have been linked to good health [3, 9] such as curcumin [10], anthocyanins [11], tea catechins [12], carotenoids (e.g. lycopene and lutein) [13] and chlorophylls [3].

6.3 NATURAL DYES

The main aim of work described in this chapter is to evaluate the effectiveness of anodic oxidation processes for the degradation of nine natural plant extracts (spinach, green tea, saffron, curcumin from turmeric, annatto, beetroot, sumac, roselle and henna), and one natural animal-derived colourant (cochineal).

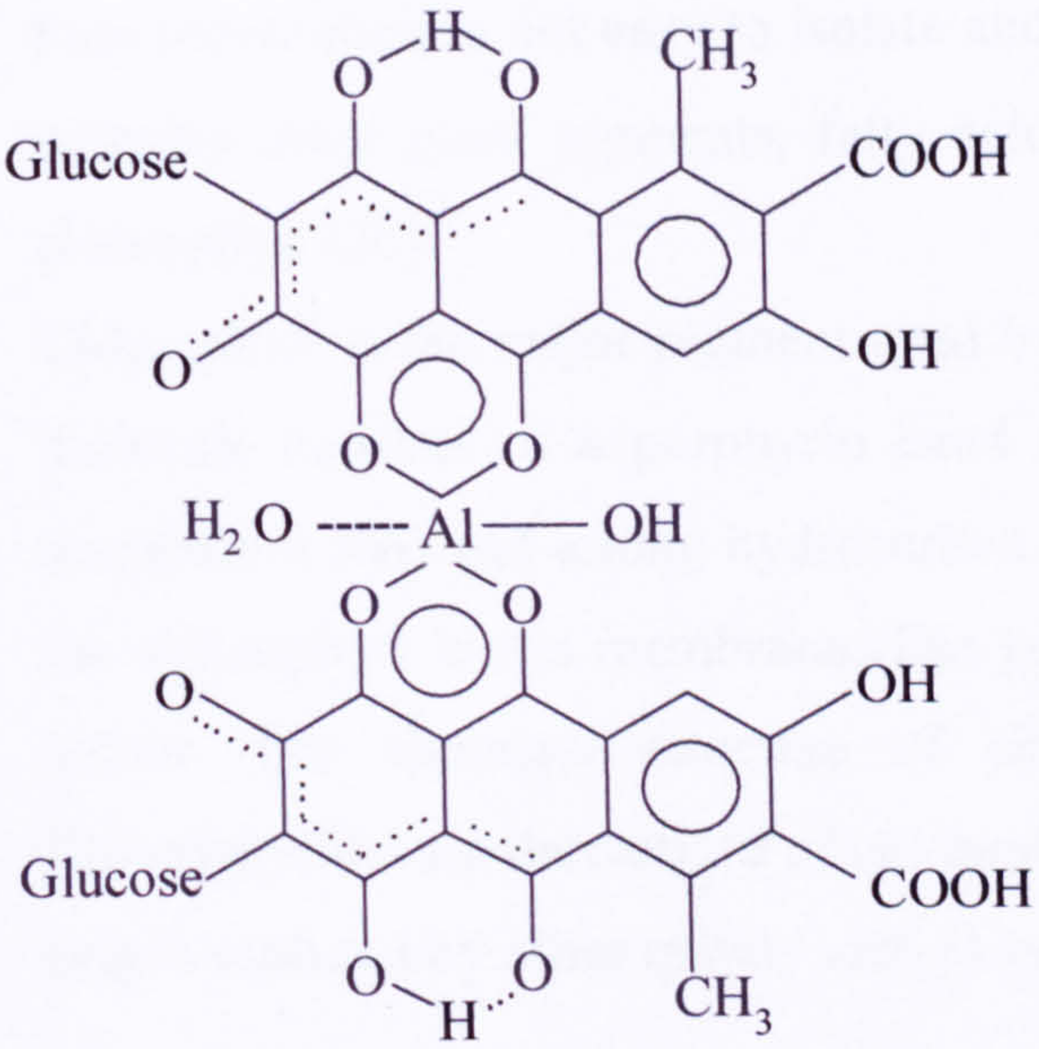
A brief account on each of these natural colourant extracts is presented in the following subsections. These include chemical structures of the main colouring components, pictures of the natural dyes where available are presented in plates.

Degradation products from some plant extracts are predicted and compared with the degradation products reported in the literature; and obtained during the degradation methods such as heat, acid, enzymatic or biological treatments discussed in section 6.6.

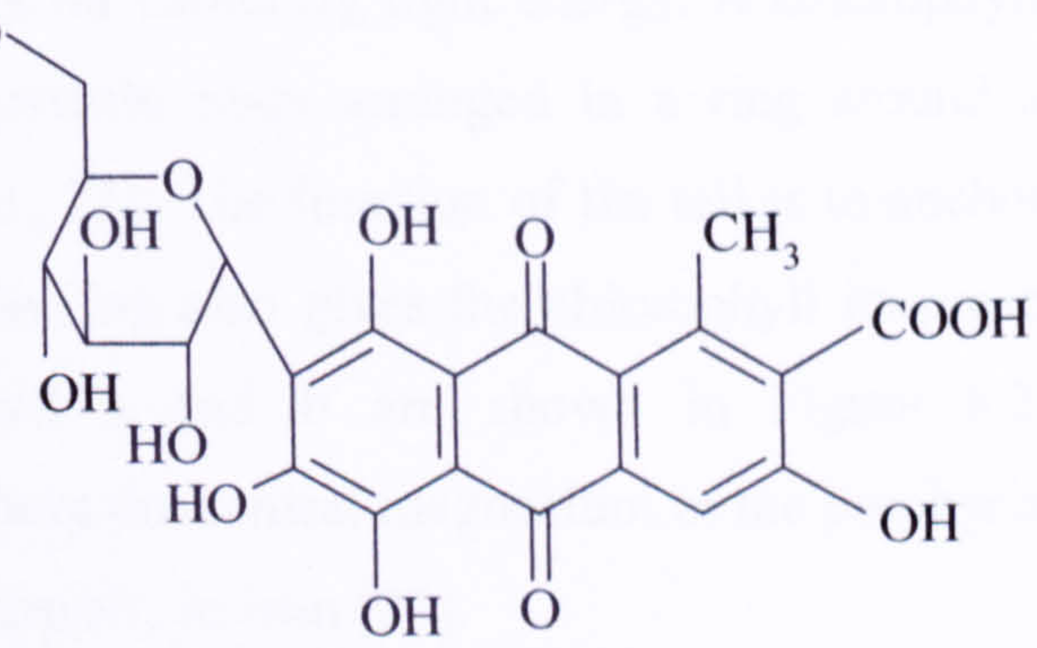
6.3.1 Carmine (Cochineal), *Coccus dactylopius*, *Coccus cacti.*

Cochineal is obtained from the bodies of the female insect *Coccus cacti*, living on a cactus which grows in Mexico [14]. Cochineal pigments extracted from the dried insects are dark red powders and carminic acid is the active colouring principle of both carmine and (the less pure) cochineal, as shown in Figure 6.1 [15].

It takes around 70,000 insects to make one pound of cochineal [16]. It is a permitted food additive, and has an E number 120. Plate 6.1 shows a plump female cochineal insect which has just given birth to several tiny nymphs. Her minute legs are concealed by a protective cottony mass, which she secrets around her body. The red body fluids are the source of cochineal dye [16].



Carmine



Carminic acid

Figure 6.1: Chemical structures of cochineal pigments carmine and carminic acid.

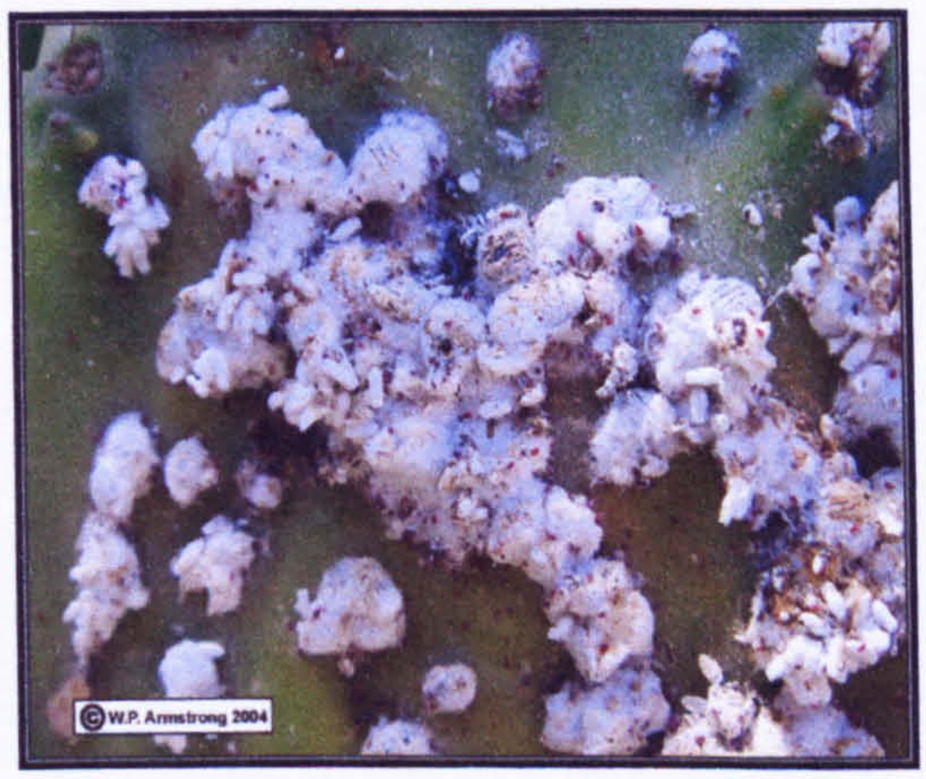


Plate 6.1: Cochineal insects on a prickly pear cactus stem (Lanzarote Island, Spain); details of clusters of cochineal beetles and cochineal insect *Coccus dactylopius* [16]

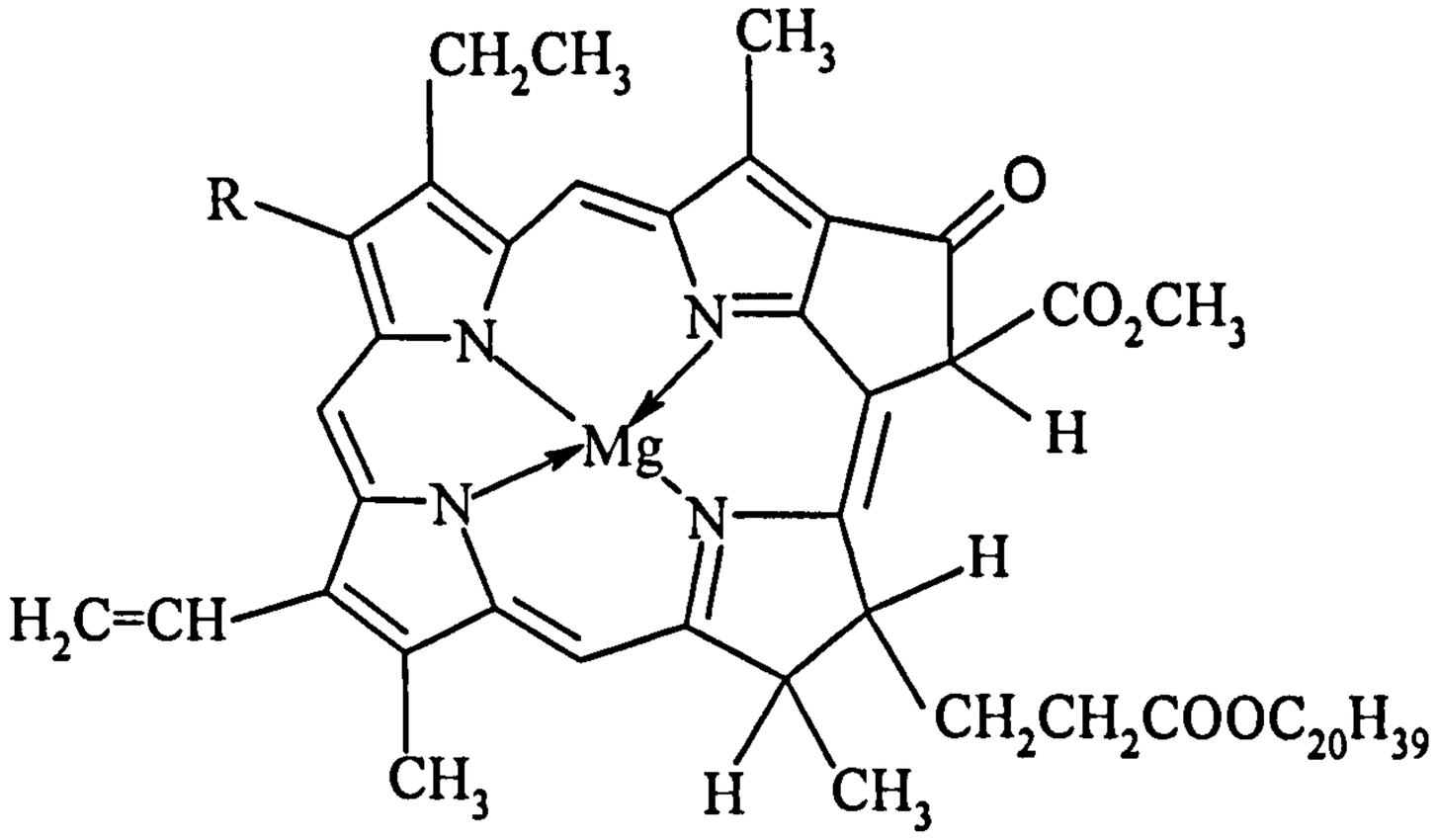
6.3.2 Spinach; *Spinacea oleracea* L., Chenopodiaceae, Chlorophylls

Spinach originated in Persia, spread through much of Asia, and from Spain to the rest of Europe [17]. Spinach is one of the important leafy vegetables consumed all over the world. It is consumed fresh, pureed or processed [18]. Chlorophyll contents as high as 1 mg/g can be found in spinach [19].

Pure chlorophyll is not easy to isolate and the chlorophyll which is commercially available contains other plant pigments, fatty acids and phosphatides, and is known as technical chlorophyll [20].

Chlorophyll is the major pigment used by plants for capturing light energy. A chlorophyll molecule consists of a porphyrin head (four pyrrole rings arranged in a ring around a magnesium ion) and a long hydrocarbon tail [21, 22]. The function of the tail is to anchor the chlorophyll in the membrane. The porphyrin ring also gives the chlorophyll its green colour. The chemical structure of chlorophyll a and b are shown in Figure 6.2. Chlorophyllins are derivatives of chlorophyll where the central magnesium in the porphyrin ring is replaced by other metals such as cobalt, copper, or iron [23].

There are four types of chlorophyll; chlorophyll a is found in all higher plants, algae and cyanobacteria, chlorophyll b in higher plants and green algae, chlorophyll c in diatoms, dinoflagellatea and brown algae, and chlorophyll d in red algae only [5, 21, 24].



Chlorophyll a R = CH_3
Chlorophyll b R = CHO

Figure 6.2: Chemical structures of chlorophylls from spinach

6.3.3 Green Tea, *Camellia sinensis*, *Thea sinensis*, Theaceae; Tea catechins; Polyphenols.

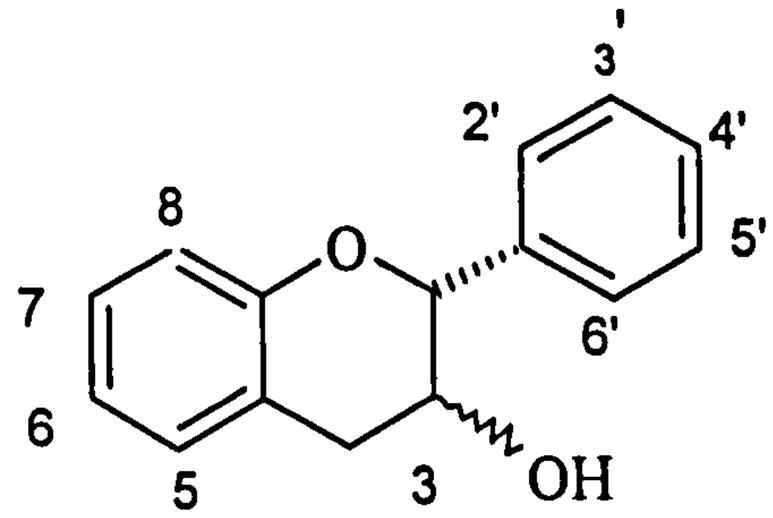
Ancient China was the birth-place of tea and the Chinese tell this story about it. Over 5000 years ago, they say, the Emperor Shen Nung was sitting beneath a tree enjoying a bowl of

hot water when a leaf from a wild tea plant fell into the bowl. He enjoyed the new infusion so much that began regularly using tea leaves with hot water to make a refreshing drink. The habit caught on, and soon tea gardens had spread throughout the Far East [25].

Europeans discovered tea in the 17th century- Samuel Pepys describes in his diary how the drink was enjoyed in smart circles in London, Amsterdam and Paris as long ago as1668 [26]. The Dutch East India Company began to import the leaves from China which as the world's only tea producer was unable to cope with the increased demand and sent poor quality leaves to Europe. During the 18th century, the British smuggled plants out of China to break the Chinese monopoly and planted tea in India, Ceylon and East Africa [27].

The procedure of tea fermentation substantially affects the tea composition and teas can be generally divided into three basic groups. Green tea (non-fermented) is derived directly from drying and steaming of fresh tea leaves; oolong tea is prepared when fresh tea leaves are subjected to partial fermentation before drying; and black tea undergoes full fermentation before drying and steaming. The fermentation is an oxidative process, in which catechins, major polyphenolic components of green tea leaves, are oxidized or condensed to larger polyphenolic molecules such as theaflavins and thearubigins [28].

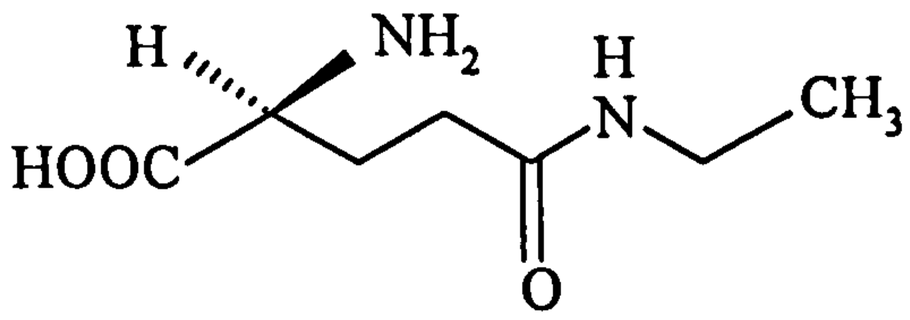
Green tea catechins are, structurally, primarily flavanols. The main catechins in green tea are (-)-epigallocatechin gallate ((-)-EGCG), (-)-epigallocatechin (-)-EGC), (-)-epicatechin gallate ((-)-ECG) and (-)-epicatechin (-)-EC) [29, 30]. The chemical structures of the catechins and their epimers are illustrated in Figure 6.3



Catechin (2R, 3S) 5=7= 3'= 4'= OH
Epigallocatechin (2R, 3R) 5=7= 3'= 4'= OH
Epicatechin gallate (2R, 3S) 5=7= 3'= 4'= OH
Epigallocatechin gallate (2R, 3R) 5=7=3'=4'=5'= OH

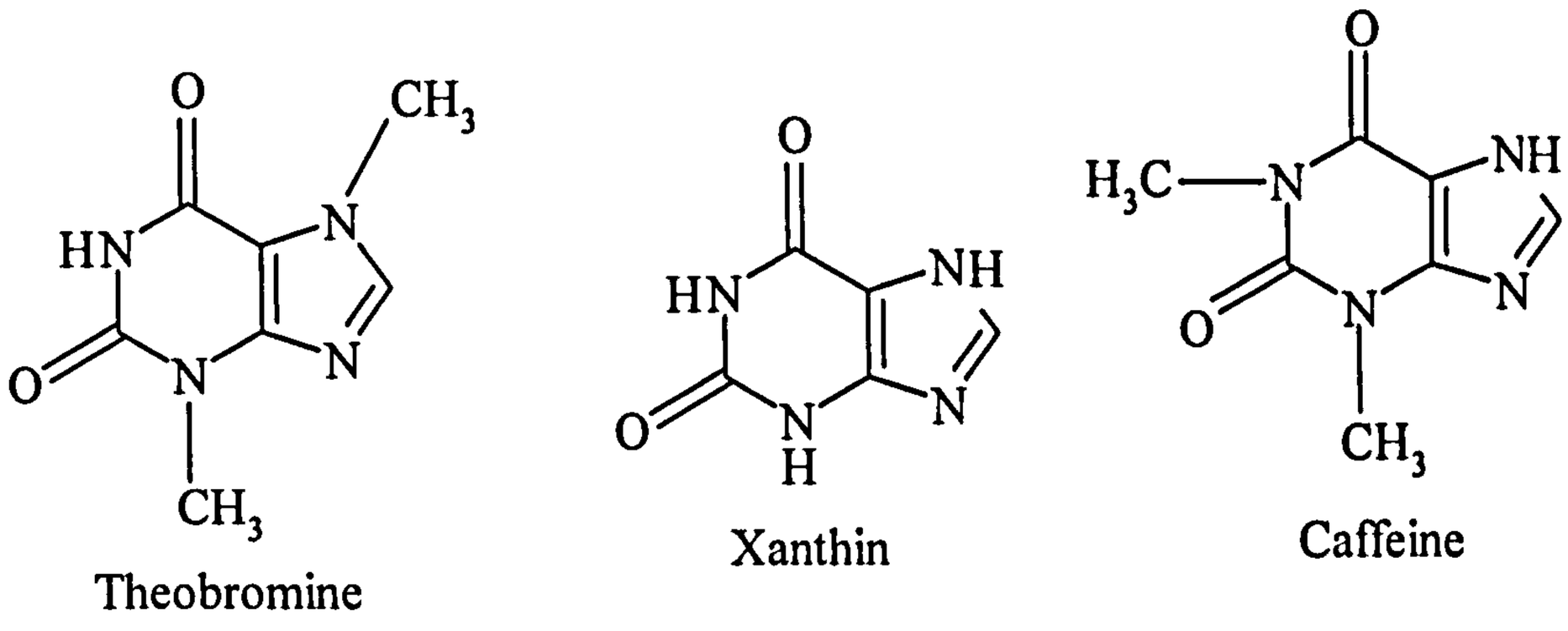
Figure 6.3: Chemical structures of tea catechins and their epimers

The main tea phenolic acid is gallic acids. Teas also contain certain amount of caffeine, a plant alkaloid occurring also in some other popular beverages such as coffee. Caffeine also has attracted much scientific and public attention during the past years due to its stimulatory effects [31, 32]. Theanine is a unique amino acid found almost solely in tea plants and is the main component responsible for the exotic taste of green tea. Figures 6.4 and 6.5 show the chemical structures of theanine [33] and the alkaloids caffeine, xanthin and theobromine respectively.



Theanine

Figure 6.4: Chemical structure of theanine



Theobromine Xanthin Caffeine

Figure 6.5: Chemical structures of alkaloid moieties of tea leaves

In the past decade, considerable attention has been focused on the improvement of human health by consumption of functional food [12] and tea, originally prepared from the leaves of *Camellia sinensis*, has been re-investigated in many studies for its excellent pharmaceutical properties [28]. Polyphenols, especially catechins and phenolic acids, have been considered the main players in these beneficial effects on the human health [12].

6.3.4 Saffron; *Crocus sativus*; *Iridaceae*

Saffron is the dried stigmas of *Crocus sativus* and the most expensive spice used in industry [34], with many different uses as drug [35], textile dye [36], perfume [37] and culinary

adjunct [38]. It is mainly valued as a food additive for tasting, flavouring and colouring [39], as well as for its therapeutic properties as antidepressant [40], anticonvulsant [41], antitumoral [37, 42], and antioxidant [13].

The name Saffron comes from Arabic za'faran, which mean yellow [37]. Each flower has three stigmas and is harvested by hand. The stigma are separated, sorted and dried. One dried stigma weighs about 2 mg and 150–200 stigmas are required to obtain 1 g of spice. Consequently, the operation is highly labour intensive leading to high costs [43].

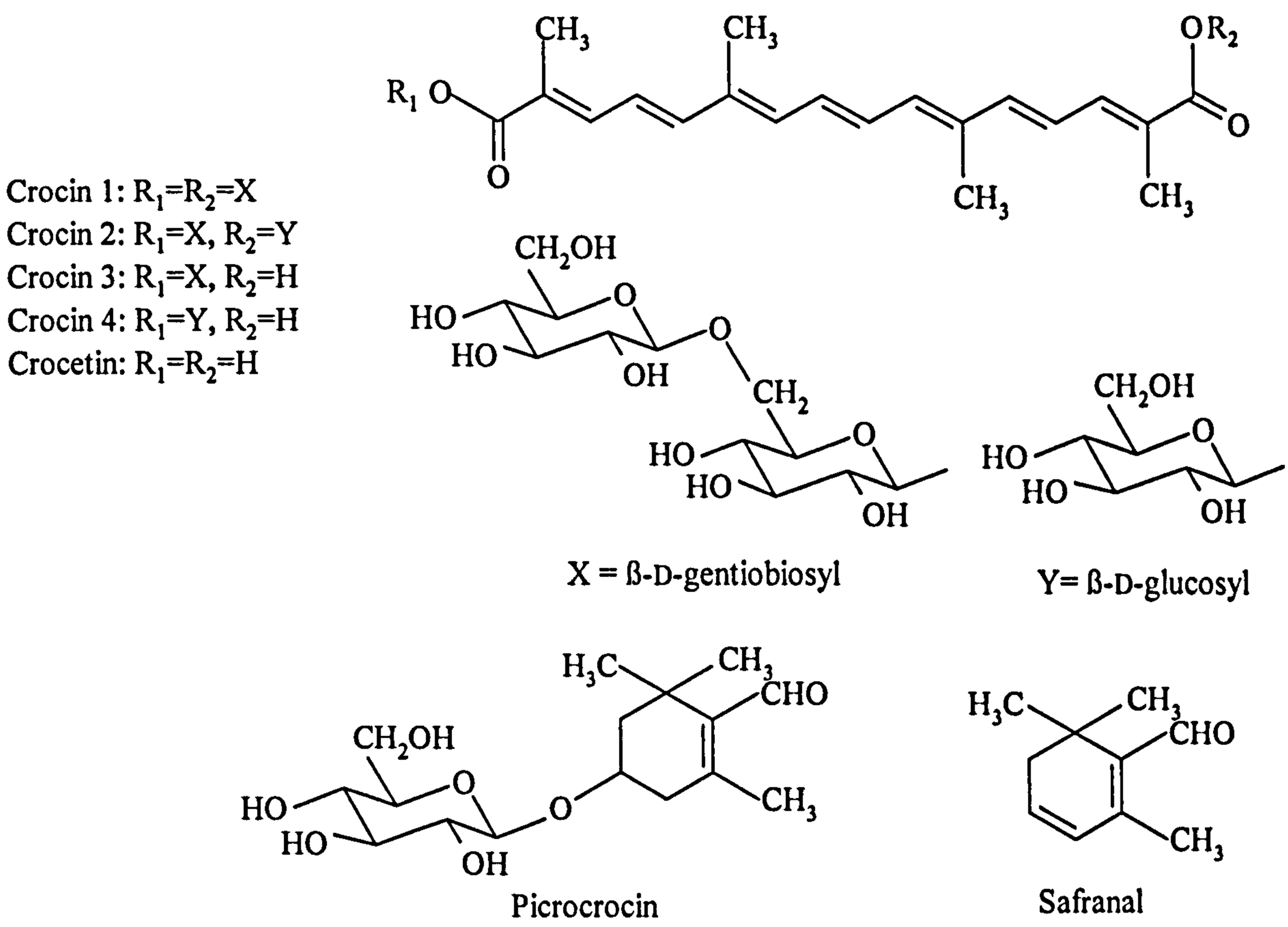


Figure 6.6: Chemical structures of saffron components

Saffron originally grew in India, Iran, Spain, Greece and other countries, and has been successfully cultivated in various places in China [44]. In mediaeval times the cultivation of saffron was widespread throughout the whole Mediterranean region and central Europe, where it was used as a dye. In England it used to be cultivated at Saffron Walden and even now can be found growing wild in that area [45]. While the world's total annual saffron production is estimated to be 190 tons, Iran produces about 90% of the total [46]. Chemical

structures of the main saffron components are shown in Figure 6.6 and Plate 6.2 shows saffron stigmas and the plant (*Crocus sativus*).

Plate 6.2: Saffron stigmas strands and saffron plant (*Crocus sativus*)

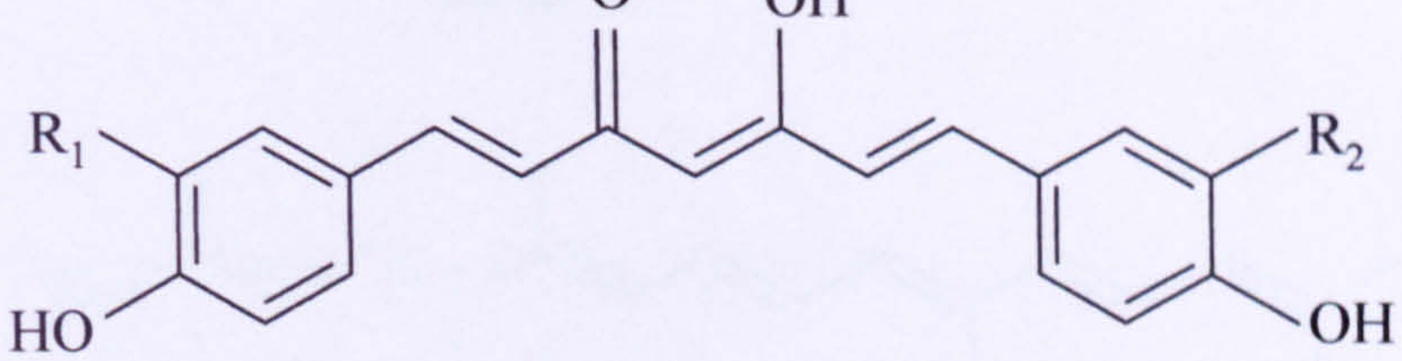
6.3.5 Turmeric, *Curcuma longa*, Curcumin, Diferuloylmethane, Zingiberaceae

The major yellow ingredient of the powdered rhizome of *Curcuma longa* L. (turmeric), (Plate 6.3) is a polyphenol molecule called curcumin (diferuloylmethane) [10]. The pigment contains other curcuminoids, mono-demethoxycurcumin and bis-demethoxycurcumin (Figure 6.7) which have one or both methoxy groups missing from the aromatic rings [47, 48]. It is a fat soluble pigment but is insoluble in aqueous medium [2]. It can be made soluble in water by the use of diluents like propylene glycol and tween. Curcumin is sensitive to light but is moderately stable to heat [2].

Curcumin can exist in at least two tautomeric forms keto and enol [49, 50]. The keto form is preferred in solid phase and the enol form in solution.

The most outstanding use of turmeric is as an important component of curries, to which it not only imparts a vivid yellow colour but also adds a distinctive pungent flavour [48]. As a food additive, its E number is E100 [20]. Curcumin is used as a dye for silk, wool, cotton, paper and wood in India and China [51].

Curcumin has also been traditionally used for centuries to treat many inflammatory disorders and for wound healing for centuries [47, 52]. Besides its extensive usage in herbal medicine, it receives growing attention in modern pharmacology [53] due to its beneficial effects including strong antioxidant and anti-inflammatory activity, and chemopreventive properties against various human malignancies [50, 54, 55].



Curcumin	$R_1 = OCH_3$	$R_2 = OCH_3$
mono-desmethoxycurcumin	$R_1 = OCH_3$	$R_2 = H$
bis-desmethoxycurcumin	$R_1 = H$	$R_2 = H$

Figure 6.7: Chemical structures of turmeric components (*Curcuma longa*)

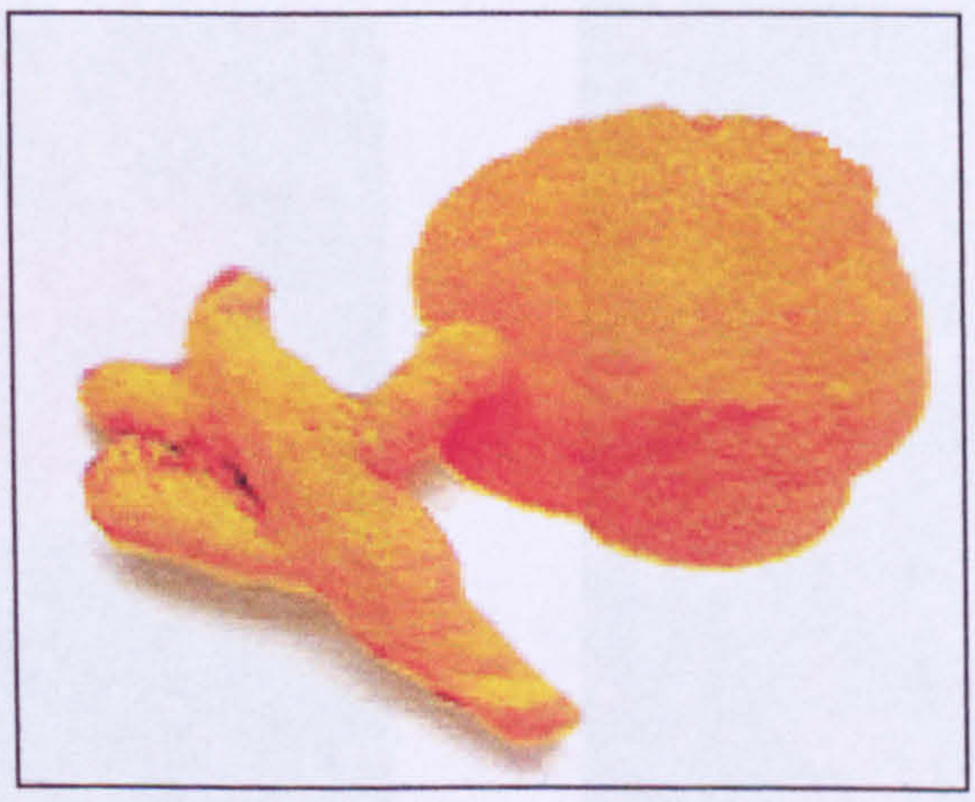


Plate 6.3: Turmeric root, and ground turmeric (*Curcuma longa*)

6.3.6 Annatto, *Bixa orellana L.*; Bixaceae

Annatto is a natural colouring material, extracted from the pericap of the seeds of *Bixa orellana* L. Plant (Plate 6.4). It is orange yellow in colour and oil soluble. The major colouring component is the di-apo carotenoid, bixin [56]. Bixin is the liposoluble 9′-*cis*-bixin, which is the monomethyl ester of the water-soluble 9′-*cis*-norbixin. In addition to bixin and norbixin, numerous other pigments have been characterised from annatto extracts.

Figure 6.8 shows the chemical structure of bixin and norbixin. Norbixin is obtained by alkaline hydrolysis of bixin to give a water soluble di-carboxylic acid [48].

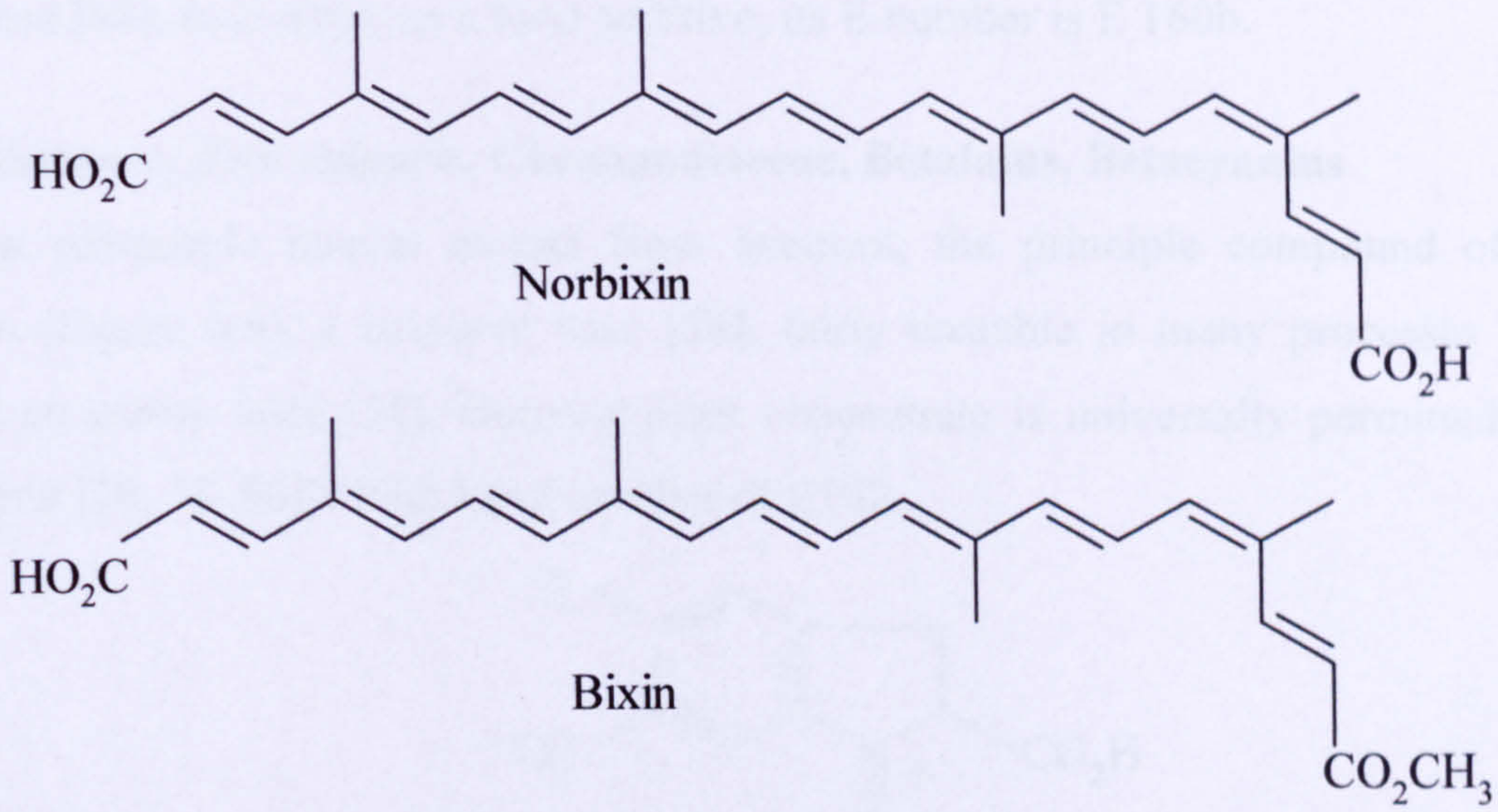


Figure 6.8: Chemical structures of bixin and norbixin in annatto (*Bixa orellana*)

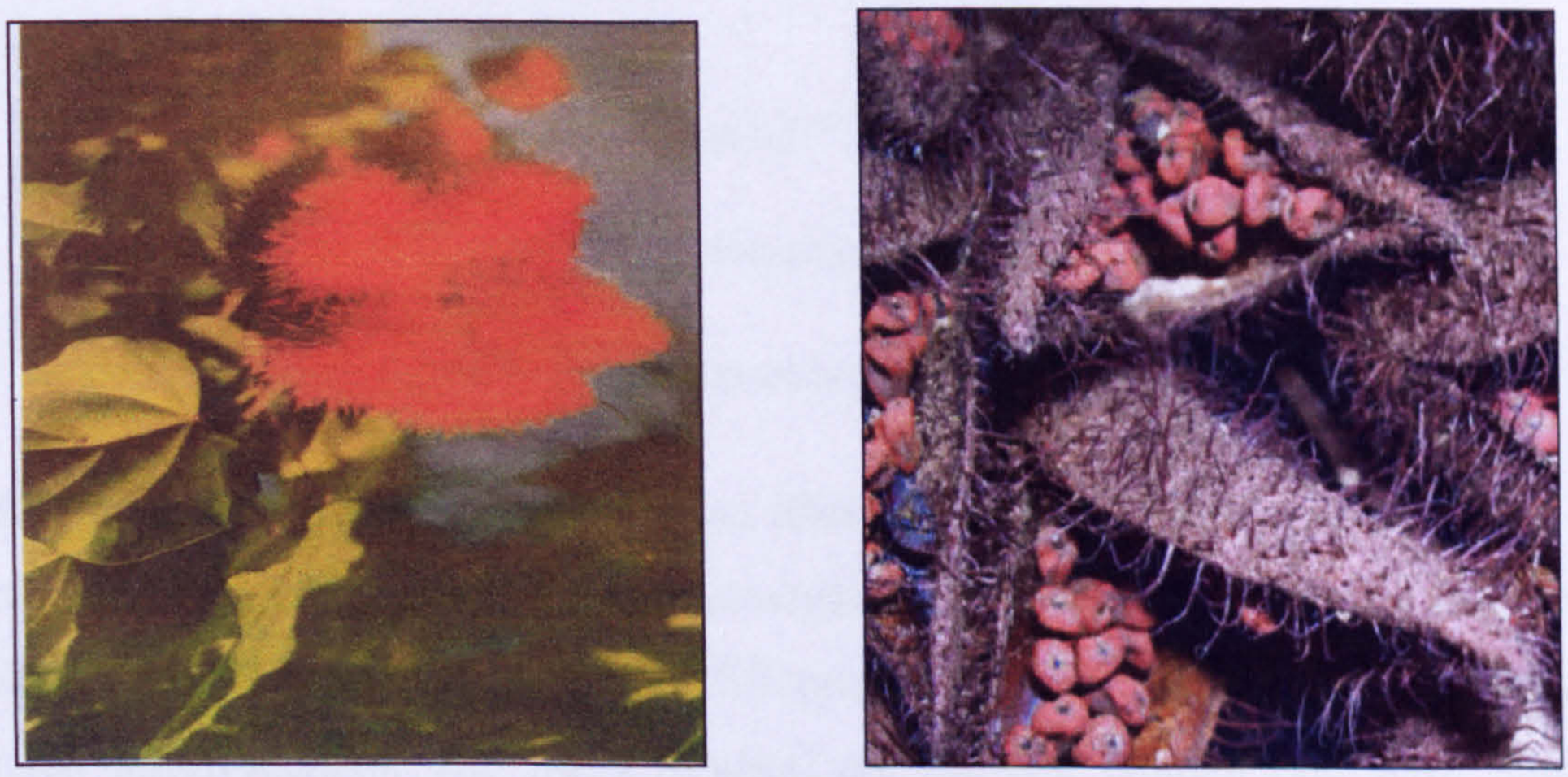


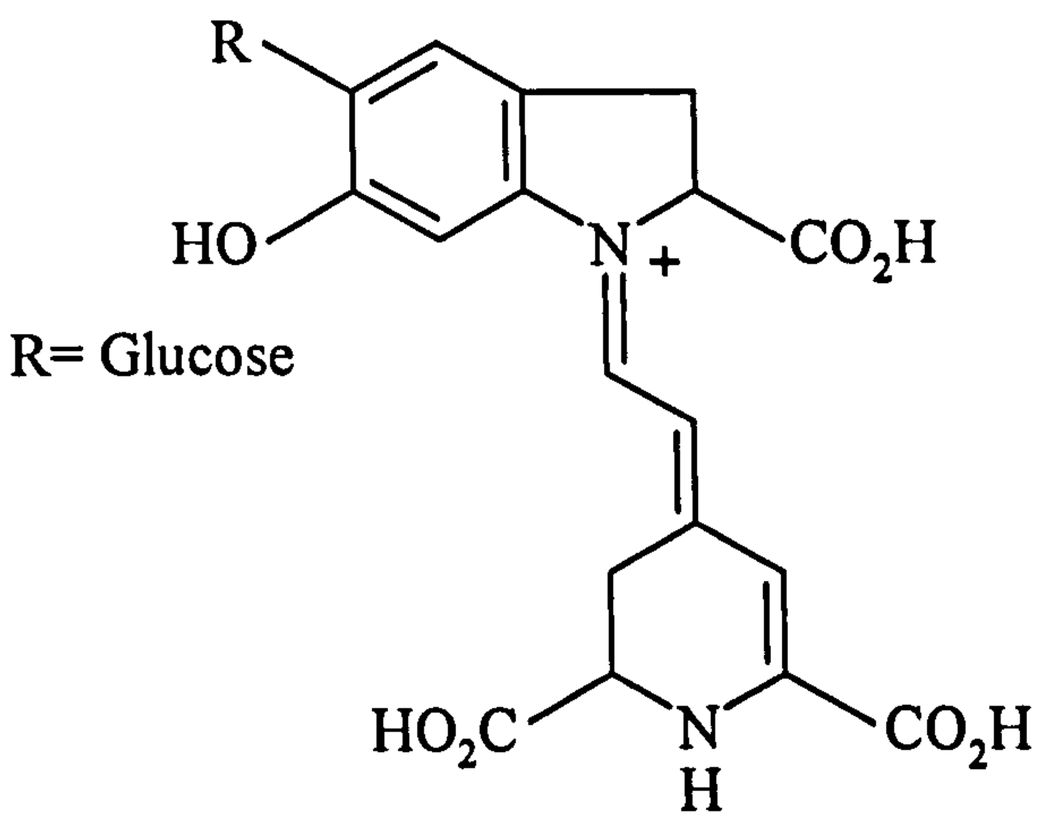
Plate 6.4: Annatto plant (*bixa orellana*) and a stem from an annatto tree and red seeds in a dried capsules Source: [48]

Annatto extracts are generally formulated to impart colour shades in the range red-orange-yellow in different foods [57]. The major uses of oil-soluble annatto colour are in dairy and fat-based products and snack foods [20, 58, 59].

It has been suggested that over 2000 seeds have to be harvested to get just one gram of bixin and to produce one gallon of cheese colour, 240,000 seeds would have to be harvested [48]. In Europe, as a food additive, its E number is E 160b.

6.3.7 Beetroot, *Beta vulgaris*, Chenopodiaceae, Betalains, Betacyanins

A deep red-purple natural extract from beetroot, the principle compound of which is betanin (Figure 6.9), a coloured base [58], fairly unstable in many processes which can impart an earthy taste [58]. Beetroot-juice concentrate is universally permitted as a food colourant [20, 58, 60] which has a number of E162.



Betanin

Figure 6.9: Chemical structures of betanin (beetroot red)

6.3.8 Sumac, *Rhus glapra*; *Rhus cotinus*; *Rhus typhina*, Ancardiaceae

Sumac is a shrub which reaches 3-4 m in height in the wild. It bears pinnate leaves with six to eight pairs of small oval leaflets of different size [Plate 6.5], and has white flowers in terminal inflorescences. The fruits (drupes) are red and contain one seed. Sumac was cultivated until 1970s in Spain, Italy, Turkey, Iran and some Mediterranean Arabian countries. Its powdered leaves were using as a tanning agent because of its high tannin content [61]. There are over 250 species of sumac, some varieties of which are poisonous [62].

Sumac is a tart, red-purple spice, and is obtained by grinding the berries of the Middle Eastern sumac shrub. Sumac is a souring agent in Middle Eastern cookery, used in place of

vinegar or lemon juice [62], where it is sprinkled liberally over rice, kebabs, fish and salads. It is often mixed with freshly cut onions and eaten as an appetizer [62].

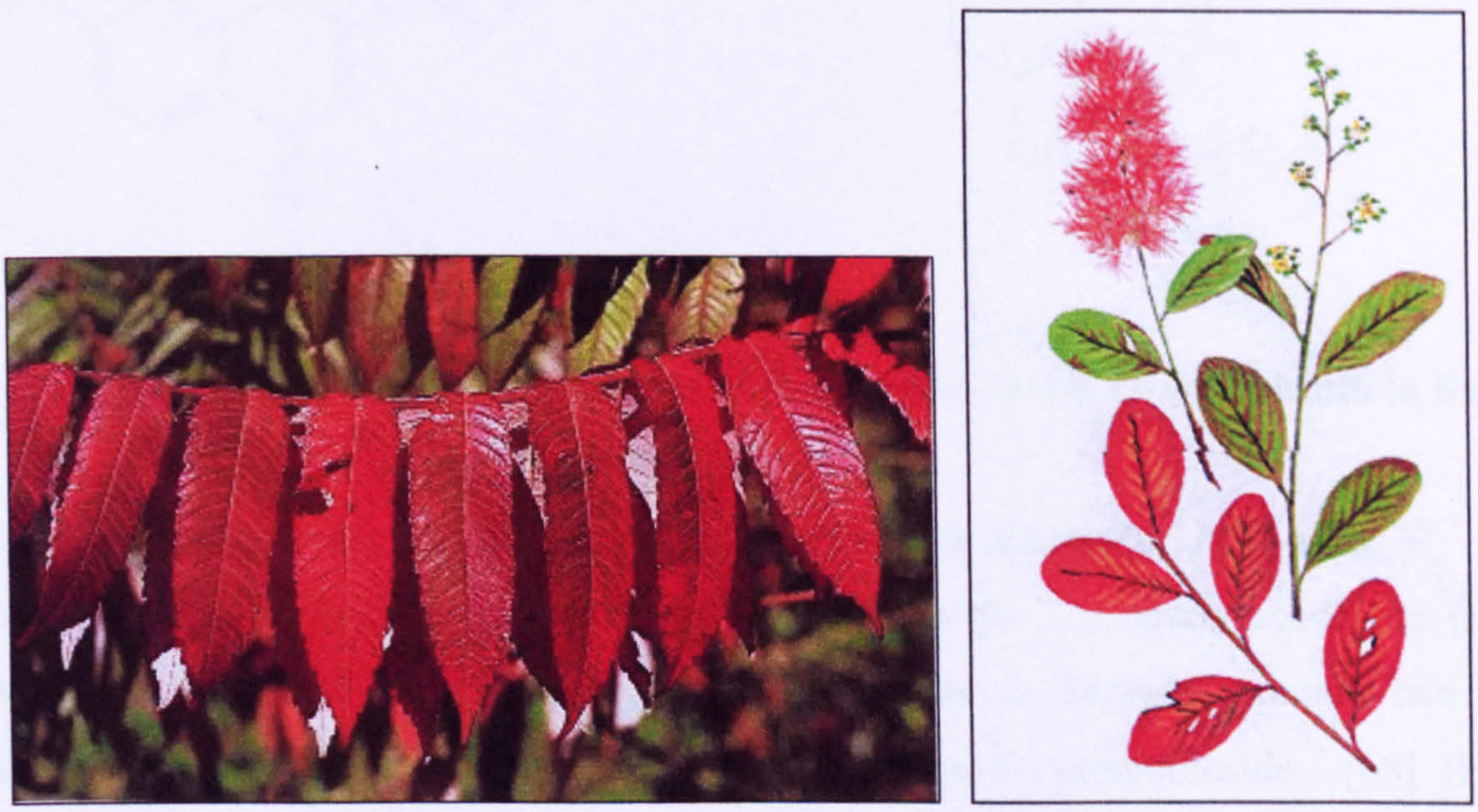
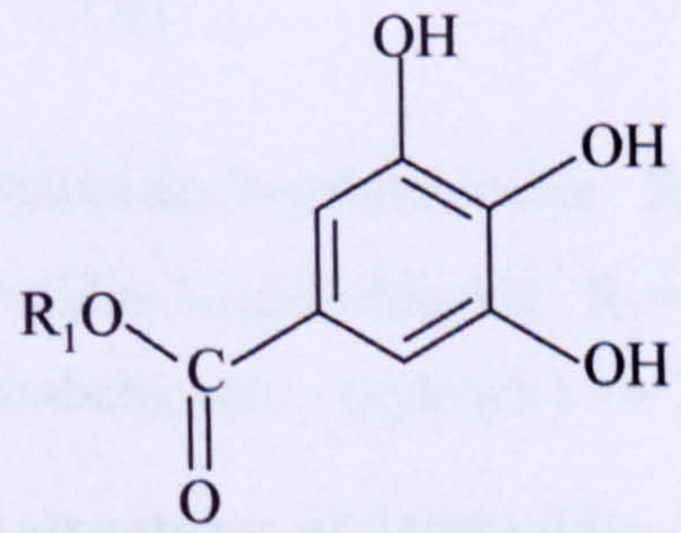


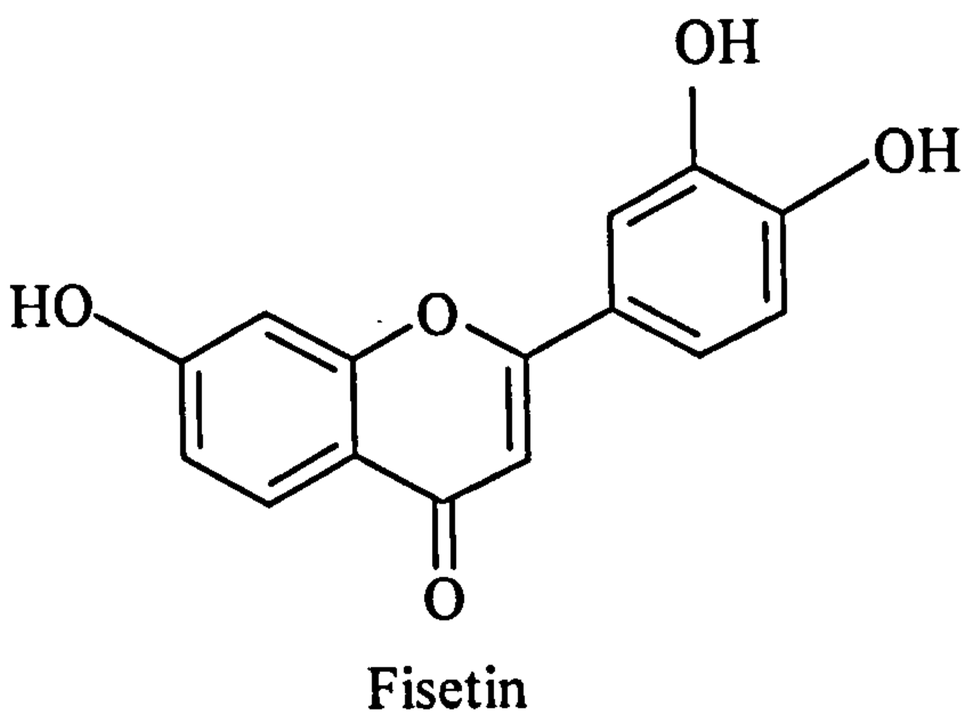
Plate 6.5: Sumac leaves and sumac plant (*Rhus typhina*) [63]

The main compounds present in *Rhus* family are hydrolysable gallotannins [61, 64]. Its basic structural unit is the polyol D-glucose, esterified by gallic acid at its hydroxyl groups (Figure 6.10). In addition to gallotannins [65], *Rhus* leaves contain substantial amounts of flavonoids, fisetin, myricetin [66] (Figure 6.11) and quercetin [67].

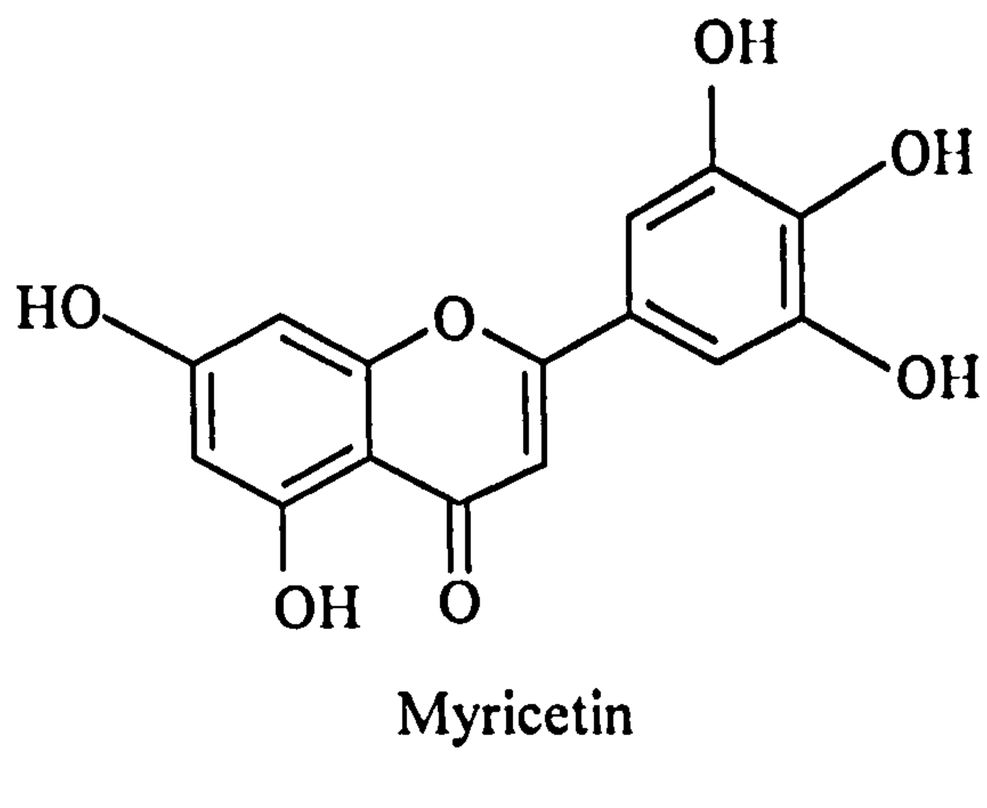


Hydrolysable tannins (e.g. gallic acid derivatives)
R_1=glucose:monogalloyl-glucose

Figure 6.10: Chemical Structures of gallotannins from sumac



Fisetin

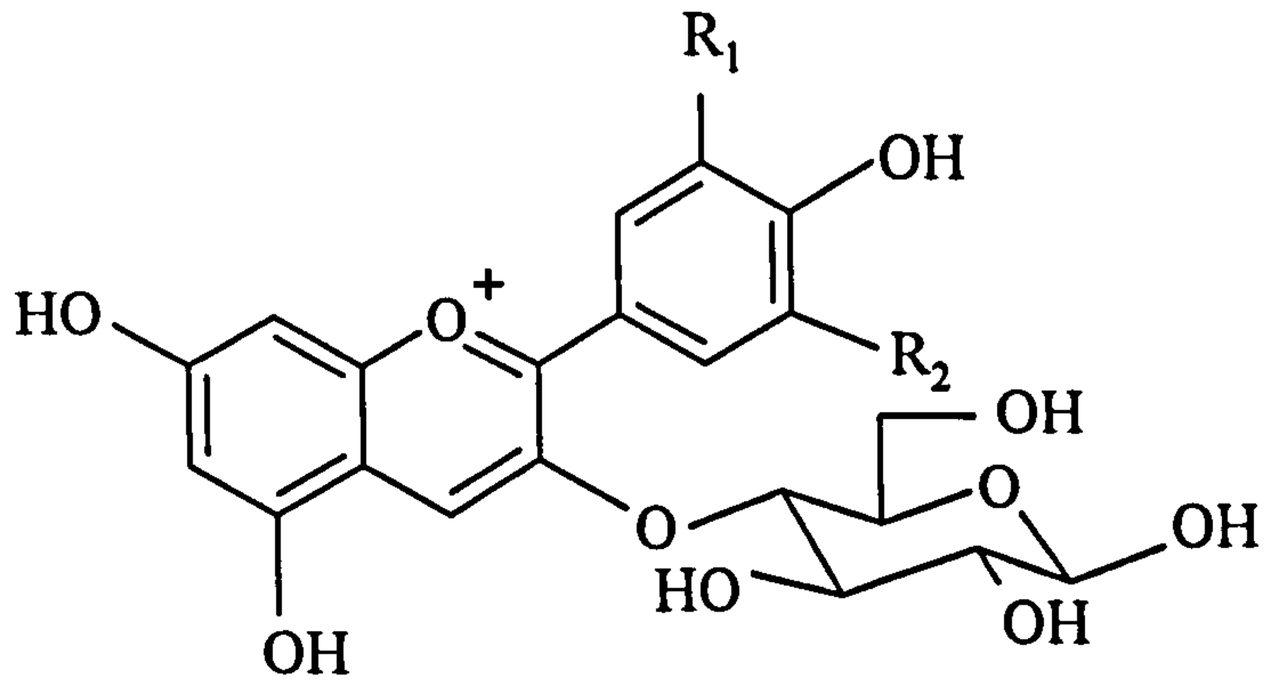


Myricetin

Figure 6.11: Chemical structures of flavonoids; fisetin and myricetin in Sumac

6.3.9 Roselle; Karkadé; Sorrel; Sudanese tea; *Hibiscus sabdariffa*; Malvacea

Aqueous extracts from dry calyces of *Hibiscus sabdariffa* L., variety sabdariffa (ruber) (Plate 6.6), a tropical annual shrub known as roselle or karkade, contain two main anthocyanins: delphinidin-3-sambubioside and cyanidin-3- sambubioside [68] (Figure 6.12).



Delphinidin-3-sambubioside $R_1 = R_2 = OH$

Cyanidin-3-sambubioside $R_1 = OH$; $R_2 = H$

Sambubioside - (xylosyl-1 → 2-glucode)

Figure 6.12: Chemical structures of delphinidin-3-sambubioside and cyanidin-3-sambubioside

The dry calyces of *H. sabdariffa* yield as much as 1.5% (w/w) pigment that has transmission spectral features very similar to those of Red No.2 (amaranth) [68]. It was introduced to the West Indies in the 18th century it was cultivated mainly as an ornamental

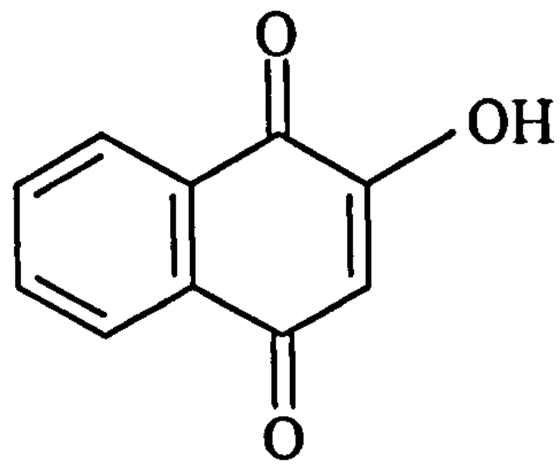
plant and partly for fibre. The crop is cultivated extensively at present in India, Thailand, Senegal and Egypt for its pleasant red coloured calyxes which are used for making jam and bottled drinks [69].

Plate 6.6: Roselle (*Hibiscus sabdariffa*) plant

Being high in anthocyanin [68] roselle petal is both a good colourant and potentially a good source of antioxidants [11, 70].

6.3.10 Henna, (*Lawsonia inermis* L.); Lythraceae

Henna, a natural product obtained from the crushed leaves of *Lawsonia inermis*, has for centuries been used, as a cosmetic agent to dye the skin, hair, and nails of people in many Middle Eastern countries and Muslim world [7, 71, 72]. It is native to and grows wild throughout the Middle East, North Africa and the Indian sub-continent. Henna is planted today primarily as an ornamental hedge, but is probably best known for the dried, ground leaves. Traditionally used to produce the colourfast red-orange pigment, lawsone [Figure 6.13] [72, 73]. It contains many healing substances like tannin and other glue-like substances [74].



Lawsone

Figure 6.13: Chemical structure of Lawsone (Henna)

6.4 ANALYSIS OF NATURAL FOOD PIGMENTS

Several methods have been developed to analyze the components of natural food dyes including colorimetric measurement [39], UV-Vis [21, 24, 36, 38, 57, 67], UV-Visible-MS [75, 76], thin-layer chromatography (TLC) [21, 77- 79], gas chromatography (GC) [56, 75, 79], high-performance liquid chromatography (HPLC) with a UV-visible light absorbance detector [21, 15, 22, 24, 47, 53, 55, 77, 80, 81] or a photodiode array detector (PDA) [44, 46, 56, 57, 61, 68, 76, 82] and LC [83, 84], MS [57, 75, 84-86], GC-MS [57] are the most powerful analytical separation methods.

Other methods of analysis such as IR [75], FT-IR-Raman [43], NMR [57, 75, 84], XRD [87], Gel Filtration [64], Phase conjugation [88], Florescence spectrometry [89], Laser excited molecular fluorescence [90], Electron Paramagnetic Resonance (EPR) spectroscopy [28], Multiresponse Modeling [91] and Flow rate properties using concentric cylinders rotational viscometer [92], have been generally used for separation and qualitative analysis studies.

The achievements in the use of chromatographic and electrophoretic techniques including thin-layer chromatography, high-performance liquid chromatography and capillary electrophoresis for the separation and quantitative determination of pharmacologically interesting plant pigments in various sample matrices for use in medicine, foods and food products are surveyed and critically evaluated by Sun et al. [93].

Cyclic voltammetry (CV), an analytical method based on redox processes were previously developed for monitoring the composition of tea samples [31, 94-96] and to investigate the behaviour of tea components under various experimental conditions [30, 97, 98].

The electrochemical properties of some hydroxyl-1, 4-naphthoquinones of plant origin, namely juglon and lawsone, have been investigated using thin layer voltammetry on pyrolytic graphite electrodes [99]. In recent years, capillary electrophoresis (CE) has been applied to the analysis of various food ingredients [14, 34].

Literature reports of studies on electrochemical colour removal and degradation of natural dye extracts is apparently scarce. Such studies, however, help in understanding of electrochemical behaviour of natural dyes. Also limited information is available concerning the application of natural dyes in foods, and there exists a need to investigate the use of such natural dyes in a variety of foods, particularly their stability during storage. The results will be useful in the application of natural dyes in a number of foods instead of the permitted synthetic colours.

6.5 EXPERIMENTAL

6.5.1 Electrolysis Set-up

Electrochemical degradation experiments were conducted in a bench-top undivided electrolytic Pyrex glass cell, with a working sample volume of 2 litres (Plate 6.7). The internal dimension of the cell was 14 cm × 19 cm × 14.3 cm (width × length × depth). The two anodes and one cathode were positioned vertically and parallel to each other with an inter electrode gap of 1 cm. The size of stainless steel plate cathode was 0.15 cm × 10.8 cm × 14.7 cm (thickness × width × length). The anode used in the study was a commercially available titanium mesh coated with Platinum. The size of each mesh anode was 6.5 cm × 11.5 cm (width × length). All experiments were conducted at ambient temperature. DC power supply (Thurlby model PL154, RS Components, Ltd., England), having an input of 230 V and variable output of 0-15 V with maximum current of 4 A was used as a direct current source. Magnetic stirring (KIKA RO8 model, Germany) was used in order to keep the solutions in the compartment well mixed during electrochemical oxidation.

The pH of the sample was measured using Mettler Toledo pH meter (model Delta 320, UK). A Perkin-Elmer Lambda 9 UV-visible Spectrophotometer was used in this work for the

determination of dye concentrations at the maximum absorbance in the range of 200-700 nm. Total organic carbon (TOC) was determined by using a model 700 (O.I. Corporation, Texas) TOC analyzer. The instrument was operated at room temperature and 5 ml samples were injected. All solutions for TOC were prepared in deionised water.

Two litres of solutions of each dye were prepared by dissolving the required amount of the natural dye extract in deionised water to make up 50 ppm of dye concentration. At the beginning of each experiment the electrolytic cell was filled with 2 litres of dye solution and the required amount of the electrolyte was added to the solution. During the experiments, the pH of the solution was monitored constantly. Each experiment was run for 480 minutes or otherwise specified time depending on the nature of the experiment, and the solution was kept agitated constantly by a magnetic stirrer. About 20 ml of the solution was sampled at intervals from the middle of the electrolytic cell by a glass pipette. Experiments were performed in duplicate and found to be reproducible.

To evaluate colour removal by the electrochemical method, the disappearance of the absorbance peak in the visible range of the solutions of the investigated dyes was monitored.

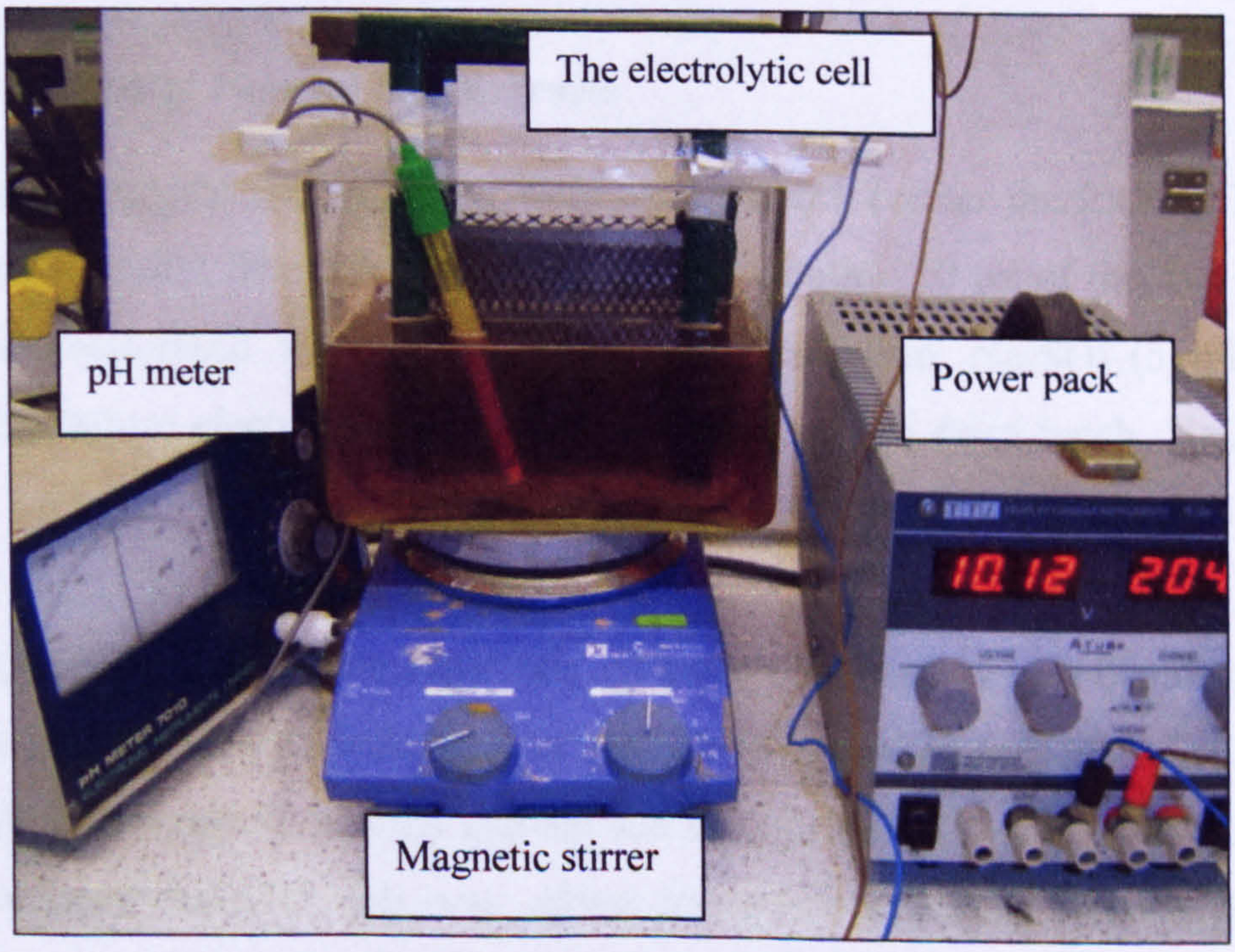


Plate 6.7: Experimental set-up for electrolytic oxidation of natural food dyes

6.5.2 Materials and Natural Dyes

Experiments were carried out to study the electrolytic oxidation of the following natural dyes:

Natural Food Colours: carmine in propandiol (Langdale red), binary mixture of curcumin and annatto in propandiol (Langdale yellow) were purchased from Tesco, Uxbridge.

Dry Leaves: green tea, roselle (karkade), henna were purchased from local shops in Tripoli, Libya.

Dry Stigmas Strands: saffron (Abushiba; Iranian origin) was a gift from Dr Amani Alshirawi from Bahrain.

Dry Powders: turmeric was obtained from local herbal shop in Tripoli; sumac was purchased from local shop in Southall, London.

Fresh Vegetables: beetroot and spinach leaves were purchased from Tesco in Uxbridge.

Three sets of experiments were conducted for carmine, saffron, green tea, spinach and Langdale yellow. These experiments were run separately in aqueous solution, aqueous NaCl and aqueous Na_2SO_4 as electrolytes. While only one experiment using aqueous NaCl was run for turmeric, sumac, beetroot, roselle and henna.

6.5.3 Preparation of Natural Dye Extracts

Carmine and Langdale yellow colour were used without further processing. Three batches of stock solution of 2 litres each were prepared by diluting 10 ml of the dye solution. One batch was electrolysed without addition of an electrolyte, Na_2SO_4 (5 g/l) was added immediately before electrolysis of the second batch, to the third batch, NaCl (5 g/l) was added.

The beetroot and spinach were separately chopped and crushed in a blender; and, in each case, a weighed amount of material was mechanically shaken in boiled distilled water for 30 minutes. The chopped material drained and the filtrate was made up to 2 L solution. In case of beetroot NaCl (5 g/l) was added immediately before electrolysis. The same procedure was used three times in the case of spinach extracts but with the addition of

Na_2SO_4 (5 g/l) and NaCl (5 g/l) to two batches separately before running the electrolysis. The third batch was subjected to electrolysis without using any electrolyte. Three other stock solutions of raw fresh spinach extracts were prepared (without boiling). To one stock NaCl (5 g/l) was added before running the electrolysis. The second stock solution was boiled for 60 minutes and samples were taken in 15 minutes intervals and followed with the UV-visible analysis. The third stock solution was used to take samples for analysis on UV-visible spectrometer.

Saffron stigmas strands were soaked in 200 ml of water for 10 minute, followed by boiling with distilled water at 95°C for 30 minutes. The strands were removed by filtration and the filtrate was made up to 2 L with distilled water and this solution was then subjected to electrolysis. The same procedure was repeated twice but with the addition of Na_2SO_4 (5 g/l) and NaCl (5 g/l) separately to the working solutions before running the electrolysis.

The dry leaves of green tea, the calyces of karkade (roselle) and henna leaves were separately boiled in distilled water at 95°C for 30 minutes. The leaves were removed by filtration and the filtrate in each case was diluted to 2 L with distilled water and (NaCl 5 g/l) was added to each solution immediately before the solutions of the extracts subjected to electrolyses. The same procedure was followed in preparing two other batches of green tea extracts. One batch was electrolysed without adding electrolyte, to the second batch Na_2SO_4 (5 g/l) was added immediately before electrolyses.

Turmeric powder and sumac dry crush were separately boiled in distilled water at 95°C for 30 minutes. The residues were removed by filtration and the filtrate in each case was diluted to 2 L with distilled water and (NaCl 5 g/l) was added to each solution immediately before the solutions of the extracts subjected to electrolyses.

6.6 RESULTS AND DISCUSSION

Temporal changes in the concentration of the studied natural dyes were monitored by examining the variations in maximum absorptions in the visible spectra. Electrolysis

experiments were carried out at the natural pH and a range of constant current (0.011-3.997 A). The experimental processes and the results are presented in each section individually.

6.6.1 Degradation of Carmine (Cochineal) by Electrolytic Process

The UV/visible spectrum of carmine in (a) aqueous solution, (b) aqueous Na_2SO_4 and (c) aqueous NaCl are shown in Figure 6.14 and the percentage degradation / removal data are shown in (Tables 6.3-6.5).

The UV/visible spectrum of carmine exhibited a sharp maximal absorbance at 292 nm and a less intense band at 344 nm in UV region and a broad band with two absorbance peaks at 526 and 563 nm in visible region.

In aqueous solution of carmine, the peaks at 526 and 563 nm shifted to longer wavelength (bathochromic effect) and decreased slightly. Only 27% colour removal is achieved during the 360 minutes of electrolysis with little fading of the pink red colour to light purple and a change of pH from 6.3 to 4.5 was observed during the course of electrolysis (Table 6.3).

In aqueous Na_2SO_4 solution of carmine, the peaks at 526 and 563 nm shifted to the blue region (hypsochromic effect) and decreased continuously with 69% colour removal is achieved during the 15 minutes of electrolysis. The pink red colour of the carmine discharged after 120 minutes electrolysis, and after 360 minutes 92% colour removal is attained (Table 6.4).

In the case of aqueous NaCl solution the pink red colour of the carmine discharged completely after 2 minutes electrolysis, and with a rapid decrease of the absorbance (hypochromic effect) at pH, which varied between 6.2-4.3, and 97% colour removal achieved during the course of 240 minutes (Table 6.5). However, after 30 minutes electrolysis the absorbance peak at 292 nm increased and shifted to longer wavelength (bathochromic effect). The results from the UV spectra and TOC data (31%) indicate the formation of intermediate products which are persistent and remained in solution even after 240 minutes of the electrolysis (Table 6.6).

Table 6.3: Electrochemical decolourisation of carmine in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.3	15.48	Pink-red	0
15	5.6	15.46	Light purple	15
30	5.0	15.45	Light purple	17
60	5.6	15.26	Light purple	21
120	6.2	15.26	Light purple	21
240	5.8	15.28	Light purple	23
360	4.5	15.30	Light purple	27

Conditions: current, 0.011 A; temperature, ambient; concentration (carmine 5 ml/L)

Table 6.4: Electrochemical decolourisation of carmine in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.6	15.33	Pink-red	0
15	11.9	14.42	Pale pink	69
30	11.5	14.21	Baby pink	70
60	11.6	13.70	Baby pink	74
120	4.8	14.62	Colourless	81
240	4.6	14.83	Colourless	87
360	4.6	15.52	Colourless	92

Conditions: current, 2.0 A; temperature, ambient; concentration (carmine 5 ml/L; Na_2SO_4, 5 g/L)

Table 6.5: Electrochemical decolourisation of carmine in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.2	7.12	Pink-red	0
2	4.0	7.14	Colourless	89
15	3.9	6.95	Colourless	94
30	3.9	6.11	Colourless	95
60	4.0	6.79	Colourless	95
120	4.4	6.79	Colourless	96
180	4.2	6.80	Colourless	96
240	4.3	6.80	Colourless	97

Conditions: current, 2.0 A; temperature, ambient; concentration (carmine 5 ml/l; NaCl, 5 g/l)

Table 6.6: TOC data during the electrolysis of carmine extract in aqueous sodium chloride

Time (min)	TOC (ppm)	TOC % Degradation
0	154	0
30	150	03
60	149	04
120	139	10
180	130	16
240	106	31

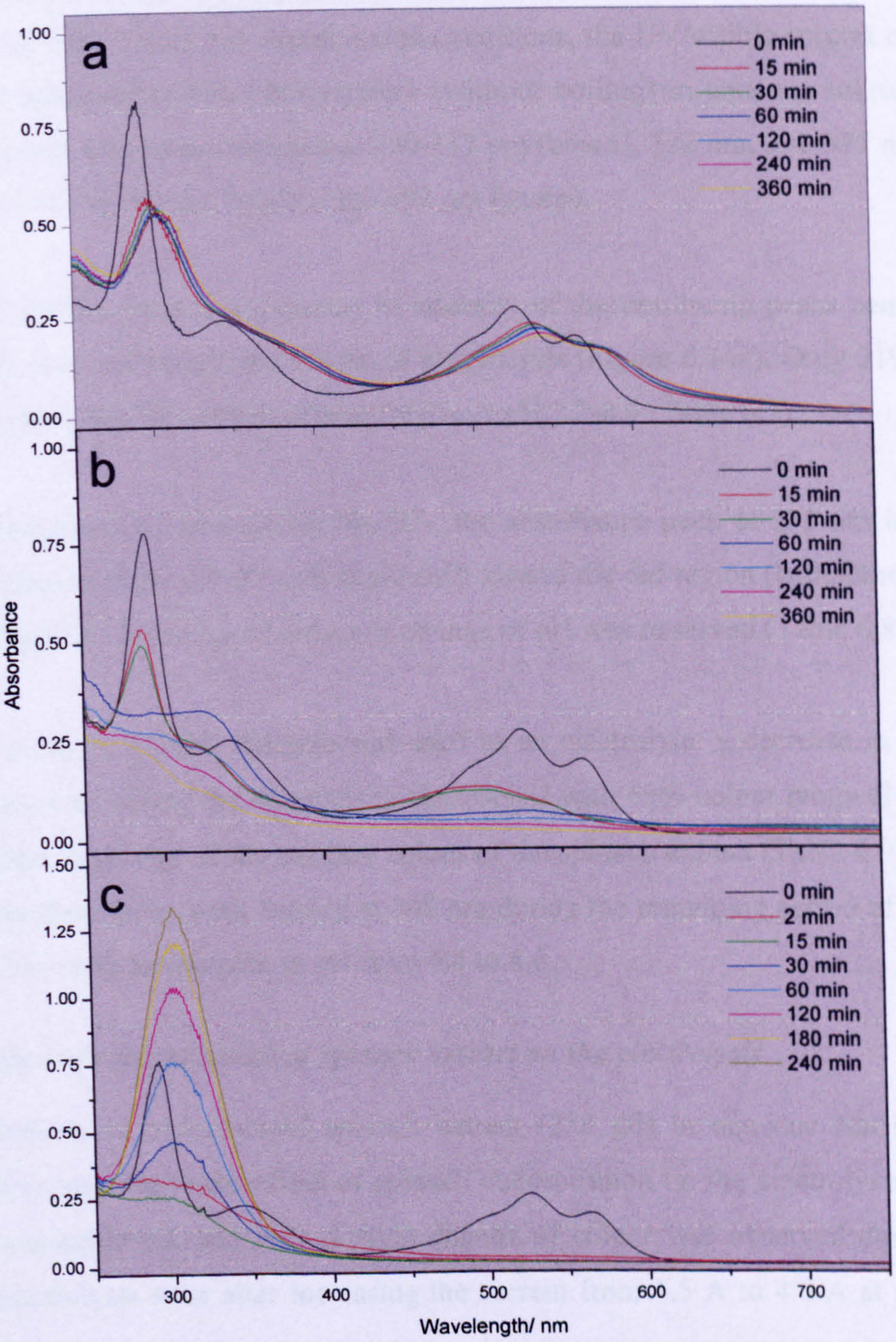


Figure 6.14: UV-Visible spectra showing the electrolytic destruction of carmine (cochineal extract) in (a) aqueous solution, (b) aqueous Na_2SO_4 and (c) aqueous NaCl

6.6.2 Degradation of Spinach Extract by Electrolytic Process

Generally, spinach solutions display characteristic maximum absorbance at 430-450 nm and at 685 nm [90]. Under our experimental conditions, the UV/visible spectra of the fresh raw spinach extracted at room temperature (without boiling) in aqueous solution (Figure 6.17a) displayed absorbance maxima at 250-317 nm (broad), 372 nm, 331-377 nm (centred at 356 nm), 454 and 492 nm (sharp), and 692 nm (sharp).

In aqueous spinach extract, a decrease in intensity of the two hump peaks centred at 269 and 352 nm occurred during the course of electrolysis (Figure 6.16a). Only 21% colour is removed during the 480 minutes of electrolysis at pH 7.2-8.0 (Table 6.7).

For the spinach extract in aqueous Na_2SO_4, the absorbance peak at 235 nm increased in intensity (hyperchromic effect) with slight shift toward the red region (bathochromic effect) (Figure 6.16b). No discharge of colour or change of pH was observed (Table 6.8).

When the aqueous sodium chloride was used as an electrolyte, a decrease in absorbance intensity occurred during the 60 minutes electrolysis with 69% colour removal is achieved with complete discharge of the original colour of the spinach extract (Table 6.9). However, a new sharp absorbance peak formed at 305 nm during the remaining period of electrolysis (Figure 6.16c) with an increase in pH from 6.4 to 8.6.

6.6.2.1 Effect of concentration of spinach extract on the electrolysis

The electrolysis of concentrated spinach extract (250 g/l) in aqueous NaCl (5g/l) was conducted to investigate the effect of spinach concentration on the electrolysis. No colour removal was achieved, and only a slight change of colour was observed during the 180 minutes electrolysis even after increasing the current from 1.5 A to 4.0 A at pH (4.6-6.0) (Table 6.10).

6.6.2.2 Effect of Heating on the Stability of Spinach Extract

An experiment was conducted to investigate the thermal stability of the chlorophylls and other components of spinach extract during boiling in aqueous solution (Table 6.11). The

UV/visible spectrum of the boiled spinach extract (Figure 6.17b) showed an increase in intensity (hyperchromic effect) of the absorbance peaks at 250-317 nm and 345 nm after 5 minute electrolysis, and a shift toward longer wavelength observed during the remaining time of electrolysis period. After 30 minutes of electrolysis, a shoulder developed at 385 nm. An increase in pH from 6.7 to 9.5 was observed during the course of electrolysis and the olive green colour turned to dull yellow.

It was reported by Nisha et al. [100] that chlorophyll is degraded by the replacement of magnesium by hydrogen and acid produced during heating. Discolouration in leaves due to loss of chlorophyll is accompanied by browning. The authors have also reported that during thermal processing, the colour changes from bright green to olive green due to the conversion of chlorophyll to pheophytin and pyropheophytin (Figure 6.15). Our results are in accordance with the results reported in the literature [100].

6.6.2.3 Electrolysis of fresh raw spinach extracted at room temperature in aqueous NaCl

The UV/visible spectrum of the spinach extracted at room temperature (without boiling) in aqueous NaCl solution (Figure 6.17c) shows a continuous decrease in the intensity (hypochromic effect) of the absorbance maxima at 454 and 492 nm (sharp), and 692 nm (sharp) during the course of electrolysis. Although 95% of colour removal was achieved in 60 minutes with only slight change of pH (6.7-5.9) and colour was discharged after 30 minutes (Table 6.12). However, the UV region of the spectrum shows organic materials remains in the solution.

Table 6.7: Electrochemical decolourisation of spinach in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	7.2	15.05	Light olive	0
15	6.8	15.16	Light olive	07
30	8.0	15.18	Light olive	14
60	6.8	14.90	Light olive	15
120	7.8	15.58	Light olive	18
240	7.2	13.98	Light olive	21
360	6.9	14.55	Light olive	14
480	8.0	14.62	Light olive	21

Conditions: current, 0.246 A; temperature, ambient; concentration (spinach 15 g/l)

Table 6.8: Electrochemical decolourisation of spinach in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.7	11.40	Light olive	0
15	6.4	12.84	Pale yellow	0
30	6.3	13.09	Pale yellow	0
60	6.4	12.19	Pale yellow	0
120	6.4	11.40	Pale yellow	0
240	6.7	11.04	Pale yellow	0
360	6.6	11.06	Pale yellow	0
480	6.6	11.31	Pale yellow	0

Conditions: current, 2.0 A; temperature, ambient; concentration (spinach 15 g/l; Na_2SO_4, 5 g/l)

Table 6.9: Electrochemical decolourisation of spinach in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.4	6.78	Light olive	0
15	5.6	6.94	Pale olive	04
30	5.3	7.07	Pale yellow	30
60	6.3	6.59	Colourless	69
120	7.5	6.59	Colourless	69
240	8.2	6.72	Colourless	69
360	8.4	6.73	Colourless	69
480	8.6	6.85	Colourless	69

Conditions: current, 2.0 A; temperature, ambient; concentration (spinach 15 g/l; NaCl, 5 g/l)

Table 6.10: Electrochemical decolourisation of concentrated spinach in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.6	4.01	Olive green	0
5	4.6	4.07	Yellow	0
15	4.6	4.15	Olive green	0
30	5.9	4.21	Olive green	0
60	5.8	4.40	Dark yellow	0
150	5.9	4.19	Dark yellow	0
180	6.0	5.98	Dark yellow	0

Conditions: current, 1.5 A; 0-150 min; 3.997 A at 180 min,; temperature, ambient; concentration (spinach 250 g/l; NaCl, 5 g/l).

Table 6.11: Thermal colour decolourisation of raw fresh spinach in aqueous solution

Time (min)	pH	Colour	% Removal
0	6.7	Bright green	0
5	10.3	Olive green	0
10	10.2	Dull yellow brown	0
20	9.0	Dull yellow brown	0
30	9.5	Dull yellow brown	0

Conditions: temperature, 100°C; concentration (spinach 15 g/l)

Table 6.12: Electrochemical decolourisation of raw fresh spinach extracted at room temperature (without processing) in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.7	6.09	Bright green	0
5	6.2	6.54	Olive green	39
10	6.6	7.26	Olive green	81
20	6.2	8.00	Olive green	88
30	5.9	8.24	Colourless	92
40	6.0	8.22	Colourless	93
50	6.2	8.06	Colourless	97
60	5.9	7.93	Colourless	95

Conditions: current, 2.0 A; temperature, ambient; concentration (spinach 50 g/l; NaCl, 5 g/l)

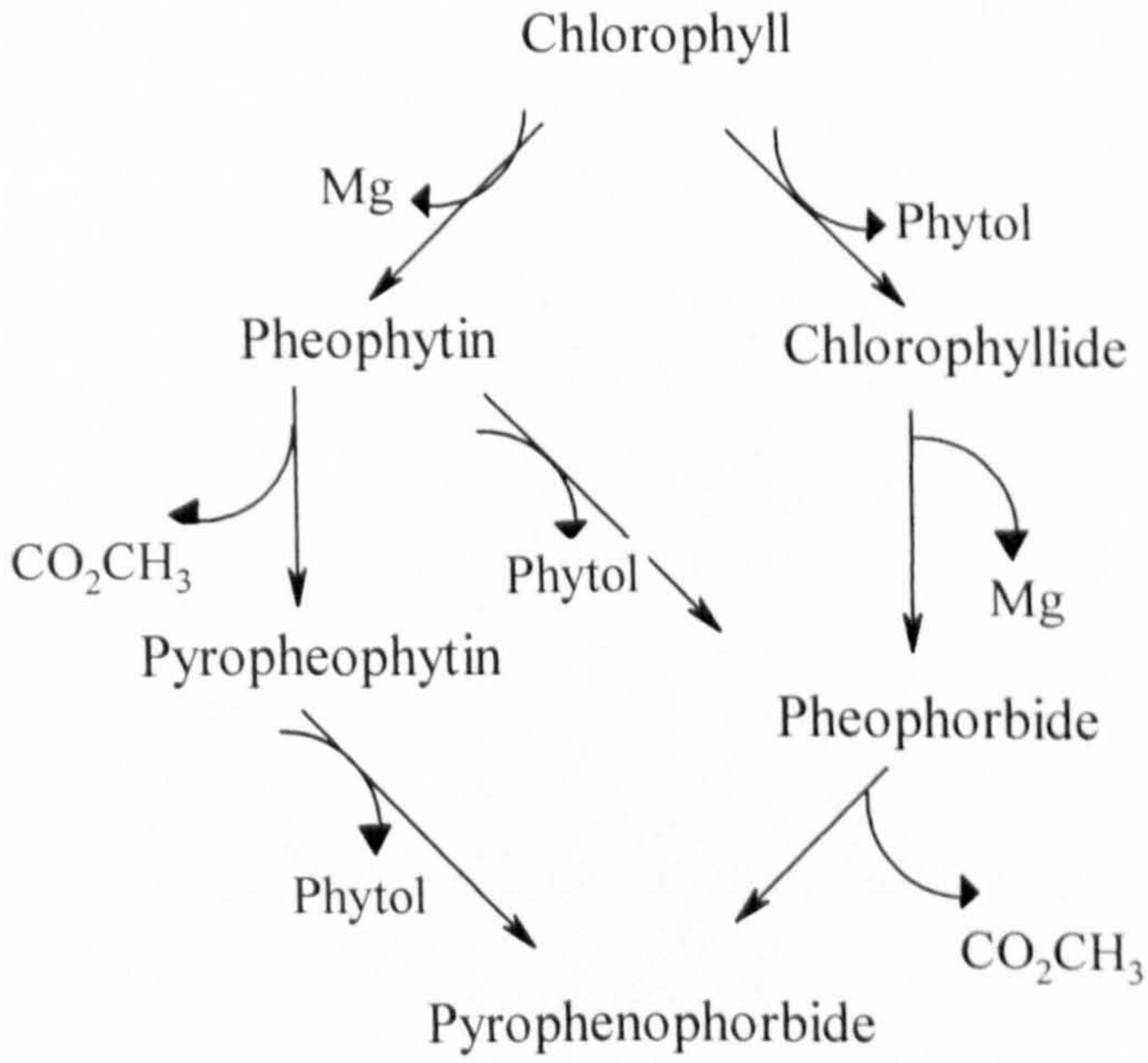


Figure 6.15: Schematic representation of chlorophyll degradation [91]

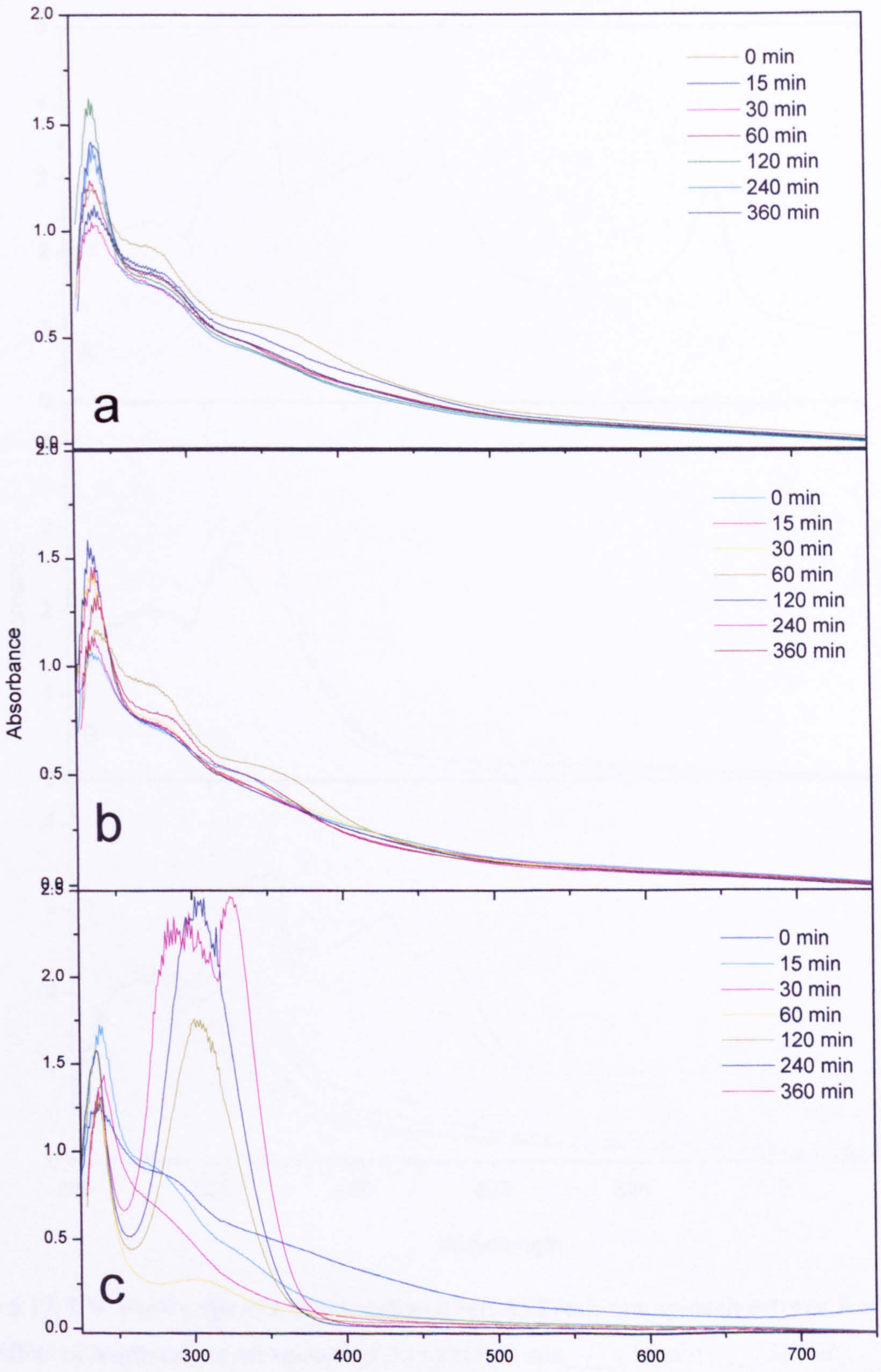


Figure 6.16: UV-Visible spectra showing the electrolytic destruction of spinach extract in (a) aqueous solution, (b) aqueous Na_2SO_4 and (c) aqueous NaCl

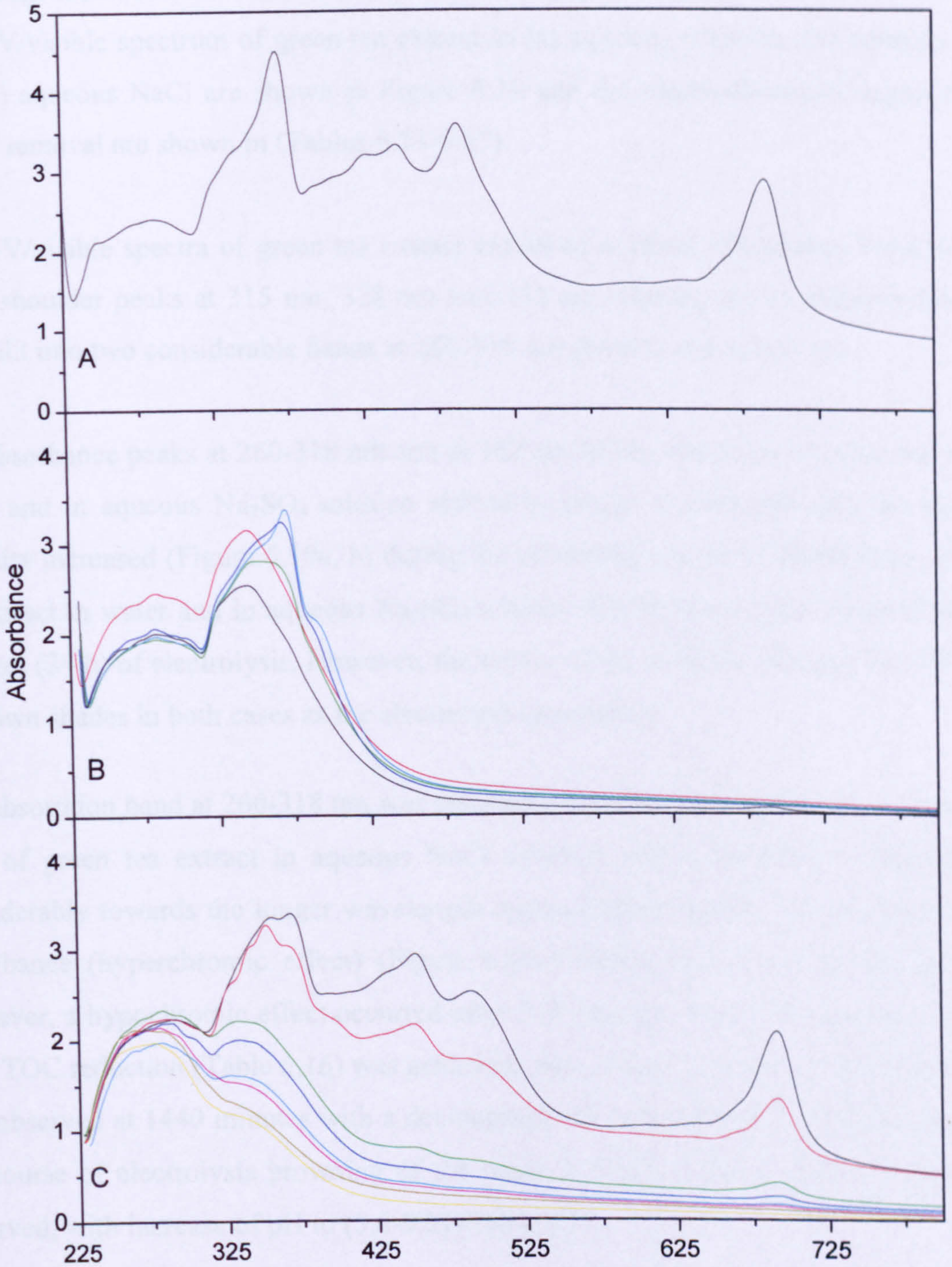


Figure 6.17: UV-Visible Spectra of spinach extract: A) Fresh raw spinach extract: 0 min____, **B) Effect of temperature on spinach-chlorophyll**: 0 min____, 15 min____, 30 min____, 45 min____ and 60____, **C) Electrolysis of fresh raw spinach in aqueous NaCl solution**: 0 min____, 5 min____, 10 min____, 20 min____, 30 min____, 40 min____, 50 min____ and 60 min____.

6.6.3 Degradation of Green Tea extract by Electrolytic Process

The UV/visible spectrum of green tea extract in (a) aqueous solution, (b) aqueous Na_2SO_4 and (c) aqueous NaCl are shown in Figure 6.19 and the electrochemical degradation and colour removal are shown in (Tables 6.13-6.15).

The UV/visible spectra of green tea extract exhibited a broad absorbance band with three small shoulder peaks at 315 nm, 328 nm and 342 nm. During the 15 minutes electrolysis this split into two considerable bands at 260-318 nm (broad) and at 362 nm.

The absorbance peaks at 260-318 nm and at 362 nm in the spectrum of green tea extract in water and in aqueous Na_2SO_4 solution shifted to longer wavelength and the absorbance intensity increased (Figure 6.19a, b) during the remaining course of electrolysis. The green tea extract in water and in aqueous Na_2SO_4 solution showed no colour removal after 1440 minutes (24 h) of electrolysis. However, the colour of the solution changed from dull green to brown shades in both cases as the electrolysis proceeded.

The absorption band at 260-318 nm was selected to monitor the concentration changes with time of green tea extract in aqueous NaCl solution, since the band at 362 nm shifted considerably towards the longer wavelength region (bathochromic effect) with increase in absorbance (hyperchromic effect) (Figure 6.19c) during the course of the electrolysis. However, a hypochromic effect occurred after 240 minutes when 35% colour removal and 22% TOC reduction (Table 6.16) was achieved, after which a dramatic hyperchromic effect was observed at 1440 minutes with a development of a shoulder peak 382-402 nm. During the course of electrolysis browning of the aqueous NaCl solution after 120 minutes was observed, with increase of pH to (5.6-9.0) (Table 6.15).

Maiti et al. [101] reported that the polyphenolic catechins in green tea extract typically display characteristic absorbance maxima at 212 and 272 nm. The browning of the extract during the course of electrolysis may indicate the oxidation of catechins to condensed tannins as reported by Janeiro and Brett [96] (Figure 6.18).

Table 6.13: Electrochemical decolourisation of green tea in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.1	12.52	Dull green	0
15	5.2	11.60	Dull green	0
30	5.2	11.30	Dull green	0
60	5.0	11.15	Dull green	0
120	4.6	14.40	Light olive	0
240	4.4	15.48	Yellow-honey	0
360	4.4	13.90	Yellow-honey	0
480	4.3	12.45	Light brown	0
600	4.2	12.55	Light brown	0
1440	4.6	12.39	Light brown	0

Conditions: current, 0.208 A; temperature, ambient; concentration (green tea, 5 g/L)

Table 6.14: Electrochemical decolourisation of green tea in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.3	13.45	Dull green	0
15	4.4	13.28	Light olive	0
30	4.3	12.72	Light olive	0
60	4.2	11.95	Yellow olive	0
120	4.2	11.34	Yellow	0
240	4.2	11.08	Dark yellow	0
360	4.3	10.96	Brown-olive	0
480	4.2	10.73	Brown-olive	0
600	4.3	10.70	Brown-olive	0
1440	5.2	10.70	Brown	0

Conditions: current, 2.0 A; temperature, ambient; concentration (green tea, 5 g/L; Na_2SO_4, 5 g/L)

Table 6.15: Electrochemical decolourisation of green tea in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.6	9.73	Dull green	0
15	6.3	9.46	Olive yellow	28
30	4.7	9.12	Olive yellow	—
60	5.6	8.65	Honey	—
120	6.2	8.10	Brown-honey	—
240	6.2	8.02	Honey	35
360	6.6	8.14	Light yellow	—
480	7.2	8.30	Pale yellow	—
600	9.0	8.45	Pale yellow	—
1440	9.0	8.98	Colourless	—

Conditions: current, 2.0 A; temperature, ambient; concentration (green tea 5 g/l; NaCl, 5 g/l)

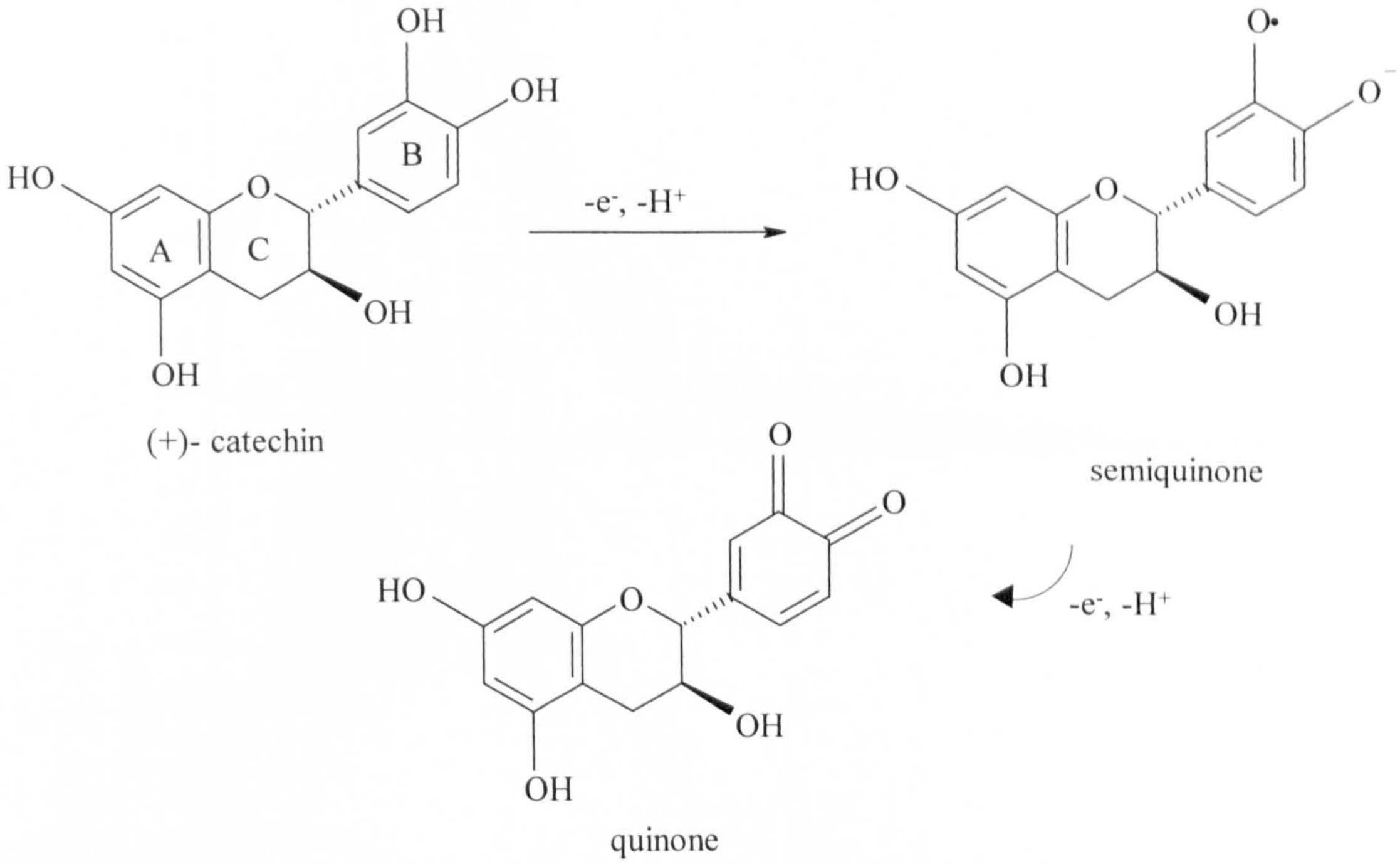


Figure 6.18: Mechanism of oxidation of catechin as suggested by Janeiro and Brett [96]

Table 6.16: TOC data during the electrolysis of green tea extract in aqueous sodium chloride

Time (min)	TOC (ppm)	TOC % Degradation
0	132.3	0
30	121.5	08
60	116.0	12
120	115.0	13
240	111.5	16
360	103.0	22

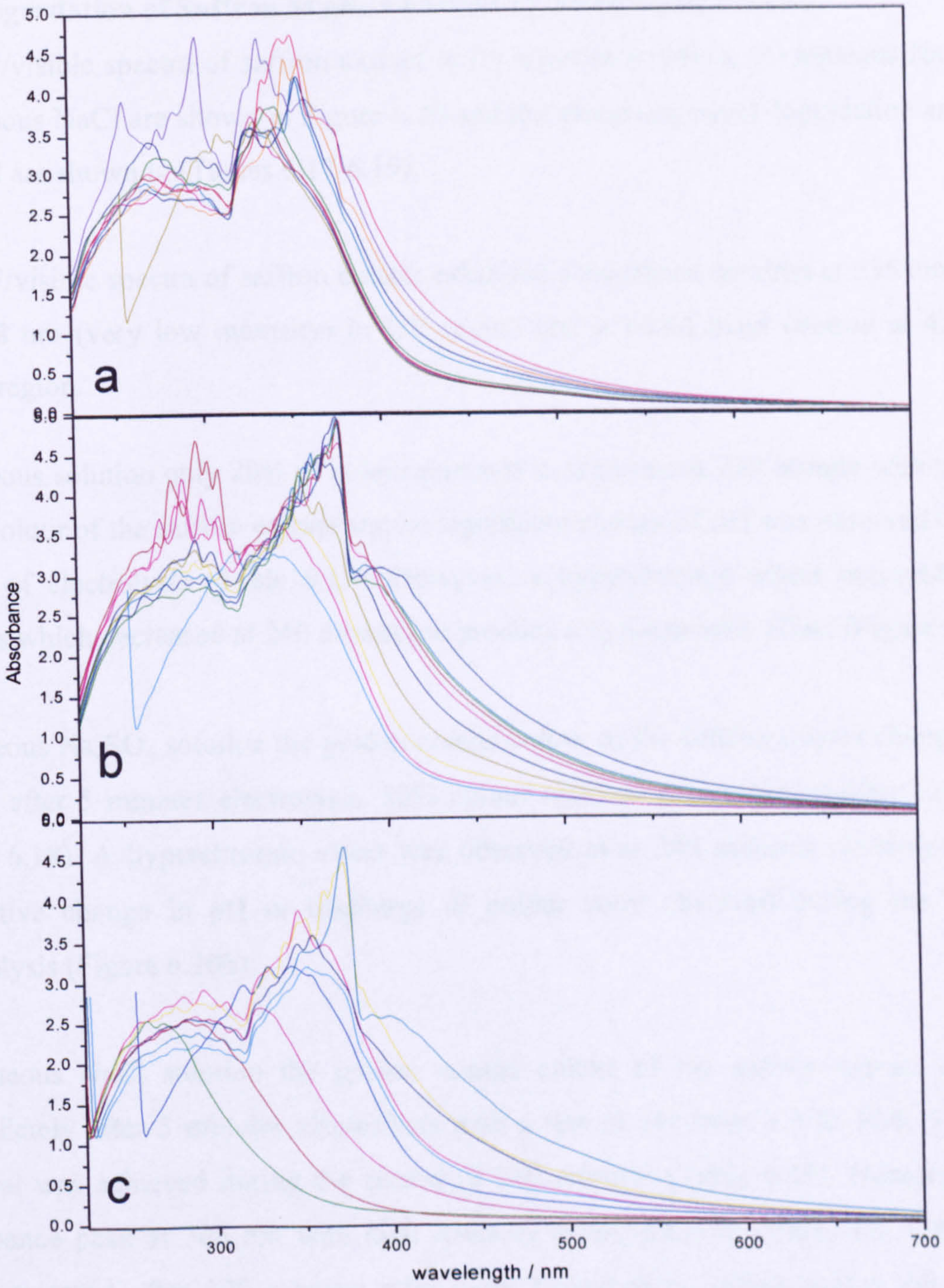


Figure 6.19: UV-Visible spectra showing the electrolytic destruction of green tea extract in (a) aqueous solution: 0 min____, 15 min____, 30 min____, 60 min____, 120 min ____, 240 min ____, 360 min____, 480 min____, 600 min____, 1440 min____.

(b) aqueous Na_2SO_4 solution: 0 min____, 15 min____, 30 min____, 60 min____, 120 min ____, 240 min ____, 360 min____, 480 min____, 600 min____, 1440 min____.

(c) aqueous NaCl solution: 0 min____, 15 min____, 30 min____, 60 min____, 240 min ____, 360 min____, 480 min____, 600 min____, 1440 min____.

6.6.4 Degradation of Saffron Stigmas Extract by Electrolytic Process

The UV/visible spectra of saffron extract in (a) aqueous solution, (b) aqueous Na_2SO_4 and (c) aqueous NaCl are shown in Figure 6.20 and the electrochemical degradation and colour removal are shown in (Tables 6.17-6.19).

The UV/visible spectra of saffron extract exhibited absorbance maxima at 235 nm, 262 nm and 348 nm (very low intensity) in UV region and a broad band centred at 439 nm in visible region.

In aqueous solution only 20% of colour removal is achieved at 240 minute with no change in the colour of the saffron extract and no significant change of pH was observed during the course of electrolysis (Table 6.17). However, a hyperchromic effect occurred after 30 minutes which decreased at 240 minutes to produce a hypochromic effect (Figure 6.20 a).

In aqueous Na_2SO_4 solution the golden orange colour of the saffron extract changed to oily orange after 5 minutes electrolysis. 32% colour removal was achieved after 120 minutes (Table 6.18). A hyperchromic effect was observed after 240 minutes electrolysis and no distinctive change in pH or discharge of colour were observed during the course of electrolysis (Figure 6.20b).

In aqueous NaCl solution the golden orange colour of the saffron extract discharged immediately after 5 minutes electrolysis with a rise of pH from 6.3 to 10.0. 97% colour removal was achieved during the course of 240 minutes (Table 6.19). However, a sharp absorbance peak at 303 nm with high intensity (hyperchromic effect) and bathochromic effect emerged after 120 minutes with more hypochromic effect during the remaining course of the electrolysis time (Figure 6.20c). This result indicates the degradation of the extended conjugated system in saffron and the formation of conjugated degradation products with increasing time of electrolysis.

However, the UV spectra and the TOC data (20% reduction) (Table 6.20) indicate the formation of intermediate products after 120 minutes which persist during the remaining 240 minutes of the electrolysis.

Table 6.17: Electrochemical decolourisation of saffron extract in aqueous extract

Time (min)	pH	Voltage	Colour	% Removal
0	5.6	15.30	Orange-gold	0
5	5.7	14.23	Orange-gold	07
15	5.6	14.23	Orange-gold	16
30	5.6	14.05	Orange-gold	17
60	5.6	13.98	Orange-gold	-
120	6.2	13.92	Orange-gold	-
240	6.6	13.88	Orange-gold	20

Conditions: current, 0.024 A; temperature, ambient; concentration (saffron, 1 g/l)

Table 6.18: Electrochemical decolourisation of saffron extract in aqueous sodium sulphate

Time (min)	pH	Voltage	Colour	% Removal
0	7.9	14.03	Orange-gold	0
5	6.2	14.08	Oily-orange	11
15	6.5	13.72	Oily-orange	17
30	6.6	13.28	Oily-orange	18
60	6.7	12.63	Oily-orange	19
120	6.0	11.44	Oily-orange	32
240	7.3	10.89	Oily-orange	-

Conditions: current, 2.086 A; temperature, ambient; concentration (saffron, 1 g/l; Na_2SO_4, 5 g/l)

Table 6.19: Electrochemical decolourisation of saffron extract in aqueous sodium chloride

Time (min)	pH	Voltage	Colour	% Removal
0	6.3	9.53	Orange-gold	0
5	10.0	9.55	Colourless	92
15	9.3	9.27	Colourless	92
30	9.0	9.00	Colourless	94
60	8.9	8.50	Colourless	94
120	9.0	8.36	Colourless	95
240	9.0	8.46	Colourless	97

Conditions: current, 2.032 A; temperature, ambient; concentration (saffron, 1 g/l; NaCl, 5 g/l)

Table 6.20: TOC data during the electrolysis of saffron extract in aqueous sodium chloride

Time (min)	TOC (ppm)	TOC % Degradation
0	183.0	0
15	161.6	12
30	158.0	14
60	156.0	15
90	153.0	16
120	150.8	18
240	147.0	20

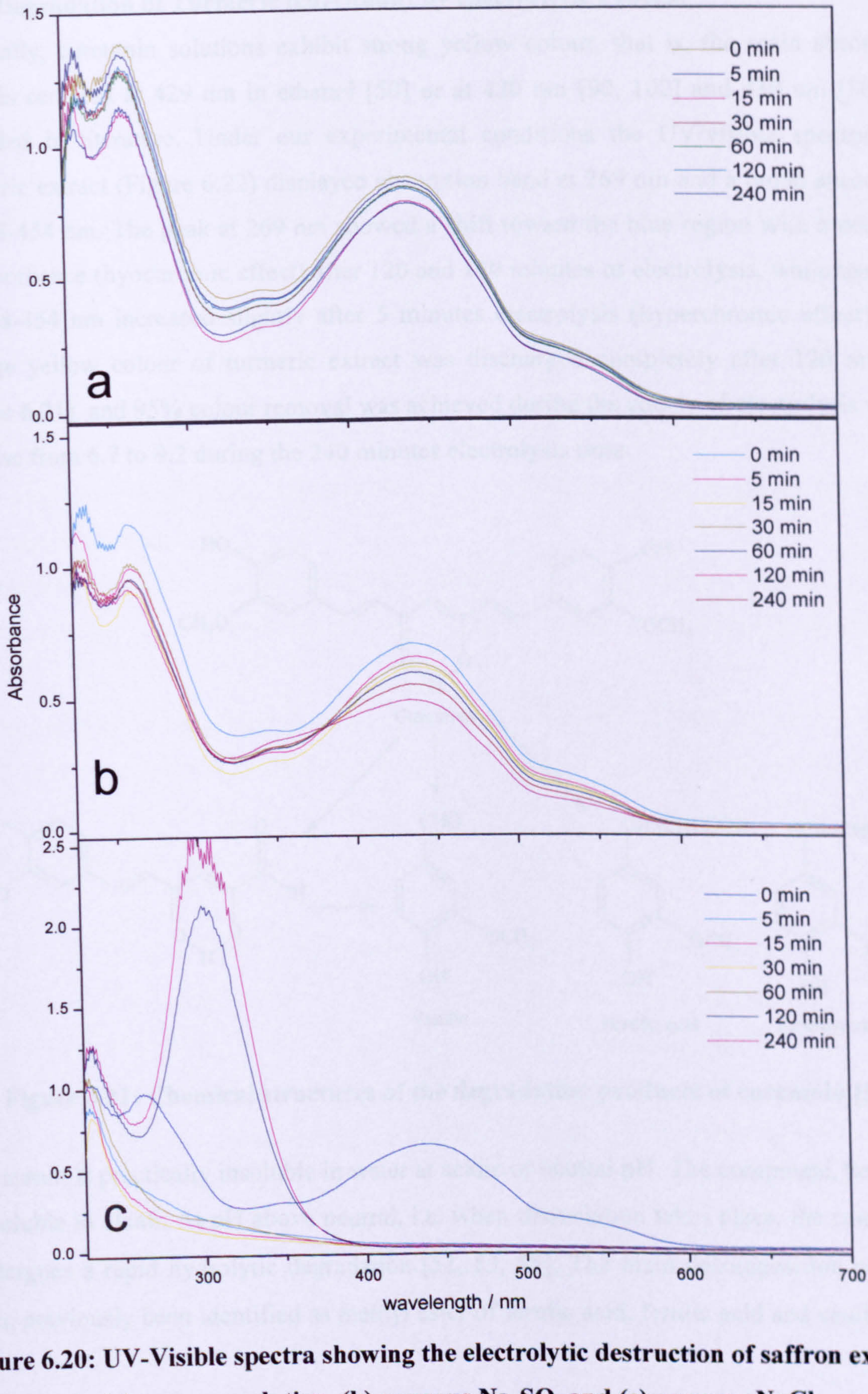


Figure 6.20: UV-Visible spectra showing the electrolytic destruction of saffron extract in (a) aqueous solution, (b) aqueous Na_2SO_4 and (c) aqueous NaCl

6.6.5 Degradation of Turmeric (curcumin) by Electrolytic Process

Generally, curcumin solutions exhibit strong yellow colour, that is, the main absorption band is centered at 429 nm in ethanol [50] or at 420 nm [90, 102] and 430 nm [103] as recorded in literature. Under our experimental conditions the UV/visible spectrum of turmeric extract (Figure 6.22) displayed absorption band at 269 nm and a broad absorption at 418-454 nm. The peak at 269 nm showed a shift toward the blue region with a decrease in absorbance (hyochromic effect) after 120 and 180 minutes of electrolysis, while the band at 418-454 nm increased slightly after 5 minutes electrolysis (hyperchromic effect). The orange yellow colour of turmeric extract was discharged completely after 120 minutes (Table 6.21), and 95% colour removal was achieved during the course of electrolysis with a pH rise from 6.7 to 9.2 during the 240 minutes electrolysis time.

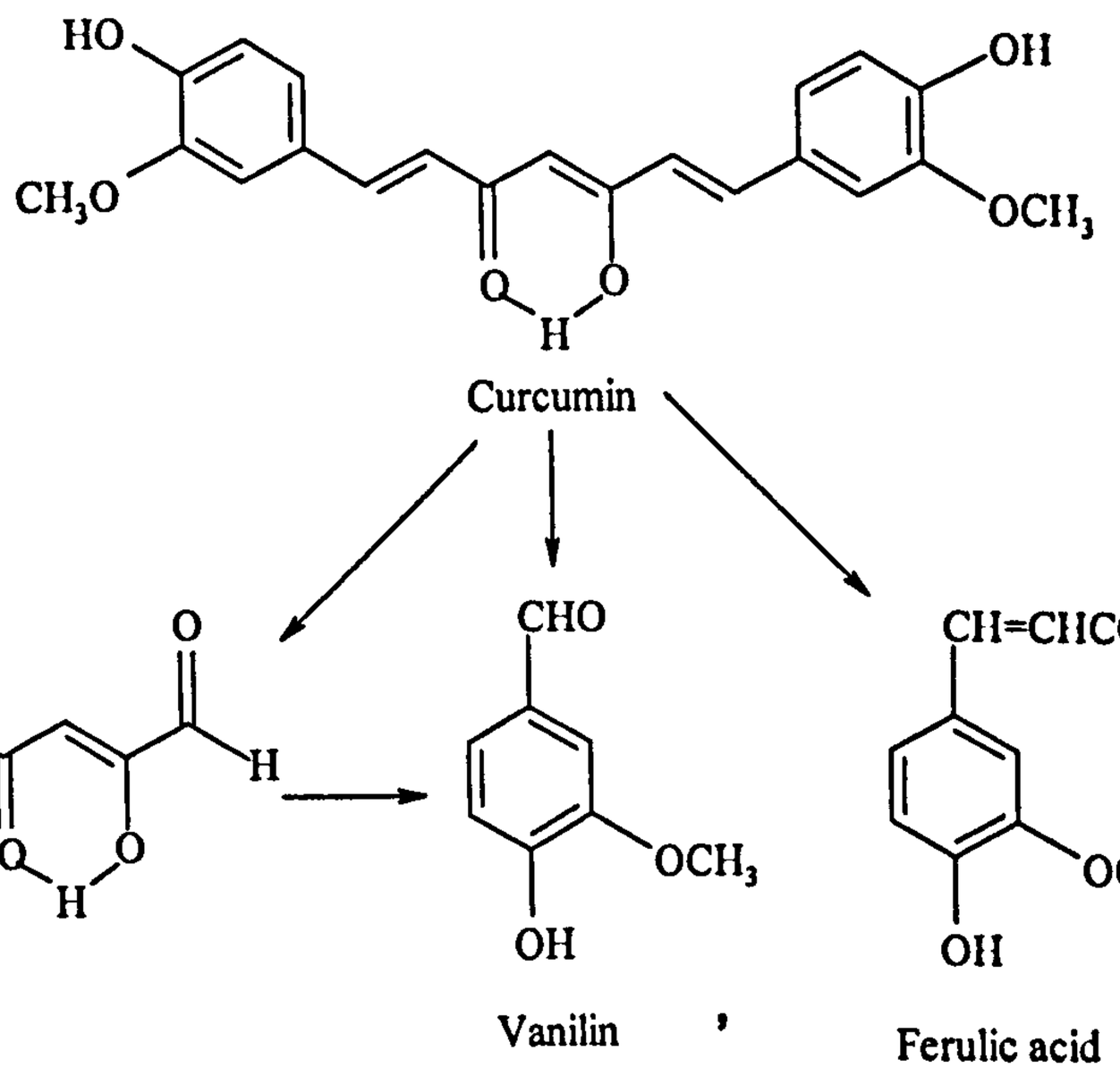


Figure 6.21: Chemical structures of the degradation products of curcumin [53]

Curcumin is practically insoluble in water at acidic or neutral pH. The compound, however, is soluble in alkali. At pH above neutral, i.e. when dissociation takes place, the compound undergoes a rapid hydrolytic degradation [52, 53, 55]. The main decomposition products have previously been identified as methyl ester of ferulic acid, ferulic acid and vanillin; the

latter being secondary product formed by hydrolysis of methyl ester of ferulic acid [47, 53, 55] (Figure 6.21).

Table 6.21: Electrochemical decolourisation of turmeric extract in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.7	6.35	Orange-yellow	0
5	7.3	6.43	Orange-yellow	31
60	10.6	6.45	Yellow	33
120	9.9	6.16	Colourless	86
180	9.5	6.22	Colourless	95
240	9.2	6.27	Colourless	95

Conditions: current, 1.5 A; temperature, ambient; concentration (turmeric 5 g/l; NaCl, 5 g/l)

6.6.6 Degradation of Binary Mixture of Annatto and Curcumin (Langdale Yellow) by Electrolytic Process

The electrolysis of Langdale Yellow binary mixture in aqueous solution (Table 6.22) shows no colour removal or change of the original colour, and the pH varies only slightly (4.5-5.9).

The electrolysis of Langdale yellow binary mixture in aqueous solution of Na_2SO_4 (Table 6.23) shows only slight change of colour from yellow to pale yellow during the 120 minutes electrolysis process. However, a reduction in the pH values from 6.3 to 1.2 was observed during the reaction.

The UV/visible spectrum of the degraded binary mixture of annatto and curcumin in aqueous solution of NaCl (Figure 6.22) displayed a well-defined absorbance at 439 nm in the visible region and 247 nm in the UV region. Typically bixin and norbixin the colouring matters of annatto exhibits absorbance maxima at 470, 501 nm for bixin and 453, 482 nm for norbixin have been reported [104]. In another manuscript, the absorbance maxima for bixin are at 448, 480 nm [105].

The corresponding TOC data of the binary mixture in aqueous NaCl are given in Table 6.25. TOC values decreases over the 120 minutes electrolysis period with 46% reduction of the organic material (TOC) of the Langdale dye mixture. The dye in aqueous NaCl (Table 6.24)

showed that the yellow colour discharged completely and that 90% of colour removal is achieved after 10 minutes with dramatic rise in pH from 4.7 to 9.2, and at 25 minutes the colour removal of the dye reached a plateau of 95%. The results obtained from the UV spectra and the TOC data showed that organic material remains in the solution (Table 6.25).

The thermal stability of annatto food colouring has been studied in model systems and foods. The findings indicated that annatto is readily degraded to form both coloured degradation products and the aromatics *m*-xylene and to a lesser extent, toluene [15, 56]. Lancaster and Lawrence mentioned that on heating in solution, *cis*-bixin is partially converted into the *trans* isomer and yellow degradation products [15].

Table 6.22: Electrochemical decolourisation of Langdale yellow (annatto & curcumin) extract in aqueous solution

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.5	14.75	Oily- yellow	n.a.
10	4.3	14.53	Oily- yellow	n.a.
15	4.3	14.42	Oily- yellow	n.a.
20	4.1	14.41	Oily- yellow	n.a.
25	4.3	14.57	Oily- yellow	n.a.
30	4.9	15.00	Oily- yellow	n.a.
60	5.5	15.53	Oily- yellow	n.a.
120	5.9	15.63	Oily- yellow	n.a.

Conditions: current, 0.015 A; temperature, ambient; concentration, (Langdale yellow 5 ml/l), n.a.; not analysed.

Table 6.23: Electrochemical decolourisation of Langdale yellow (annatto & curcumin) extract in aqueous sodium sulphate

Time (min)	pH	Voltage (V)	Colour	% Removal
0	6.3	12.90	Oily- yellow	n.a.
3	3.4	12.89	Yellow	n.a.
10	2.7	12.87	Yellow	n.a.
15	2.3	12.85	Yellow	n.a.
20	2.2	12.76	Yellow	n.a.
25	2.0	12.60	Yellow	n.a.
30	1.9	12.63	Yellow	n.a.
60	1.2	12.15	Yellow	n.a.
120	1.2	12.80	Pale yellow	n.a.

Conditions: current, 1.555 A; temperature, ambient; concentration, (Langdale yellow 5 ml/l; Na_2SO_4, 5 g/l), n.a.; not analysed

Table 6.24: Electrochemical decolourisation of Langdale yellow (annatto & curcumin) extract in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	4.7	4.90	Oily- yellow	0
10	8.9	4.23	Colourless	90
15	9.8	4.27	Colourless	94
20	9.5	4.30	Colourless	94
25	9.1	4.33	Colourless	95
30	9.0	4.34	Colourless	95
60	9.2	4.34	Colourless	95
120	9.2	4.24	Colourless	95

Conditions: current, 2.0 A; temperature, ambient; concentration, (Langdale yellow 5 ml/l; NaCl, 5 g/l)

Table 6.25: TOC data during the electrolysis of Langdale yellow (annatto & curcumin) in aqueous sodium chloride

Time (min)	TOC (ppm)	TOC % Degradation
0	6.1	0
10	4.6	24
15	4.5	26
20	4.2	31
25	4.0	34
30	3.9	36
60	3.8	38
120	3.3	46

6.6.7 Degradation of Beetroot by Electrolytic Process

The UV/visible spectrum of the beetroot extract in aqueous NaCl (Figure 6.22) exhibited two absorbance maxima at 342 nm and a broad band at 527 nm in the visible region and one absorbance maximum at 279 nm. Typically betacyanins have absorbance maximum at 534-552 nm [106]. The results showed hypsochromic effect by as much as 20 nm after 15 minutes and also there is a change of pH from 5.4 to 6.6. Although 98% of colour removal is achieved after 240 minutes (Table 6.26), the UV absorbance shows that organic material remains in the aqueous solution.

Table 6.26: Electrochemical decolourisation of beetroot extract in aqueous sodium chloride

Time (min)	pH	Voltage (V)	Colour	% Removal
0	5.4	4.16	Yellow-brown	0
15	5.6	4.29	Yellow-brown	37
40	5.7	4.35	Dark brown	57
60	6.2	6.29	Light brown	67
90	6.3	6.29	Light brown	73
120	6.7	6.29	Yellow	88
180	6.4	6.08	Colourless	95
240	6.6	6.07	Colourless	98

Conditions: current, 3.998 A; temperature, ambient; concentration (beetroot 63 g/l; NaCl, 5 g/l)

It was reported by Hancock [5] that betanin is most stable at pH 4.0-5.0. It degrades with increasing temperature, the colour is destroyed by UV and radiation, and oxidation darkens the beetroot and causes loss of the colour. Patkai et al. [107] investigated the decomposition of the main beetroot colourings betanin and vulgaxanthine, as a function of temperature and pH value in acetate and citrate buffer solutions in a temperature range between 60 and 80°C and pH range of 3.3-6.2. No isolation or identification of degradation products was attempted in their investigation.

6.6.8 Degradation of Sumac by Electrolytic Process

The UV/visible spectrum of the sumac extract in aqueous NaCl (Figure 6.22) exhibited two absorbance maxima at 280 nm and 327nm. The peak in the UV region at 280nm corresponds to gallotannin (hydrolysable tannins) which is in accordance with the value reported in literature [61, 64, 80]. Niemetz and Gross [64] reported the isolation of ten polygallotannins from sumac: e.g., β- glucogallin (1-*O*-galloyl- β-D-glucose); 1,2,3,4,6-pentagalloylglucose; 3-*O*-digalloyl-1,2,4,6-tetra-*O*-galloyl β-D-glucose. Methyl gallate (3, 4, 5-trihydroxy benzoic acid), 4-methoxy-3,5-dihydroxy benzoic acid, gallic acid, tannic acid and ellagitannins were also identified in sumac extract by Saxena et al. [65]. Fisetin, myricetin [66] and quercetin [67] were also reported to occur in sumac leaves.

A shift to longer wavelength was observed from 327 nm to 338 nm after 30 minutes electrolysis time. This bathochromic shift is indicative of extended conjugation that may

have occurred as a result of electrolysis (Table 6.27). Only 14% colour removal was achieved in 60 minutes at pH values of (3.5-2.7). The UV absorbance in Figure 6.22 showed that organic materials remained in the extract. This may be attributed to the presence of the above organic constituents reported to occur in sumac.

Table 6.27: Electrochemical decolourisation of sumac extract in aqueous sodium chloride

Time	pH	Voltage (V)	Colour	% Removal
0	3.5	6.23	Tart red purple	0
30	3.5	6.12	Yellow brown	11
60	3.3	6.10	Yellow brown	14
120	3.2	6.10	Yellow brown	n.a.
180	3.2	6.09	Light yellow	n.a.
240	2.7	6.09	Pale yellow	n.a.

Conditions: current, 4.0 A; temperature, ambient; concentration (sumac, 5 g/l; NaCl, 5 g/l)
n.a.; not analysed

6.6.9 Degradation of Roselle (Karkade) by Electrolytic Process

The UV/visible spectrum of roselle extract in aqueous NaCl (Figure 6.22) shows a broad peak at 529 nm in the visible region and two absorbance maxima at 332 nm and a broad band centred at 271 nm in UV region. The anthocyanin delphinidin, in roselle extract reported to show an absorbance maximum at 520 nm [68, 70].

Fluctuations (hypochromic and hyperchromic effects) in the results were obtained together with the changes in the percentage of colour removal values of the roselle extract with time (Table 6.28) were unexplained. A continuous hypochromic effect was observed after 30 minutes with 89% colour removal. However, a hypochromic effect occurred after 40 minutes followed by a hypochromic at 60 minutes with 93% colour removal. At 90 minutes another hyperchromic effect was observed, and then a hypochromic effect was seen during the remaining time of the electrolysis. Only a slight change from the natural acidic pH values occurred (1.6-2.2) during the course of electrolysis. No change in colour removed was observed when the electrolysis was conducted using 50 g/l of roselle calyces (Table 6.29) for 180 minute with current of 2.0 A at pH values of (1.9-2.2).

Gradinaru et al. [68] studied the thermal stability of isolated anthocyanin from *H. sabdariffa* (roselle) in aqueous solutions. Their findings reported that oxygen and heat cause oxidation of anthocyanins to yield colourless or brown pigments, and suggested the oxidation of o-dihydroxyphenols to quinones and subsequent reaction between quinones and anthocyanins [68].

Table 6.28: Electrochemical decolourisation of roselle (karkadé) extract in aqueous sodium chloride

Time (min)	pH	Voltage	Colour	% Removal
0	1.6	5.90	Ruby-red	0
15	1.6	6.08	Brown	14
30	1.6	6.12	Yellow	89
45	1.7	6.25	Yellow	-
60	2.2	7.08	Pale yellow	93
90	2.2	7.09	Pale yellow	-
120	2.2	7.10	Pale yellow	-
180	2.2	7.12	Pale yellow	-
240	2.2	6.92	Colourless	98

Conditions: current, 1.572 A; temperature, ambient; concentration (karkadé 5 g/l; NaCl, 5 g/l)

Table 6.29: Electrochemical decolourisation of concentrated roselle (karkadé) extract in aqueous sodium chloride

Time (min)	pH	Voltage	Colour	% Removal
0	1.9	5.90	Ruby-red	0
30	2.0	6.08	Ruby-red	0
60	2.0	6.12	Ruby-red	0
120	2.2	6.25	Ruby-red	0

Conditions: current, 1.440 A; temperature, ambient; concentration (karkadé 50 g/l; NaCl, 5 g/l)

6.6.10 Degradation of Henna Extract by Electrolytic Process

The UV/visible spectrum of henna extract in aqueous NaCl (Figure 6.22) shows two distinctive absorbance peaks at 322-376 nm and 390 nm (shoulder) and a broad band centred at 283 nm in UV region. A hypsochromic effect was also observed after 120 minutes with disappearance of the shoulder absorbance at 390 nm. A change in the pH also occurred from slightly acidic to neutral (5.0-7.8) (Table 6.30).

The brown orange colour disappeared after 360 minutes and the colour removal reached 97% at 420 minutes of electrolysis period. However, the UV region absorbance shows that organic materials in henna extract remain in the electrolysed solution after 480 minutes electrolysis. This could be attributed to the resistance of the anthraquinone moiety in lawsone (α-hydroxy naphthoquinone), the main colouring matter in henna as suggested by Robinson et al. [108] that anthraquinone-based dyes are most resistant to degradation due to their fused aromatic ring structure. It was reported in literature that Lawsone has absorbance maxima at 452 nm [103], and 275, 335 nm [105].

Other constituents known to occur in henna extract are tannin, gallic acid, 1,2-dihydroxy-4-O-glucosyl-oxynaphthalene and 2,3,4,6-tetrahydroxyacetophenone, 2-β-D-glucopyranoside [109]. Flavonoid pigments were also found in henna leaves [110].

Table 6.30: Electrochemical decolourisation of henna extract in aqueous sodium chloride

Time (min)	pH	Voltage	Colour	% Removal
0	5.0	5.45	Brown-orange	0
120	5.9	5.55	Honey-yellow	59
180	6.4	5.82	Yellow	86
300	6.0	5.90	Pale yellow	89
360	7.3	5.92	Colourless	96
420	7. 6	5.92	Colourless	97
480	7.8	6.00	Colourless	97

Conditions: current, 3.998 A; temperature, ambient; concentration, 5 g/l; NaCl, 5 g/l)

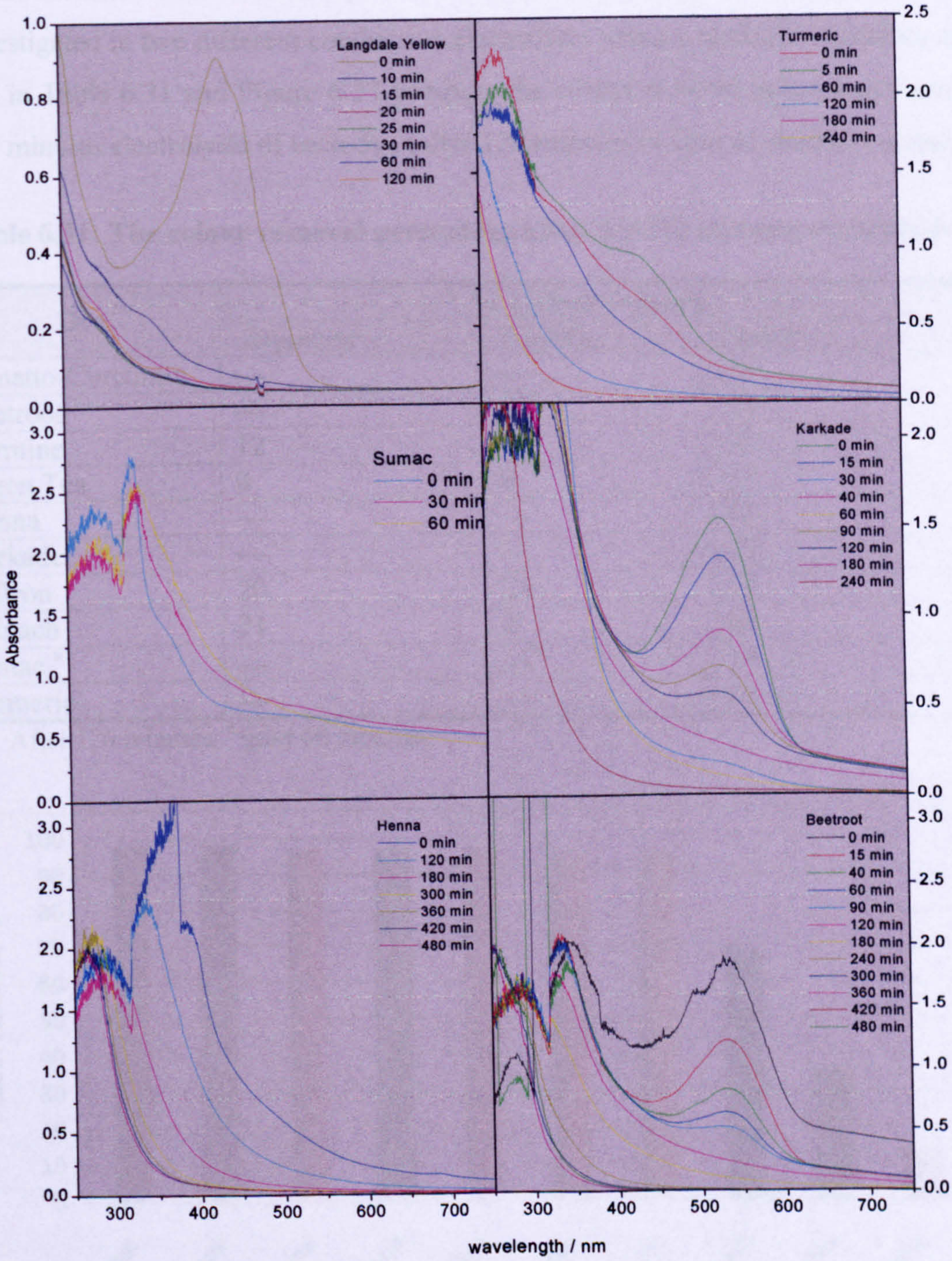


Figure 6.22: UV-Visible spectra during the electrolytic destruction of turmeric, roselle (karkade), sumac, Langdale yellow (annatto and curcumin), beetroot and henna using NaCl as an electrolyte

6.7 CONCLUSIONS

The electrochemical treatment of aqueous solutions containing natural dye extracts has been investigated in two different conductive electrolytes using a platinised titanium anode. The data in Table 6.31 and Figure 6.23 compare the colour removal percentages achieved after 240 minutes electrolysis of each dye (after 120 minutes in case of annatto-curcumin).

Table 6.31: The colour removal percentage after the 240 minutes electrolysis

Dye	% Colour removal		
	Aqueous	Na_2SO_4	NaCl
Annatto-Curcumin [i]	—	—	95
Beetroot	—	—	98
Carmine	12	87	97
Green Tea	0	0	35
Henna	—	—	97
Karkade	—	—	98
Saffron	20	25	97
Spinach	21	0	69
Sumac [ii]	—	—	14
Turmeric	—	—	95

[i] After 120 minutes, [ii] after 60 minutes

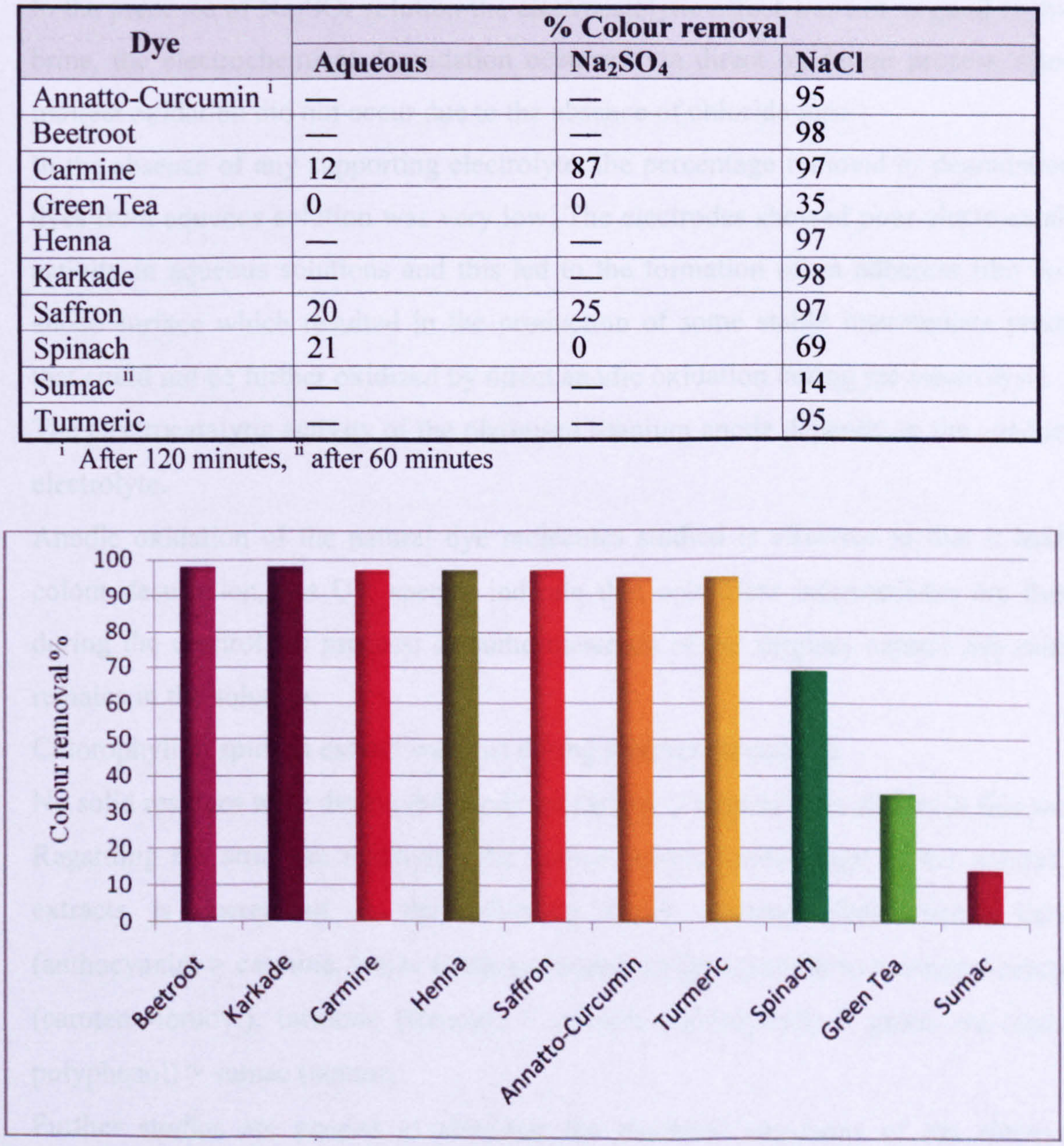


Figure 6.23: Colour removal percentages of the natural dyes in aqueous NaCl solutions after 240 minutes electrolysis

The main findings of this study are given below:

- The addition of electrolytes improved the efficiency of the process and generally increased the percentage removal of dyes from aqueous solutions.
- The highest electrolytic activity was achieved in the presence of NaCl (5 g/l) and this increase in the degradation and percentage colour removal is attributed to both direct as well as indirect oxidation occurring simultaneously.
- In the presence of Na_2SO_4 solution the electrocatalytic effect was not as good as that in brine, the electrochemical degradation occurred via direct oxidation process whereas indirect oxidation did not occur due to the absence of chloride ions.
- In the absence of any supporting electrolyte, the percentage removal or degradation of dyes from aqueous solution was very low. The electrodes showed poor electrocatalytic activity in aqueous solutions and this led to the formation of an adherent film on the anode surface which resulted in the production of some stable intermediate products that could not be further oxidized by direct anodic oxidation during the electrolysis.
- The electrocatalytic activity of the platinised titanium anode depends on the conductive electrolyte.
- Anodic oxidation of the natural dye molecules studied is effective in that it leads to colour destruction, but UV spectra indicate that colourless intermediates are formed during the electrolytic process; or some materials of the original natural dye mixture remains in the solution.
- Chlorophyll in spinach extract was lost during thermal processing.
- No solid residues were during the anodic oxidation of natural dyes studies in this work.
- Regarding the structure reactivity, the colour removal percentage of the natural dye extracts is decreasing in the following order: beetroot (betacyanin), karkade (anthocyanin) > carmine, henna (anthraquinone), saffron (carotene) > annatto-curcumin (carotene-feruoyl), turmeric (feruoyl) > spinach (chlorophyll) > green tea (catechin polyphenol) > sumac (tannin)
- Further studies are needed to elucidate the chemical structures of the electrolytic degradation products of the dyes/pigments studied in this work.

6.7 REFERENCES

1. J.B. Hallagan, D.C. Allen J.F. Borzellec, *Food Chem. Toxicol.*, 1995, **33**, 515-528.
2. H.B. Sowbhagya, S. Smitha, S.R. Sampathu, N. Krishnamurthy, S. Bhattacharya, *J. Food Eng.*, 2005, **67**, 367-371.
3. http://europa.eu.int/comm/food/fs/sfp/flav_index_en.html, EU legislation on food additives (20/06/2006).
4. A. Downham and P. Collins, *Int. J. Food Sci. Technol.*, 2000, **35**, 5-22.
5. U. Wissgott and K. Bortlik, *Trends Food Sci. Technol.*, 1996, **7**, 298-302.
6. M. Hancock, Potential for Colourants from Plant Sources in England & Wales, 1997, ST0106, Arable Crops & Horticulture Division, ADAS Boxworth, Cambridge, UK.
7. J.S. Anderson, *J. S. D. C.*, 2000, **116**, 193-196.
8. S.L. Chua and N. Levell, *J. Am. Acad. Dermatol.*, March 2005, P34.
9. A. Schieber, F.C. Stintzing, R. Carle, *Trends Food Sci. Technol.*, 2001, **12**, 401-413.
10. K.I. Priyadarsini, D.K. Maity, G.H. Naik, M.S. Kumar, M.K. Unnikrishnan, J.G. Satav, H. Mohan, *Free Radic. Biol. Med.*, 2003, **35**, 475-484.
11. Y.-C. Chang, K.-X. Huang, A.-C. Huang, Y.-C. Ho, C.-J. Wang, *Food Chem. Toxicol.*, 2006, **44**, 1015-1023.
12. C. Dufresne and E. Farnworth, *J. Nut. Biochem.*, 2001, **12**, 404-421.
13. S. Chatterjee, T.B. Poduval, J.C. Tilak, T.P.A. Devasagayam, *Clin. Chim. Acta,* 2005, **352**, 155-163.
14. T. Watanabe and S. Terabe, *J. Chromatogr. A*, 2000, **880**, 311-322.
15. F.E. Lancaster and J.F. Lawrence, *J. Chromatogr. A*, 1996, **732**, 394-398.
16. W.P. Armstrong, (A newsletter of Natural History Trivia) http:/waynesword.palomar.edu/ecoph3.htm, cochineal (14/06/03).
17. file://A:\Spinach\Spinach.htm, spinach (04/02/2004)
18. V. A.-E. King, C.-F. Liu, Y.-J. Liu, *Food Res. Int.*, 2001, **34**, 167-175.
19. T. Bohn and T. Walczyk, *J. Chromatogr. A*, 2004, **1024**, 123-128.
20. M. Hanssen and J. Marsden, E for Additives, (The Complete Number Guide), 1985, Wellingborough, Northamptonshire: Thornson Publishers Ltd.
21. B. Schoefs, *Trends Food Sci. Technol.*, 2002, **13**, 361-371.

22. B. López-Ayerra, M.A. Murcia, F. Garcia-Carmona, *Food Chem.*, 1998, **61**, 113-118.
23. A. Sheppard, www.purlife.com/overview.htm, Chlorophyll and Cancer (11/02/2005).
24. S.S. Teng and B.H. Chen, *Food Chem.*, 1999, **65**, 367-373.
25. D.S. Wheeler and W.J. Wheeler, *Drug Development Research*, 2004, **61**, 45-65.
26. www.pepysdiary.com/p/360.php, Tea, (10/3/2006).
27. A.J. Hennessy, 1998, *Chem. Ind.*, 1998, 518-519.
28. M. Polovka, V. Brezová, A. Staško, *Biophys. Chem.*, 2003, **106**, 39-56.
29. D. Labbé, A. Tremblay, L. Bazinet, *Sep. Purif. Technol.*, 2006, **49**, 1-9.
30. H. Wang, G.J. Provan, K. Helliwell, *Trends Food Sci. Technol.*, 2000, **11**, 152-160.
31. Y. Zuo, H. Chen, Y. Deng, *Talanta*, 2002, **57**, 307-316.
32. A. McIntyre, Folk for Common Ailments, 1994, Gaia Books Ltd., Toronto, Ontario. Canada.
33. L.R. Juneja, D.-C. Chen, T. Okubo, Y. Nagato, H. Yokogoshi, *Trends Food Technol.*, 1999, **10**, 199-204.
34. M. Zougagh, B.M. Simonet, A. Ríos, M. Valcarcel, *J. Chromatogr. A*, 2005, **1085**, 293-298.
35. D. Potteron, Culpeper's, Colour Herbal, 1999, Foulsham, London-New York-Toronto-Sydney.
36. E. Tsatsaroni, M. Liakopoulou-Kyriakides, I. Eleftheriadis, *Dyes Pigm.*, 1998, **37**, 307-315.
37. F.I. Abdullaev and J.J. Espinosa-Aguirre, *Cancer Detect. Prev.*, 2004, **28**, 426-432.
38. O. Orfanou and M. Tsimidou, *Food Chem.*, 1996, **57**, 463-469.
39. K. Selim, M. Tsimidou, C.G. Biliaderis, *Food Chem.*, 2000, **71**, 199-206.
40. A.A. Noorbala, S. Aknondzadeh, N. Tahmacebi-Pour, A.H. Jamshidi, *J. Ethnopharmacol.*, 2005, **97**, 281-284.
41. H. Hosseinzadeh and F. Talebzadeh, *Fitoterapia*, 2005, **76**, 722-724.
42. M. Ashrafi, S.Z. Bathaie, M. Taghikhani, A.A. Moosavi-Movahedi, *Int. J. Biol. Macromol.*, 2005, **36**, 246-252.

43. P.A. Tarantilis, A. Beljebbar, M. Manfait, M. Polssiou, *Spectrochim. Acta*, Part A, 1998, **54**, 651-657.

44. P. Lozano, M.R. Castellar, M.J. Simancas, J.L. Iborra, *J. Chromatogr. A*, 1999, **830**, 477-483.

45. F. Starý and V. Jiràsek, Herbs, A Concise Guide in Colour, 1973, Artia Hamlyn Ltd., London, New York, Sydney, Toronto.

46. H. Caballero-Ortega, R. Pereda-Miranda, F.I. Abdullaev, *Food Chem.*, 2007, **100**, 1126-1131.

47. E. Pfeiffer, S. Höle, A.M. Solyom, M. Metzler, *J. food Eng.*, 2003, **56**, 257-259.

48. wwwchem.umimona.edu.jm/lectures/turmeric.html, Jamaican grown Turmeric, 11/06/2005.

49. M. Bernabé-Pineda, María Teresa Ramírez-Silva, M. Romero-Romo, E. González-Vergara, A. Rojas-Hernández, *Spectrochim. Acta Part A*, 2004, **60**, 1091-1097

50. F. Zsila, Z. Bikádi, M Simonyi, *Bioorg. Med. Chem.*, 2004, **12**, 3239-3245.

51. R.K. Gupta and L. Balasubrahmanyam, *World Patent Information*, 1998, **20**, 185-191.

52. A. Paradkar, A.A. Ambike, B.K. Jadhav, K.R. Mahadik, *Int. J. Pharm.*, 2004, **271**, 281-286.

53. Y.-J. Wang, M.-H. Pan, A.-L. Cheng, L.-I. Lin, Y.-S. Ho, C.-Y. Hsieh, J.-K. Lin, *J. Pharm. Biomed. Anal.*, 1997, **15**, 1867-1876.

54. G.R. Pillai, A.S. Srivastava1, T.I. Hassanein, D.P. Chauhan, E. Carrier, *Cancer Lett.*, 2004, **208**, 163-170.

55. H.H. Tønnesen, M. Másson, T. Loftsson, *Int. J. Pharm.*, 2002, **244**, 127-135.

56. M.J. Scotter, L. Castle, G.P. Appleton, *Food Chem.*, 2001, **74**, 365-375.

57. M.J. Scotter, *Food Chem.*, 1995, **53**, 177-185.

58. www.bryngollie.freeserve.co.uk, E Numbers (08/11/2003).

59. D.R. Tennant and M. O'Callaghan, *Food Res. Int.*, 2005, **38**, 911-917

60. G.J. Kapadia, H. Tokuda, T. Konoshima, H. Nishino, *Cancer Lett.*, 1996, **100**, 211-214.

61. A. Zalacain, M. Prodanov, M. Carmona, G.L. Alonso, *Biosystem Eng.*, 2003, **84**, 211-216.

62. www.silk.net/sirene/spices.htm, Spices (16/10/2002).
63. http://scifun.chem.wisc.edu/chemweek/fallcolr/fallcolr.html, sumac (11/02/2005)
64. R. Niemetz and G.G. Gross, *Phytochemistry*, 1998, **49**, 327-332.
65. G. Saxena, A.R. McCutcheon, S. Farmer, G.H.N. Towers, R.E.W. Hancock, *J. Ethnopharmacol.*, 1994, **42**, 95-99
66. J.M. Watt, B. Brandwijk, M. Gerdina, 1962, Medicinal and Poisonous Plants of Southern and Eastern Africa, Livingstone, Edinburgh, London, UK.
67. Y. Seino, M. Nagao, T. Yahagi, T. Sugimura, T. Yasuda, S. Nishimura, *Mutat. Res.*, 1978, **58**, 225-229.
68. G. Gradinaru, C.G. Biliaderis, S. Kallithraka, P. Kefales, C. Garcia-Viguera, *Food Chem.*, 2003, **83**, 423-436.
69. T.O. Omobuwajo, L.A. Sanni, Y.A. Balami, *J. Food Eng.*, 2000, **45**, 37-41.
70. P.- J. Tsai, J. MaIntosh, P. Pearce, B. Camden, B.R. Jordan, *Food Res. Int.*, 2002, **35**, 351-356.
71. D.C. McMillan, S.D. Sarvate, J.E. Oatis, Jr., D.J. Jollow, *Toxicol. Sci.*, 2004, **82**, 647-655.
72. B. Bonev 2003, www.hennapage.com/henna/mainindex.html, Lawsone (14/07/2005).
73. www.eastonwest.co.uk/scieihenna.html, henna (11/02/2005).
74. www.bodyminderevival.com/henna.htm, Henna (02/03/2003).
75. N.S. Zarghami and D.E. Heinz, *Phytochemistry*, 1971, **10**, 2755-2761.
76. P.A. Tarantilis, G. Tsoupras, M. Polssiou, *J. Chromatogr. A*, 1995, **699**, 107-118.
77. B. Schoefs, *Trends Anal. Chem.*, 2003, **22**, 335-339.
78. J. Sherma, *J. Chromatogr. A*, 2000, **880**, 129-147.
79. V. Sujata, G.A. Ravishanker, L.V. Venkataraman, J. *Chromatogr. A*, 1992, **624**, 497-502.
80. J.U. Niehaus and G.G. Gross, *Phytochemistry*, 1997, **45**, 1555-1560.
81. K. Saitoh, I. Awaka, N. Suzuki, *J. Chromatogr. A*, 1995, **693**, 176-180.
82. P.A. Tarantilis, M. Polssiou, M. Manfait, *J. Chromatogr. A*, 1994, **664**, 55-61
83. P.S. Negi and S.K. Roy, *Food Res. Int.*, 2001, **34**, 283-287.

84. S. Sang, S. Tian, X. Meng, R.E. Stark, R.T. Rosen, C.S. Yang, C.-T. Ho, *Tetrahedron Lett.*, 2002, **43**, 7129-7133.
85. M. Gross, H. Baer, H.M. Fales, *Phytochemistry*, 1975, **14**, 2263-2266.
86. T. Chakrabartty, G. Poddar, J. st. Pyrek, *Phytochemistry*, 1982, **21**, 1814-1816.
87. H. Suhaimi, F.B. Ahmed, S.E. Friberg, *J. Pharm. Sci.*, 1995, **84**, 376-380.
88. T. Keinonen, P. Riihola, V.-P. Leppänen, J. Parkkinen, T. Jaaskelainen, *Opt. Mater.*, 1997, **7**, 95-101.
89. Y.X. Tan, J.-H. Jiang, H.L. Wu, H. Cui, R.-Q. Yu, *Anal. Chem. Acta*, 2000, **412**, 195-202.
90. www.chemufl.edu/~kampehs/classes/2047 L/2047L Lab8 Chlorophyl2002.pdf, Microsoft Internet.
91. M.A.J.S. van Boekel, *Food Res. Int.*, 1999, **32**, 261-269.
92. B.H. Hassan and A.I. Hobani, *J. Food Eng.*, 1998, **35**, 459-470.
93. X. Sun, X. Yang, E. Wang, *Anal. Chim., Acta*, 2005, **547**, 153-157.
94. P.A. Kilmartin, C.F. Hsu, *Food Chem.*, 2003, **82**, 501-512.
95. M. Gizdavic-Nikolaidis, J. Travas-Sejdic, G.A. Bowmaker, R.P. Cooney, P.A. Kilmartin, *Synth. Met.*, 2004, **140**, 225-232.
96. P. Janeiro and A.M.O. Brett, *Anal. Chem. Acta*, 2004, **518**, 109-115.
97. R. Ito, A. Yamamoto, S. Kodama, K. Kato, Y. Yoshimura, A. Matsunaga, H. Nakazawa, *Food Chem.*, 2003, **83**, 563-568.
98. M. Obanda, P.O. Owuor, R. Mang'oka, M. M. Kavoi, *Food Chem.*, 2000, **85**, 163-173
99. S.A. Petrova, M.V. Kolodyazhny, O.S. Kesenzhek, *J. Electroanal. Chem.*, 1990, **277**, 189-196.
100. P. Nisha, R. S. Singhal, A. B. Pandit, *J. Food Eng.*, 2004, **64**, 135-142
101. T. K. Maiti, J. Chatterjee, and S. Dasgupta, *Biochem. Biophys. Res. Commun.*, 2003, **308**, 64-67
102. D. Gopinath, M. R. Ahmed, K. Gomathi, K. Chitra, P.K. Sehgal, R. Jayakumar, *Biomaterials*, 2004, **25**, 1911-1917
103. www.sigmaaldrich.com
104. wwwchem.uwimona.edu.jm: 1104/lectures/annatto.html 01/07/2005

105. R.C. Weast, M. J. Astle, W. H. Beyer, Eds. CRC Handbook of chemistry and physics, 1979, 59th Ed. CRC Press, Inc. Boca Raton Fl.

106. www2.unil.ch/lpc/docs/theses/zaiko/intro.pdf, anthocyanin versus betalain (06/06/2007).

107. G. Patkai, J. Barta, I. Varsănyi, *Cancer Lett.*, 1997, **114**, 105-106.

108. T. Robinson, G. McMullan, R. Marchant, P. Nigam, *Bioresour. Technol.*, 2001, **77**, 247-255.

109. T. Kawamura, Y. Hisata, K. Okuda, T. Takeda, T. Tanaka, *Natural Medicines*, 2000, **54**, 86-89.

110. A. El-Gadi and S. Bshana, Usages of some plants in Libyan Folk-Medicine, 1989, National Book Room, Benghazi, Libya

CHAPTER 7

CONCLUSION

CHAPTER 7
CONCLUSIONS

The work described in this thesis is concerned with the application of electrochemical methods to solve the environmental pollution problems associated with the disposal of effluent streams originating from food and textile industries.

In the electrochemical technique, the main reagent is the electron, called 'Clean Reagent' which may degrade all the organics present in the effluent directly into CO_2, H_2O, N_2, NO_3^-, and SO_4^- without generating any secondary pollutant or by-product/sludge. The process commonly referred to as electrochemical mineralization. The electrochemical technique offers high removal efficiencies and has lower temperature requirements compared to non-electrochemical treatment. Above all, the electrochemical reactors are compact, simple and the rate of pollutants removal may be very rapid.

The main objectives of this research work were:

- To highlight the problems associated with the management of textile effluent streams containing dyes.
- To optimise the electrochemical processes for the removal and destruction of synthetic textile dyes in aqueous solutions.
- To apply the electrochemical processes for the removal and destruction of synthetic food colours.
- To investigate the application of simple techniques to extract natural dyes from different plants.
- To investigate the application of natural-derived colourants for dyeing textile fabrics.
- To apply the electrochemical processes for the removal of residual natural pigments and dyes in aqueous solutions.

In conclusion, the work described in this thesis showed the potential for the exploitation of various aspects of electrochemistry in the control of environmental problems caused by synthetic hazardous dye materials in wastewater effluents. A simple electrochemical process can be used to remove dye molecules from aqueous solution containing a suitable

supporting electrolyte. However, the use of sodium chloride as a supporting electrolyte could lead to produce some intermediate compounds and a complete mineralisation may not be achieved during the process. The application of natural dyes as alternative source for dyeing textile fabrics was found to be an attractive option for reducing the cost associated with the management and treatment of wastewater streams originating from textile applications. The wastewater streams containing residual concentration of natural dyes can easily be treated in a sewage treatment plant.

7.1 RECOMMENDATION FOR DYE PRODUCTION AND FOR THE TREATMENT OF WASTEWATER IN LIBYA

The waste management hierarchy is a nationally and internationally accepted guide when determining the Best Practicable Environmental Option (BPEO). It represents a chain of priority for waste management, extending from the ideal of prevention (avoidance) and reduction to the last resort of disposal (Figure 7.1).

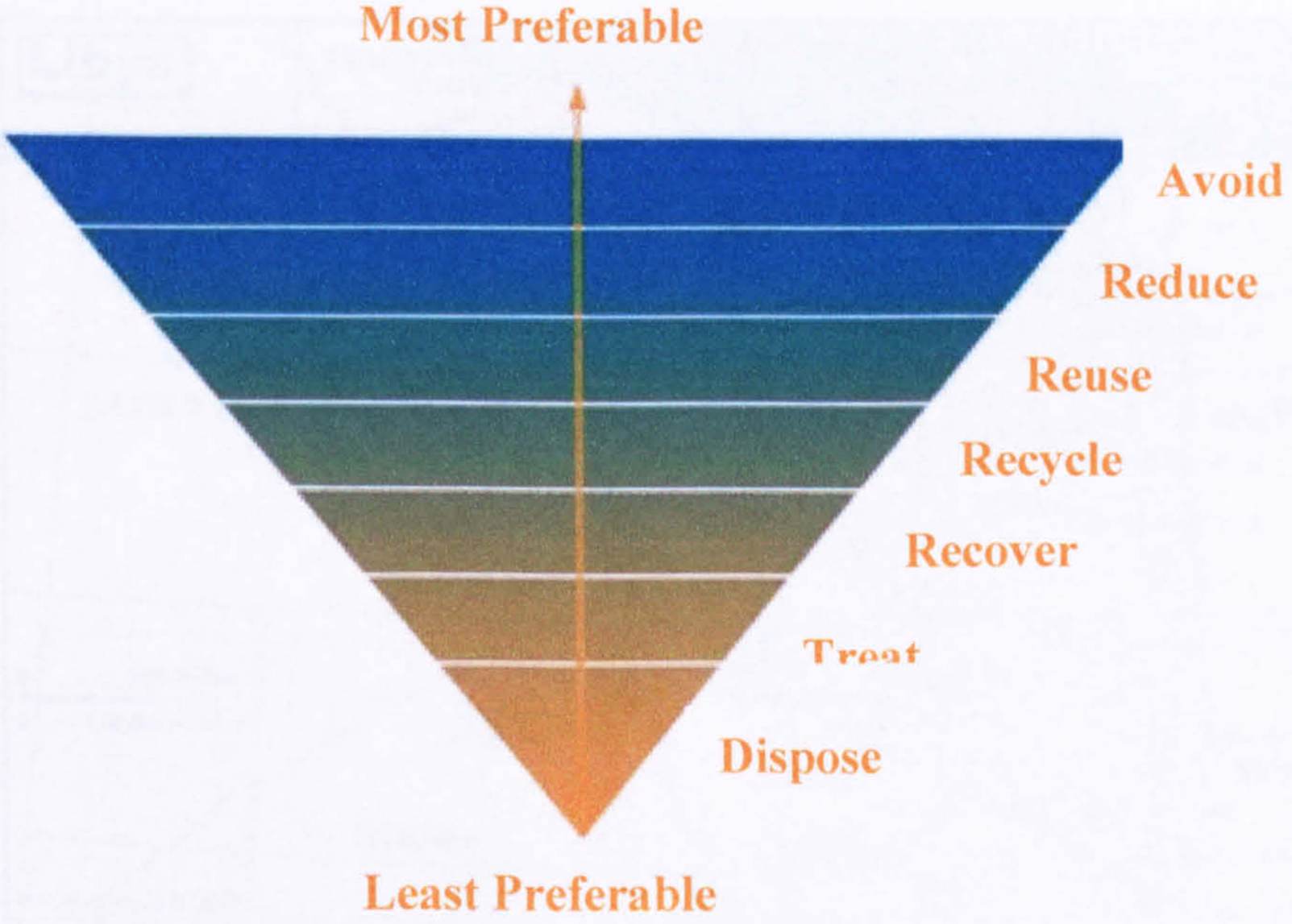


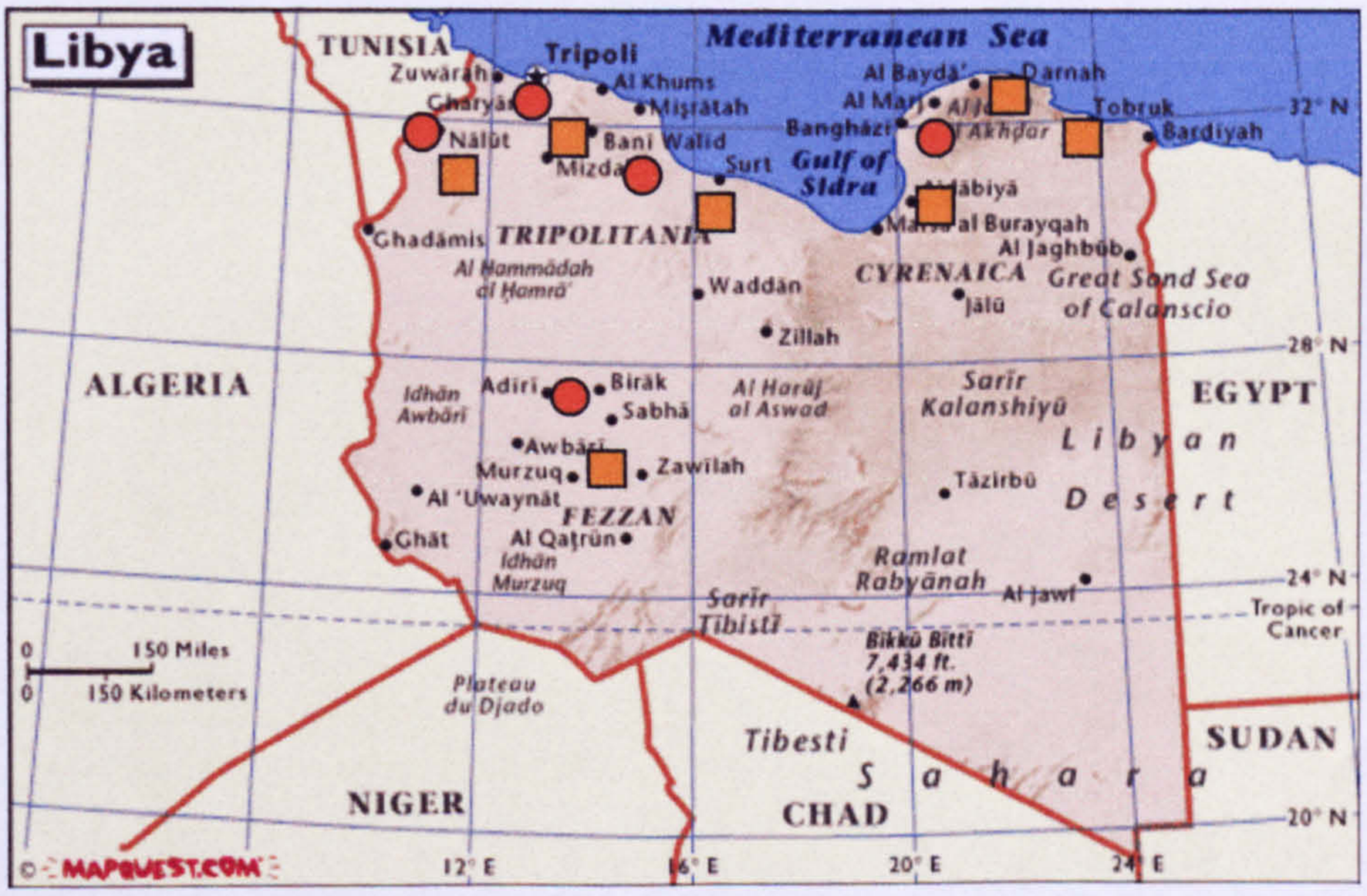
Figure 7.1: The waste management hierarchy

The aim of the waste management hierarchy is to extract the maximum practical benefits from products and to generate the minimum amount of waste. Source reduction involves efforts to reduce hazardous waste and other materials by modifying industrial production. It

also involves changes in manufacturing technology, raw material inputs, and product formulation. At times, the term "pollution prevention" may refer to source reduction.

At present, there are two main textile-processing complexes at Tripoli and Bani Walid, in Libya. There are other small textile and food industries located in different parts of the country. The locations of these factories are marked with dots and squares on the map in Figure 7.2

These textile and food industries are responsible for producing effluent containing low concentrations of coloured organic pollutants which include dyes, pigments and heavy metals. The discharges of toxic effluent streams from the textile and the food industries are directly fed to the water basins without using any procedures to control water pollution. Regular and direct discharge of wastewater has contaminated and disrupted the environmental ecosystem of the country.



● Textile complex factories, ■ Food processing factories

Figure 7.2 Location of textile and food industries in Libya

A change in attitude is now urgently needed to save the natural environment of Libya from the danger of serious pollution. The uses of natural dyes in textile industry along with the

implementation of stringent environmental regulations are now required to reduce the level of environmental contamination associated the management of textile effluent streams.

Figure 7.3 shows the present situation of waste management of synthetic dyes and food colours from aqueous solutions in Libya and Figure 7.4 outlines a new approach developed as a part of this study for the management of wastewater containing dyes.

Present situation

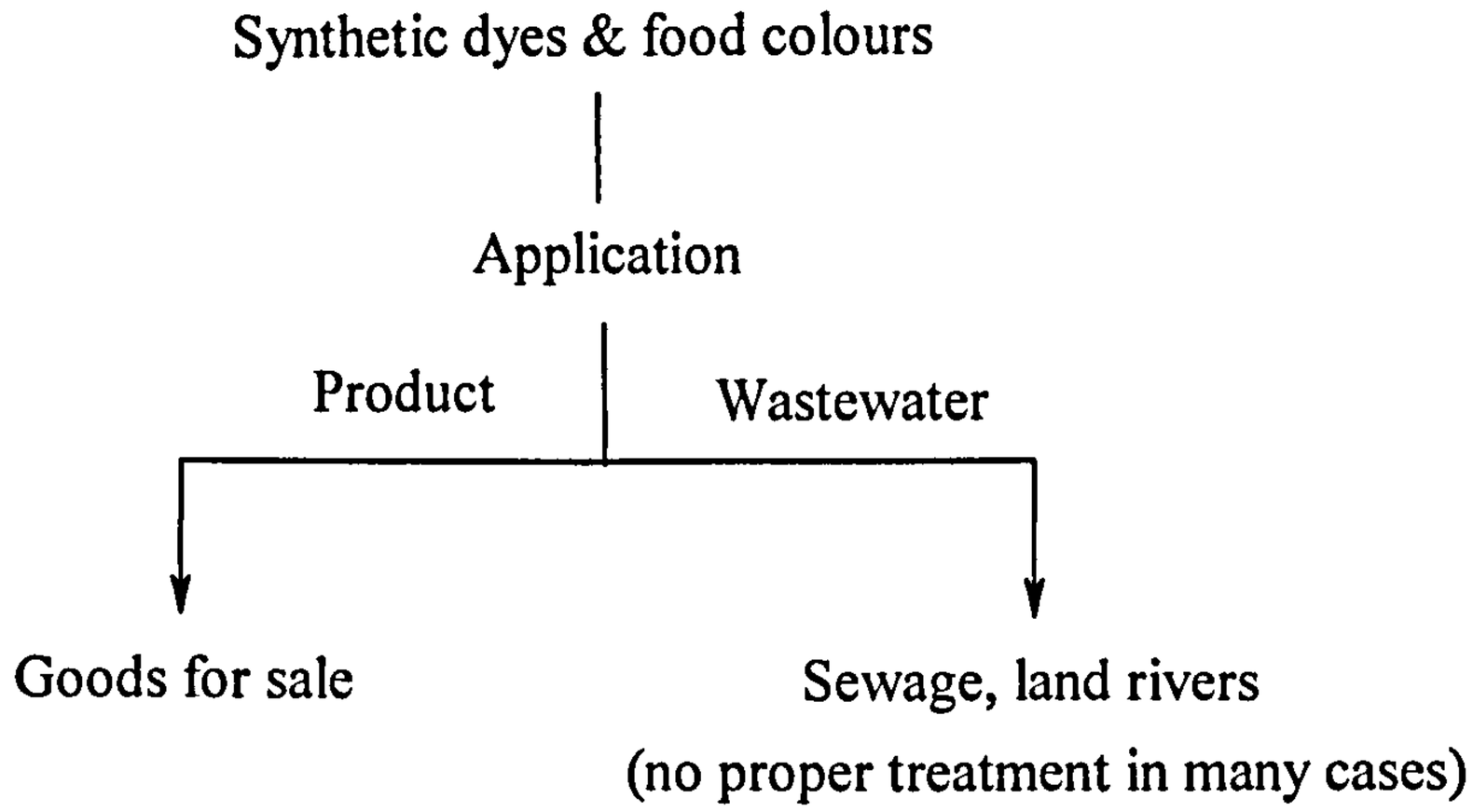


Figure 7.3: Present situation of waste management of dyes

Proposed management

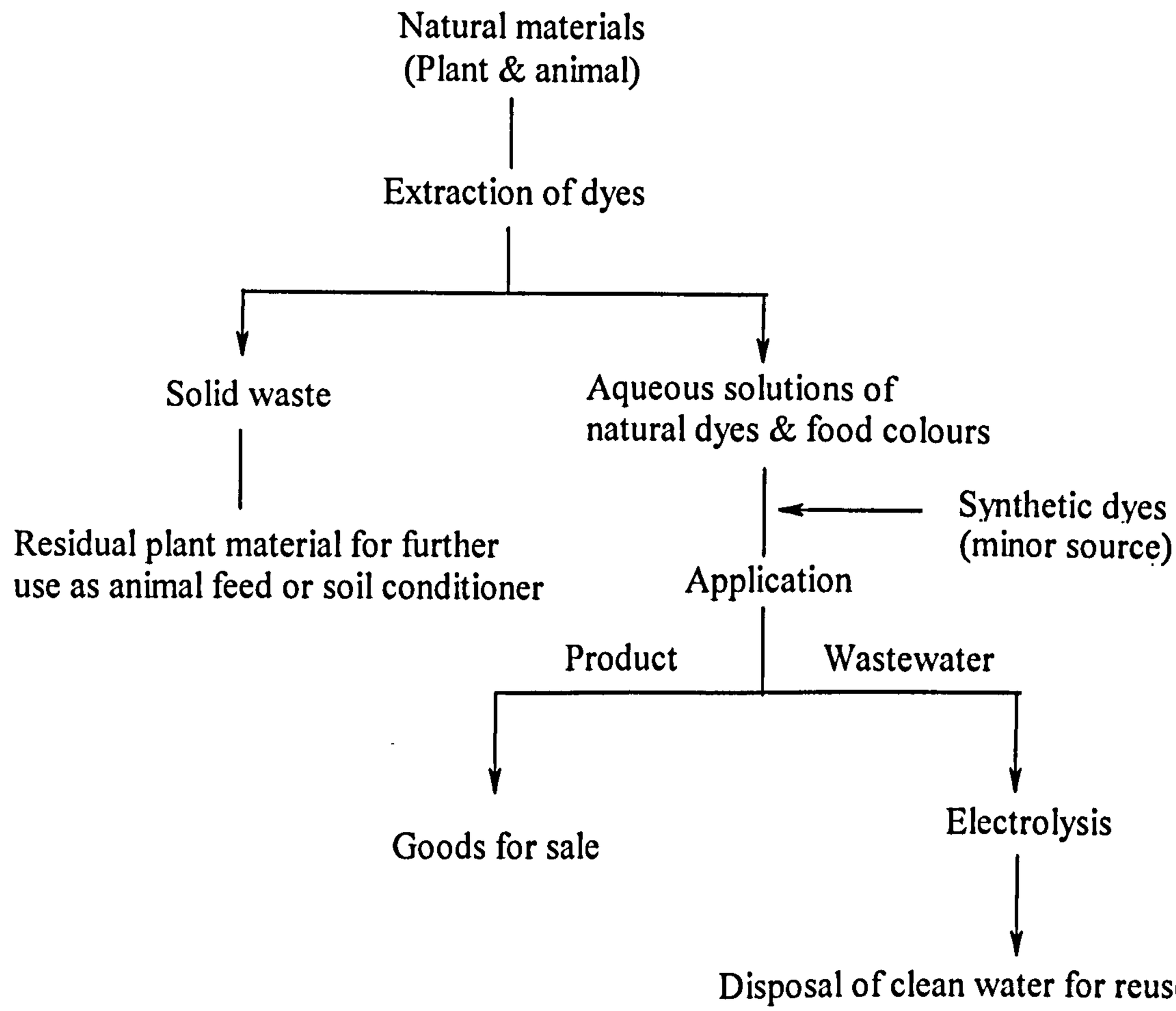


Figure 7.4: Proposed study and development of waste management of dyes

7.2 RECOMMENDATIONS FOR FUTURE WORK

Further investigation is required to identify and elucidate the chemical structures of the intermediate breakdown products and the final compounds present in the solution after the electrochemical oxidation and their toxicity level to the living organisms.

Regarding using natural dyes as an alternative to synthetic dyes, the following research areas are required to be conducted for future work:

- To improve the quality and yield of colourants from the plant by selection, conventional breeding, and by genetic manipulation and transformation.
- Development of large scale, efficient production and harvesting methods.
- To develop efficient systems of dye plant production (e.g., nutrition, pest, weed and disease control, husbandry, suitable rotations and soil types).
- To increase the efficiency of extraction of the dye from the plant.
- Storage issues related to dyestuffs and dye extracts.
- To determine the environmental impact of cultivating dye plant species.
- Markets for dyes and finished products.
- Consumer awareness of the renewable aspects of natural dyes, their wide colour palette, and good performance.
- A further area for work is the development of alternative uses for natural dyestuffs, e.g., as chemical sources for other products or non-dye uses for glucosinolates such as pest control.
- To investigate the antibacterial activity for tannins containing plants which could be very useful in developing clothing for infants, elderly and infirm people to protect them against common infections.