Development and Optimisation of Treatment Technologies For Environmental Pollution Control

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

By

Saboor Javaid

Institute for the Environment
Brunel University, London
United Kingdom

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DEDICATION

This thesis is dedicated to the memory of my loving late mother, Mrs Mussawar Javaid, who is still sorely missed 'God bless her'

&

Those who died in the devastating earthquake, October 2005 in Kashmir, Pakistan

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ABSTRACT

A number of sustainable and economically viable treatment methodologies have been developed and optimised to combat environmental pollution problems associated with the diversity and scattered nature of industries in Pakistan.

The use of both electro-precipitation and electro-oxidation processes are shown to lead to the removal of dyes from textile effluent streams originating from various operations. The use of the electro-precipitation process, however, leads to a secondary disposal problem because sludge produced has to be disposed of safely. The use of an electro-oxidation process does not produce sludge but is unable to remove some of the organic impurities from industrial textile effluent. Both processes do, however, result in colour removal from dye effluents with the degradation of dyes during electro-oxidation proceeding through the formation of different intermediate species before mineralization leading to complete mineralization in 30-40 minutes. Ames tests confirm that the treated effluent streams from both electro-precipitation and electro-oxidation processes are non-mutagenic.

The electro-precipitation process with mild steel anodes is also be used for the treatment of leather effluent streams to remove chromium by producing a mixed Cr(III) / Fe(III) hydroxide sludge. The same treatment process was successfully used for the simultaneous removal of dyes and chromium from mixed textile/leather effluent streams. The electro-precipitation process developed has been successfully tested on pilot scale at a textile mill in Faisalabad, Pakistan.

A number of transition metal supported catalysts were shown to be ineffective in the oxidation of volatile organic compounds. For this reason a method of preparing platinum group metal catalysts on inert supports at low temperatures was developed and used to oxidise toluene, as an indicator of volatile organic compounds. The preferred catalyst support is γ-Al_2O_3 which can be in the form of spheres or washcoated monoliths. In the case of γ-Al_2O_3 spheres and the γ-Al_2O_3 washcoated monolith complete oxidation of toluene was achieved at the relatively low temperatures of 236 and 268°C.

A number of novel room temperature ionic liquids (RTILs) were synthesised, characterised and their potential application for selective extraction of copper from industrial wastes is also reported. The solubility studies of different metal oxides in the RTIL, 1-(2-cyanoethyl)-3-methylimidazolium bromide, show that it can be used for the selective extraction of copper from industrial waste samples containing other metal oxides. This RTIL has the ability to selectively dissolve, copper, copper oxide and copper sulfide when the reaction is carried out in the presence of water

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GLOSSARY OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AL	Aluminium
BOD	Biochemical Oxygen Demand
BTEX	Benzene, Toluene, Ethylene and Xylene
CFB	Conventional Continuous-Flow Bio-filter
COD	Chemical Oxygen Demand
CPI	Cell Per Square Inch
CNS	Central Nervous System
DDT	Dichlorodiphenyltrichloroethane
DEFRA	Department for Environment Food and Rural Affairs
DOE	Department of the Environment
EQS	Environmental Quality Standards
ES&H	Environment Safety and Health
ETPI	Environmental Technology Programme for Industry
EP	European Patent
FID	Flame Ionisation Detector
GC	Gas Chromatography
Gr	Graphite
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HPLC	High Pressure Liquid Chromatography
ICME	International Council on Metals and the Environment
ICRCL	Interdepartmental Committee for the Redevelopment of Contaminated Land
IR	Infra Red Spectroscopy
M	Mutagenic
MEK	Methyl Ethyl Ketone
MCL	Maximum Contaminant Level
MM	Mixed Metal
MS	Mild Steel

MS	Mass Spectroscopy
MW	Microwave
NCSR	National Conservation Strategy Report
ND	Not Determine
NEQS	National Environmental Quality Standards
NM	Non-Mutagenic
NOEC	No Observed Effect Concentration
PAIs	Pesticide Active Ingredients
PCCI	Pakistan Chambers of Commerce and Industry
PEC	Predicted Environmental Concentration
PEPA	Pakistan Environmental Protection Agency
PHE	Potentially Harmful Element
PNEC	Predicted No Effect Concentration
POPs	Persistent Organic Pollutants
RDA	Recommended Daily Allowances
RO	Reverse Osmosis
RTILs	Room Temperature Ionic Liquids
SBB	Sequencing Batch Bio-filter
SEPA	Swedish Environmental Protection Agency
SDPI	Sustainable Development Policy Institute
SS	Stainless Steel
SS	Suspended Solids
TCDD	Tetrachlorodibenzo-P-Dioxin
TDS	Total Dissolved Solids
TM	Titanium Mesh
UV/Vis	UV/Visible Spectroscopy
UV/Vis	Uv/Visible Spectroscopy
US	United States
VOCs	Volatile Organic Compounds
WHO	World Health Organization
WTO	World Trade Organization
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

CHAPTER 1

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

There has been an immense change in the global environmental scenario during the last three decades. A large number of national and international organizations are now campaigning for action to control environmental pollution problems associated with various industrial activities. Governments have established departments for the environment and there has been a flurry of environmental law-making. This period is regarded as the 'new environmentalism', which had several roots, such as:

- Developed nations grew more affluent resulting in greater interest in a cleaner environment.
- There were sharp reminders in the 1952 smog in London and the mercury poisoning from fish in Japan, that pollution can kill [1].
- The accident in Bhopal, India, which claimed 4000 lives and injured tens of thousands more in December 1984, heightened concerns that protection measures were needed to reduce potential risk to the public from exposure to airborne toxic chemicals.
- There was evidence that DDT does not just vanish when sprayed on crops but that it accumulates alarmingly in plants and animals.
- There was public alarm over the environmental impact of nuclear weapon testing in the atmosphere, especially in the Pacific Ocean [2].

1.2 WHAT IS POLLUTION?

To define pollution may appear straightforward at first glance, e.g. "too high concentration of any chemical in any location". Scientists, politicians, legislators, enforcers and the public freely and frequently use the term, and the perception of its meaning is as diverse as the people who use it. There is one fundamental property of pollution, however, which is that it has an adverse effect, directly or indirectly, on life or on quality of life. If it does not affect life in any way then it should be described as contamination, not pollution. Since the biosphere interacts with all other quarters of the

globe (Figure 1.1), pollution may be anything which affects the hydrosphere, the lithosphere and the atmosphere – or water, soil and air, i.e., pollution acts predominantly upon an ecosystem

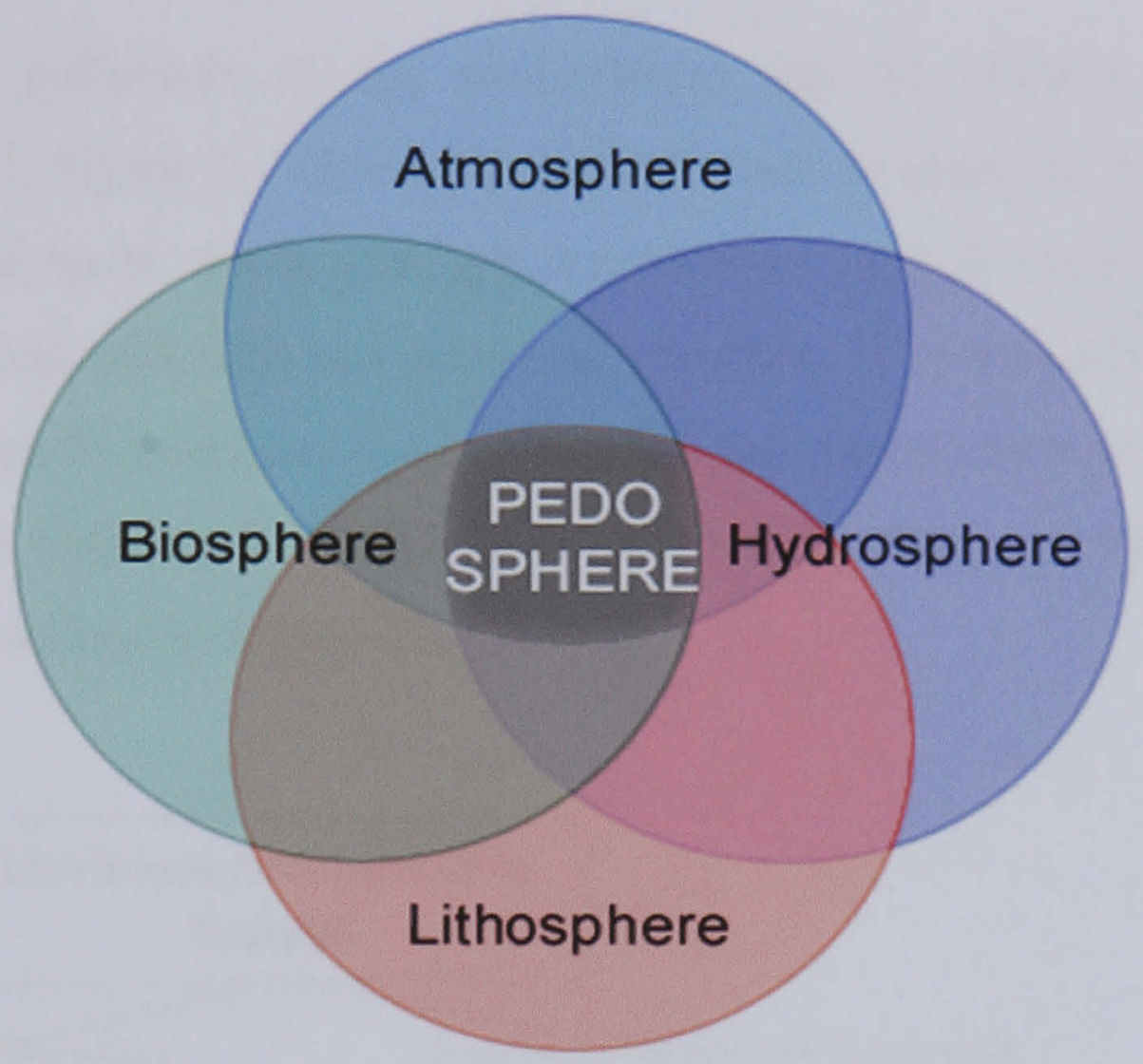

Figure 1.1: Global environmental system

Pollutants are materials that affect the global environment, with a detrimental effect on the biosphere. They may be chemical in nature but results could also be harmful physical phenomena, e.g. greenhouse gases leading to global warming. Those pollutants of a chemical nature, e.g. synthetic organic dyes, chromium from leather effluent, volatile organic compounds (VOCs) and heavy metals are the major concern of this thesis and the development of technologies to combat the problems associated with these pollutants are described in detail in later chapters.

1.3 SOURCES OF POLLUTION

In pollution science, the source refers to the site that has the potential to introduce pollutants into one of the three main environmental sectors, namely water, soil and atmosphere [3,4]. The concentrations of potentially harmful elements in soil, surface waters and groundwaters, or dust may arise from natural sources such as metalliferous ores and specific types of rocks such as black shales. A significant proportion of pollutants in the environment, for example, arise as a result of man's activities. These include emissions from textile, leather, electroplating, metal mining, smelting and

refining, power generation, manufacturing and transport, urban and household activities, waste disposal to landfill, combustion processes, the use of agricultural materials including pesticides and fertilizers, and the utilization/disposal of sewage sludge on farmland [5].

The sources of pollutants in the environment can be divided into natural and anthropogenic [3]. Figure 1.2 shows the outline waste streams for which the treatment technologies need to be developed and optimised to control environmental pollution problems associated with different industrial activities. The research work described in this thesis has been focussed on the development and optimisation of sustainable, robust and economically viable technologies to combat the problems associated with some of waste streams described in Figure 1.2.

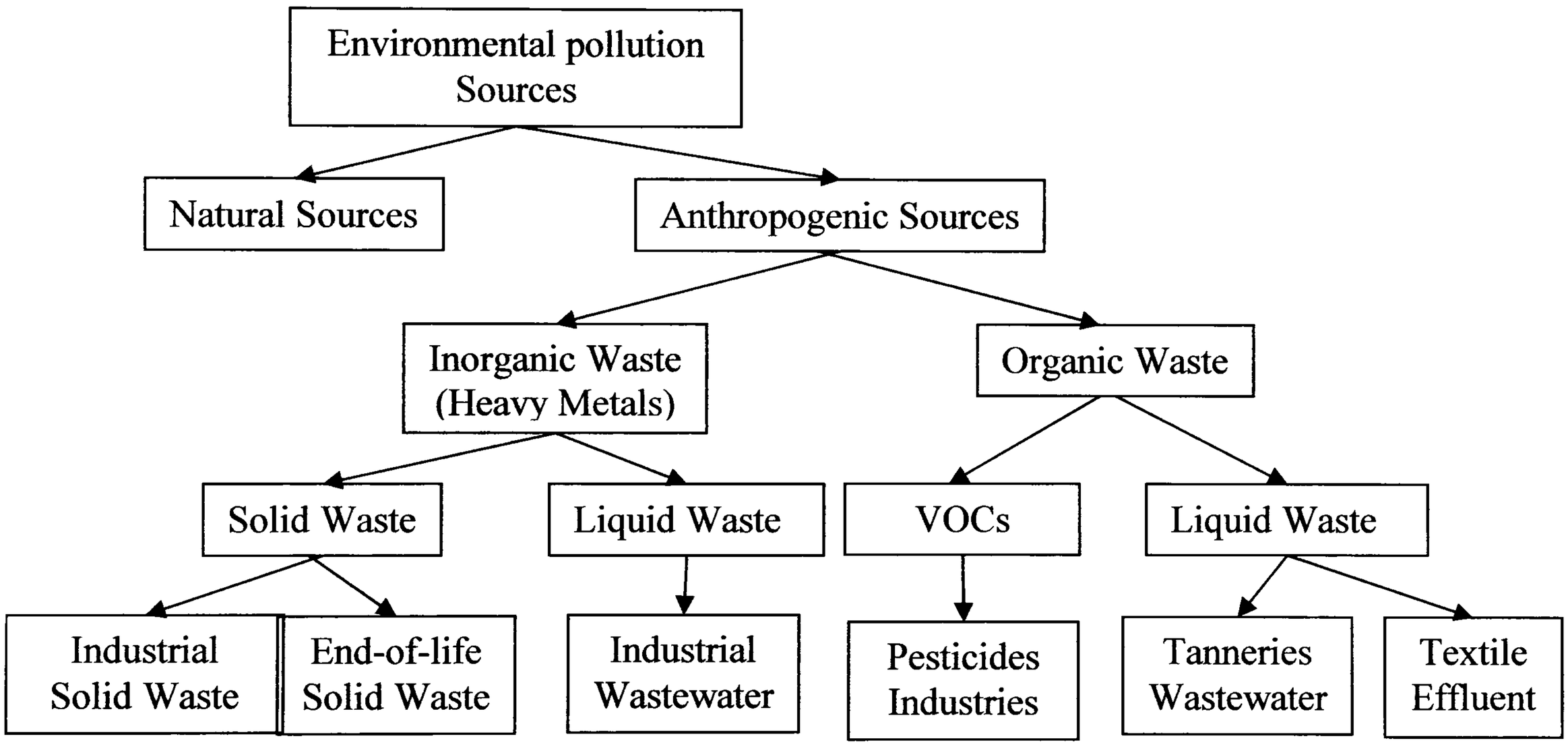

Figure 1.2: Environmental pollution sources and the nature of pollutants.

The following sections deal with contamination by natural and anthropogenic sources using heavy metals and organic pollutant as examples.

1.3.1 Natural Sources of Pollution

Background concentrations of heavy metals vary considerably depending on the geochemical nature of the underlying geological environment [3,5]. Some of the naturally occurring rocks are enriched with various metals including nickel, chromium,

lead, tin, uranium, molybdenum, arsenic, cadmium, and mercury. These natural sources can be responsible for high metal concentrations in the surface environment. Potentially harmful elements arising from these sources are closely related to their natural geochemical association [5-7].

The normal processes of weathering of rocks and the chemical breakdown of their minerals result in the redistribution of metals into the surface environment. Consequently, all metals are an inherent part of the natural environment, occurring in a great variety of forms or species [8]. In some parts of the world soils can contain up to 2500 ppm of arsenic and up to 2000 ppm of copper compared with the normal background concentrations of <5-40 ppm for arsenic and 2-60 ppm for copper. Soils containing high concentrations of other metals such as lead, zinc, cadmium, antimony and mercury are also found in many countries. These diverse, widespread, and in some cases detrimental, occurrences of metals in the biosphere are a result of natural processes [5].

'Natural background concentration' is the concentration of a species that is present due to natural causes only, while 'background metal concentration' is, for a soil, the concentration of a metal in that soil at sufficient distance from known mobile or point sources of contamination such that it is representative of typical soils for the region in question [9]. Background concentrations usually represent a negligible risk to the environment [10]. This is not the case, however, where elevated naturally occurring concentrations are found. These could give rise to difficulty in determining contamination levels relative to background concentrations, because they cannot represent background values which establish a reference level corresponding to unpolluted or non-anthropogenic conditions.

In the European Union legislation, the definition of pollution requires the contaminant to have been 'introduced by man'. The question then arises as to whether the elevated naturally occurring concentrations of some heavy metals should be regarded only as 'contamination'. This does not mean, however, that they will not cause harm. Petts et al. [11] suggest that the tendency to leave 'natural' contamination out of the regulatory definition is likely to be influenced by:

- The large target areas which would be covered
- The inherent political and psychological difficulty of accepting that areas where people have lived for centuries may be harmful to health
- Public perceptions, concerns and priorities relating to industrial pollution and the view that industry is the primary pollution source
- The difficulties and cost of dealing with 'natural' contamination
- The relative ease with which regulatory action can be directed to anthropogenic sources

It is very important to understand the magnitude of natural sources in order to develop approaches to assess the risk posed by metals in the environment. In terms of contaminated land regulation, there is the problem of whether or not any sites where elevated concentrations occur naturally should be designated as contaminated land. Thus, in the absence of a statutory definition of contamination arising from natural sources, it is unlikely that a regulator would try to find someone responsible for the contamination. If the contamination causes unacceptable threats to human health and the environment, regulators cannot take action against the owner of the land if the elevated values are from natural sources. In cases where high concentrations of metals result from both natural and anthropogenic sources, it is important that natural sources of contamination be distinguished from anthropogenic sources. In particular, when a liability issue is involved, this may cause difficulties in determining the extent to which the potentially liable person should be responsible for the contamination. Therefore, natural baseline information must always be taken into account when assessing the degree to which anthropogenic sources may have given rise to environmental pollution. Significant data gaps and uncertainties remain about the relative contribution of natural and anthropogenic sources of metals in various environmental media [8].

1.3.2 Anthropogenic Sources of Contamination

There are three principal areas of human activity which result in the liberation of pollutants into the natural environment: industry, agriculture and domestic life. Industrial activities are the major source of chemical pollutants and most environmental problems relate to the presence of excessive amounts of potentially harmful elements in water, soil or the atmosphere [3]. Among others, the harmful elements include heavy

metals and organic pollutants in various forms that flow into the environmental sectors and disperse having potential to harm humans, animals and plants and, in certain cases, may lead to death.

Anthropogenic sources of pollution can be divided into two groups *viz*: inorganic and organic and can be solids, liquids or gases.

1.3.2.1 Inorganic Pollutants

The main sources of anthropogenic heavy metal pollution are described in general in this section.

Mining Activities

The principal sources of potentially harmful metal species pollution from mines and associated mineral processing plants are water, solid wastes and airborne emissions. Water from mines, concentrators and tailing ponds frequently enters the drainage system. The waters are often highly acidic and, besides high concentrations of potentially harmful elements in solution, may carry potentially harmful element-rich particulates. Broken rocks and ore frequently find their way into the streams and rivers. Potentially harmful element-rich airborne contamination arises principally from dust blown off storage piles. A wide range of potentially harmful elements may be involved depending on the source [3]. The ultimate sources of metal contamination from mines are ore minerals and they may have several metals associated with them (Table 1.1). Many of these metals have already contaminated the environment in the vicinity of mines [12]. Discharges from non-ferrous metal mines may still contain high metal concentrations even after 100-150 years from cessation of mining activities. There may also be widespread pollution of the groundwater [13]. Some base metal mines contain large amounts of pyrite and marcasite and the oxidative weathering of these materials results in very acidic mine drainage water. In addition, the spoil tips associated with these mines contain metal sulfides that can be solubilised by bacterial activity involving species such as *thiobacillus thiooxidans* and *thiobacillus ferrooxidans*. Drainage waters from these sources have pH values as low as 2.6 and are heavily contaminated with metals such as zinc, cadmium and nickel [14]. Some common ore minerals of non-ferrous metals are listed in Table 1.1.

Smelting Operations

When the sulfide ore minerals are smelted to obtain the metals, it is necessary to roast or sinter the ores in air in order to convert the sulfides to oxides, which are subsequently reduced to the metal. This process gives rise to large amounts of sulphur dioxide; therefore metal smelters are among the major sources of atmospheric pollution [12]. Smelting activity may also result in very high concentrations of metals in the immediate vicinity and downwind of smelters because of atmospheric dispersions of particles mainly in the direction of the prevailing wind [15-16]. Metal concentrations in these areas tend to decrease rapidly with soil depth and distance from the smelter [17].

Table 1.1: Common ore minerals of non-ferrous metals [12].

Metal	Ore Minerals	Associated Heavy Metals
Ag	Ag_2S, PbS	Au, Cu, Sb, Zn, Pb, Se, Te
As	FeAsS, AsS	As, Au, Ag, Sb, Hg, u, Bi
	Cu ores	Mo, Sn, Cu
Au	Native Au, $AuTe_2$, $(Au, Ag)Te_2$	Te, AG, As, Sb, Hg, Se
Ba	$BaSO_4$	Pb, Zn
Bi	Pb ores	Sb, As
Cd	ZnS	Zn, Pb, Cu
Cr	$FeCr_2O_4$	Ni, Co
Cu	$CuFeS_2$, Cu_5FeS_4,	An, Cd, Pb, As, Se, Sb, Ni, Pt, Mo, Au, Te
	Cu_2S,Cu_3AsS_4 CuS, native Cu	
Hg	HgS, Native Hg, Zn ores	Sb, Se, Te, Ag, Zn, Pb
Mn	MnO_2	Various (e.g. Fe,Co, Ni, Zn, Pb)
Mo	MoS_2	Cu, Re, W, Sn
Ni	$(Ni,Fe)_9S_8$,NiAs,$(Co,Ni)_3S_4$	Co, Cr, As, Pt, Se, Te
Pb	PbS	Ag, Zn, Cu, Cd, Sb, Tl, Se, Te
Pt	Native Pt, $PtAs_2$	Ni, Cu, Cr
Sb	Sb_2S_3, Ag_3SbS_3	Ag, Au, Hg, As
Se	Cu ores	As, Sb, Cu, Ag, Au
Sn	SnO_2, $Cu_2(Fe,Zn)SnS_4$	Nb, Ta, W, Rb
U	U_3O_8	V, As, Mo, Se, Pb, Cu, Co, Ag
V	V_2O_5, VS_4	U
W	WO_3, $CaWO_4$	Mo, Sn
Zn	ZnS	Cd, Cu, Pb, As, Se, Sb, Ag, Au, In

Industrial Activities

In this section the concept of 'industrial' waste is described with examples. Waste is generated by different industrial activities and can be solid, liquid or gaseous. The major sources of waste, both solid and liquid, are municipal and industrial. This research is aimed at dealing with industrial waste, in particular solid and liquid industrial wastes from the chemical, petrochemical, pharmaceutical, pesticides, mining and textile industries and tanneries.

The term industrial solid waste refers to all wastes produced by industrial operations or derived from manufacturing processes [18]. Industrial solid wastes encompass food wastes, ash, construction and demolition wastes, special wastes, hazardous wastes and inorganic and organic wastes from processing and manufacturing industries [19].

The solid wastes generated are classified according to their composition. In surveys of waste the following categories have been identified.

- Paper and cardboard, including office materials, packaging and industrial paper.
- Glass, including bottles from the eating establishments, packaging and construction wastes, car windshields and raw materials from factories manufacturing lamps, mirrors, window panels, and glassworks in general.
- Plastics, including packaging and various other wastes (packaging materials containing hazardous products are included in the hazardous waste group).
- Wood, including splinters, sawdust and other residues from the wood sector activities, in furniture factories and sawmills.
- Metals (e.g., iron, aluminium, bronze, lead, copper, steel and brass) from packaging, construction materials, automobile mechanics and metal sector transformation processes.
- Textiles, including clothing, industry wastes (mainly jute and cotton) and upholstery (both fabric and leather).
- Inert wastes from the construction sector industries. These include demolition wastes, sand, gravel and other wastes.
- Solid wastes from bars, restaurants and food sector industries. Their composition is essentially organic with a small amount of packaging, paper, glass, etc [18].

Industries have traditionally managed their waste products by discharging them into the environment without prior treatment. This practice resulted in an increase of pollution and produced negative environmental impacts. Recent legislation has, however, resulted in a change in the whole concept of waste and effluent control and the emphasis is now on reuse, recycle and recovery before final disposal [20]. For this reason it is reasonable to assume that the projected quantities of waste may be significantly reduced with the development of new clean-up technology and waste minimization schemes [21].

1.3.2.2 Organic Pollutants

A number of organic pollutants are described in this section as examples of the problems associated with organic chemicals in the environment. A great number of industries such as textile, paper/pulp, printing, coke, petroleum, pesticide, paint, solvent, pharmaceuticals and wood-preserving chemicals, consume large volumes of water and organic based chemicals. These organic chemicals have large differences in chemical composition, molecular weight, toxicity etc. Many persist in the environment for long periods of time and hence are known as persistent organic pollutants that can cause serious health and environmental problems. There is growing concern about organic pollutants that have a potential for causing neurological disorders, suppressing the immune system, increasing the risk of cancer and causing endocrine disruption etc. Organic pollutants can be transported by air and water and many move through the soil. Effluents of many industries may also contain undesired quantities of organic pollutants and therefore need to be treated before their discharge into any medium.

Many persistent organic pollutants were widely used during the boom in industrial production after World War II, when thousands of synthetic chemicals were introduced into commercial use. Many of these chemicals proved beneficial for pest control, crop production and industry. These chemicals, however, can also produce unforeseen effects on human health and the environment especially when they are stable molecules and can accumulate and pass from one species to another through the food chain [22-30]. To address this concern, a conference was held in Stockholm, Sweden, in May 2001 where the treaty known as the Stockholm Convention was signed by more than 90 countries who promised to reduce or eliminate the production, use and release of twelve key persistent organic pollutants (Table 1.2), which are know as "the dirty dozen''.

Table 1.2: The key persistent organic pollutants – the dirty dozen

Persistent Organic Pollutants	USE
Aldrin	Crop insecticide (corn, cotton)
Chlordane	Crop insecticide (cotton, citrus, vegetable potatoes)
DDT	Crop insecticide (cotton)
Dieldrin	Crop insecticide (corn, cotton)
Endrin	Crop insecticide (grains, cotton)
Heptachlor	Crop insecticide (termites and soil insects)
Hexachlorobenzene	Fungicide for seed treatment
Mirex	Insecticide (termites, fire ants)
Toxaphene	Insecticide (livestock and crop)
PCBs e.g. 2,4-D and 2,4,5-T	Industrial chemical (heat exchange fluid for electrical transformers, paint and plastic additive)
Dioxins	Unintentionally produced during combustion
Furans	Unintentionally produced during combustion

Globally, an alarming level of pesticides has been reported in air water and soil as well as in foods and biological materials. Some of these pesticides have been reported to be persistent, toxic, mutagenic and carcinogenic. Pesticide contamination of water systems is also a major concern as residues reach the aquatic environment through manufacturing plants, direct surface run-off, leaching, careless disposal of empty containers, equipment washings, etc. Pesticides are divided into many classes, of which the most important are organochlorine and organophosphorous compounds. The chemical stability of organochlorine compounds is reflected in their resistance to microbial degradation. The lipophilic nature, hydrophobicity and low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues and subsequent magnification of concentrations in organisms progressing up the food chain. Organophosphorous pesticides on the other hand are known to degrade rapidly depending on their formulation, method of application, climate and the growing stage of the plant. The most important and common pollutants among organochlorine pesticides are dichlorodiphenyl-trichloroethane and its metabolites, polychlorinated biphenyls, hexachloro-cyclohexane isomers, chlordane related compounds, hexachlorobenzene, cyclodienes, dieldrin, etc. The wide range of pesticides used makes it extremely difficult to produce a single method for pesticide disposal that applies universally [31-58].

Phenol and its derivatives are another group of organic pollutants which are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential to harm human health. It should be noted that the contamination of drinking water by phenolics even at concentration of 0.005mg l^{-1} could bring about significant taste and odour problems making it unfit for use. Human consumption of phenol-contaminated water can cause severe pain leading to damage of the capillaries ultimately causing death. Phenol-containing water when chlorinated during disinfection of water also results in the formation of chlorophenols. The most important pollution sources containing phenols and phenolic compounds such as nitrophenols, chlorophenols, are the wastewaters from the iron-steel, coke, petroleum, pesticide, paint, solvent, pharmaceutical, wood preserving chemicals and paper and pulp industries [54-57].

1.4 THE POLLUTANT LINKAGE CONCEPT

Environmental pollution means that there is a presence of hazardous substances or constituents that pose unacceptable risks to the environment, humans, animals, plants or ecological receptors. Pollution risk assessment uses a pollutant model which refers to the relationship between a pollutant and a receptor. This section, therefore, describes the concept of heavy metal contamination and guideline concentrations, contamination pathways and target or receptor.

A **contaminant** is a substance which has the potential to cause harm or to cause pollution of controlled waters.

A **pathway** consists of one or more routes or means by, or through, which a receptor is being, or could be exposed to or affected by the **contaminant**.

A **receptor** is the receiving system that could be harmed by a contaminant and it falls into one of the following categories a) human beings, b) ecological systems, c) buildings, d) crops and e) controlled waters.

To form a pollutant linkage, contaminants, pathways and receptors must directly relate to each other and be present in a specific identified area. When these requirements are met the relevant linkage is said to be a significant pollutant linkage. In this section contamination with heavy metals is used to illustrate the pollution linkage concept.

1.4.1 Heavy Metal Contamination and Guideline Concentrations

The heavy metal poisoning of humans is rare and is usually from industrial or domestic sources rather than from the natural environment. Excessive exposure to lead has been detected in a study of blood lead concentrations in the Leadhills historical mining area of southern Scotland, although no symptoms of ill-health were detected [59]. High blood lead levels, however, were reported in children from the historical metalliferous mining areas of Derbyshire [60]. Even though lead poisoning was a hazard in the lead mines of Derbyshire, there is no firm evidence of significant ill health amongst people exposed to high concentrations of lead in this area and other similar areas. For instance, although high soil-lead concentrations are transferred to the child via the soil-dust-hand-mouth pathway, blood lead levels within an old lead mining village in the Pennines, UK, were found within the normal national range, because of the extremely low solubility of pyromorphite, the end-product of the weathering of lead compounds [61].

A guideline value is a criterion for deciding what trigger level is acceptable to plants, animals and humans and the standard to which contaminated land should be remediated, but the guideline value approach has been subjected to much criticism [62]. A central problem is whether the guideline value is based on sufficient information on metal speciation and bioavailability, toxicity, dose-response relationship etc. in dealing with heavy metal contamination from contaminated land. The advisory guideline values in the UK (Table 1.3 & 1.4), for example, have a number of weaknesses [62]. Including the limited range of contaminants covered; the lack of action values for some substances; trigger levels not derived in a consistent way for all substances; a lack of consideration of environmental hazards; the lack of consideration of metal speciation and leachability and the lack of linked and strictly specified sampling and analytical protocols [3].

Dickson [63] summarised common problems associated with advisory soil guideline values. These guideline values address (1) only widely acknowledged zootoxic and phytotoxic metals and (2) cover an incomplete range of situations ignoring synergistic, antagonistic and additive effects of metals; (3) use metal concentration and not speciation; (4) make no allowance for soil type, pH and organic matter; (5) lack any guidance for land which is currently in use and (6) do not specify or validate analytical methods for detecting contaminants in soil. The Department for Environment Food and

Rural Affairs (DEFRA) in the UK funded research to investigate the derivation of generic risk-linked guideline concentrations for potentially harmful elements and other contaminants in soil over several years [64]. The aim was to base the guidelines on the modelling of toxicological data although this may be made difficult in some cases by the lack of a reliable dose-response relationship between the concentrations of potentially harmful elements in soil and the level of risk to human health [3].

Table 1.3: Provisional soil guideline concentrations for the assessment and redevelopment of contaminated land adapted from International Concentration and Redevelopment of Contaminated Land (ICRCL)

Contaminants	**Planned Uses**	**Threshold Trigger Concentration (Mg/kg air-dried soil)**
Group A: Contaminants which may pose hazards to health		
Arsenic	Domestic gardens, allotments	10
	Parks, playing field, open spaces	40
Cadmium	Domestic gardens, allotments	3
	Parks, playing field, open spaces	15
Chromium (Total)	Domestic gardens, allotments	600
	Parks, playing field, open spaces	1000
Lead	Domestic gardens, allotments	500
	Parks, playing field, open spaces	2000
Mercury	Domestic gardens, allotments	1
	Parks, playing field, open spaces	20
Selenium	Domestic gardens, allotments	3
	Parks, playing field, open spaces	6
Group B: contaminants which are phytotoxic but not normally hazards to health		
Boron (Water-soluble) (2)	Any uses where plants are to be grown (1,5)	3
Copper (3,4)	Any uses where plants are to be grown (1,5)	130
Nickel (3,4)	Any uses where plants are to be grown (1,5)	70
Zinc (3,4)	Any uses where plants are to be grown (1,5)	300

Notes on Table 1.3

(1) The soil pH is assumed to be about 6.5 and should be maintained at this value. If the pH falls, the toxic effects and the uptake of these elements will be increased.

(2) Determined by standard ADAS method (soluble in hot water)

(3) Total concentration (extractable by nitric/perchloric acids)

(4) The phototoxic effects of copper, nickel and zinc may be additive. The trigger concentrations given are those applicable to acid sandy soils. In neutral or alkaline soils, phytotoxic effects are unlikely at these concentrations.

(5) Grass is more resistant to phytotoxic effects than are most plants and its growth may not be adversely affected at these concentrations.

Conditions for the Values in Table 1.3

- *All values are for concentrations determined on 'spot' samples based on an adequate site investigation carried out prior to development. They do not apply to analysis of averaged, bulked or composite samples, nor to sites, which have already been developed. All proposed values are tentative.*
- *The lower values in Group-A are similar to the limits for metal content of sewage sludge applied to agricultural land. The values in Group-B are those above which phytotoxicity is possible.*
- *If all sample values are below the threshold concentrations then the site may be regarded as uncontaminated as far as the hazards from these contaminants are concerned. Above these concentrations, remedial action may be needed.*

Table 1.4: Guidelines for toxic element trigger concentrations in mine spoil contaminated 'soil', in mg/kg air-dry weight adapted from ICRCL [65].

Element	Threshold Trigger Concentration (a)	Maximum (Action Trigger) Concentrations (Values not to be exceeded for use as specified)	
		For grazing livestock (b)	For crop growth (c) (Risk of phytotoxicity)
Arsenic	50	500	1000
Cadmium	3	30	50
Copper	250	500	250
Fluoride	500	1000	--
Lead	300	1000	--
Zinc	1000	3000	1000

Notes on Table 1.4

(a) These concentrations are acceptable only when soil contamination is derived from mine spoil. In other situations the elements may be present in forms which are more available to plants and animals when lower trigger concentrations will be appropriate.

(b) For calves, sheep and horses, assuming that plant uptake is normal, the stock is continuously exposed to these concentrations and it is proposed to manage the sward in such a way that only a relatively low level of soil contamination of herbage will occur. In such cases, the soil ingestion may be much higher.

(c) *For clover and the more productive sown grass species assuming a soil pH of at least 6.0. Metal tolerant cultivars are available, but these are intended for amenity or recreation after-uses and advice should be sought before they are used in agricultural mixtures.*

1.4.2 Contamination Pathways

The pathway is the route (both direct and indirect) in the environment by which contaminants may reach the targets of concern. In other words, it is the link between the source and the possibly exposed target. Within the pathway, chemical release mechanisms (e.g. leaching), transport mechanisms (e.g. groundwater flow), transfer mechanisms (e.g. sorption) and transformation mechanisms (e.g. biodegradation) will be important in determining the concentration of a contaminant at the point at which the target is exposed. The chemical form and physical properties of the contaminant determine the behaviour in the environment. For potential adverse human health effects, a chemical must be toxic, mobile and in a bio-available form.

In the environment, a chemical may change its characteristics by combination with other entities and its concentration may be modified by dispersion, dilution, degradation and adsorption [4]. Metals and their compounds may for example be released as solutions, colloids or suspended particles in aqueous effluents, or as gases, aerosols or dusts from smelter stacks, ore stockpiles and tailings or during transportation. Having

been released, they follow normal geochemical and ecological pathways until they reach sinks such as sediments, soils or biota [66].

The dispersion or transfer of contaminants along the food chain may be by three major pathways i.e. uptake by crops, livestock and people. Factors that affect potentially harmful element mobility in the soil and hence their availability to the growing plants and crops include physical (structure, penetrability), chemical (pH, speciation, concentration) and biological factors [67]. The risk of poisoning livestock is almost totally dependent on the concentration of toxic elements in the soil and the quantity of soil ingested, rather than on the concentration of the potentially harmful elements in the herbage, which is usually very much less than in the soil [3].

The main pathways of transfer of potentially harmful elements from sources to human are water, soil, dust and food. The full understanding of the pathways of exposure is an essential part of the risk assessment framework for contaminated sites. There are several likely pathways of human exposure [68], such as:

- Ingestion of contaminated soil and dust
- Dermal contact with soil and dust
- Inhalation of dust
- Inhalation of vapours
- Intake of drinking water
- Intake of vegetables grown on the contaminated site
- Intake of fish from nearby surface water

1.4.2.1 Speciation and Bioavailability

The bioavailability and hazard potential of a metal can vary greatly between different forms and species of metals. Thus, identification of each metal species present is important. Bioavailability means the potential for a substance in the environment to be incorporated by living organisms [8]. Rarely is all the substance that is ingested or otherwise taken into an organism absorbed by that organism. This means that a value for total metal in a real environmental sample is almost always an overestimate of the amount of the metal that is available for biological absorption [9]. Environmental parameters, such as pH, redox potential, organic matter, salinity, temperature, particle

size, etc. can significantly influence the behaviour and bioavailability of metals within the medium of interest [69].

Each metal occurs in hundreds of different minerals or compounds in nature [7]. Speciation is the identification of the exact nature of the phase containing the metal. Speciation of metals thus involves determination of the physical and chemical forms of the metal-containing species. This includes the evaluation of free metal ions, inorganic and organic complexes, and organometallic compounds and solid soil phases containing the metal [70]. Metal species (particularly those in solution) are inherently labile, in that they have a tendency to change form under different environmental conditions. Metals are subject to a variety of physico-chemical processes, including complexation and disassociation, oxidation and reduction, precipitation and dissolution, and adsorption and absorption. In addition, some metals may undergo microbial transformations that are reversible and that can either increase or decrease the availability of metals, depending on local physico-chemical conditions. Different metal species present different solubilities and availabilities to living organisms [70]. Metal speciation plays a critical role in the determination of bioavailability for human health and environmental risk.

Most heavy metals have a tendency to convert, over time, to less soluble and mobile forms that are not bioavailable [8]. Soil pH is often regarded as the most important factor controlling the chemical behaviour of metals in soils. For instance, metallic cations such as Cu^{2+} and Mn^{2+} are most mobile under acid conditions, and an increase in pH reduces their solubility and bioavailability. Some metallic anions, however, such as molybdate and selenate become more soluble and available with increasing pH [71]. When determining the bioavailability (or potential availability) of metals in soil, a number of different analytical methods have been used, and there has been misunderstanding and confusion with regard to the terms used to describe the potential availability of metals.

Often risk assessments and environmental quality standards consider only the total concentration of the substance for example, a metal. If the basis of risk assessment is to establish the potential risk, total concentration may not be the primary concern, as many heavy metals are held in complexes and mineral structures that render them relatively

immobile with respect to plant and animal uptake [11]. Understanding the speciation and thus bioavailability of a metal improves our understanding of the potential for exposure. [70]. A standard exposure assessment assumes that the total concentration of a metal is bioavailable and able to be absorbed. Evidence shows, however, that most of the metals in soil are in a highly insoluble form and are not absorbed upon ingestion of soil. A scientifically complete exposure assessment should take into account any available data on differences in bioavailability of different forms of metals [8]. For example, Van Assche *et al* [72] have carried out environmental risk assessment for the essential element zinc, integrating bioavailability with the natural pH range, essentiality, slowing ecotoxic and homeostatic ranges.

Total concentrations may be used as initial indicators of the presence of particular contaminants (i.e. as a screening mechanism) [11]. When the concentration exceeds the trigger concentration, then site-specific risk assessment, which must consider bioavailability and other factors, should be carried out. In this regard, risk assessment is a particularly important methodology. In all kinds of risk assessment, the importance of consideration of bioavailability is paramount. While the significance of metal speciation has been recognised in the scientific community for many years, it has usually not been given adequate emphasis in risk assessment and risk management, often because of insufficient data on specific metal species and their bioavailability.

New research is helping to distinguish the different risks that are associated with different metal species, which should permit increased attention to metal speciation regulatory decision-making [8]. To ensure progress in this area, criteria for determining the acceptability of analytical methodologies need to be developed. The need for low-cost, reproducible analytical methodologies for speciation to reduce uncertainty in risk assessment must be emphasised.

1.4.3 Contamination Targets or Receptors

According to Petts *et al* [4], a sensitive target must be present if a risk is to be realised. The target (sometimes referred to as the receptor or the endpoint in ecological assessments) is the point at which damage may occur if the contaminant is present at a level sufficient to cause the harm. Petts *et al* [4] have suggested five types of targets that may be of the concern:

- Environmental quality: soil contamination, air pollution, surface-water pollution and groundwater pollution.
- Flora and fauna: stress, reproductive effects, reduced growth, toxic effects, teratogenicity, death and loss of habitat.
- Humans: toxic effects, carcinogenicity, teratogenicity, mutagenicity, death, sensitisation and adverse health effects as a result of stress.
- Materials and buildings: deterioration of materials by chemical attack, corrosion.
- Socio-economic: loss of land value, additional costs to develop, costs of long-term monitoring, delays in selling/developing land, stress in affected populations, perceived loss of amenity, disruption to personal plans and fear, particularly of potential adverse health impacts.

1.4.3.1 Essentiality and Toxicity

The existence of potentially harmful substances in the environment need not always be of toxic concern. The level of toxicity of a substance relates to the amount that causes an adverse effect and to some extent the nature of the effect [73]. Many non-ferrous metals are essential nutrients for humans and other organisms. All living species are absolutely dependent on the presence of metal salts in their food in order to maintain their life and reproductive capacity. Because non-ferrous metals are abundant constituents of the earth's crust, it is not surprising that life forms have become dependent on many metals. Inadequate availability of essential metals can lead to serious health or environmental problems as much as can an over-abundance of the same metals [8]. Many elements such as copper, selenium and zinc are essential at low concentrations but may be toxic at higher concentrations or at very low 'deficiency' concentrations. "Essential" means that they are necessary for plant, animal and human health and growth [5]. Man and animals require copper, cobalt, iron, manganese, molybdenum, selenium and zinc whereas plants require the metals copper, iron, manganese, molybdenum, nickel and zinc.

The toxic effects of an element are measured by its dose-response relationship. In assessing the risk of those elements to plants, animals and human health, it is important to take dose-response assessment and exposure assessment into account. While metal toxicity in plants, animals and humans is dependent on various factors, the balance between essential and toxicity levels is difficult to quantify. Essential roles for arsenic,

nickel, tin and vanadium have also been established in animal nutrition. In plants, deficiencies may limit normal growth, development and reproduction, at times leading to visible symptoms and reduction of crop yield and quality. Trace element deficiency is a serious matter in humans, particularly in infants, leading to abnormalities in bone, skin and liver development as well as in the mental development. Excessive amounts of some of these metals may be toxic to plant and/or animal life or may affect the quality of water or foodstuffs for human consumption [5]. In some circumstances, elements may have either antagonistic or synergistic effects on the biological properties of other elements. A toxic element may be either helpful in reducing the toxic effects of another, or add to its toxic effect [73]. Some plant species are more susceptible to deficiencies of metal than others, while some are more tolerant to large amounts than others. Some plants grow only in soils containing high concentrations of specific metals particularly copper, nickel and cobalt in mining areas [5].

The incorporation of ecological risk assessment into the regulatory process is relatively new and poses a number of scientific questions and research requirements. Methods of aquatic and terrestrial toxicity testing have been proposed but must be viewed with caution as they require more rigorous evaluation and refinement. Ecological risk from exposure to heavy metals and other substances has been related to the criteria of toxicity, bioaccumulation and persistence. There is some doubt, however, as to the validity of applying the values derived from tests to field situations. While industrial exposure to many metals, and, in particular, to certain compounds of metals, that may be toxic at the much higher exposures encountered in the occupational settings, there are relatively few proven cases of human mortality resulting from metal contamination of the environment [5].

A number of data sets (such as geochemical data, including geographical distribution, metal speciation and nutritional data) are required to adequately address essentiality. The development of essentiality-toxicity curves for species requires further effort and research. Traditional methodology for safety assessment, in animals, humans or plants, may result in estimates of tolerable levels protective of human health or ecosystems, which are less than recommended daily allowances (RDA) for nutritionally essential metals. Therefore, for risk assessment of metals and their inorganic compounds, consideration of the adverse effects of deficiency must be considered in addition to the

potential for toxicity at higher exposures [69]. In risk assessment methodology, the "predicted environmental concentration" (PEC) of a substance is compared with its "predicted no effect concentration" (PNEC), the environmental level at which no adverse effect on ecosystem function is to be expected.

Environmental concentrations can be estimated from model predictions but follow, preferably, from straightforward environmental monitoring. The PNEC is derived from ecotoxicity data obtained on distinct organisms under laboratory conditions. In spite of the artificial nature of such data and their lack of connection with the higher levels of ecosystem organisation, this approach might be the only one feasible for assessing the multitude of man-made existing and new chemicals.

Current methods for PNEC determination include the safety factor approach and the statistical extrapolation model. When applied to the natural essential elements, however, several conceptual problems and inconsistencies with biological reality arise. As a general approach in risk assessment, a safety factor is applied to the lowest ecotoxicity values observed in a database on a given substance. The safety factor varies with the uncertainty of the ecotoxicity value that is referred to. When applied to natural essential elements, however, such an approach often leads to PNECs or tolerable levels below the essential element's natural concentration range and the acceptable daily intake. At the same time, such PNECs would also be situated at concentrations that are deficient for many organisms in the ecosystem. The safety factor approach is thus not applicable to essential elements [72]. Therefore, the need to develop specific approaches for the assessment of risk associated to the exposure of essential elements has been recently recognized [74].

The new alternative approach for essential elements takes their natural occurrence (including bioavailability), their essentiality and potential toxicity into account. In the case of essential elements, since there are significant risks associated with low intakes as well as high intakes, the relationship between intake/exposure level and risk has in fact a U shape (Figure 1.3). That is, there are risks of deficiency associated with low intakes and risks of toxicity associated with high intakes. For essential elements, risk assessment for humans requires the definition of the normal homeostatic range for the metal of concern. Ideally, when assessing risk to organisms in the environment,

information at the population or community level should be available. Since this is rarely the case, experimental animals and plants have to be used to estimate a range of no observed effect concentration (NOEC) for toxicity. As some metals fulfil a nutritional function, test concentrations need to be reduced below the NOEC for toxicity for a few representative organisms in order to define the deficiency dose-response curve for the organisms living in a given habitat [69]. In other words, in an alternative risk assessment for essential elements there is a need to estimate exposure range in organisms in selected habitats, then to establish the range of deficiency curve and of toxicity for environmental organisms. In addition, it must be considered that essential elements can be rate limiting at both the deficiency and toxicity side of the homeostatic range.

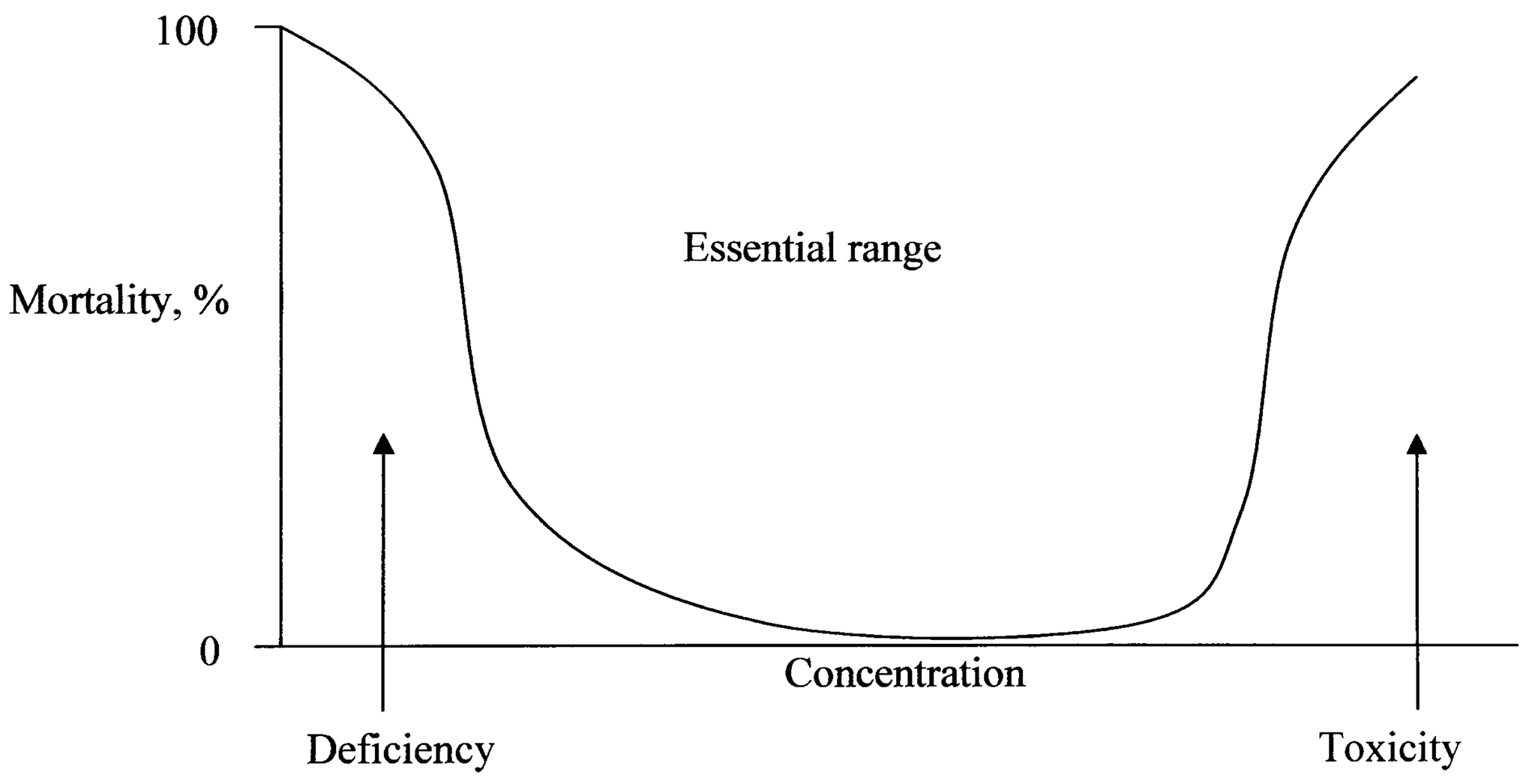

Figure1.3: Relationship between intake level and risk

1.5 ENVIRONMENTAL POLLUTION IN PAKISTAN

Over the past few decades, Pakistan has focused on achieving self-sufficiency in food production, meeting energy demands, increasing fertilisers and agrochemical production, slowing population growth, and increasing economic growth rather than on curtailing pollution or other environmental hazards. As a result, no attention was paid to combat pollution problems because environmental issues have not been the government's top priority [75].

At present, Pakistan has a very small industrial base but the indications are that the industrial activities will increase enormously over the next 10 years. Most of the existing industrial units do not pose any danger to the environment. The national and provincial environmental protection authorities point out approximately 21 sub-sectors of industries which come under the head of polluting industries. Out of these 21 only six have been marked as most dangerous and are included in Red List [75]. The Pink and White Lists are also there. The industries in the white list are environmental friendly. The six highly polluting industries are: Textile, Leather, Pesticides, Fertilisers, Cement, Sugar and Paper. The activities of these industries have created a number of environmental problems such as degradation of water and soil quality, pollution of marine environment and degradation of human health [76].

The number of small scale industrial processing units is growing every year since 1970 and the solid wastes and wastewater streams originating from these units contain heavy metals and other toxic chemicals. It is alarming that most of these small scale units have started without proper planning and waste treatment plants. They just dispose of untreated toxic waste into nearby drains, canals or rivers. Lahore, Faisalabad, Karachi, Sialkot contribute major pollution loads into their water bodies. These disposal practices have resulted in the deterioration of both water and soil quality. Polluted water streams also pose a serious threat to the marine environment, as the channel water is contaminated with toxic chemicals. Animals drink water out of polluted water bodies, ailing ponds, rivers and streams. This sickens the animals and some may even die [77]. Extreme pollution of river Ravi near Lahore has destroyed the once existing 42 species of fish and the bird life around the river has migrated to other areas. Survival of small invertebrates, micro fauna and flora is also threatened [77].

According to the Pakistan Environmental Protection Agency (PEPA), 9000 million gallons of wastewater having 20,000 tons of BOD_5 loading are daily discharged into canals, rivers and other water bodies from the industrial sector [77]. Most of these canals and rivers are a part of the irrigation system in Pakistan. Since 69 % of this water is used for agricultural purpose, irrigation water containing high levels of contaminants can cause damage to the soil. Groundwater quality has also suffered from rapidly increasing use of pesticides and fertilizers aimed at promoting more intensive cropping and facilitating self-sufficiency in food production [77].

The unplanned expansion of various small scale industrial processing units, especially in textile and leather sectors, and the increased public awareness regarding the environmental pollution problems have created a situation where the discussion on environmental issues have become a more salient feature in recent years. The pressure on both national and provincial governments to safeguard ecosystem and human health as well as the prudent use of natural resources has made environmental protection increasingly important. In an attempt to redress the previous inattention to the nation's mounting environmental problems, in 1992 the government issued its National Conservation Strategy Report (NCSR) [75].

The National Conservation Strategy Report has documented that solid and liquid wastes originating from various industries are the major source of water pollution in the country and also the cause of widespread waterborne diseases. Most of the untreated wastewater streams go into canals and rivers, whereas low-lying land is generally used for solid waste disposal. The National Conservation Strategy Report has raised concerns about industrial toxic wastes which are also being dumped without any treatment. Another important issue is the contamination of shallow groundwater near urban industries that discharge wastes directly into the ground [75].

Air pollution has also become a major problem in most cities. There are no controls on vehicular emissions, which account for 90 percent of atmospheric pollutants. The NCSR claims that the average Pakistani vehicle emits twenty-five times as much carbon monoxide, twenty times as many hydrocarbons, and more than three times as much nitrous oxide in grams per kilometre as the average vehicle in the United States.

Building on the Pakistan Environmental Protection Ordinance of 1983, the NCSR stipulated three goals for the country's environmental protection efforts: (1) conservation of natural resources; (2) promotion of sustainable development; and (3) improvement of efficiency in the use and management of resources. Fourteen programme areas were targeted for priority implementation, including energy efficiency improvements, renewable resource development/deployment, pollution prevention/reduction, urban waste management, institutional support of common resources, and integration of population and environmental programs [75].

In addition, in 1997 Pakistan instituted National Environmental Quality Standards (NEQS) on municipal and liquid industrial effluents and industrial gaseous emissions, motor vehicle exhaust, and noise. This attempt to legislate environmental protection has fallen short, as regulations have not been enforced strongly. In addition, enforcement does not imply effectiveness, and even if regulations were strictly enforced, many industries would be unable to comply. For instance when environmental regulations were implemented in 1997, only 3 % of industries were able to pass the test for compliance. National attention towards environmental issues has increased recently because, under provisions of a World Trade Organization (WTO) agreement, Pakistan will have difficulty in exporting products from industries without adequate environmental safeguards [75].

Following early successes in the implementation of Pakistan's National Conservation Strategy, progress on environmental pollution control has stalled due to institutional failure and lack of funds. A report released by the Ministry of Environment in January 2000 showed that Pakistan currently spends about $17 million per year on pollution-related cleanup; however, $84 million is needed to correct the country's environmental problems, and $1.8 billion per year in losses from environmental damage [78]. The Sustainable Development Policy Institute (SDPI) has estimated that the government allocates just 0.04 % of the total public sector development program budget on the environment, and 70 % of the funds for environment are loans from foreign lenders [79]. The SDPI has estimated the staggering cost of environmental neglect in Pakistan as between 3-5 % of GDP, projected to reach 4-8 % by 2010 [79].

1.5.1 Textile, leather and chemical industries in Pakistan

Textile, leather and chemical are three of the most polluting industries and, within these industries, producing cloth, tanning leather and producing pesticides are the most polluting processes. This section, highlights some of the main environmental pollution problems associated with textile, leather and chemical industries because of their economic significance and their pollution impact. The textile industry ranks as number one in terms of exports, value added and employment. Leather ranks third in terms of exports and, while it is less significant in terms of value added or employment, it is the most polluting of all the industries. There are a limited number of chemical industries in Pakistan and most of them are involved in manufacturing fertilisers, pesticides and pesticides active

ingredients. The production of these chemicals usually involves the use of organic compounds and the main environmental pollution problem associated with these industries is the emission of volatile organic compounds (VOCs) into the environment. All these industries are highly damaging to the environment and human, plant and animal life. The damage to the environment is likely to increase due to the export related increase in the production of textile and leather products.

Textile Industry

Textile industry is considered as the backbone of Pakistan economy as it is the most important industrial sector of Pakistan in terms of export and labour force employment [80]. The importance of this industry can be judged by the fact that the present government is determined to expand the activities of textile industry and this is reiterated by Omer Ayub Khan, Minister of Finance, during his 2005-06 budget speech.

> *Mr Speaker, the private sector has invested $4 billion in textile industry and textile exports are touching the $10 billion mark. Karachi Textile City is being established. Garments cities are being set up both at Lahore and Karachi. The growth in the textile sector can be judged from 18 % increase in the production of cotton yarn, 28.45 % increase in the production of cotton and 45 % increase in the production of ginned cotton. We have made a commitment that we will add value to the cotton of Pakistan and Pakistan will become the symbol of the best cloth in the world.*

At present, around 700 textile-processing units are currently working in the country. The locations of these units are marked by dots on the map in Figure 1.4. These units carry out various textile processes and the wastewater originating from most of these units are discharged into canals and rivers. The Lyari River, which runs through Karachi, Pakistan's largest industrial city, is an open drain for both raw sewage and untreated industrial effluents. Most industrial effluents come from an industrial estate with some 300 major industries and almost three times as many small units. Three-fifths of the units are textile mills. Most other industries in Karachi also discharge untreated effluents into the nearest water body.

Similar situations exist in Lahore where textile wastewater is allowed to flow into River Ravi and in the case of Faisalabad, Gujranwala, Hyderabad, Kasur, Sheikhupura, Peshawar, Rawalpindi or Sialkot into the nearest channel, surface water drains and the irrigation canals. Municipal wastewater, industrial wastewater and mixed wastewater streams, in some towns and industrial estates, are allowed to flow into open fields where they form lagoons and from there they flow into channels of the streams.

Figure 1.4: Location of textile industries in Pakistan

Textile effluents contain high biochemical oxygen demand (BOD), suspended solids (SS) such as fibre and grease, chemical oxygen demand (COD), and total dissolved solids (TDS) [81]. The textile effluent is usually alkaline, strong smelling and coloured by chemicals used in the dyeing processes. High BOD and COD lower the dissolved oxygen of the receiving waters; threaten aquatic life and damaging both the aesthetic value and water use quality downstream. High COD also results in obnoxious odours, toxic sulfides. Suspended solids raise water turbidity, reduce light penetration and hence plant production. They settle to the bottom where they destroy fish spawning grounds and other organisms that serve as fish food. Fish gills can also be plugged if SS are high. TDS are the inorganic salts and substances that are dissolved in the water. This process accelerates corrosion in the water systems and pipes and depresses crop yields if used for irrigation.

Metals and compounds such as chromium and phenol, which are used in textile processing, are known to be carcinogenic. All textile effluents contain residual concentration of synthetic dyes and most of these dyes are also believed to be carcinogenic and allergy inducing [81].

To get a sense of how polluting the effluents are, the data in Table 1.5 reports the results of the audits of the three textile units in Pakistan relative to PEPA standards and EPA standards in the USA [80, 83].

Table 1.5: Measured contamination levels and discharge standards in the textile sector

Parameter	Measured Level mg/L	Pakistan EPA Standard mg/L	US EPA Standards mg/L
pH	8-9	6-10	6-9
BOD	112-120	80	58
COD	430-480	150	524
TSS	25-1,200	150	157
TDS	2,300-3,600	3,500	-
Total Chromium	0.05-0.30	1	0.9
Phenol	Not detected	0.1	0.9
Sulfide	0.07-15.0	1	1.75

Textile industries use huge amount of water and it is estimated that all 700 textile processing units require about 50 million gallons per day of water and most these units meet their requirement by extracting the sub-soil water or by the tanker water suppliers. The sub-soil waters of the two major textile centres of the country, Karachi and Faisalabad, are highly saline and as such are not suitable for producing high quality finished textile products. Some of the major textile units have adopted the reverse osmosis (RO) process for demineralisation of brackish water. This technique, however, is very expensive and cannot be adopted by small scale units to solve the problem of water scarcity. The Pakistan Environmental Protection Agency is encouraging industry to use suitable wastewater treatment systems to remove toxic impurities and the treated wastewater would then be available for reuse [83].

Environmental pollution problems associated with textile industries are well known and some of them have been highlighted in this section. With increasing public awareness regarding the issues of environmental pollution, this successful business is striving to achieve the goals of responsible environmental behaviour. To enhance and sustain the textile exports of Pakistan it is essential to address the associated environmental problems on urgent basis. The new regime of international trade under World Trade Organization (WTO) demands that the production of textile products must comply with the national and international environmental standards. If these standards were not followed precisely, the Pakistani textile products would not be accepted in the international markets [82, 83].

Leather Industry

The leather industry is the second biggest export-oriented industry in the manufacturing sector and third in the overall exports of Pakistan. At present, according to the Pakistan Tanners Association, there are 526 tanneries in Karachi, Lahore, Multan, Kasur, Faisalabad, Peshawar, Gujranwala, and Sialkot, with the majority of leather production taking place in medium-size tanneries (14). Although the production of leather has been steadily increasing but the supply has not been able to keep up with demand. To help leather industry in order to meet the growing demand, the government has currently allowed wet-blue (unfinished) and skins to be imported duty-free.

In Pakistan, leather tanning has been ranked as one of the most polluting activities compared to other manufacturing sector activities. It also has one of the highest toxic intensity per unit of output [84]. Converting hides into leather is a heavily chemical intensive process utilizing roughly 130 chemicals. The main chemicals used in the various processing stages include sodium sulfide, lime powder, ammonium sulfate, sodium chloride, sulfuric acid, chromium sulfate, sulfonated and sulfated oils, formaldehyde, pigments, dyes and anti-fungual agents. The processing stages are pre-tanning (soaking, unhairing and liming, fleshing, deliming, washing, bating and de-greasing), tanning (pickling, chrome tanning, wet-blue storage, sorting, splitting and shaving), wet finishing (wet back, neutralization, retanning, washing, fat liquoring, dyeing and washing), dry machine process (drying, stacking/toggling, shaving,

trimming and pressing), and finishing (buffing, spraying/coating, drying and glazing/polishing).

Pollution or wastes resulting from these processes are air, solid and primarily liquid. Hydrogen sulfide and ammonia are the major gases released into the atmosphere. However, the emissions of these gases are lower than the national environmental quality standards. Most of the solid wastes, which contain proteins and chromium, are bought by poultry feed manufacturers. The chicken feeds prepared from tanneries solid wastes are likely to cause direct entry of chromium into the food chain. The results of tests conducted by the Pakistan Tanners Association showed that the poultry feed prepared from tanneries solid waste contained high level of chromium. Leather shavings are used as cheap fuel in kilns causing the release of chromium into the environment. The remaining solid wastes are usually illegally dumped around the factory area on unutilised lands. These solid wastes contain metal contents, such as chromium and aluminium, which have a detrimental effect on plant growth [84].

In the course of processing of hides into leather, roughly 50-150 litre of water is used per one kilogram of converted leather [84]. Thus effluents discharged from tanneries are voluminous, highly coloured, contain a heavy sediment load including toxic metallic compounds, chemicals, biologically oxidisable materials and large quantities of putrefying suspended matter. Tannery effluents, without any pre-treatment, are discharged indiscriminately into water bodies or open land, resulting in contamination of surface as well as sub-surface water. The leather tannery operations are also polluting canals and river and threatening their use for domestic and irrigation purposes [84].

The rampant discharge of untreated effluents from tanneries is a growing problem facing the leather industry in Pakistan. Export of tanned leather is on the increase following a decline of leather production in the developed world due to more stringent environmental controls. The increase of tanneries in Pakistan is causing severe environmental degradation. Due to a need for foreign exchange, the national government is encouraging the growth of tanneries by offering these industries export rebates while at the same time lagging on implementing the sparse existing governmental environment regulations in leather tanning. The combination of an increasing demand for the product and a lack of government regulation are aggravating

whatever fragile balance existed between the Pakistani leather trade and the environment.

As in the case of textile effluents, the audits generated data enabling me to compare the effluent parameters relative to Pakistan and USA EPA standards [85].

Table 1.6: Measured contamination levels and discharge standards in the leather sector

Parameter	Measured Level mg/L	Pakistan EPA Standard mg/L	US EPA Standards mg/L
pH	7.4-9.8	6-10	6-9
BOD_5	1,740-11,050	80	58
COD	3,800-41,300	150	524
TSS	440-890	150	157
TDS	10,580-20,000	3,500	-
Total Chromium	3.0-133.0	1	0.9
Sulfide	0.0-288.0	1	1.75

Data in Table 1.6 show that there is much more to be concerned about in the leather industry relative to the textile industry since leather production effluents far exceeded both Pakistani and US EPA standards on all counts.

The government's policy of encouraging the growth of the leather industry with little regulation is compounding the environmental problem in Pakistan. Although some NGOs and concerned citizens are working to raise awareness of the dangers of these policies, little is being done to control the situation. Until Pakistan is forced to adhere to international norms for pollution control in its domestic leather tanneries, the situation will likely worsen at the expense of the average Pakistani citizen in terms of a declining quality of life [85].

Chemical Industries

Pakistan economy is largely based on agriculture and it is supported by one of the largest and sophisticated irrigation system in the world. At present only 27 % area of

the country is being cultivated and the indications are that this will increase over time. As a result of this increase an agriculture economy showing intentions to become industrial over the next 10 years. Most of the chemical industries in Pakistan are, therefore, either agro-based or agriculture orientated. Accordingly, consumption of chemicals is also primarily confined to agriculture. Chemical fertilisers and pesticides are the largest chemical products produced and consumed in the country. Other chemicals produced and used in the country in sizeable quantities are dyestuffs, petrochemical products, caustic soda and sulfuric acid.

With the exception of fertilizers, pesticides and chemicals for the manufacture of man-made fibres, the chemical industry in Pakistan is in nascent stage. At present, the consumption of fertilizers and pesticides per hectare use is very low in Pakistan as compared to other developed and developing countries but the consumption is bound to increase as more and more area is being cultivated. For this the environmental protection authorities are working very hard to strengthen their ability to control the rising levels of pollution in Pakistan. It is, therefore, a high time that proper environmental management skills are put in place so that the chemical industry grows into the network without any hassle. What is needed to be done for the time being is to provide help and support to industry in selecting clean and clean-up technologies to ensure pollution free environment. Most fertilizers and pesticides industries are set-up close to the larger consumption areas. In fact this type of regional concentration helps to develop and implement preventive measures more efficiently.

Industrialised countries in the developed world have stringent environmental regulations for controlling industrial pollution. The situation in Pakistan, however, is different from industrialised countries and according to the Pakistan Environmental Protection Agency nearly all chemical industries are violating the national environmental norms [85]. Chemical industries in Pakistan are supposed to comply with the National Environmental Quality Standards, which came into effect in July 1997. However, some factory owners argued that they cannot import expensive treatment systems and the government should help them to develop sustainable and economically viable treatment technologies to control pollution and went to court to challenge the laws. As a consequence, government and industry agreed to a self-monitoring system under which the latter would measure industrial emissions on its own and report them to the

authorities. In return, the environmental protection authorities will provide technical and financial help to develop suitable treatment systems to ameliorate the environmental pollution problems associated with the chemical industry.

The magnitude of environmental pollution problems is likely to increase as the country pursues its desire for industrialisation. At present, chemical industry in Pakistan has been agriculture-based and rural orientated. From hereon it will move into the high-tech, advanced and sophisticated industrialisation. With little or no infrastructure for the management of industrial wastes, it will be difficult to control environmental pollution problems emanating from these chemical industries. The Pakistan Environmental Protection Agency which is responsible for protecting, rehabilitating and improving the environment is working in close collaboration with industry to develop and implement suitable treatment technologies to combat environmental pollution problems.

1.5.2 Pakistan in the 21st Century

The Pakistani government's current focus is on economic development and poverty alleviation. Like many developing countries, Pakistan has limited resources for addressing its environmental problems. Pakistan's previous environmental record is poor, and the country has not yet been able to back up its commitment to environmental protection with action. New developments in the World Trade Organization (WTO), however, stipulate that members can face higher tariff barriers for their exports in 2005 if certain basic environmental criteria are not met. Discussions are ongoing in Pakistani government and industry circles to meet the necessary requirements. It is clear that Pakistan will need to place greater emphasis on environmental protection in order to stem the country's environmental degradation and safeguard citizens' health.

In Pakistan, apart from a few large and export-oriented industries, which have to meet environmental standards, most of the industries have no effluent treatment facilities. Some textile and leather industries are employing pollution prevention measures but these approaches have not made a dent on the status of environmental degradation since the effluent discharged from various industrial estates whether in Karachi or elsewhere is still as highly toxic as in 1997 when the Pakistan Environmental Protection Act was passed.

It is the common view of the local government and the other regulatory authorities that most industries need sympathetic rather than harsh treatment. The reason that most of the industrial units need sympathy is that they are not able to and will not be able to comply with the stringent environmental standards as set out in the Environmental Protection Act of 1997. This is because they are so hard pressed by the rising cost of imports and the tax burden that their very survival is at stake.

At present, Pakistani industries are in the same position as the Eastern European Industries were in the 1980s, when, instead of installing the treatment units to meet the environmental requirements, they chose to close down. Most small and medium size units are not able to bear the expenditure on effluent treatment and, therefore, must be provided with financial support and all the basic infrastructure facilities including waste and wastewater treatment facilities, which in the case of my country, have been ignored.

It may be added here that when the National Environmental Quality Standards (NEQS) were being introduced in 1997, and the stage was being set for levying penalties in terms of Pollution Charges as a means to control industrial pollution, the industrialists did plead their case to sympathetic approach. The levy of charges was deferred when the President of Federation of Pakistan Chambers of Commerce and Industry (FPCCI) argued that the local industry was already faced with various domestic and international problems and would not be able to bear the harsh penalties provided in the Bill that was to become Pakistan Environmental Protection Act in 1997. He made a strong plea for the small and medium size industries, particularly the textile units and the tanneries, pointing out that many of them do not have space and resources for the establishment of an effluent treatment plant.

The need of the time is to support a strategy that collectively addresses the environmental problems faced by small and medium scale industries. Their problems relate to upgrading the working conditions by adopting good housekeeping practices and improving the operation of the almost outmoded industrial units or discarding them in favour of introduction of cleaner production technologies to control pollution and subsequently to establish combined effluent treatment plants if the unit or units are located in close proximity in an industrial estate.

It was for this reason that the Environmental Technology Programme for Industry (ETPI) was established by the FPCCI in collaboration with the PEPA. The main aim of this programme was to provide funds to universities and other research organisations to develop sustainable and economically viable treatment technologies to combat the problems associated with textile, leather and chemical industries. Therefore, the remit of my research was to develop and optimise treatment systems that should be adopted by some of these major industries and could easily be transferred with suitable modification to small scale units of the same sector.

1.6 AIMS OF THIS WORK

The research work described in this thesis was partly funded by the Pakistan. The remit of the research work was to develop environmental pollution control methodologies to combat the pollution problems associated with the emissions from textile, leather, pesticides and chemical industries in Pakistan. The successful control of these emissions requires a thorough understanding of emission sources and their relative impacts. Most of these industries are small establishments scattered throughout the country, which do not have the resources to purchase expensive treatment technologies needed to reduce emissions to water, air and land. Clearly, controlling the emissions from these widely distributed facilities is a complex task requiring careful regulatory strategies along with the availability of economically viable add-on treatment methodologies. The PEPA has tried to solve the emission problems by establishing centralised treatment units. These attempts have failed because the systems were not able to cope with the mixed effluent streams and the transport systems to deliver liquid and solid wastes from industry to the treatment site were poor and not properly organised. The main aim of the work described in this thesis is to develop and optimise sustainable, robust and economically viable add-on treatment technologies to control emissions from materials and chemical manufacturing facilities. The industry must be able to use local expertise and materials to manufacture and install the treatment units on site. The specific objectives of this research work are:

1. To develop treatment technologies, based on electrochemical cell systems, to remove dyes from textile effluent streams.
2. To develop treatment technologies, based on electrochemical cell systems, to remove chromium from leather effluent streams.

3. To investigate the possibility of using a waste from one industry to treat the waste of another in order to achieve an overall waste minimisation objective.
4. To investigate the possibility of developing treatment technologies that can be used for the treatment of mixed textile and leather effluent streams.
5. To develop treatment technologies based on catalytic oxidation process to reduce volatile organic compounds VOCs emissions from pesticides and pesticides active ingredients manufacturing industries.
6. To synthesise, characterise and investigate the potential use of room temperature ionic liquids (RTILs) for the selective extraction of heavy metal from low-grade ores and solid industrial wastes.

1.7 SCOPE OF THIS WORK

Background information on environmental pollution problems associated with both inorganic and organic pollutants has been given in this introductory chapter. This chapter has also highlighted some of the major environmental pollution problems associated with textile, leather and chemical industries in Pakistan. The descriptions of all the analytical techniques used through out the work have been outlined in the second chapter. In chapter three the development of treatment technologies suitable to remove dye molecules from textile wastewater and chromium from leather effluent streams is presented. The description of a treatment system suitable for the simultaneous removal of dyes and chromium from mixed textile and leather effluents streams is also presented in chapter three of this thesis. The development and optimisation of a catalytic oxidation technology suitable to control the emissions of volatile organic compounds (VOCs) from pesticides manufacturing industries is described in chapter four. The synthesis, characterisation and applications of room temperature ionic liquids (RTILs) to selectively extract heavy metals from low-grade primary ores and waste material are given in chapter five. The conclusion of this work is given the final chapter.

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CHAPTER 2

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CHAPTER 2
ANALYTICAL TECHNIQUES

The analytical techniques used in this research include atomic absorption spectroscopy, X-ray powder diffraction, X-ray fluorescence spectrometry, UV/visible spectroscopy and high performance liquid chromatography. These techniques are discussed in the following sections.

2.1 ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption spectroscopy (AAS) [1] can be used to determine most metallic elements. In this method, a solution containing low concentrations of metallic ion is atomised into a vapour, which contains free atoms of the elements. A hollow cathode lamp (the source of light) emits radiation, characteristic of the element to be determined, directly through the vapour. The analyte atoms dispersed throughout the vapour absorb a proportion of the radiation thus decreasing the radiation emerging from the vapour that can be measured by the detector. A monochromator is included in the system so that energy of the desired wavelength can be isolated from that of neighbouring wavelengths emitted from the light source. The sensitivity of AAS is defined as that concentration of an element, in ppm in aqueous solution, which gives a 1% absorption signal.

The instrument used throughout the present study was a Perkin-Elmer 2380 [2], a schematic diagram of which is show in Figure 2.1.

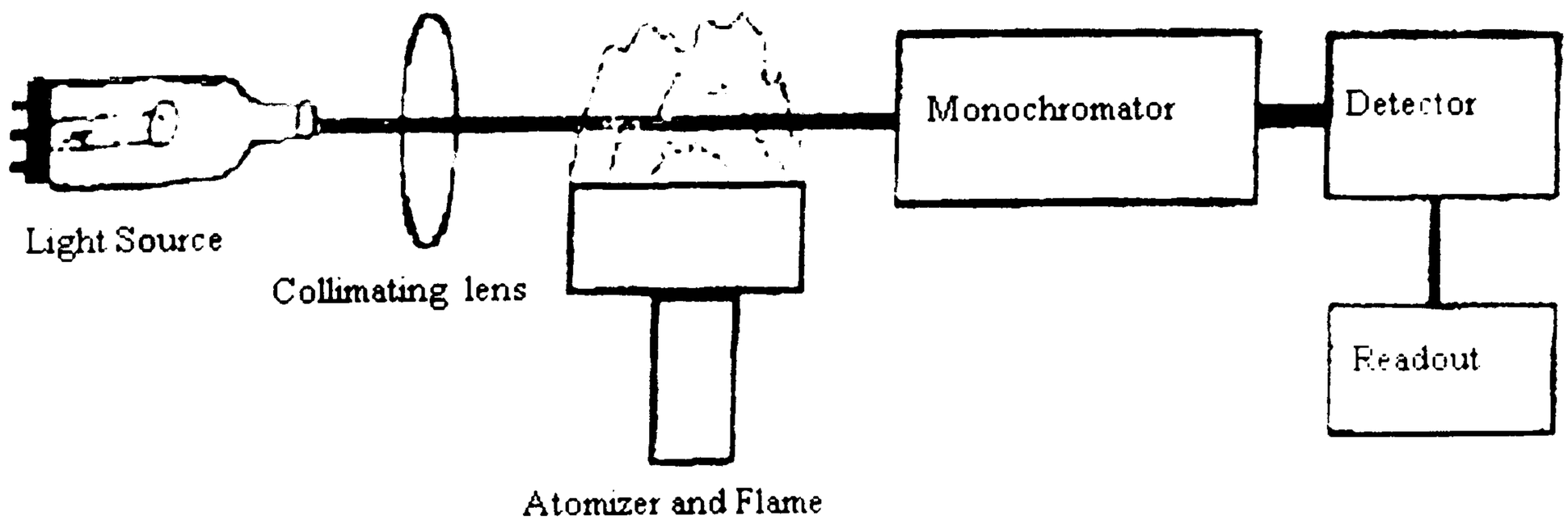

Figure 2.1: Schematic diagram of a PE2380 atomic absorption spectrometer

No technique of chemical analysis is universally applicable. Figure 2.2 shows those elements that can be analysed directly by atomic absorption. Although not used in the present research, osmium, tungsten, zirconium, hafnium, niobium, tantalum and the rare earths are better analysed by other techniques. These refractory elements present difficulties and exhibit poor sensitivity in flame atomizers. Alkali metals are easily analysed by flame emission and many workers still prefer this approach. For concentration levels below the parts per million (ppm) level, neutron activation and related nuclear techniques, when available, are considered more appropriate.

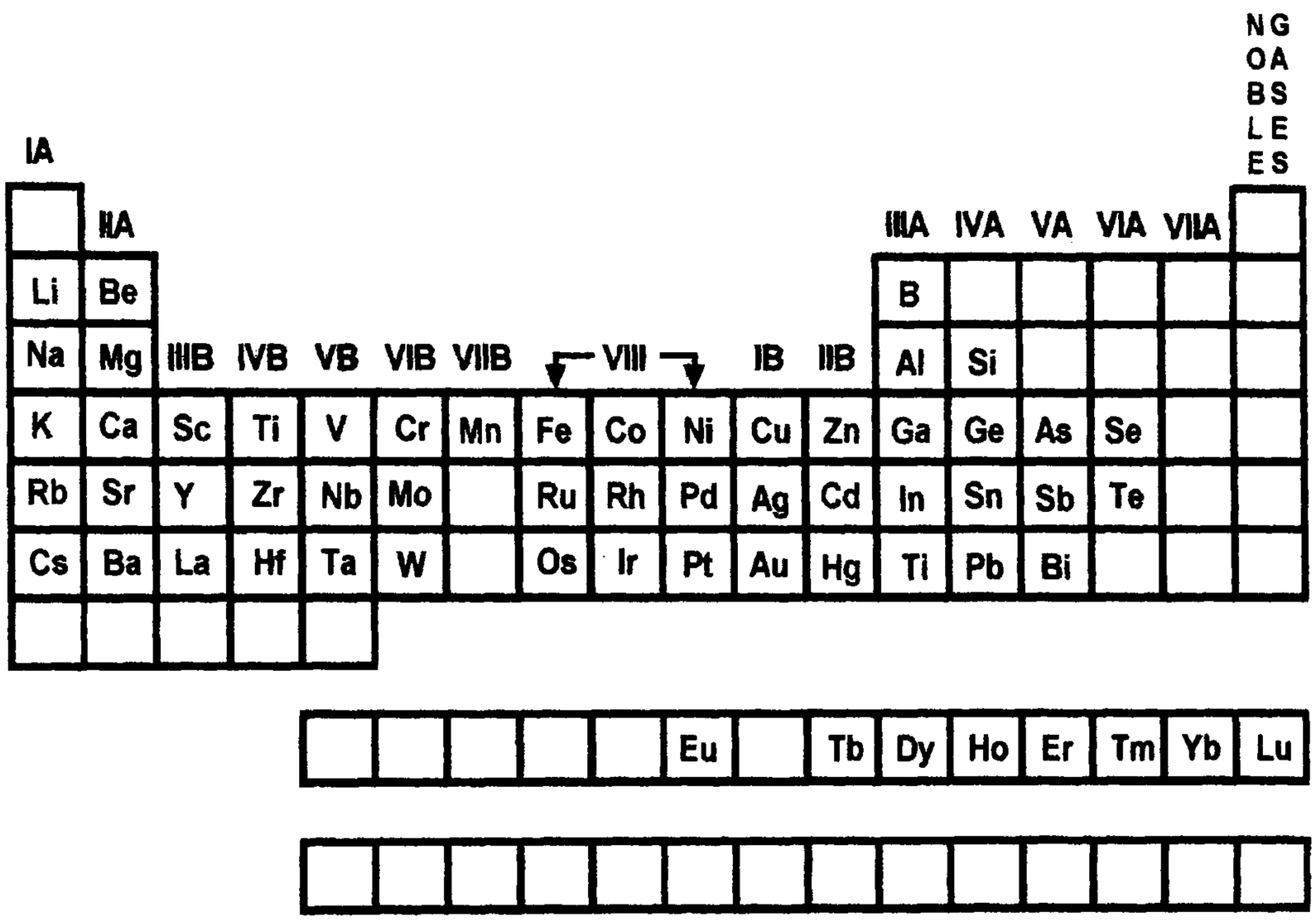

Figure 2.2: Periodic Table showing elements determinable by atomic absorption spectroscopy

2.1.1 Hollow-Cathode Lamp

Hollow-cathode lamps are the most common radiation sources for AAS. The hollow cathode lamp comprises a hollow cup cathode made from the element to be determined and a tungsten anode housed in a glass envelope containing an inert gas at low pressure Figure 2.3.

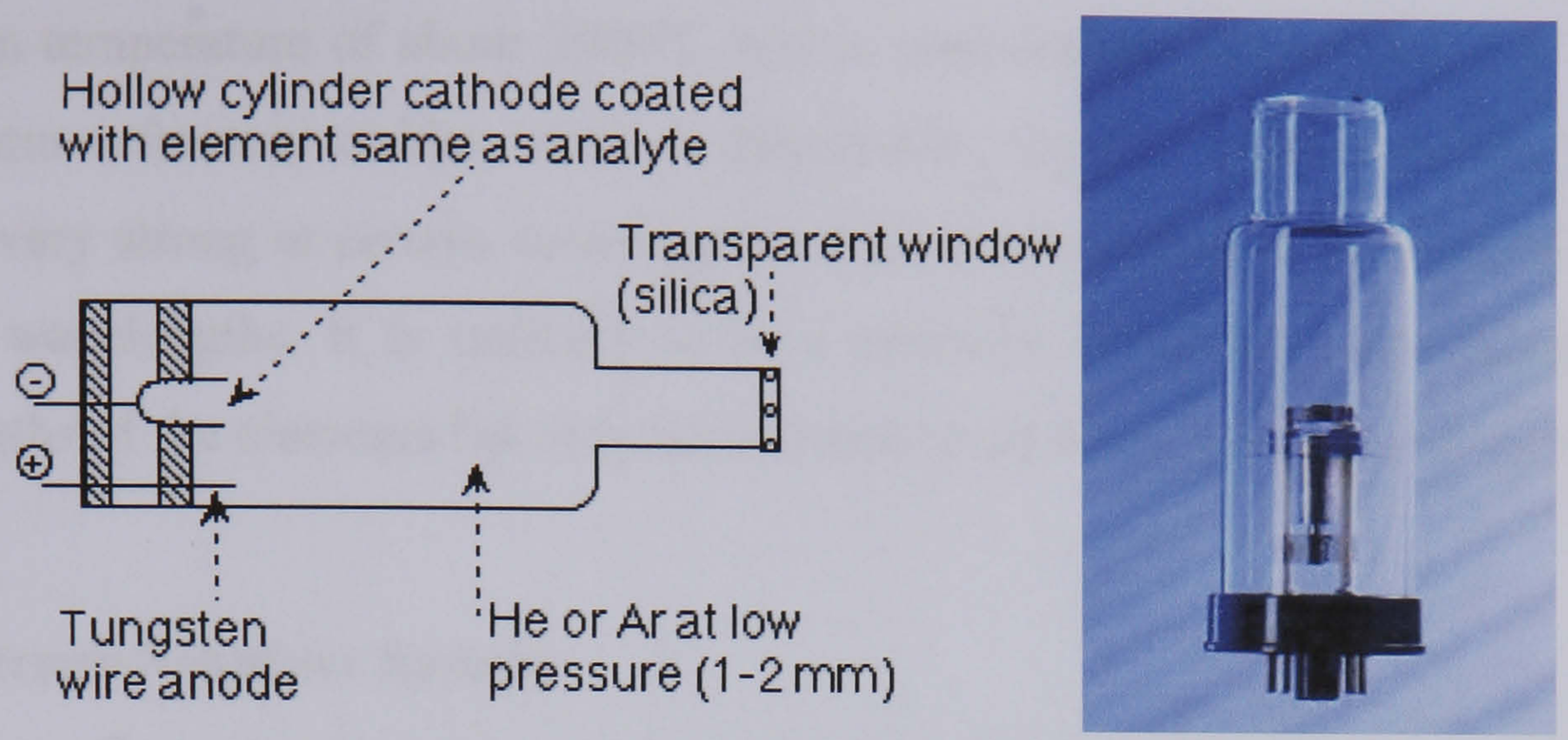

Figure 2.3: Schematic diagram of a hollow-cathode lamp

Ionisation of the inert gas occurs when a potential is applied across the electrodes, and a current of about 5 to 10 mA is generated as ions and electrons migrate to the electrodes. If the potential is sufficiently large, the gaseous cations acquire enough kinetic energy to dislodge some of the metal atoms from the cathode surface and produce an atomic cloud; this process is called sputtering [3].

Portions of the sputtered metal atoms are in excited states and thus emit their characteristic radiation as they return to the ground state. Eventually, the metal atoms diffuse back to the cathode surface or to the glass walls of the tube and are redeposited. The cylindrical configuration of the cathode tends to concentrate the radiation in a limited region of the tube; this design also enhances the probability that redeposition will occur at the cathode rather than on the glass walls. The total light obtained is subsequently passed through a monochromator, usually a grating or prism, to separate the resonance line from other nearby spectral lines.

2.1.2 Atomisation Systems

The gas combinations most often used to produce atomisation of vapours in AAS are air-acetylene and nitrous oxide-acetylene. Other rare combinations include air-hydrogen, argon-hydrogen, air-propane and air-natural gas. These cooler flames are useful for some specific determinations but in general they are more susceptible to interference effects. The temperature of the air-acetylene flame is approximately 2300°C and it may be used as an oxidising lean blue flame. Nitrous oxide-acetylene has a

maximum temperature of about 2900°C and is used for the determination of elements which form refractory oxides, such as aluminium, tin etc. Light emission from this flame is very strong at certain wavelengths causing fluctuation in the analytical results at those wavelengths. It is unlikely to be a problem, however, when using primary wavelengths of the elements but may occur when using a secondary wavelength [4,5].

2.1.3 Burner-Nebuliser System

The laminar flow premix system is the only type of burner in general use for AAS. A liquid sample is introduced into a burner through the nebuliser by venturi action of the nebuliser oxidant. Figure 2.5 shows a cross-section of the nebuliser premix burner assembly. As the sample passes through the nebuliser, the liquid stream is broken into a droplet spray. In addition to a nebuliser the premix burner contains a chamber and a burner head. Premix chambers are designed to mix the fuel, oxidant and sample [6]. Not all of the liquid entering a premix burner passes into the flame. The premix chamber allows large droplets, which are deleterious to the absorption processes, to condense (aided by the flow spoiler system) and pass out of the chamber through the liquid drain tube. Rejection of these large drops helps to minimise light scattering effects in the flame [7,8].

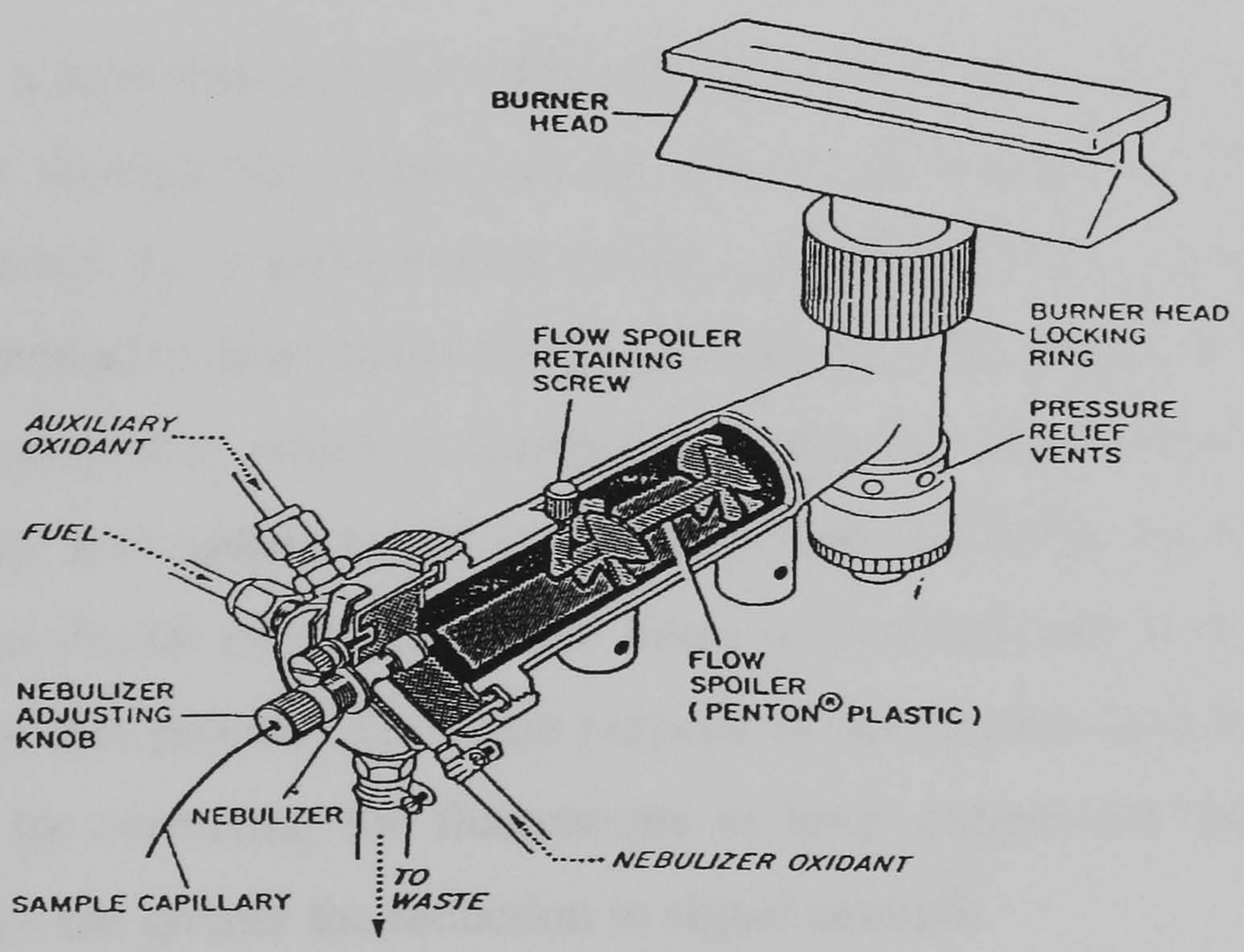

Figure 2.4: Burner-nebulizer system [5]

2.1.4 Optical System

In AAS the monochromator is placed after the atom reservoir to help diminish light-flux on the phototube. Figure 2.5 is a schematic diagram of the PE 2380, the atomic absorption spectrometer used in the present study. It is a double beam model,

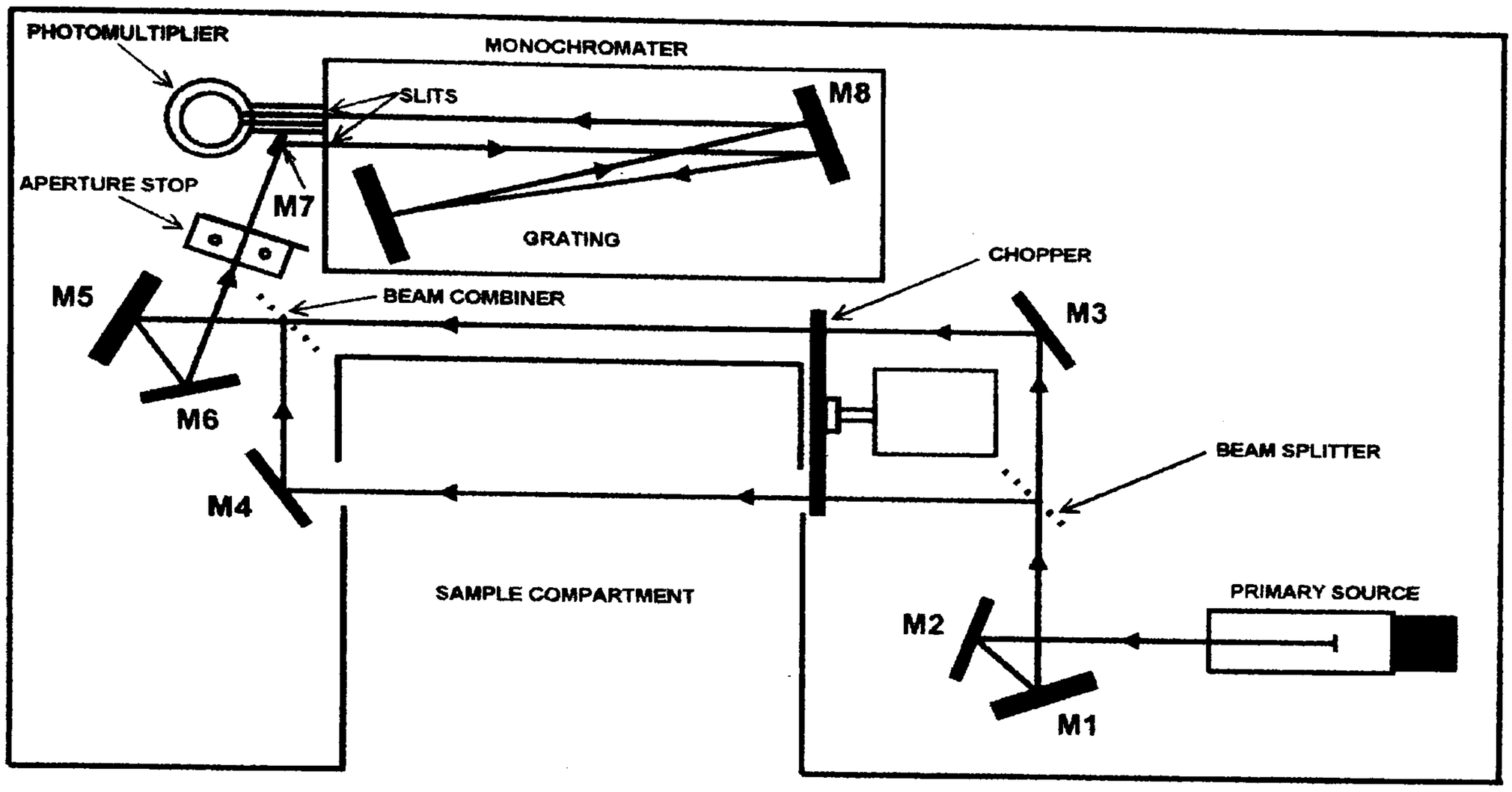

Figure 2.5: Schematic diagram of a PE2380 atomic absorption spectrometer showing the light-flux.

where a mirrored chopper splits the beam from the hollow-cathode source, one half passing through the flame and the other half around it. The two beams are then recombined by a half-silvered mirror and passed into a grating monochromator; a photomultiplier tube serves as the transducer. The output from the latter is fed to a lock-in amplifier, which is synchronised with the chopper drive. The ratio between the reference and sample signal is then amplified and fed to the readout, which may be a meter or digital recorder. Double beam instruments lose a factor of 2 in signal, as a result of this process. The main purpose of this system is to cancel instabilities in the source by correcting for fluctuations in lamp output: the more complex the optics, however, the greater the reduction in signal strength.

2.2 X-RAY POWDER DIFFRACTION

X-ray powder diffraction (XRD) [9] is a physical technique used in the characterisation of solids. It has been in use since the early part of this century for the identification of crystalline materials. In this research, a Philips 1140/00 X-ray diffractometer was used.

X-rays are electro-magnetic radiation of wavelength approximately 1Å that lie between gamma-rays and ultra-violet rays in the electromagnetic spectrum. They are produced by high energy collisions of charged particles with matter. Usually a beam of accelerated electrons is allowed to strike a metal target, such as copper, and this has sufficient energy to ionise some of the copper 1s electrons. An electron from an outer orbital (2p or 3p) immediately drops down to occupy the vacant 1s level and the energy released in the transition appears as X-radiation.

The transition energies have fixed values, therefore a characteristic spectrum of X-rays results. For copper, the 2p →1s transition called Kα, has wavelength 1.5418Å, and the 3p →1s transition, Kβ, 1.3992Å. The Kα transition is usually used in diffraction because it occurs more frequently and is more intense. In order to obtain a monochromatic X-ray beam, all other wavelengths can be filtered out. A finely powdered sample, which ideally consists of randomly orientated crystallites, has the power of scattering an X-ray beam incident on it because the separation of the atoms in a crystal sample is of the same order of magnitude as the wavelength of X-rays. In such a sample, the various lattice planes are also randomly orientated and will diffract the radiation in an analogous way to the refraction of light by an optical grating. Every crystalline substance scatters the X-rays in its own unique diffraction pattern producing a "fingerprint" of its crystalline structure. When crystals, which are regarded as being built of layers of planes, are struck by a monochromatic X-ray beam, some of the X-rays are reflected such that the angle of incidence equals the angle of reflection as shown in Figure 2.6. The rest are transmitted to be subsequently reflected by succeeding planes.

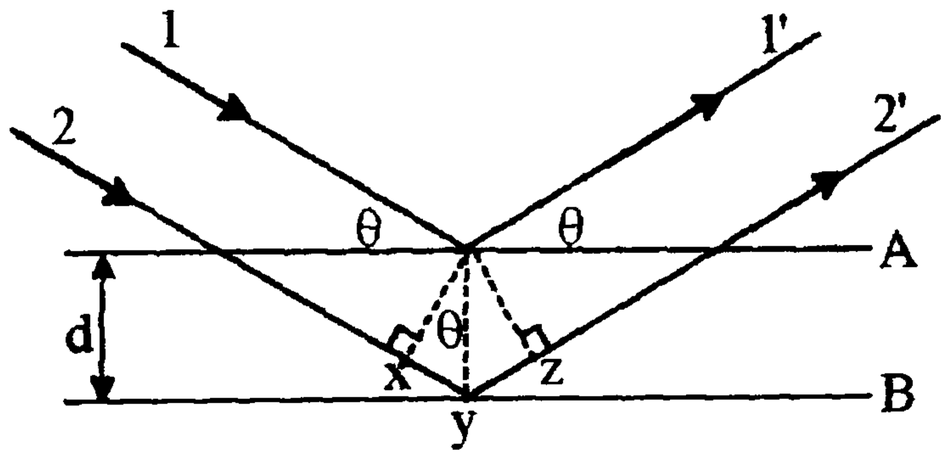

Figure 2.6: Depiction of Braggs law for X-ray diffraction.

Two X-ray beams, 1 and 2, are reflected from adjacent planes, A and B, within the crystal. For the beams to be in phase, beam 22' has to travel the extra distance xyz

compared to beam 11'. Therefore, for beams 11' and 22' to be in phase, the distance xyz must be equal to a whole number of wavelengths. The *d-spacing, d* (the perpendicular distance between pairs of adjacent planes) and the angle of incidence, or *Bragg angle, θ,* are related to the distance *xy* by:

$$xy \sim yz = d\sin\theta$$

and $xyz = 2d\sin\theta$

To be in phase $xyz = n\lambda,$ (where n is an integer)

therefore $2d\sin\theta = n\lambda$ Bragg's Law

It is only when Bragg's law is satisfied that the reflected beams are in phase and interfere constructively. At angles of incidence other than a Bragg angle, the reflected beams are out of phase and destructive interference occurs, therefore Bragg's law imposes stringent conditions on the angles at which reflection may occur that are unique to a given crystalline compound. Diffracted beams are referred to as reflections and the angle between incident and diffracted beam is denoted by 2θ and not simply θ. The basic information required in crystal structure determination may be obtained from the intensity of each reflection. Each atom has a different number of electrons and the relative scattering will vary according to this. As a result, two identical crystal lattices differing only in atoms will have different positions and intensities of refracted beams, and each crystal species will diffract X-rays in a characteristically different way [10]. Since a sample of powder contains many small crystallites that are randomly orientated, any one reflection at particular Bragg angle will result in cones of reflection [11]. These are observed as lines or peaks on the detector rather than the single points seen with single crystals. A simplistic diagram of a powder X-Ray diffractometer is shown in Figure 2.7.

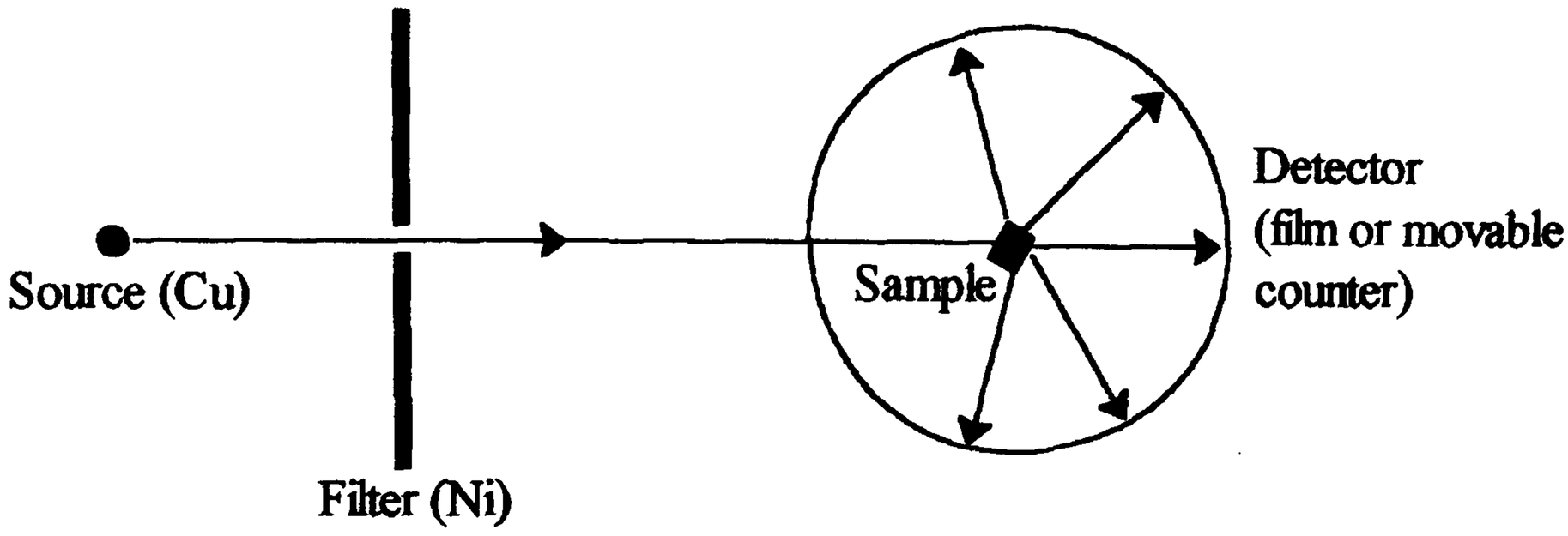

Figure 2.7: A simplified diffractometer arrangement.

2.2.1. Interpretation

The d-spacing and their intensities are the most important features of a powder pattern. The d-spacing (positions) of the lines in a powder pattern are governed by the values of the basic repeat pattern of the crystalline material represented by its unit cell parameters (the length of the cell sides a, b, c, and the angles between the cell sides α, β, γ). The intensities provide information on the types of atoms present in the sample. Intensities are recorded relative to the intensity of the strongest line of the pattern, which is arbitrarily assigned 100. For a particular substance, the line positions are essentially fixed and are characteristic of that substance. Intensities may vary somewhat from sample to sample, depending on the method of sample preparation and instrument conditions.

The substance can be identified from its powder pattern either by the indirect method, visual comparison of the pattern of the unknown sample with those of likely substances, or by the direct method, where the key spacings are measured and examined against indices of known compounds. The powder method can be used for the quantitative analysis of crystalline phases.

2.3 X-RAY FLUORESCENCE SPECTROMETRY

Energy dispersive X-ray fluorescence spectrometry (XRF) is an instrumental technique that provides elemental analysis for all elements with an atomic number of 11 (sodium) or greater [12-14]. X-rays are produced in an X-ray tube by bombarding a rhodium-plated copper anode with electrons. X-ray fluorescence is induced in elements by the bombardment of the sample by primary X-rays from the X-ray tube. In this research, an Oxford Instruments XR-300 X-ray Fluorescence Spectrometer was used.

2.3.1 Fluorescence

When the atoms in a sample are bombarded by high-energy X-ray photons, the energy carried by these photons is attenuated and partially transferred to the atoms of the specimen, exciting and ejecting bound electrons from their energy levels. If the energy of the impacting X-ray photon is great enough it may penetrate the atom structure through to an inner shell before this transfer of energy occurs. This leaves the atom in an ionised but unstable state. The laws of the atom mean that it will return to its most stable (lowest energy) ground state. This is achieved by electrons from higher energy electron shells dropping down to lower energy shells, with a free electron filling the gap.

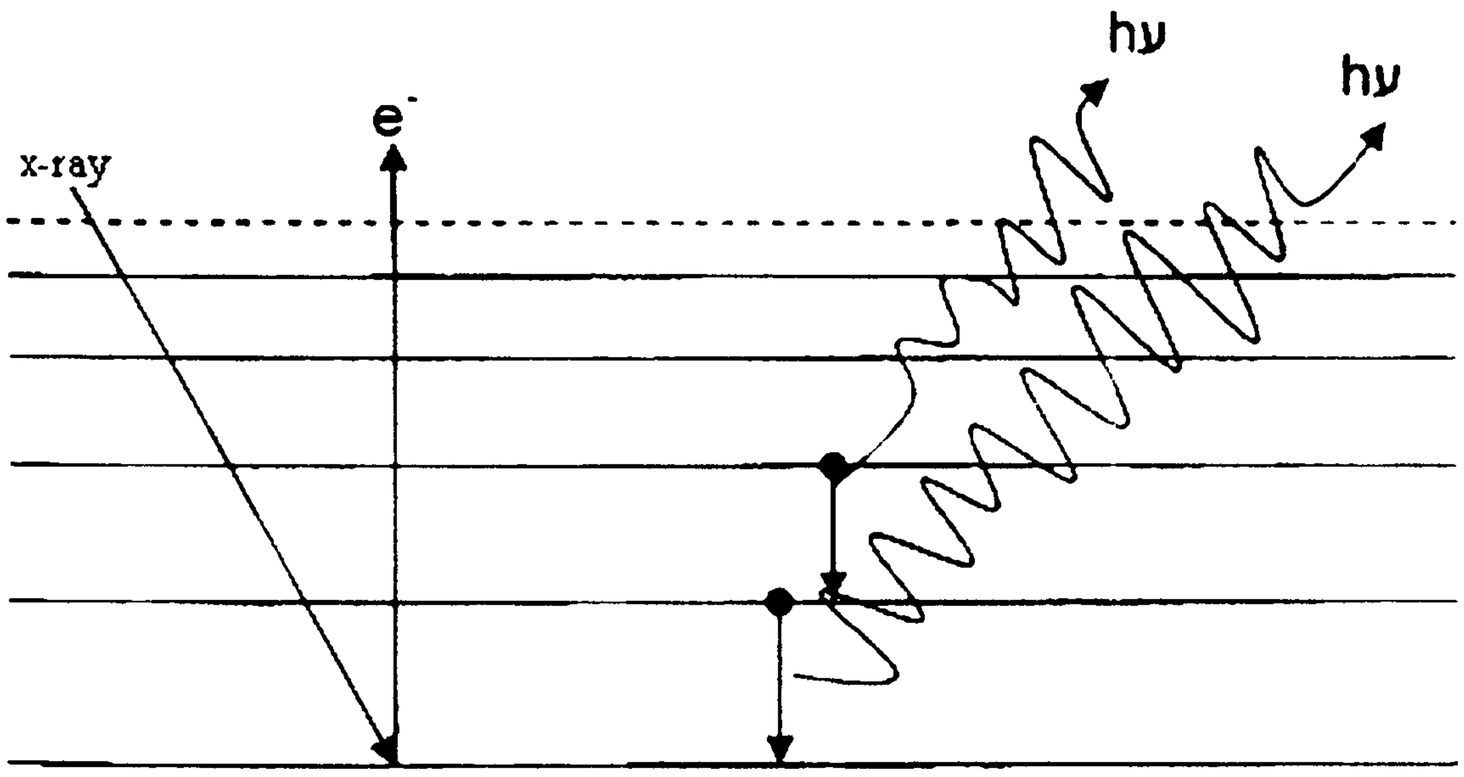

Figure 2.8: Concept of fluorescence

When an electron moves from a higher to a lower energy level, the extra energy possessed by the electron is dissipated by the release of a photon of electromagnetic radiation (fluorescence), the energy of which is determined by the sharply defined quantum energy levels of the atom. These energy levels are unique to each element and, therefore, the energy of the resulting photon is characteristic of the element from which it was produced and is known as the characteristic radiation. If the original electron was ejected from a K shell, the resultant radiation is known as a K line, with L or M shells likewise giving L or M lines [15].

2.3.2 Detection

The resultant secondary X-rays are analysed by an Energy Dispersive (ED) system, which consists of devices to detect the X-rays, measure their energy and compute the data. X-rays pass through a thin beryllium window into a cooled, reverse biased, lithium drifted silicon crystal. The crystal converts the X-ray energy into a pulse of electrical

charge. The charge is converted into a voltage pulse by a pre-amplifier, which also amplifies the pulse to a high enough level to be passed along cables to the pulse processor. The pulse is then converted to a digital signal and put into a multi-channel analyser, from where it can de viewed and analysed [16].

2.4 UV/VISIBLE SPECTROSCOPY

UV/visible spectroscopy (UV/VIS) examines the absorption spectra of a sample, obtained by the spectroscopic analysis of the light transmitted by the absorbing sample, which is placed between the light source and the spectroscope. UV/VIS is the measurement of the wavelength and intensity of absorption of near ultraviolet and visible light by a sample. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels. UV/VIS is usually applied to molecules and inorganic ions and complexes in solution [17]. In this research a Perkin Elmer, Model No. Lambda 9 was used. UV/visible spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law.

2.4.1 Instrumentation

The light source in UV/VIS is usually a hydrogen or deuterium lamp for UV measurements and a tungsten lamp for visible measurements. The wavelengths of these continuous light sources are selected with a wavelength separator such as a prism or grating monochromator. Spectra are obtained scanning the wavelength separator and quantitative measurements can be made from a spectrum or at a single wavelength.

2.4.2 Operation

The system used in this work is a dual beam system. Figure 2.9 is a schematic diagram of a typical dual-beam UV/visible spectrometer that operates between 200-400nm for the UV region and between 400-800nm for the visible region.

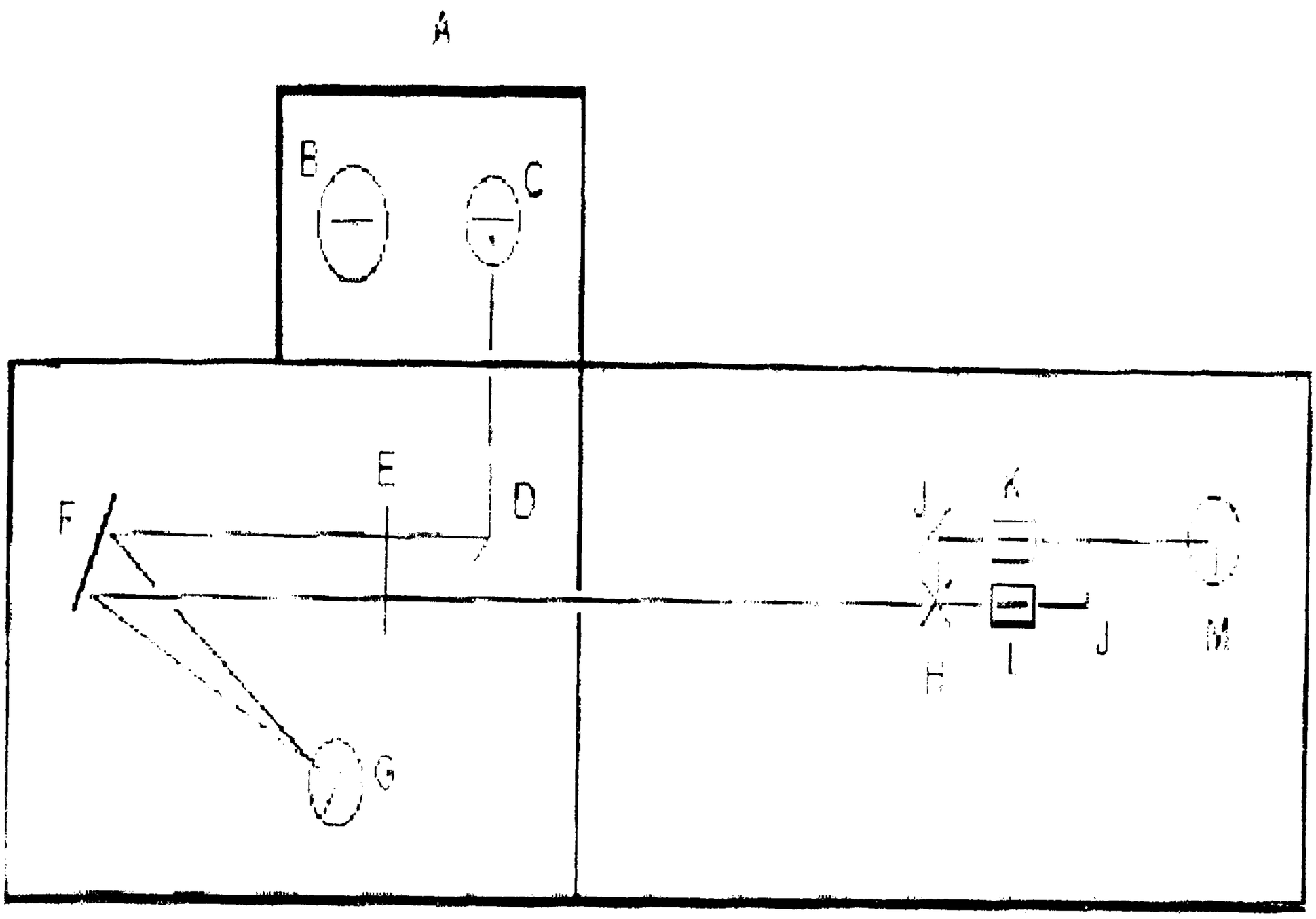

Figure 2.9: A schematic diagram of a UV/visible spectrometer

The light source (A) contains two lamps, a hydrogen lamp (B efficient for UV) or a tungsten lamp (C-visible and near–IR up to ~ 2um). The light selected is passed through a filter (D) and slits (E), and is reflected on the collimator mirror (F) to the monochromator (G), which can be either a lattice or quartz prism type. The monochromator rotates slowly and is mechanically coupled to a registering device. At a particular time, the light of a wavelength to be detected is reflected from the collimator mirror (F) to the dual beam part of the instrument. There, two rapidly rotating mirrors (H) divide the beam in two beams, one going through a reference cell (K) and one through the sample cell (L), into a detector (M), which with UV spectra is typically a photomultiplier. With UV/VIS a photoelectric cell (e.g. PbS) is used [18].

As a result of the mechanical and electronic operation of the instrument, a spectrum in the form of a rectangular plot is obtained. The abscissa (x-axis) indicates the wavelength, and the ordinate (y-axis) records absorbance.

$$A = \text{Log } I_o / I$$

where I_o = intensity of the light through reference cell

I = intensity of the light through sample cell.

The cells are made of quartz for UV spectra, but for visible spectra, cells made of special glass can be used. When recording spectra at 1 < 200nm, a special quartz cell must be used, and the sample must be degassed under an inert (nitrogen) atmosphere. The path length of the cell is typically 1cm.

Table 2.1: Spectrum of visible radiation

Wavelength, Colour, Complementary Hue	
<380nm, ultraviolet	380-420nm, violet, yellow- green
420-440nm, violet-blue, yellow	440-470nm, blue, orange
470-500nm, blue-green, red	500-520nm, green, purple
520-550nm, yellow-green, violet	550-580nm, yellow, violet -blue
580-620nm, orange, blue	620-680nm, red, blue-green
680-780nm, purple, green	<780nm, near-infrared

UV range – 200 to 350nm, Visible range – 350-700nm

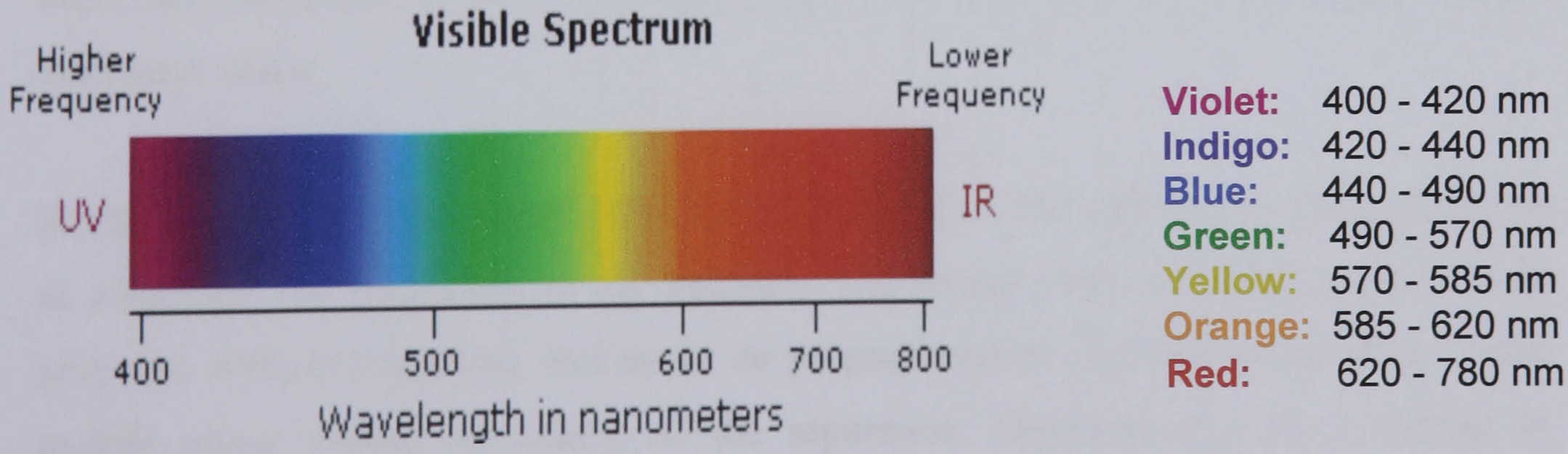

Figure 2.10: Spectrum of visible radiation

2.5 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

2.5.1 History of HPLC

High performance liquid chromatography (HPLC) was developed in the mid-1970s and quickly improved with the development of column packing materials and the additional convenience of on-line detectors. In the late 1970s, new methods, including reverse phase liquid chromatography, allowed for improved separation between very similar compounds [19]. By the 1980s HPLC was commonly used for the separation of chemical compounds, with new improving separation, identification, purification and quantification far in advance of previous techniques. Computers and automation added to the convenience of HPLC. Improvements in the types of columns and thus reproducibility were made as such terms as micro-column, affinity columns and fast HPLC began to emerge.

2.5.2 Principles of HPLC

HPLC is a popular method of analysis because it is not limited by the volatility or stability of the sample compound. HPLC is a form of liquid chromatography used to separate compounds in solution. HPLC instruments consist of a reservoir of a mobile phase, a pump, an injector, a separation column containing a stationary phase and a detector (Figure 2.11). Compounds are separated by injecting a sample on to the column. The different components in the sample pass through the column at different rates due to differences in their partition behaviour between the mobile phase and the stationary phase.

In this research a Cecil, Model No.CE1100 was used. The mobile phase was degassed to eliminate the formation of air bubbles. The pump used provided a steady high pressure, without pulsation, and could be programmed to vary the composition of the mobile phase during the course of the separation. Detectors rely on a change in refractive index, UV/visible absorption or fluorescence, after excitation with a suitable wavelength, to detect the separated compounds [20].

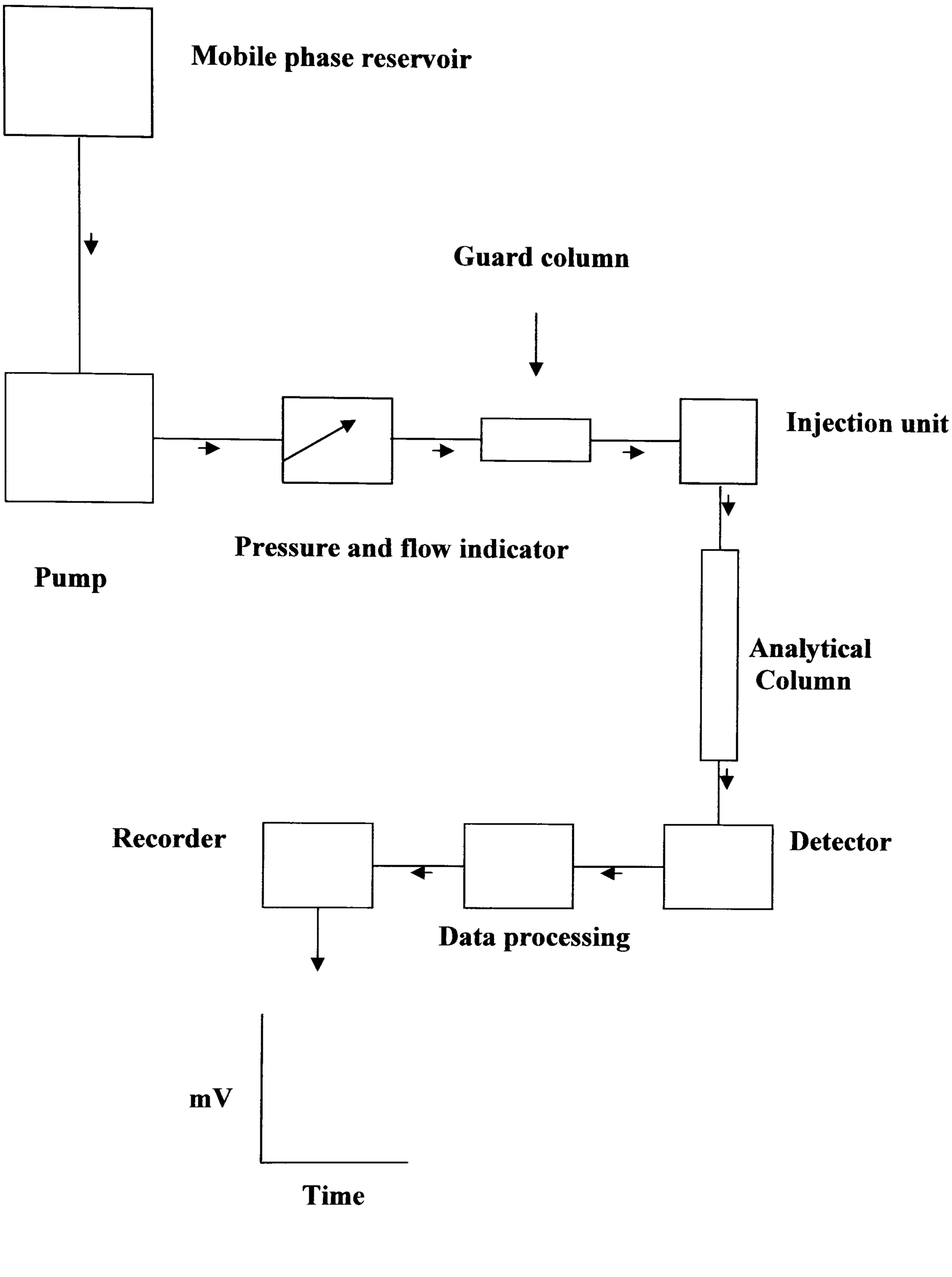

Figure 2.11: Block diagram of HPLC instrument

2.5.3 HPLC Applications

HPLC is the most widely used analytical technique for separation, identification, purification and quantification of organic compounds [21].

Purification refers to the process of separating or extracting target compounds from other possibly structurally related compounds or contaminants. Each compound should have a characteristic peak under certain chromatographic conditions. Depending on what compound is to be separated and how closely related the sample component molecules are, the chromatographer may choose the mobile phase, to allow adequate separation in order to collect or extract the desired compound as it elutes from the stationary phase. The migration of the compounds and contaminants through the column need to differ enough so that the desired compound can be collected or extracted without undesired compound.

Identification of compounds by HPLC is a crucial part of any HPLC assay. In order to identify any compound by HPLC a detector must first be selected. Once the detector is selected and is set to optimal detection settings, a separation assay must be developed. The parameters of this assay should be such that a distinct peak of the known sample is observed in the chromatogram. The identifying peak should have a reasonable retention time and should be well separated from extraneous peaks at the detection levels at which the essay will be performed. To alter the retention time of a compound, several parameters can be manipulated. The first is the choice of the column, then the mobile phase and lastly the flow rate. Identifying a compound by HPLC is accomplished by searching the literature database or by trial and error. A sample of a known compound must be utilised in order to assure identification of the unknown compound. Identification of compounds can be assured by combining two or more detection methods.

Quantification of compounds by HPLC is the process of determining the unknown concentration of a known compound in a solution. It involves injecting a series of known concentrations of the standard compound solution into the HPLC for detection. The chromatogram of these known concentrations will give a series of peaks that correlate to the concentration of the compound injected [21].

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CHAPTER 3

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CHAPTER 3

ELECTROCHEMICAL TREATMENT OF TEXTILE AND LEATHER EFFLUENT STREAMS

3.1 INTRODUCTION

The work described in this chapter extends CER research on removal of colour by adsorption to the use of electrochemical treatment in textile and leather effluent streams. The specific objectives of the work described in this chapter are:

1. To develop economically viable treatment technologies, based on electrochemical cell systems, to remove/destroy dye molecules from textile effluent streams.
2. To develop economically viable treatment technologies, based on electro-precipitation process, to remove chromium (VI) and other toxic pollutants from leather effluent streams.
3. To investigate the possibility of using a waste from one industry to treat the waste of another to achieve the overall waste minimisation an objective set out by the environmental legislative bodies in Pakistan. In order to prove this concept, experiments were conducted to achieve the simultaneous removal of chromium (VI) and dye molecules from mixed leather/textile effluent using an electro-precipitation process with mild steel electrodes.
4. To develop, design, construct and use prototype units to investigate the effectiveness of the developed technologies on an industrial scale.

3.2 TEXTILE EFFLUENT

3.2.1 Introduction

All over the world, various levels of government have imposed increasingly stringent regulations on the amount and type of waste material that can be discharged into the environment. The pace of the changes in regulation has created a situation where the priority of industry lies in the removal of toxic pollutants, with the recovery of reusable material as a secondary consideration. Existing technologies cannot achieve the lower consent levels set by the environmental legislative bodies and therefore an attempt must

be made to improve or develop new technologies to combat this environmental pollution problem [1].

Like many other industrial effluents, textile industry wastewater varies significantly, not only in quantity, but also in composition [2]. Textile effluents, apart from causing colour, often render the water toxic and produce many waterborne diseases. The dyes present can also hamper the soil fertility by suppressing the growth of nitrogen fixing *cyanobacteria*. Consequently, the need to treat effluent coloured by dye molecules, prior to discharge into receiving water, has attracted considerable research interest.

Dyestuffs and pigments are harmful to the aquatic life in rivers where they have been discharged by textile industries. The wastewaters can be highly toxic and can contain a large number of metal complex dyes (including Cr or Co as complexes). As an integral constituent of many industrial dyes, aromatic amines have been suspected as being carcinogens because epidemiological data indicate an association between bladder cancer in humans and occupational exposure to such compounds. Wastewater from the textile industry is, therefore, a problem not only because of its potential toxicity but also because it may contain residual colour, which acts as an aesthetic pollutant [1-2]. Since dye bath effluent contains a complex mixture of dyes, dispersing agents, levelling agents, wetting agents and trace metals, it becomes obvious that every effort must be made to minimise the amount of such water released into the environment.

The dyestuff manufacturing and processing industries are major consumers of water. The effluent from these industries contains a small proportion of dyes, especially those which are water soluble, which imparts only a fraction of the total organic matter load to the wastewater streams. They are readily detectable, however, because of the high degree of colouration they impart to water. As far as the general public is concerned, the removal of colour from wastewater is often considered more significant than the removal of soluble colourless organic contaminants [2].

3.2.2 Treatment Methods

Many traditional and new treatment processes have been modified and developed to try to eliminate the release to surface water of the diverse chemical substances found in wastewater discharges. Many of the dyes are difficult to remove by conventional

wastewater treatment methods, as they are fairly stable to light and heat and are biologically non-degradable because of their complex molecular structure and size [3]. The technology, which imparts colour fastness and resistance to bleaching, sunlight and oxidation makes textile dyes resistant to the primary and secondary wastewater treatment systems used in municipal sewage treatment plants. For this reason it is necessary to remove colour from wastewater, using a tertiary treatment processes, before discharging effluent into the municipal sewer or directly into natural streams [4]. Removal of dyes from textile effluent can be achieved by adsorption using different adsorbents including activated carbon granules [3,5], coagulation with iron or aluminium salts [6] and also by biological [7-8] and oxidative degradation [9].

Adsorption has received considerable attention as a means of colour removal from wastewater and many adsorbents have been tried. The use of binary or tertiary silica hydroxide gels as adsorbent has, for example, been investigated for the removal of basic and reactive dyes from aqueous solution in a batch-wise operation. These gels can be regenerated by heating them to 600°C. Sorbsil silica has also been investigated in batch and fluidized bed techniques for the removal of basic dyes [10]. In general, silica shows higher adsorption capacity for basic dyes in a fluidized bed system, but is not suitable for other dyes. Polymeric resins have been investigated for dye removal and their regeneration has also been described [11].

The most widely used adsorbent is activated carbon, as it is one of the best multipurpose and efficient adsorbents known. Granular activated carbon can be regenerated at least ten times under optimum conditions. In most examples, as long as they are economical, optimized adsorption techniques can be suitably applied to most water treatment systems. Large-scale use of activated carbon granules, however, is not cost effective in a developing country like Pakistan. The main drawback of this adsorption process is the cost and the difficulty of the regeneration process. This type of expensive technology has minimum chances of its adoption in developing countries like Pakistan.

The treatment of coloured effluent water with chlorine gas is well know and leads to almost instantaneous discolouration. But, of late, it is considered that the use chlorine could lead to the formation of chlorinated chemicals, which might be more toxic than the dye itself.

Oxidation of dyes by chemical means in wastewater has also been reported and various oxidizing agents have been used. Ozone is a very good oxidizing agent for dyes and is well described in the literature. Ozone production is, however, very expensive making wastewater treatment uneconomical. If ozone can be produced by a more economical method, its use for coloured effluent water treatment may well become a mainstream method [12-13].

The removal of colour from wastewater by flocculation and sedimentation can be satisfactory but does not lead to compliance with lower consent levels. Decolouration of industrial wastewater containing reactive dyes by flocculation using reducing agents such as sodium sulfite, sodium bisulfate and iron salts has also been reported [12-14].

Biological methods are now being applied to an ever-increasing range of effluent types. Sometimes these processes are impractical and cannot be used in the treatment of effluent containing biologically resistant substances [14-16].

Physical [17] and chemical [18] treatment processes incorporate the addition of secondary chemicals to precipitate or react with the primary pollutants in the effluents. The use of high chemical doses to clean up an effluent often results in a discharge which itself remains unacceptable. Combined treatment processes are almost always required to treat a discharge in order to make it acceptable. Such combined processes can be effective in eliminating pollution, but usually require long contact time and larger contact areas to make them practical.

At present there is no economically viable method that can be used to decolourise and/or detoxify textile mill effluent in developing countries like Pakistan. Biological degradation, chemical coagulation and reverse osmosis have been shown either to be slow, inadequately effective or uneconomical. Carbon adsorption and ozonation of dye bath effluent are expensive and usually results in poor colour removal, particularly of disperse dyes [5,11,19-25].

The work described in this chapter concentrates on the use of electrochemical methods for the treatment of textile effluent streams. The main aim of this study is to develop sustainable, economically viable, simple and robust technologies which can be used on

industrial scales to combat the problems associated with textile industries in developing countries like Pakistan.

3.2.2.1 Electrochemical treatment of wastewaters

Interest in the use of electrochemical processes for the treatment of wastewater containing organic pollutants is continuing to grow. The anodic oxidation of water containing phenol is well documented [28]. The implementation of electrochemical processes in the treatment of wastewater can result in the destruction of organic contaminants and lead to a total reduction in the COD and BOD in the effluent. The method is simple and the process operating requirements and space requirements are significantly less than many conventional treatment processes. Electrochemical treatment is a relatively new technique providing certain advantages such as almost complete decolouration, operation in a moderate pH range, low final temperature and significant reduction in COD and BOD levels [16,26-28]. The present research is concerned with the operation of electrochemical reactors to treat water containing reactive, direct and disperse dyes which are commonly in use in the textile industry.

An electrochemical cell is a device that uses electrical energy to effect a chemical change. The simplest form of an electrochemical cell requires two electrodes, an electrically conducting solution and a current source. In any electrochemical method, reduction occurs at the negative electrode (the cathode) and oxidation occurs directly or indirectly at the positive electrode (the anode). There are two important methods of dye or colour removal *viz:* a) electro-precipitation and b) direct electro-oxidation.

Electro-precipitation

The electro-precipitation of organic pollutants from an aqueous solution containing sodium chloride as an electrolyte is an effective process for the removal of colour from textile effluent. Different types of electrodes (aluminium or mild steel) can be used and, because of an oxidation reaction, the anode dissolves with the *in-situ* formation of hydroxide precipitates. These hydroxide precipitates are very good adsorbent materials and will adsorb colour from textile effluent.

With an iron anode the following reactions are involved:

Anode: $Fe \rightarrow Fe^{2+} + 2\bar{e}$

Cathode: $2H_2O + 2\bar{e} \rightarrow H_2 + 2OH^-$

Overall $Fe + 2H_2O \rightarrow H_2 + Fe(OH)_2$

Direct Electro-oxidation

In the direct electro-oxidation of an organic substance in water, an electrolyte must be added to ensure that the electrolytic process is effective. Absence of the electrolyte will result in little passage of current and consequently little or no oxidation of the organic substances. Several electrolytes can be used but a sodium chloride solution is the most common. Both the recovery of heavy metals and the oxidation of organic materials (such as dyes) in wastewater can be achieved electrochemically with little consumption of chemical and without generating a sludge problem.

In the process used in this study, organic dye molecules are destroyed by oxidation as well as through the reaction with evolved chlorine from a sodium chloride electrolyte at the anode. Hydrogen evolution and hydroxyl ion formation occurs at the cathode. There are three factors causing decolourisation at the anode in an electrochemical dye removal process in which sodium chloride is used:

(1) Dye destruction by anodic oxidation (free radical formation)
(2) Active chlorine formation (acidic-Cl_2; neutral-HOCl; basic-OCl^-)
(3) Oxygen evolution

Both hypochlorite and free chlorine act as oxidizing agents and are also chemically reactive in their own right. In most dilute solutions diffusion is the only process which controls ion transfers. In the presence of an electrolyte the diffusion of organic species is high so the efficiency of the reaction is also be high. The electrode reactions involved are:

Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4\bar{e}$

$2Cl^- \rightarrow Cl_2 + 2\bar{e}$

$OH^- \rightarrow OH^\bullet + \bar{e}$

Cathode: $2H_2O + 2\bar{e} \rightarrow H_2 + 2OH^-$

In the electrolyte

$Cl_2 + 2OH^- \rightarrow H_2O + OCl^- + Cl^-$

The efficiency of these reactions can be changed by changing the electrode material.

3.2.3 Ames Test

Many of the dyes that are being used in the textile industry are carcinogenic and it is very important that the effluent streams originating from these industries be treated to reduce the risk associated with the toxic organic dye molecules. The work described in this chapter is based on the use of electro-precipitation and electro-oxidation processes for the removal of dyes from both synthetic and industrial samples. The Ames test was used to investigate the effectiveness of these treatment methods by analysing the final effluent streams for their potential mutagenicity nature.

The Ames test uses *Salmonella Typhimurium* bacteria to test for mutation. The test is a simple and accurate method for assessing cancer risk. The Ames test assumes that the first step in the development of cancer is a mutation, and therefore, a chemical that cause a mutation is likely to be a carcinogen as well.

The bacteria that are used in the Ames test are modified biologically so that they are unable to synthesise the amino acid histidine. In the absence of histidine, the bacteria cannot grow. In the test, the modified bacteria are placed in a medium that contains all of the ingredients that they need for growth, except histidine. The suspected carcinogen chemical is then added to the medium. If the test chemical is not a mutagen, no bacterial action will occur. If it is a mutagen, however, a mutation will occur, and the bacteria will revert to a form that can synthesise histidine and grow. The growth of bacteria in the test dish identifies the chemical as a mutagen (Figure 3.1).

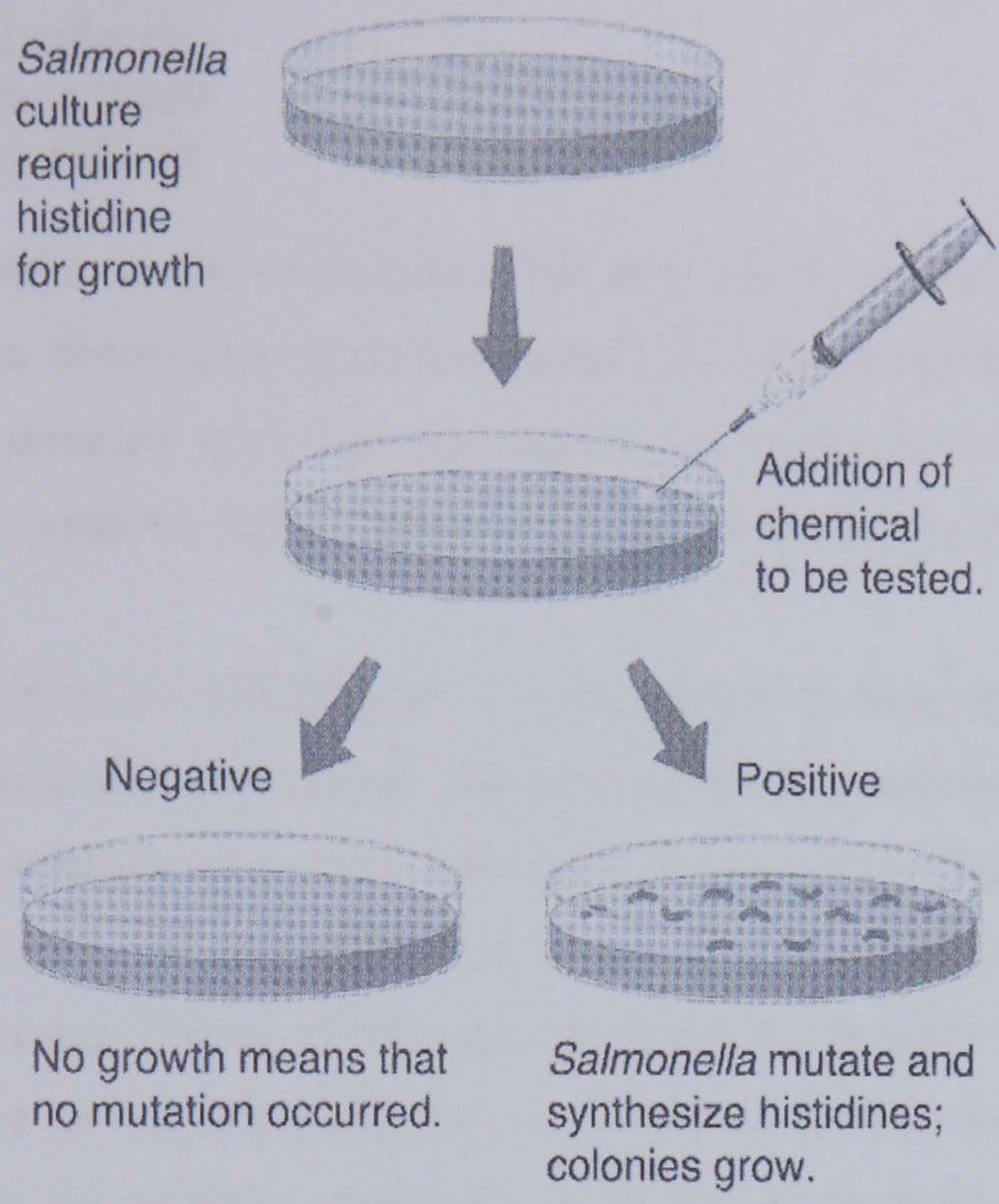


Figure 3.1: The Ames test for mutations

3.2.4 Experimental and Methodology

Before treating a known textile effluent in this work, the processes of electrochemical treatment were optimised using synthetic dye solutions. All experimental work was carried out at the National Institute of Biotechnology and Genetic Engineering, Faisalabad, Pakistan, in a close collaboration with textile industry.

The following six dyes (2 reactive, 2 direct and 2 disperse), supplied by a local textile mill from Faisalabad, Pakistan, were selected for the preparation of synthetic solutions because they are used in the majority of textile industries in Pakistan:

1. Reactive orange
2. Reactive violet
3. Direct pink
4. Direct turquoise
5. Disperse blue
6. Disperse violet

The three industrial samples supplied by a local textile mill from Faisalabad, Pakistan were:

1. Mixed effluent
2. Printing effluent
3. Dyeing effluent

Two different types of electrochemical cell were used for the treatment of textile wastewater: a) an electro-precipitation cell and b) an electro-oxidation cell. Figure 3.2 summarises the research work that was carried out using these two systems for the treatment of both synthetic and industrial solutions containing dye molecules.

The electro-precipitation cell (Figure 3.3) consisted of three plate electrodes (two anodes and one cathode). The cathode was constructed from stainless steel plate and the anodes were constructed from either mild steel or aluminium plates (5 cm x 6.5 cm). The distance between the electrodes was 1.5 cm. For each dye, separate experiments were carried out using 300 ml of 100 ppm dye solutions. In some experiments, sodium chloride was used as supporting electrolyte. A constant electric current of 0.5 amperes was applied and the voltage monitored. With the passage of an electric current, aluminium or iron ions were released from the anodes. These ions reacted with hydroxide ions generated at the cathode surface and the resulting precipitates absorbed dye from the contaminated solution. The solution was stirred at intervals with a glass rod before taking samples for analysis. After filtration of the electrolyte, the solutions were analysed by optical spectroscopy to determine the extent of colour removal. This method does, however, have the disadvantage of producing a sludge which requires disposal.

The electro-oxidation cell (Figure 3.4) consisted of two graphite rods (14 cm long and 1 cm in diameter – supplied by Fluid Dynamic International, UK) as anodes and one stainless steel or aluminium rod as cathode. Separate experiments were carried out to investigate the effects of electrode type on the anodic oxidation process by replacing the rod cathode (stainless steel or aluminium) with one titanium mesh or stainless steel plate cathode and the two graphite rod anodes with two mixed metal oxide mesh anodes (5 cm × 6.5 cm). These electrodes were also supplied by Fluid Dynamic International, UK. Some experiments were conducted to investigate the effect of the addition of sodium chloride (table salt) as a supporting electrolyte on the anodic oxidation of dye

molecules. The remaining experimental conditions were exactly the same as described for the electro-precipitation process.

The absorption of each dye solution (100 ppm) before and after treatment was measured on a Perkin Elmer, Lambda 9 UV/VIS/NIR spectrophotometer. The absorbance was measured in both the ultraviolet and visible range from 220 to 800 nm.

Microbial tests (Ames tests) were also performed to determine the potential mutagenicity nature of the treated effluent streams. The aim of these tests was to evaluate the suitability of electrochemical systems for the treatment of textile effluent on industrial scales.

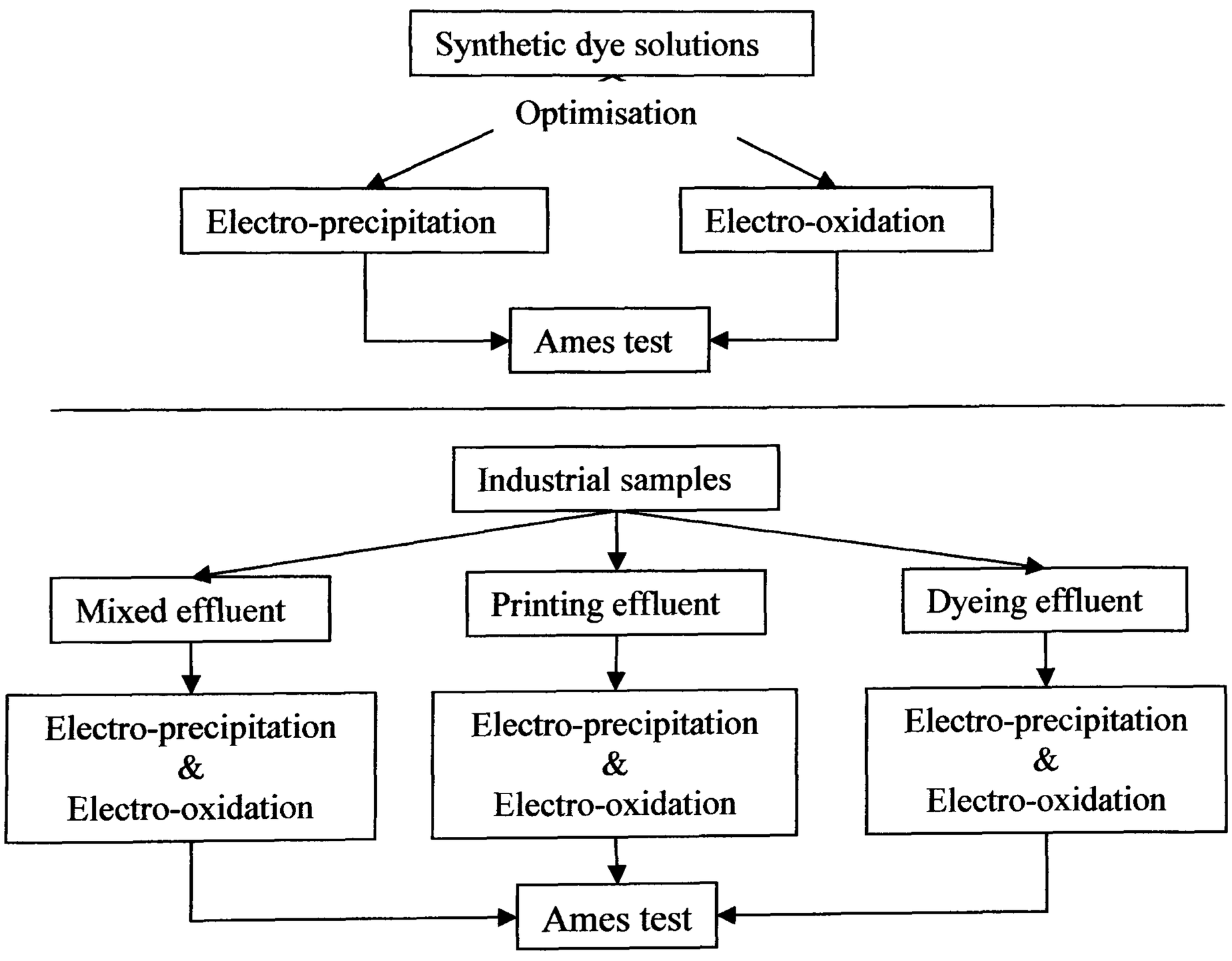


Figure 3.2: Electrochemical treatment of synthetic and industrial solutions containing dyes

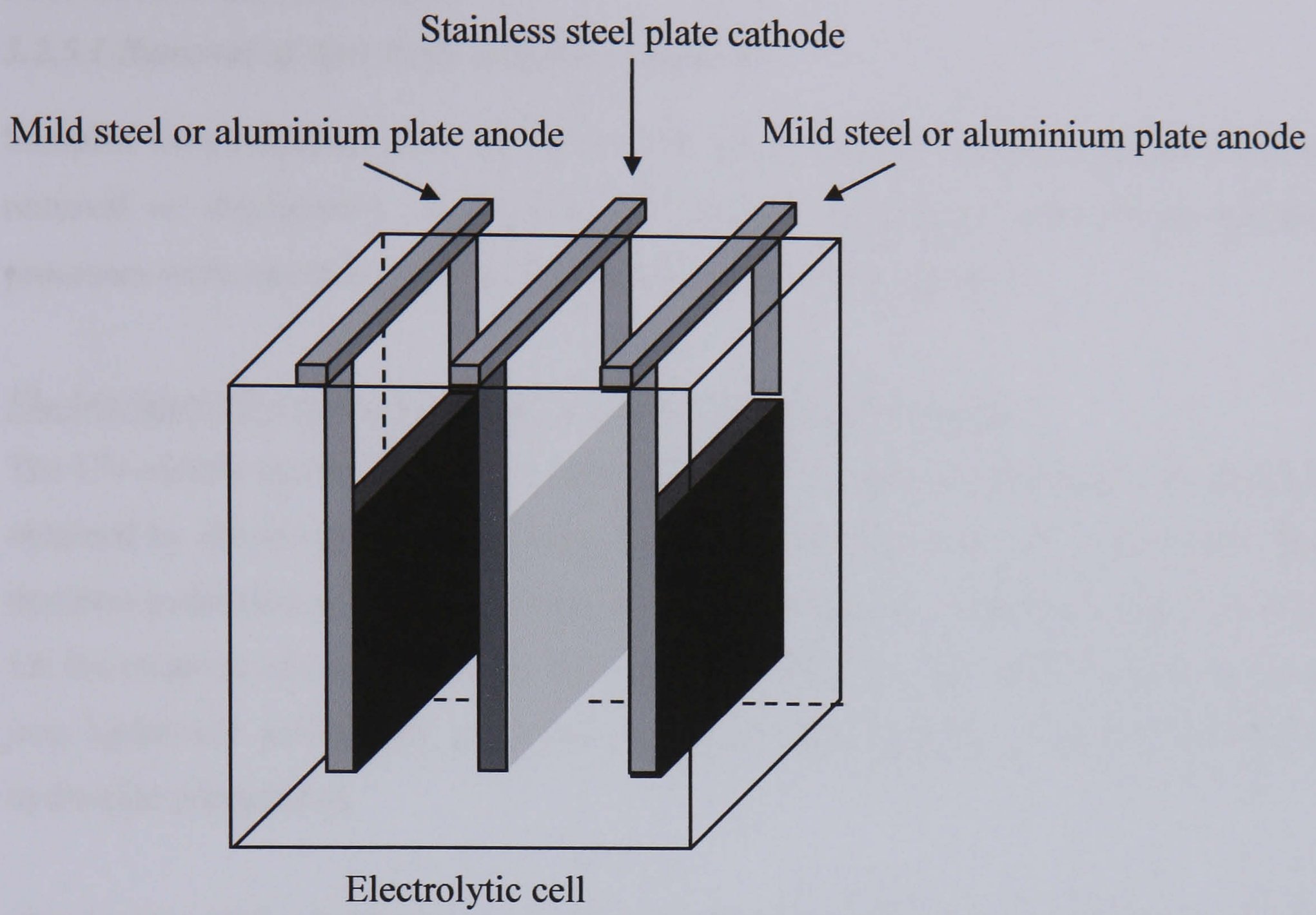


Figure 3.3: Electro-precipitation cell system

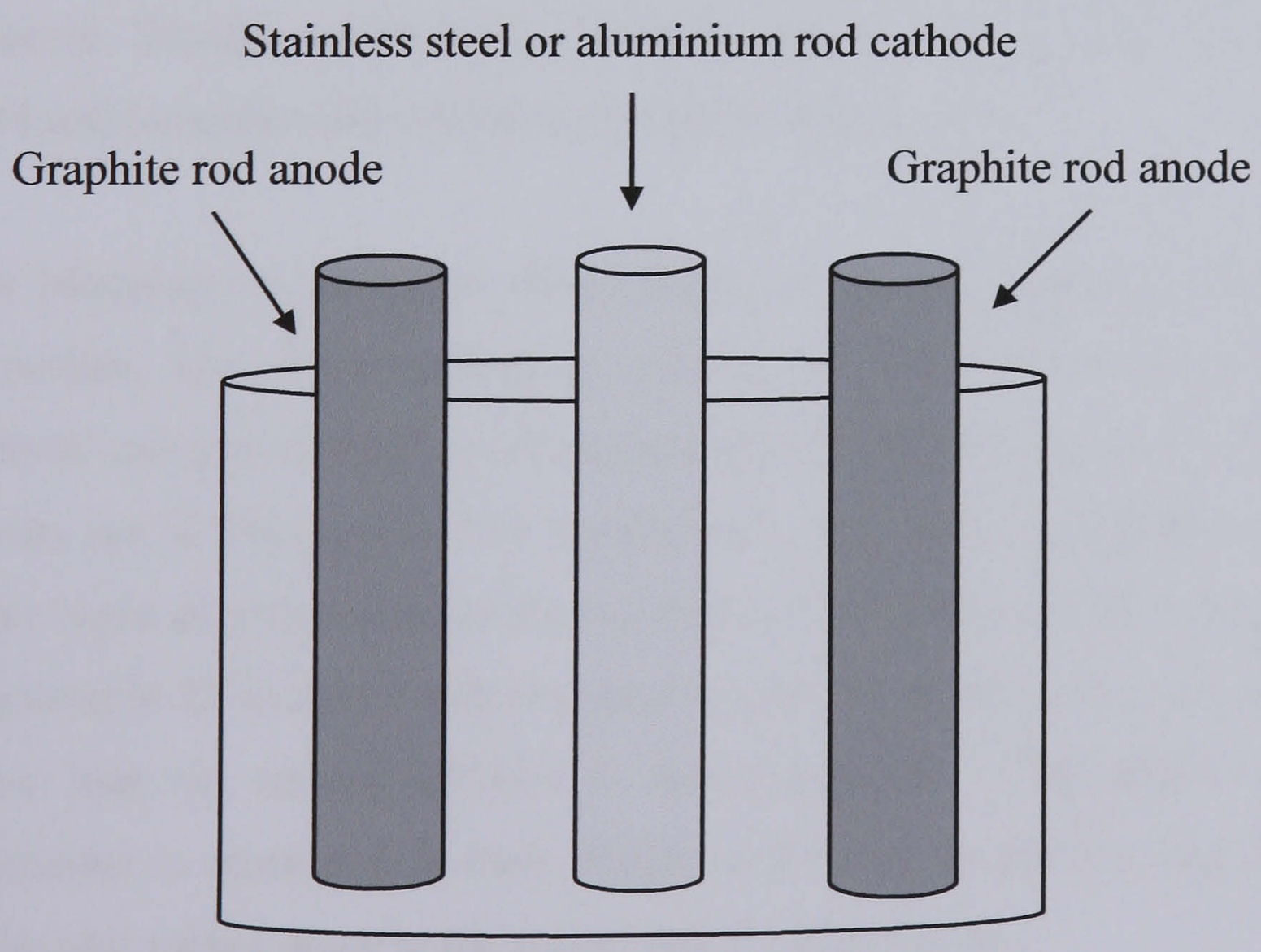


Figure 3.4: Electro-oxidation cell system

3.2.5 Results and Discussion

3.2.5.1 Removal of dyes from synthetic solutions

Samples were collected after 10, 20, 30, 40, 50, 60 and 120 minutes treatment and the removal or degradation of the dyes by electro-precipitation and electro-oxidation processes were monitored by changes in their UV- visible spectra.

Electrochemical treatment of aqueous solutions of reactive orange

The UV-visible spectra of reactive orange show that complete removal of colour can be obtained by electro-precipitation using mild steel anodes (Figure 3.5). The results show that iron hydroxide precipitates are better adsorbent materials than aluminium hydroxide for the removal of reactive orange from aqueous solution. An added benefit is that the iron hydroxide precipitates are much easier to filter than the gelatinous aluminium hydroxide precipitates.

The results obtained with the use of the direct electro-oxidation process show that the absorbance in the visible range decreased with increasing treatment time. The electro-precipitation process, however, takes only 20 minutes to remove all dye whereas electro-oxidation process takes 120 minutes to achieve the same level of colour removal. Similar results were obtained with the use of either aluminium or stainless steel rod cathode under identical conditions (Figure 3.6).

The advantage of using the direct electro-oxidation process is that there is no sludge formation. The electro-oxidation process was also carried out using titanium mesh cathode and mixed metal oxide mesh anodes for the treatment of textile effluent and the results are in Figure 3.7. The results show that these electrodes are much better than other types of electrodes for the removal of dyes and complete removal of dyes can be achieved in 20 minutes with the these electrodes. Furthermore, the data from Ames test show that the treated effluent is non-mutagenic. The higher efficiency of these electrodes is attributed to their higher surface areas and the ease of oxidation of dye molecules taking place at the mixed metal oxide anodes.

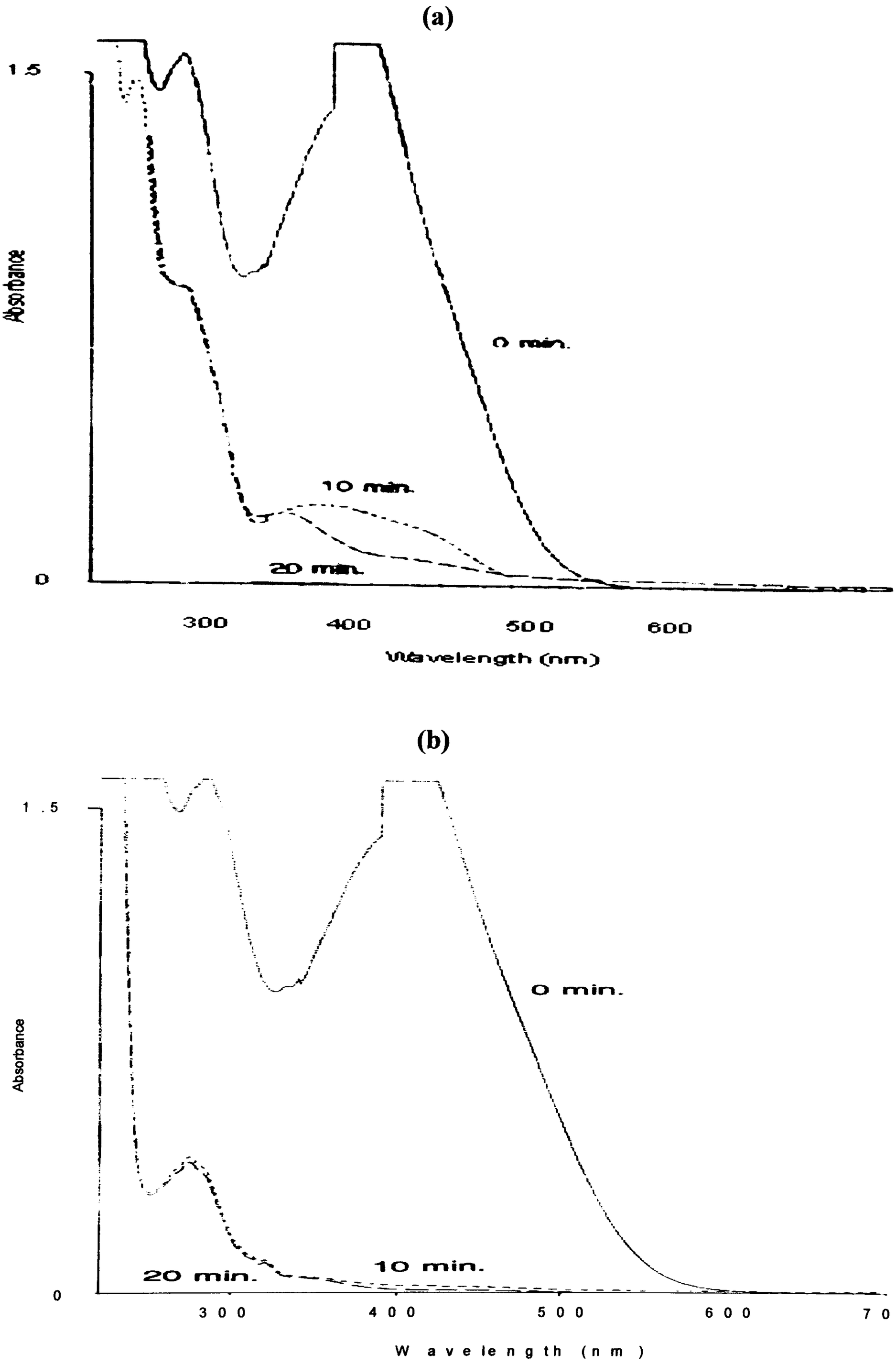


Figure 3.5: UV-visible spectra of reactive orange with time using electro-precipitation process with a) stainless steel cathode and mild steel anodes and b) stainless steel cathode and aluminium anodes.

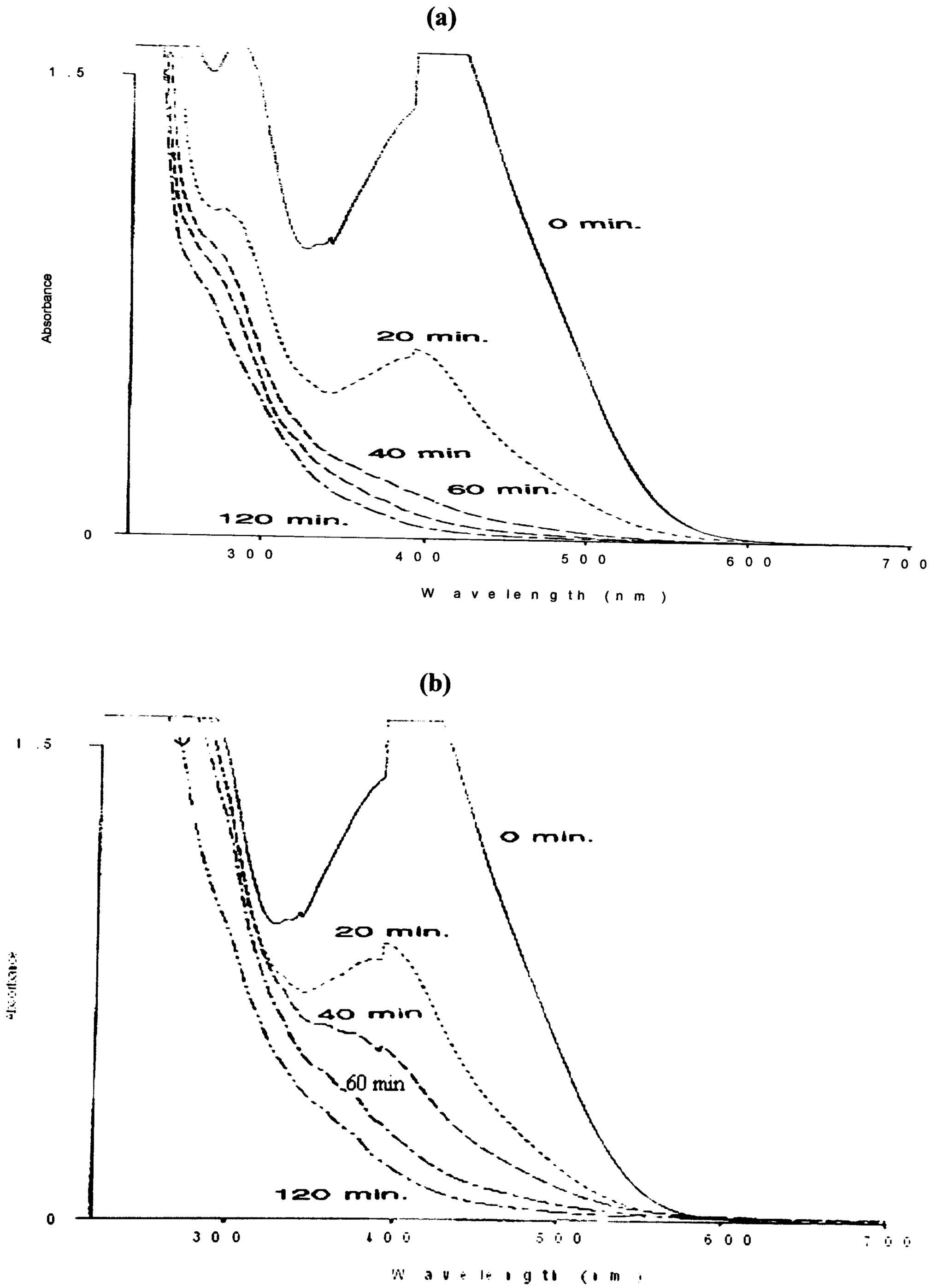


Figure 3.6: UV-visible spectra of reactive orange with time using electro-oxidation process with a) stainless steel cathode and graphite rod anodes and b) aluminium cathode and graphite rod anodes.

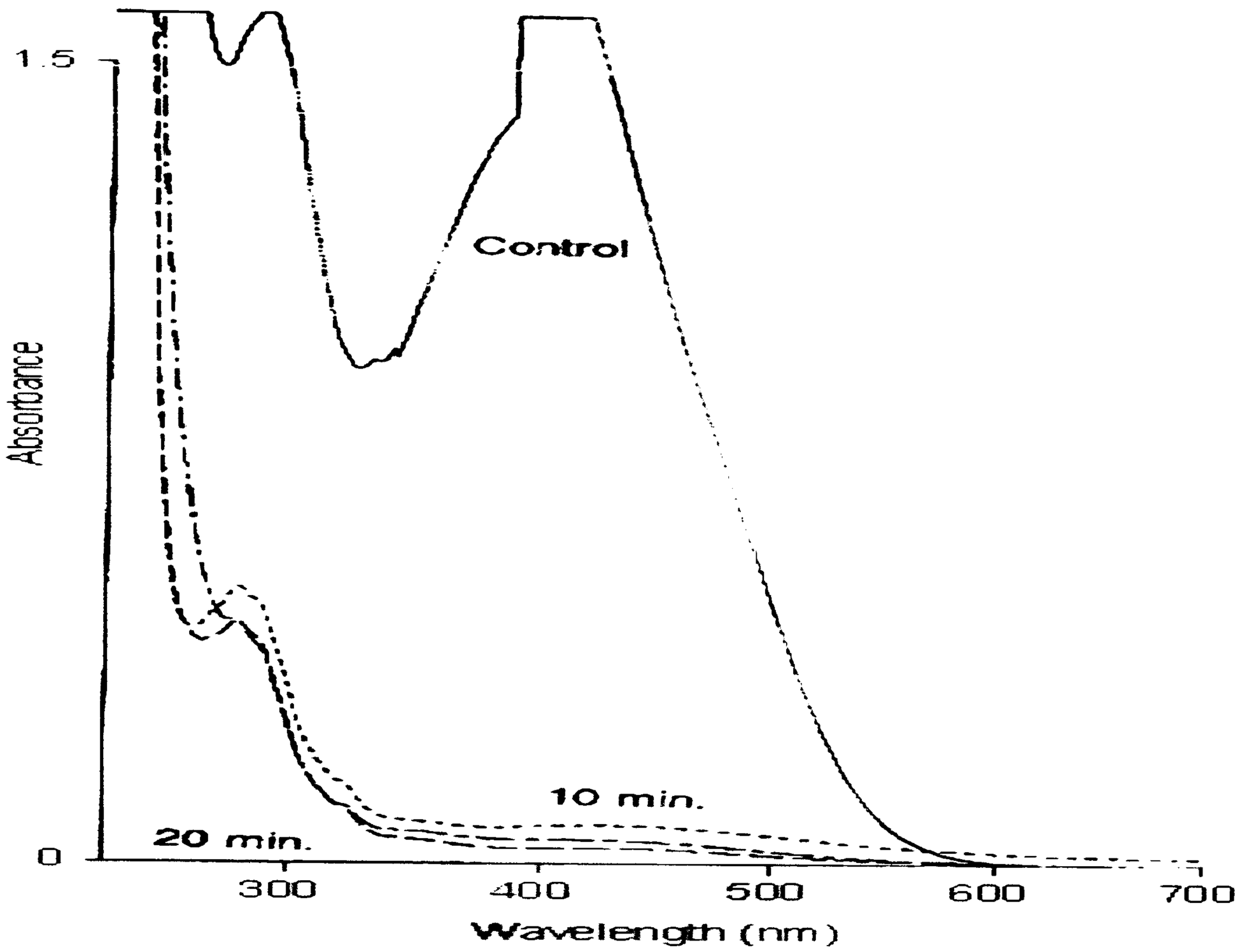


Figure 3.7: UV-visible spectra of reactive orange with time using electro-oxidation process with titanium mesh cathode and mixed metal oxides anodes.

Effect of electrolyte concentration on the removal of reactive orange

A set of experiments was carried out using 0, 2, 4, 6, 8 and 10 g/L sodium chloride as an electrolyte. The data in Figure 3.8 show that the addition of 2 g/L electrolyte increased the efficiency of the reaction from the zero concentration situation, especially at the initial stages of the reaction (Figure 3.8b). A further increase in the electrolyte concentration from 2 g to 10 g/L had no effect on the removal of dyes. The increase in the electrolyte concentration, however, decreases the energy consumption (Figure 3.9). The energy consumption was 13.2 kWh/kg without any electrolyte, which reduced to 3.4 kWh/kg with the use of 10 g/L sodium chloride (analytical grade and supplied by Merck). The decrease in energy consumption at higher concentration of sodium chloride is attributed to the increase in solution conductivity.

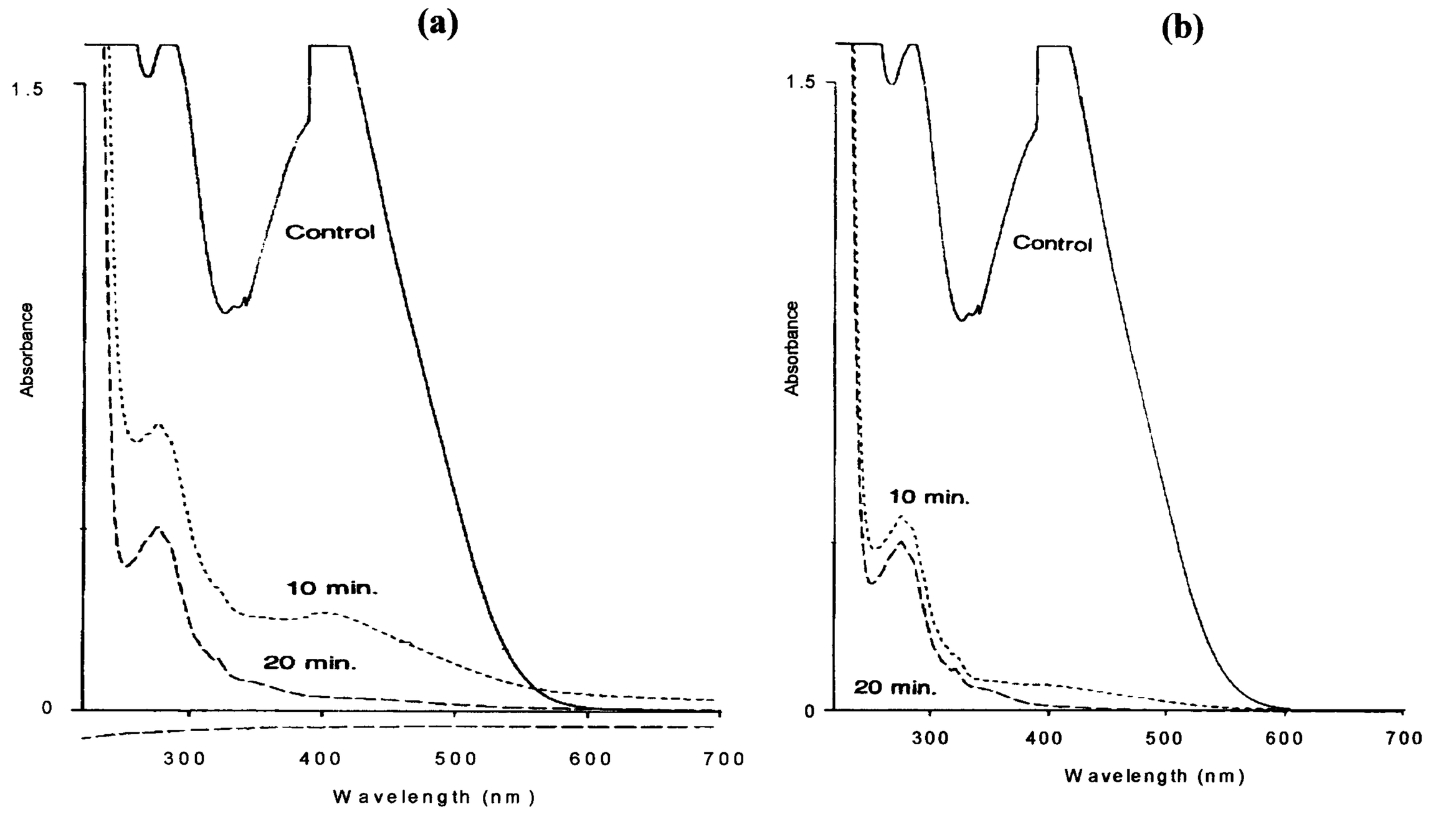


Figure 3.8: Effect of electrolyte concentration on the removal of reactive orange using electro-precipitation process with stainless steel cathodes and aluminium anodes.

(a) 0 g/L, b) 2 g/L, c) 4 g/L and d) 6 g/L sodium chloride

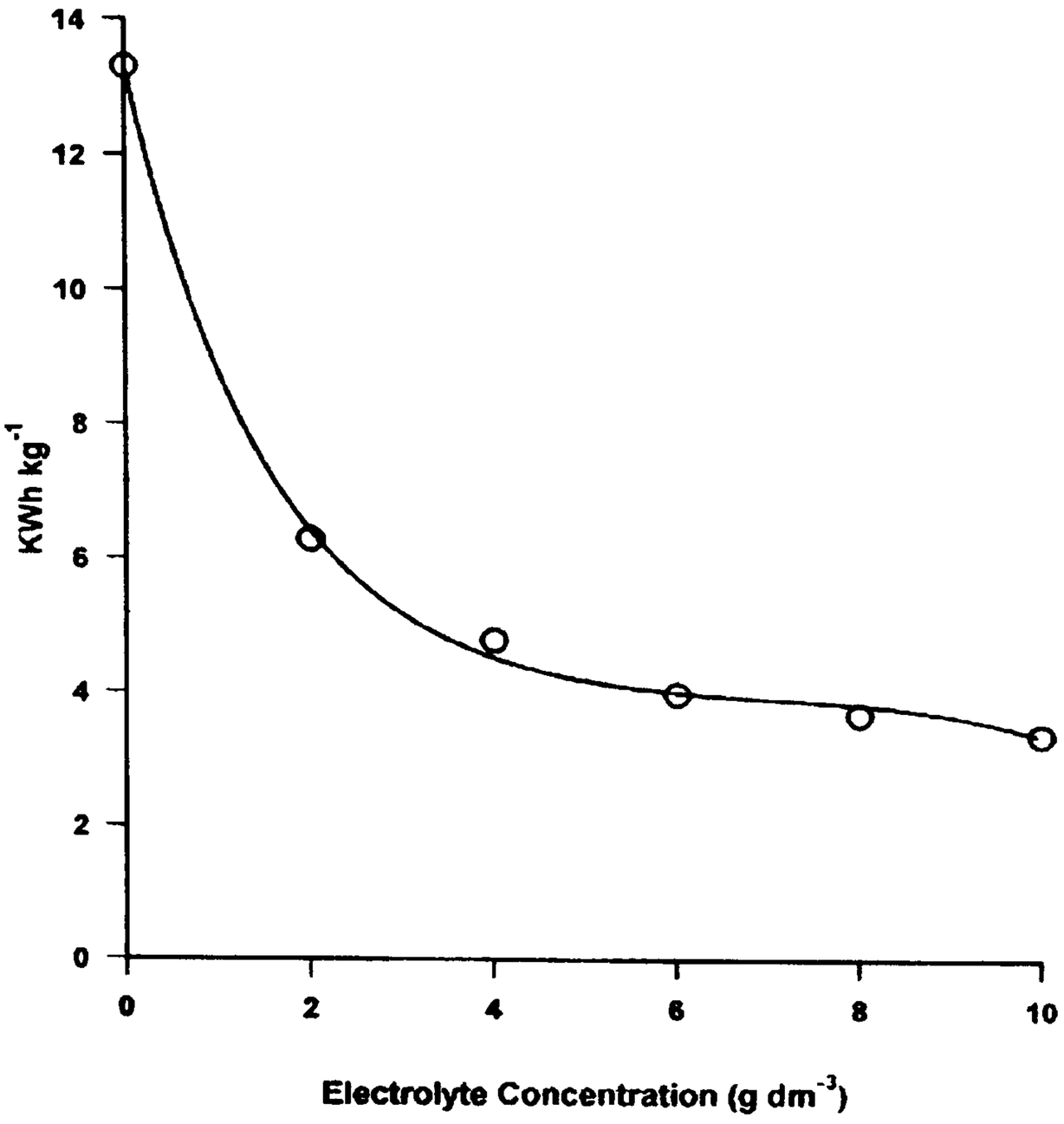


Figure 3.9: Energy consumption versus electrolyte concentration for the electro-precipitation of reactive orange

Electrochemical treatment of aqueous solutions of reactive violet

The UV-visible spectrum of reactive violet, before electrochemical treatment, shows one peak in the visible region (λ_{max} 550 nm) and two peaks in the UV region (270 nm and 345 nm). Figure 3.10 show the removal efficiency of reactive violet with time using electro-precipitation with mild steel anodes and electro-oxidation with stainless steel rod cathode and graphite rod anodes. The data show that electro-oxidation process takes longer to remove the colour component in the visible and the ultraviolet regions compared to electro-precipitation process.

The use of mild steel plate anodes during the electro-precipitation process reduces the absorbance in the visible region but there is still a small peak in the UV- region. It takes an extra 10 minutes to bring the absorbance in the visible range down to zero (Figure 3.10a). In the case of electro-oxidation process a slow but complete oxidation of reactive violet was achieved using Al rod cathode and graphite rods as anodes (Figure 3.10 b).

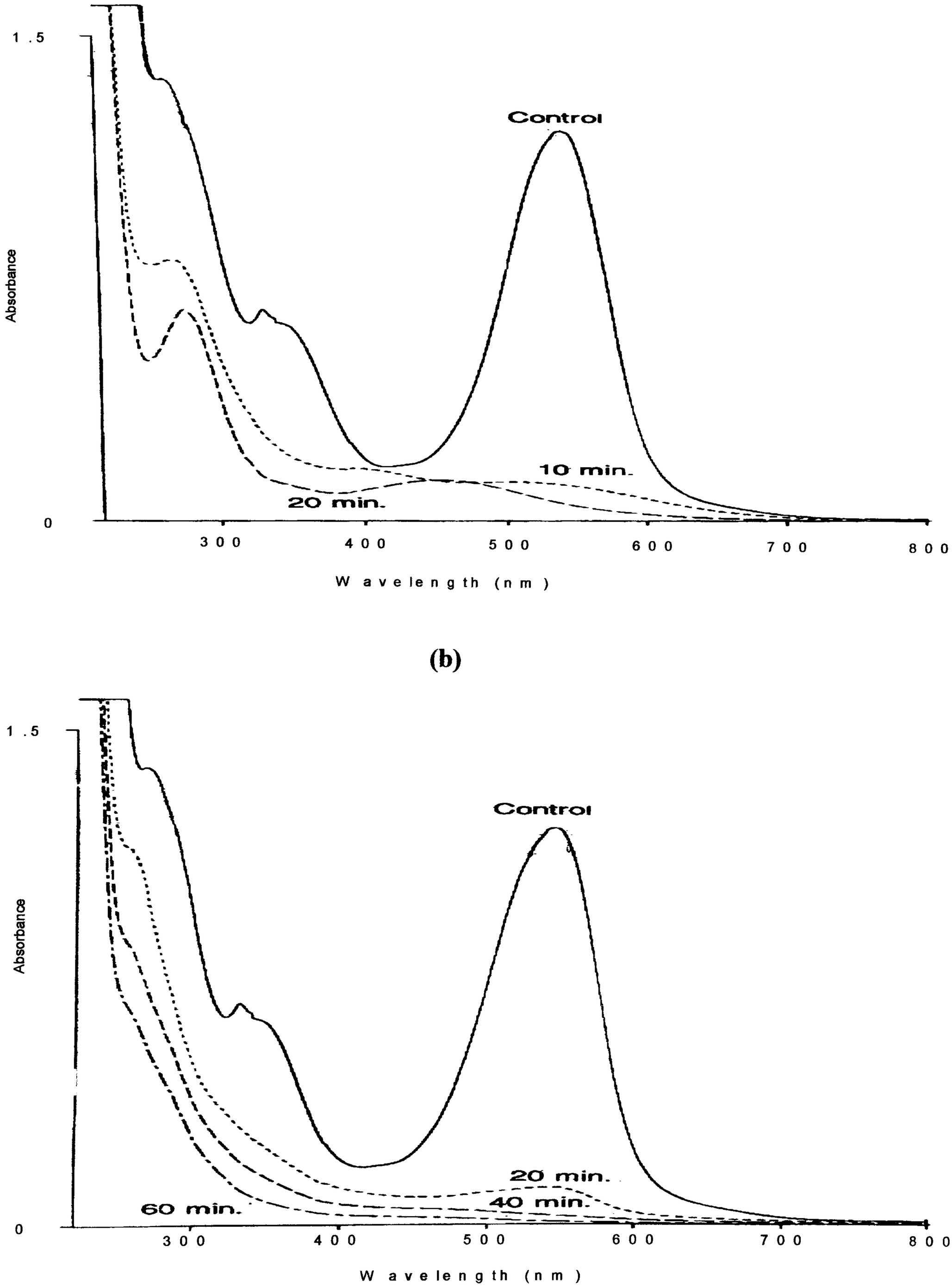


Figure 3.10: UV-visible spectra of reactive violet before and after electrochemical treatment using a) electro-precipitation process with mild steel anodes and b) electro-oxidation process with stainless steel rod cathode and graphite rods as anodes.

The results on the effect of sodium chloride concentration as an electrolyte on the electro-precipitation with aluminium anodes are give in Figure 3.11. The data indicate that no advantage in the removal of colour was obtained by increasing the electrolyte concentration from 2 to 10 g/L. A complete removal of reactive violet was not achieved even after 30 minutes of treatment time.

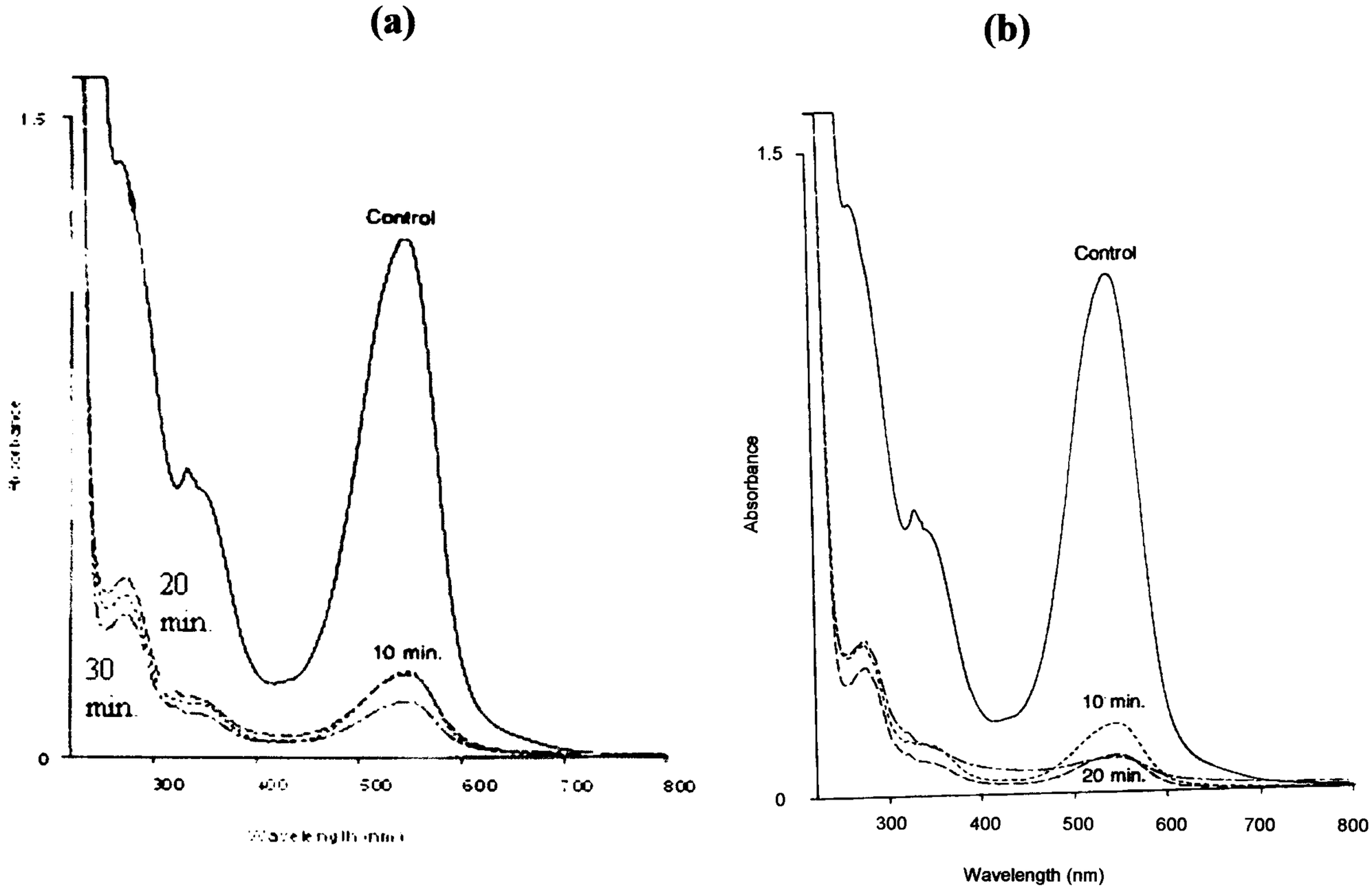


Figure 3.11: UV-visible spectra of reactive violet before and after electrochemical treatment using electro-precipitation process with aluminium anodes in the presence of a) 2g/L sodium chloride as an electrolyte b) 10g/L sodium chloride as an electrolyte

Electrochemical treatment of aqueous solutions of direct pink

The UV-visible spectra of direct pink show two peaks in the visible region (525 nm and 550 nm) and two peaks in the UV region (299 nm and 350 nm). The results obtained show that electro-precipitation using both mild steel and aluminium anodes can be used for the removal of direct pink. A complete removal of colour was obtained after 20 minutes of reaction time (Figure 3.12). No advantage in colour removal was achieved by increasing the reaction time from 20 minutes to 30 minutes. The use of mild steel anodes instead of aluminium showed that colour removal is faster, especially at the initial stages of the reaction, and the optimum reaction time for complete colour

removal is 20 minutes. The results obtained show that iron hydroxide precipitates are better adsorbents for this dye than aluminium hydroxide (Figure 3.12 a).

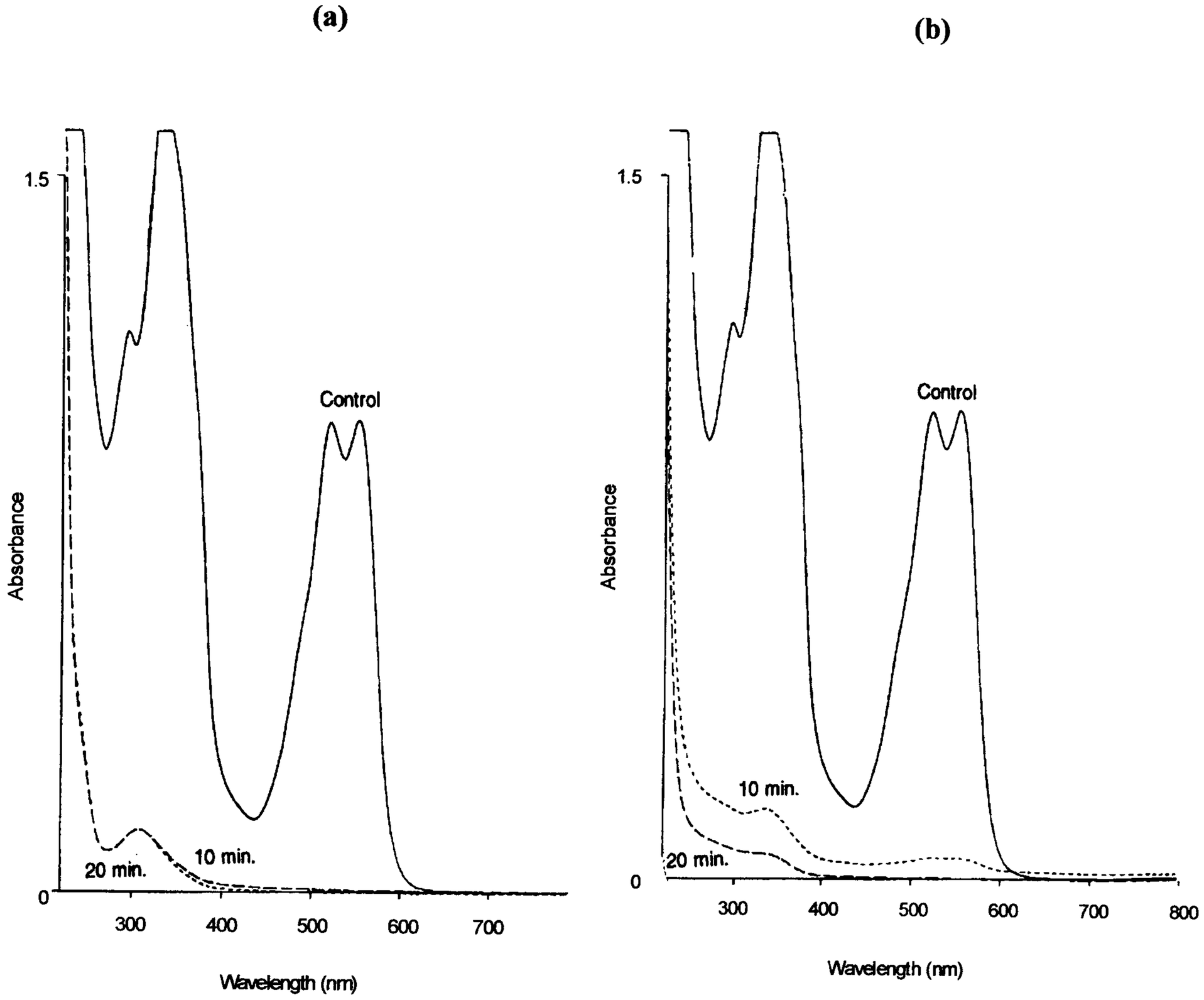


Figure 3.12: UV-visible spectra of direct pink before and after electro-precipitation process using a) mild steel anodes and b) aluminium anodes

The effects of electrode materials on the electro-oxidation of direct pink were also studied and the results are presented in Figure 3.13. The results obtained show that the electro-oxidation of direct pink is slow with the use of graphite rods as anodes (Figure 3.13a and b) and takes more than 60 minutes to achieve the complete degradation of dye molecules. The data obtained with the use of titanium mesh cathode and mixed metal oxides as anodes show that it takes only 10 minutes to drop the visible portion of the spectrum to zero but the UV- portion takes extra 10 minutes to reach the zero value (Figure 3.13c). The degradation of direct pink is slow when titanium mesh cathode was replaced with stainless steel plate cathode (Figure 3.13d) and this decrease is attributed to the reduction in the total surface area of the electrodes.

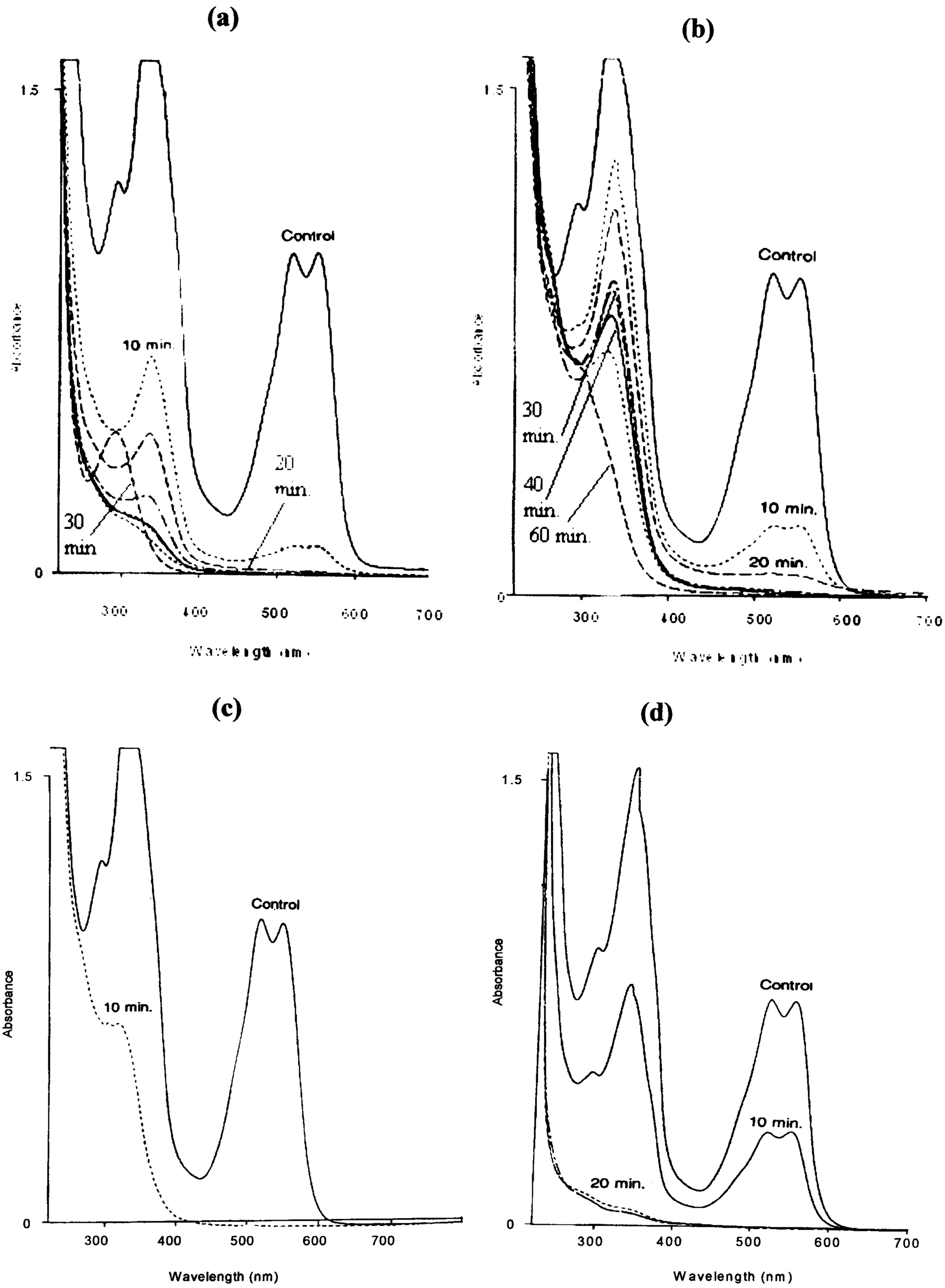


Figure 3.13: UV-visible spectra of direct pink before and after electro-oxidation process using a) stainless steel rod cathode and graphite rods as anodes b) aluminium rod cathode and graphite rods as anodes c) titanium mesh cathode and mixed metal oxide as anodes and d) stainless steel plate cathode and mixed metal oxide as anodes.

The anodic oxidation of direct pink depends upon the nature of the cathode and anode materials and the best results were obtained with the use of titanium mesh cathode and mixed metal oxide anodes (Figure 3.13c).

Anodic oxidation of direct pink was carried out in the presence of sodium chloride as a supporting electrolyte. The aim was to improve the efficiency of the electro-oxidation process with aluminium rod cathode and graphite rods as anodes. The data in Figure 3.14a show that no benefit in the degradation of direct pink was achieved with the use of sodium chloride. Experiments were also carried out to investigate the effects calcium chloride instead of sodium chloride on the anodic oxidation of direct pink. The use of 10 g/L calcium chloride as an electrolyte changed the absorbance pattern and this is attributed to the formation of turbidity in the sample solution (Figure 3.14b). The visible portion of the spectrum dropped to zero after 120 minutes of treatment but although there was evidence of some anodic oxidation in the UV portion it is clear that it does not lead to a complete mineralization of direct pink. The reduction in the percentage degradation of direct pink, in the presence of sodium chloride, may be due to the formation of some intermediate species which are responsible to slow down the overall degradation process.

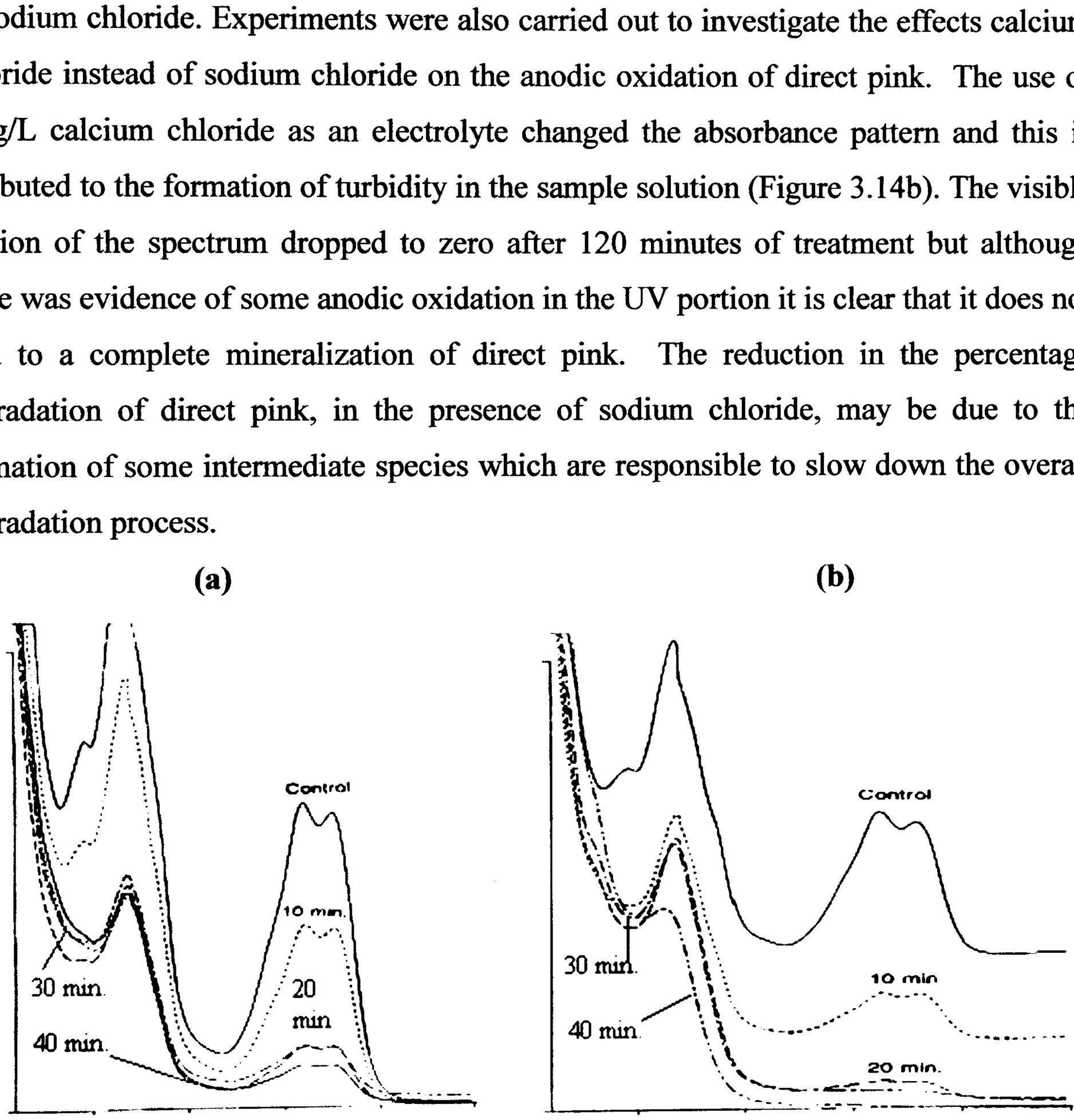


Figure 3.14: UV-visible spectra of direct pink before and after electro-oxidation process using aluminium rod cathode and graphite rods as anodes a) in the presence of sodium chloride as an electrolyte b) in the presence of calcium chloride as an electrolyte.

Electrochemical treatment of aqueous solutions of direct turquoise

The UV-visible spectra of direct turquoise show three peaks in the visible region (590 nm, 610 nm and 680 nm) and two peaks in the UV region (260 nm and 350 nm).

The spectral curves after 10 and 20 minutes treatment time using electro-precipitation process with mild steel and aluminium electrodes are given in Figures 3.15. The results show that a complete removal of direct turquoise was achieved after 20 minutes in both cases.

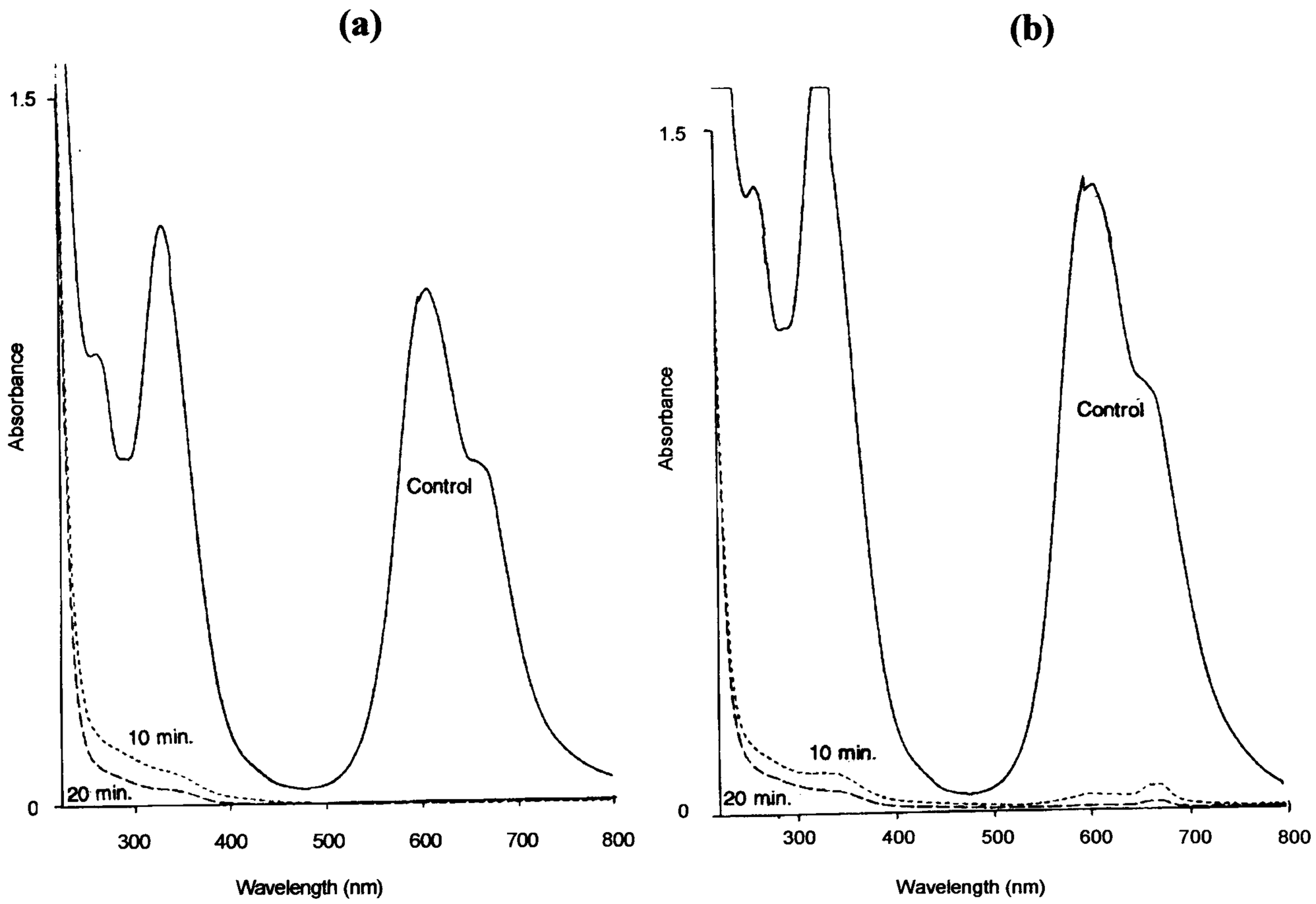


Figure 3.15: UV-visible spectra of direct turquoise before and after electro-precipitation process using a) mild steel anodes and b) aluminium anodes.

Experiments were carried out to investigate the effects of sodium chloride as an electrolyte on the electro-precipitation process using aluminium anodes. The results in Figure 3.16 show that the addition of sodium chloride did not increase the degradation of direct turquoise and similar results were obtained with 2 and 10 g/L of sodium chloride. The use of sodium chloride, however, reduces the energy consumption for the complete removal of dyes from aqueous solution.

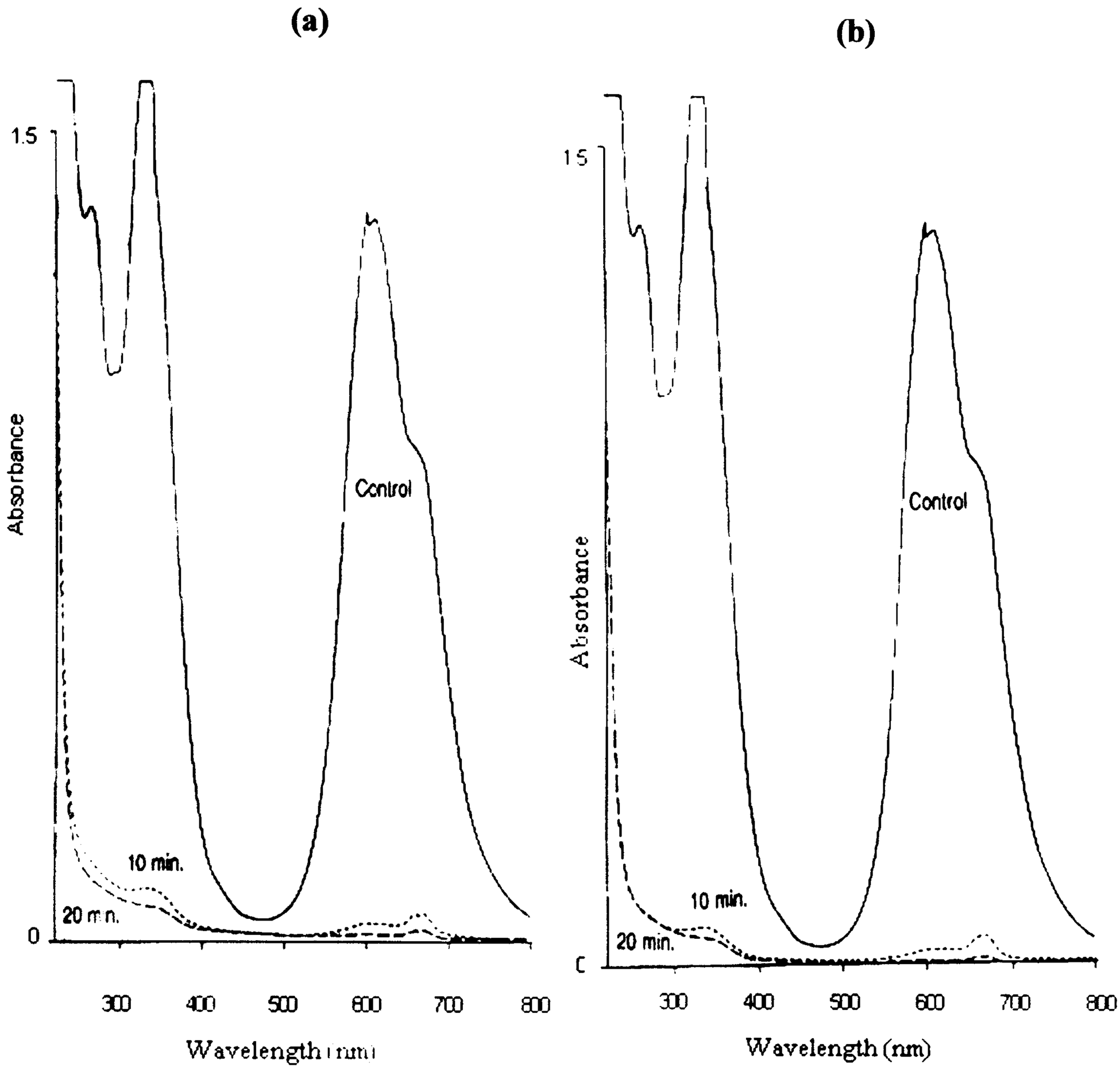


Figure 3.16: UV-visible spectra of direct turquoise before and after electro-precipitation process using aluminium anodes in the presence of a) 2 g/L sodium chloride and b) 10 g/L sodium chloride as an electrolyte.

Experiments were carried out to investigate the effect of electrode materials on the electro-oxidation of direct turquoise. Similar results were obtained with the use of both stainless steel and aluminium rod cathodes along with graphite rods as anodes (Figure 3.17a and b). The replacement of stainless rod with an aluminium rod as cathode slows down the reaction especially at the initial stages of the reaction. The electro-oxidation of direct turquoise with the use of a titanium mesh cathode and mixed metal oxide mesh anodes is very fast and 20 minutes treatment time was determined to be the optimal, corresponding with the total colour removal (Figure 3.17 c).

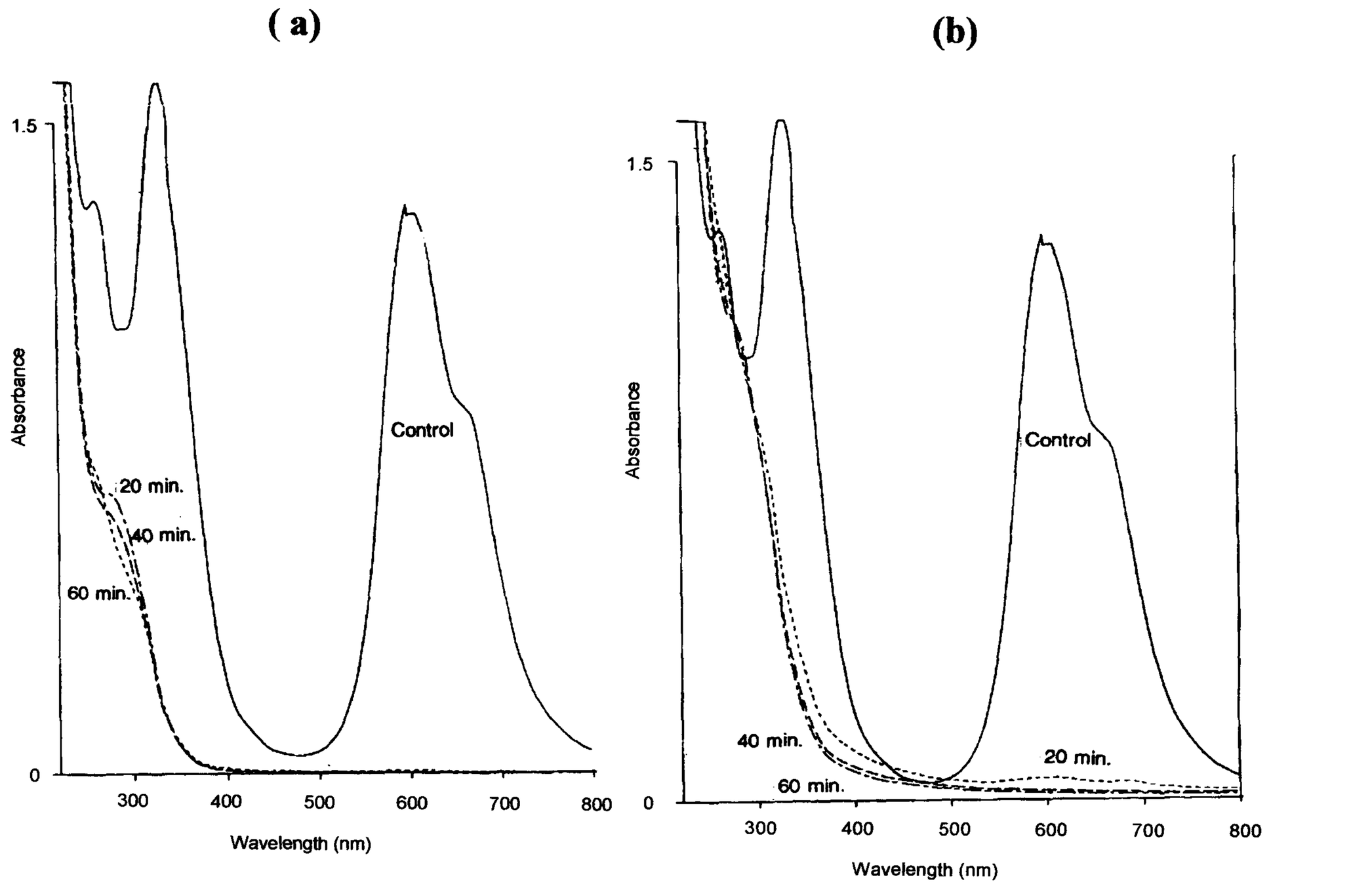


Figure 3.17: UV-visible spectra of direct turquoise before and after electro-oxidation process using a) stainless steel rod cathode and graphite rod anodes b) aluminium rod cathode and graphite rods as anodes c) titanium mesh as cathode and mixed metal oxide as anodes.

Electrochemical treatment of aqueous solutions of disperse blue

For disperse blue, the absorbance in the visible region does not given a single λ_{max} but a broad peak is obtained. The UV- portion shows one peak at 300 nm. Experiments were carried out using both aluminium and mild steel anodes during the electro-precipitation process of disperse blue. The spectral curves after 10 and 20 minutes treatment time with the use aluminium and mild steel anodes are given in Figure 3.18. The data show that similar results are obtained with the use of aluminium or mild steel electrodes. This means that both mild steel and aluminium anodes can be used for the complete removal of disperse blue with the electro-precipitation process.

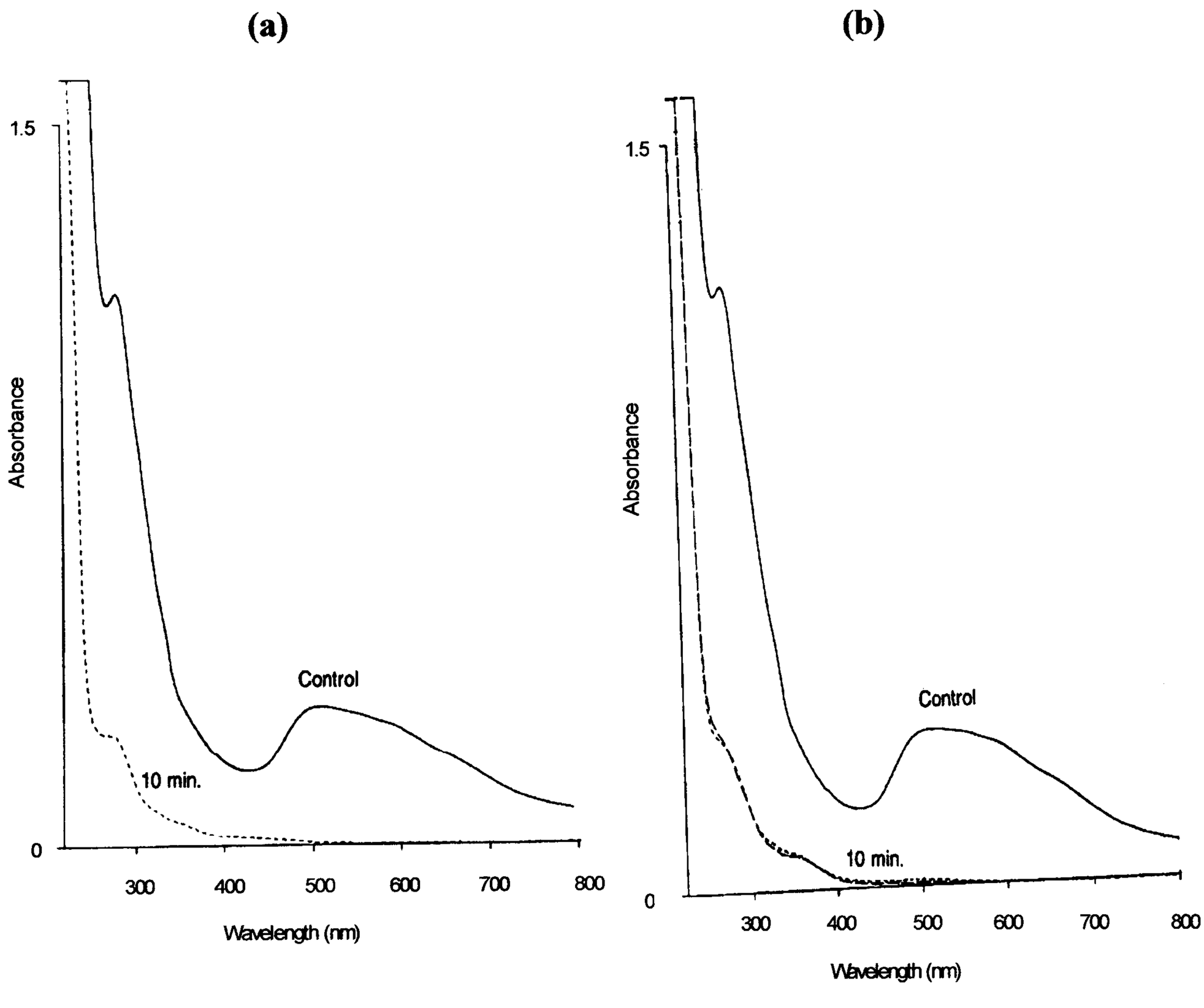


Figure 3.18: UV-visible spectra of Disperse Blue before and after electro-precipitation process using a) mild steel anodes and b) aluminium anodes.

Experiments were also carried out to investigate the effects of electrode materials on the electro-oxidation of disperse blue. The results are presented in Figure 3.19.

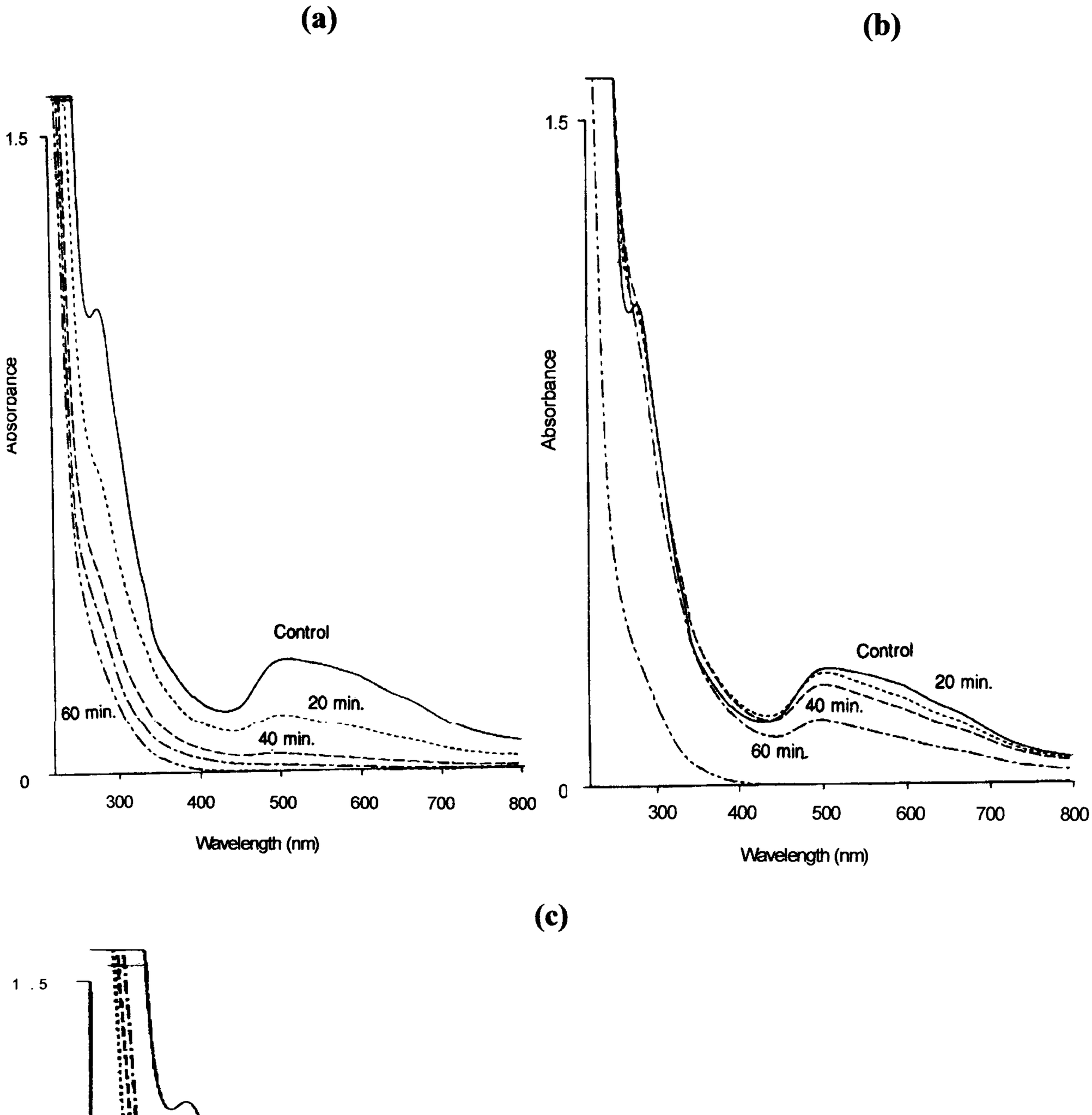


Figure 3.19: UV-visible spectra of disperse blue before and after electro-oxidation process using a) stainless steel rod cathode and graphite rods as anodes, b) aluminium rod cathode and graphite rods as anodes and c) titanium mesh cathode and mixed metal anodes.

The results in Figure 3.19 show that titanium mesh cathode and mixed metal oxide anodes are better than other types of electrodes studied in this work. The electro-oxidation process with the use of graphite anodes is slow and longer reaction time is required to obtain the same level of colour removal as with mixed metal oxide anodes.

Electrochemical treatment of aqueous solutions of disperse violet

The electro-precipitation of disperse violet using aluminium or mild steel plate anodes shows that a complete removal of dye can be achieved within 20 minutes. The reaction is slightly faster in the case of mild steel electrodes than with aluminium electrodes (Figure 3.20). The data show that 20 minutes reaction time is optimal for the total colour removal.

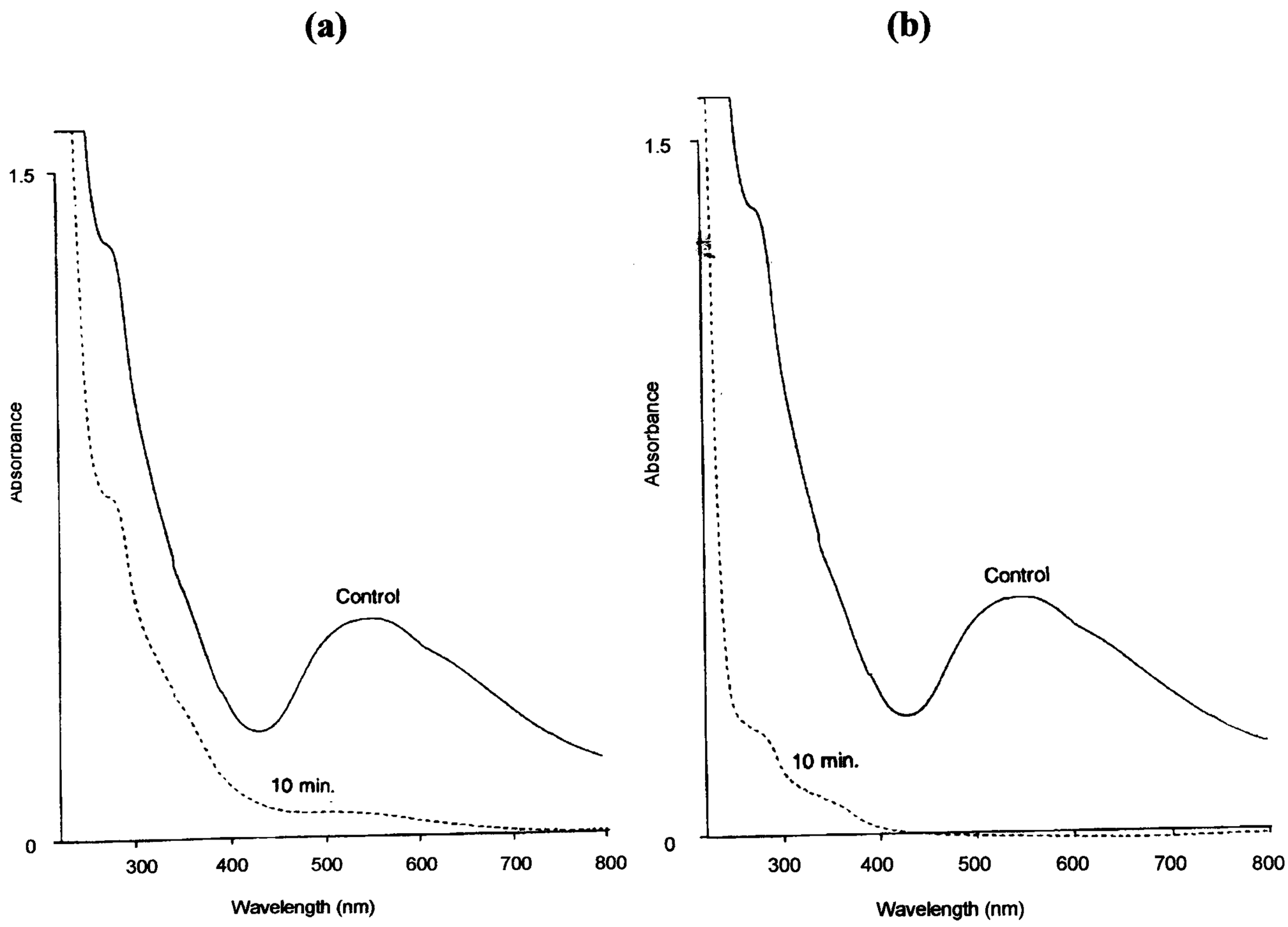


Figure 3.20: UV-visible spectra of disperse violet before and after electro-precipitation process using a) mild steel anodes and b) aluminium anodes.

The electro-oxidation of disperse violet using titanium mesh cathode and mixed metal oxide anodes was very fast and a complete degradation was achieved after only 20 minutes. The anodic oxidation with graphite anodes takes 60 minutes for the complete degradation disperse violet.

The Ames test for mutagenicity

Microbial tests were performed in the Biology Department, Azad Kashmir University, Pakistan, to determine the potential mutagenicity nature of the treated effluent streams. Mutagenicity results before and after electrochemical treatments are given in Table 3.1.

Table 3.1: Analysis of mutagenicity of synthetic dye solutions using Ames tests strains *Salmonella Typhimurium* TA98 and TA100.

No	Treatment methods	Dye sample	Time (min)	Mutagenesis Index		Result
				TA90	TA100	
1	No treatment		0	1.8	1.19	M
2	Electro-precipitation (MS-anodes)		30	1.5	1.34	NM
3	Electro-precipitation (Al-anodes)	Reactive	30	1.6	1.35	NM
4	Electro-oxidation (Gr-anodes)	orange	120	1.4	1.32	NM
5	Electro-oxidation (MM-anodes)		40	1.5	1.34	NM
6	No treatment		0	1.23	nd	M
7	Electro-precipitation (MS-anodes)		30	1.9	1.13	NM
8	Electro-precipitation (Al-anodes)	Direct pink	30	1.5	0.91	NM
9	Electro-oxidation (Gr-anodes)		60	1.7	1.18	NM
10	Electro-oxidation (MM-anodes)		40	1.6	1.14	NM
11	No treatment		0	1.7	1.82	M
12	Electro-precipitation (MS-anodes)		30	1.5	1.03	NM
13	Electro-precipitation (Al-anodes)	Direct	30	1.5	1.09	NM
14	Electro-oxidation (Gr-anodes)	turquoise	60	nd	1.02	NM
15	Electro-oxidation (MM-anodes)		40	1.6	1.07	NM
16	No treatment		0	1.6	1.02	NM
17	Electro-precipitation (MS-anodes)		30	1.6	1.07	NM
18	Electro-precipitation (Al-anodes)	Dispersed	30	1.5	1.08	NM
19	Electro-oxidation (Gr-anodes)	blue	60	1.6	1.06	NM
20	Electro-oxidation (MM-anodes)		40	1.4	1.03	NM

Mutagenesis index = number of revertants obtained in sample/number of revertants of the negative control

M = mutagenic; NM = non-mutagenic; nd = not determined; MS = mild steel;
Al = aluminium; MM = mixed metal; Gr = graphite rod

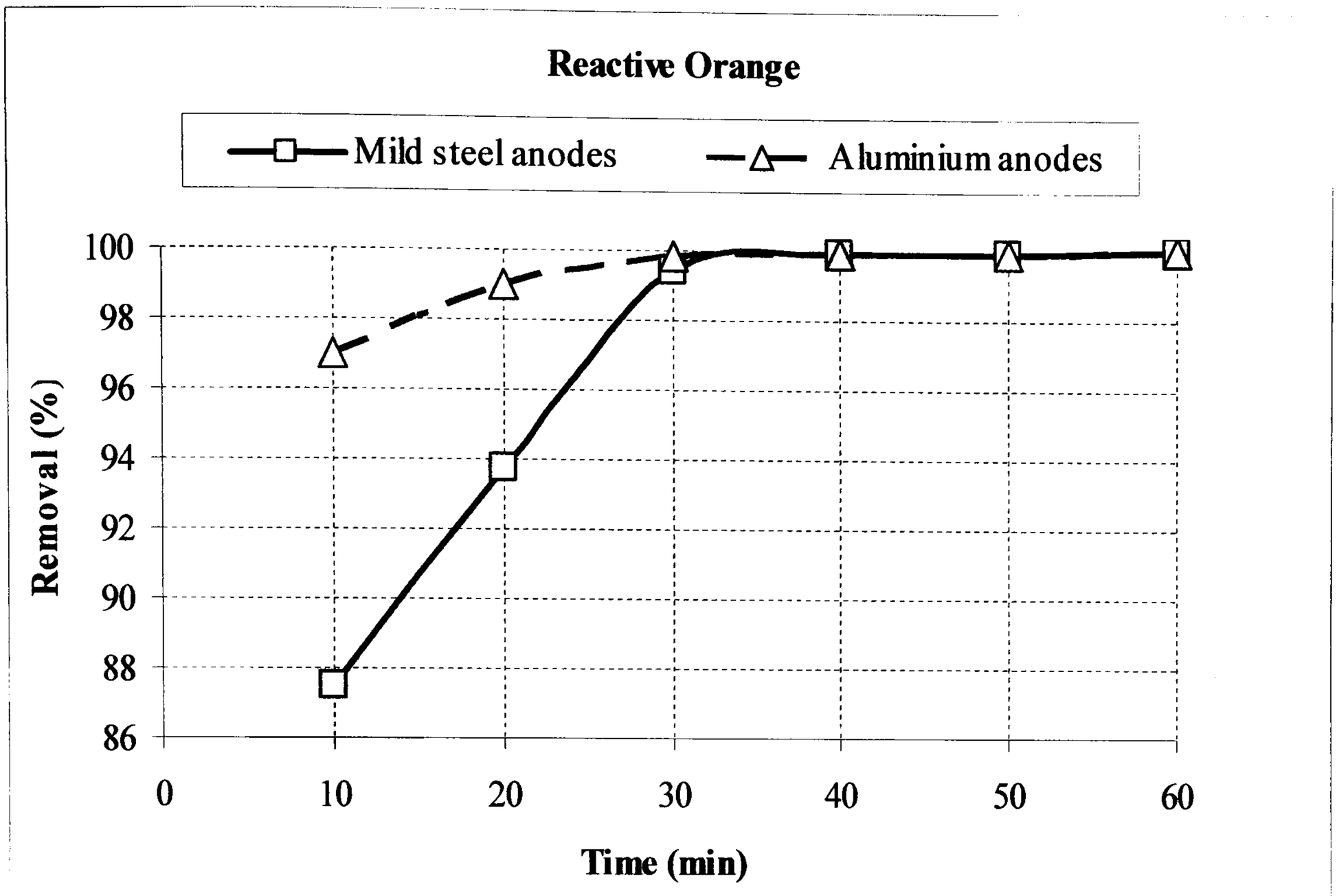
A mutagenic potential of a test item is assumed if the mutant frequency is 2.0 or higher. A dose effect relationship could underline this conclusion.
A possible mutagenic potential is assumed if the quotient ranges between 1.7 to 1.9 in combination with a dose effect relationship.
No mutagenic potential is assumed if all quotients range between 1.0 (or lower) to 1.6. A nonexistent dose effect relationship could underline this conclusion.

The percentage removal of colour (Figures 3.21-3.26) along with the data from the Ames tests (Table 3.1) show that both electro-precipitation and electro-oxidation processes can be used for the removal and degradation of reactive, direct and dispersed dyes from aqueous wastewater streams. These two electrochemical processes must be optimised for each of the dye in order to achieve a complete removal of dye molecules from aqueous wastewater streams. The removal of dye molecules depends on the electrode type and both of these processes have their advantages and disadvantages.

The results in Figures 3.21-3.23 show that an electro-precipitation process with the use of either mild steel or aluminium anodes is suitable for reactive, direct and dispersed dyes studied in this work because the final effluent streams obtained after the treatment process are non-mutagenic in nature and also the process leads to a complete removal of each dye from wastewater streams. The results show that, although, both iron hydroxide and aluminium hydroxide precipitates are equally good adsorbent materials for all of the dyes but an added benefit of the iron hydroxide precipitates is that it is much easier to filter iron hydroxide than the gelatinous aluminium hydroxide precipitates. The main disadvantage associated with this process is that it produces sludge which needs to be disposed of safely.

The results in Figures 3.24-3.26 show that the electro-oxidation process with the use of stainless steel rod cathode and graphite rods anodes can also be used for the removal of reactive, direct and disperse dyes from aqueous solutions containing no electrolyte. This electrochemical cell system, however, takes longer time to remove colour and in most cases a 60 minutes period is an optimum value for the complete removal of dyes. The addition sodium chloride can reduce the energy consumption of the process.

The electro-oxidation process with the use of titanium mesh cathode and mixed metal oxide anodes is an excellent process for the complete removal of dyes and usually takes less time to remove colour compared to the electro-oxidation process with the use of stainless steel rod cathode and graphite rods anodes. However, replacing titanium mesh cathode with stainless steel plate cathode reduces the reaction efficiency and a longer reaction time is required to achieve the same level of degradation as in the case of titanium mesh cathode. This decrease in degradation is attributed to the reduction in the total surface area. All treated effluents are non-mutagenic.



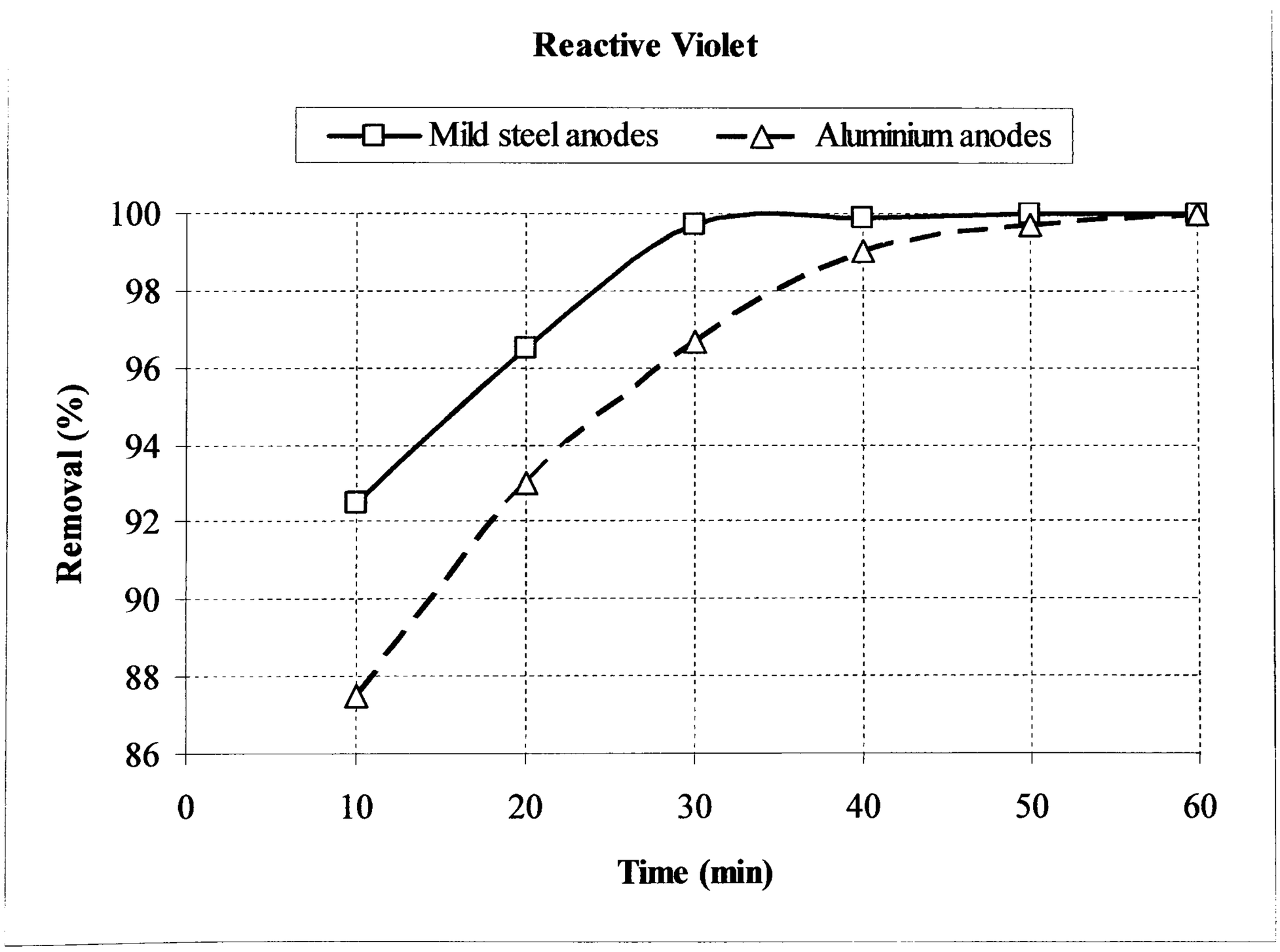


Figure 3.21: Percentage removal of reactive dyes using electro-precipitation process

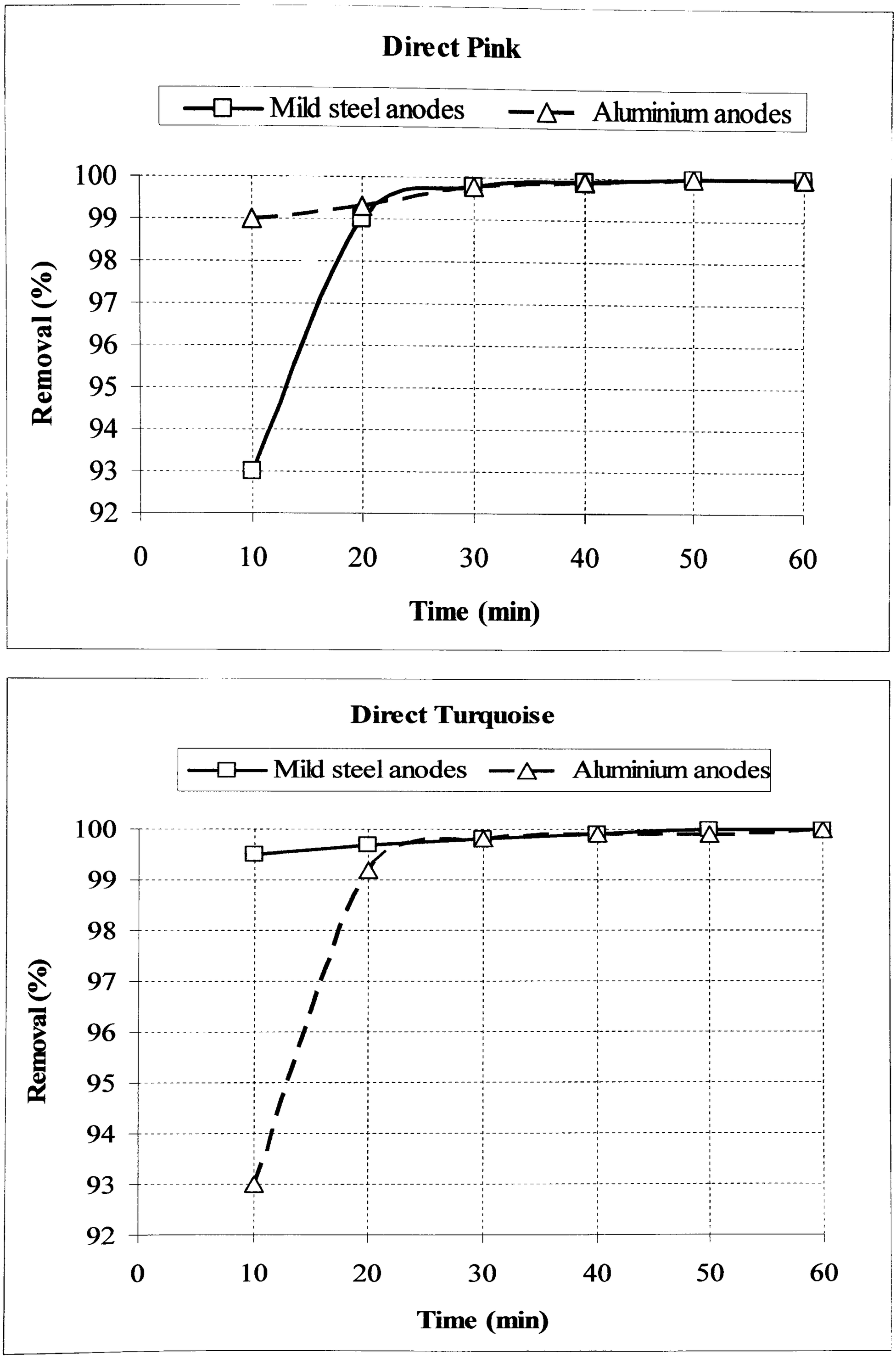


Figure 3.22: Percentage removal of direct dyes using electro-precipitation process

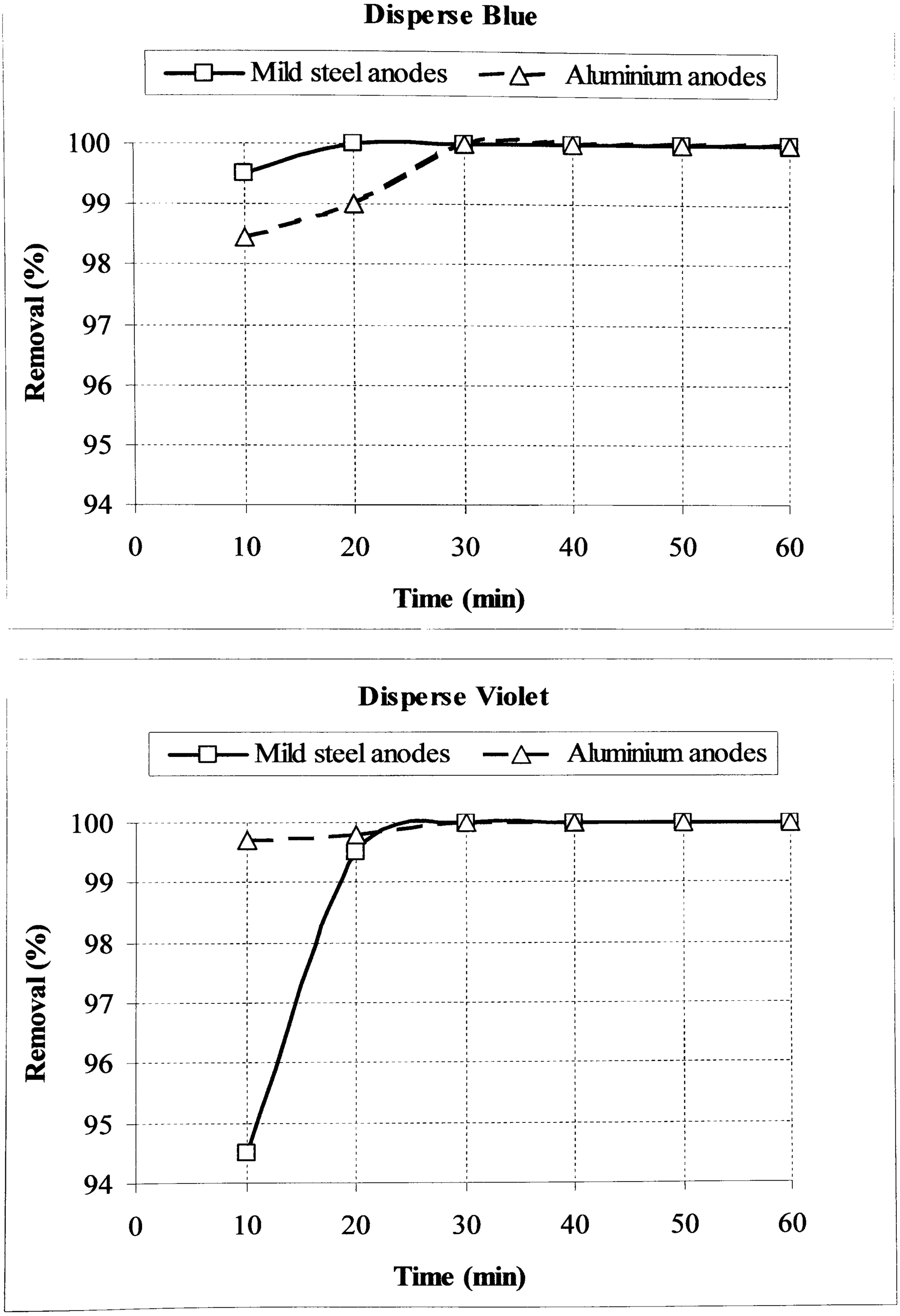
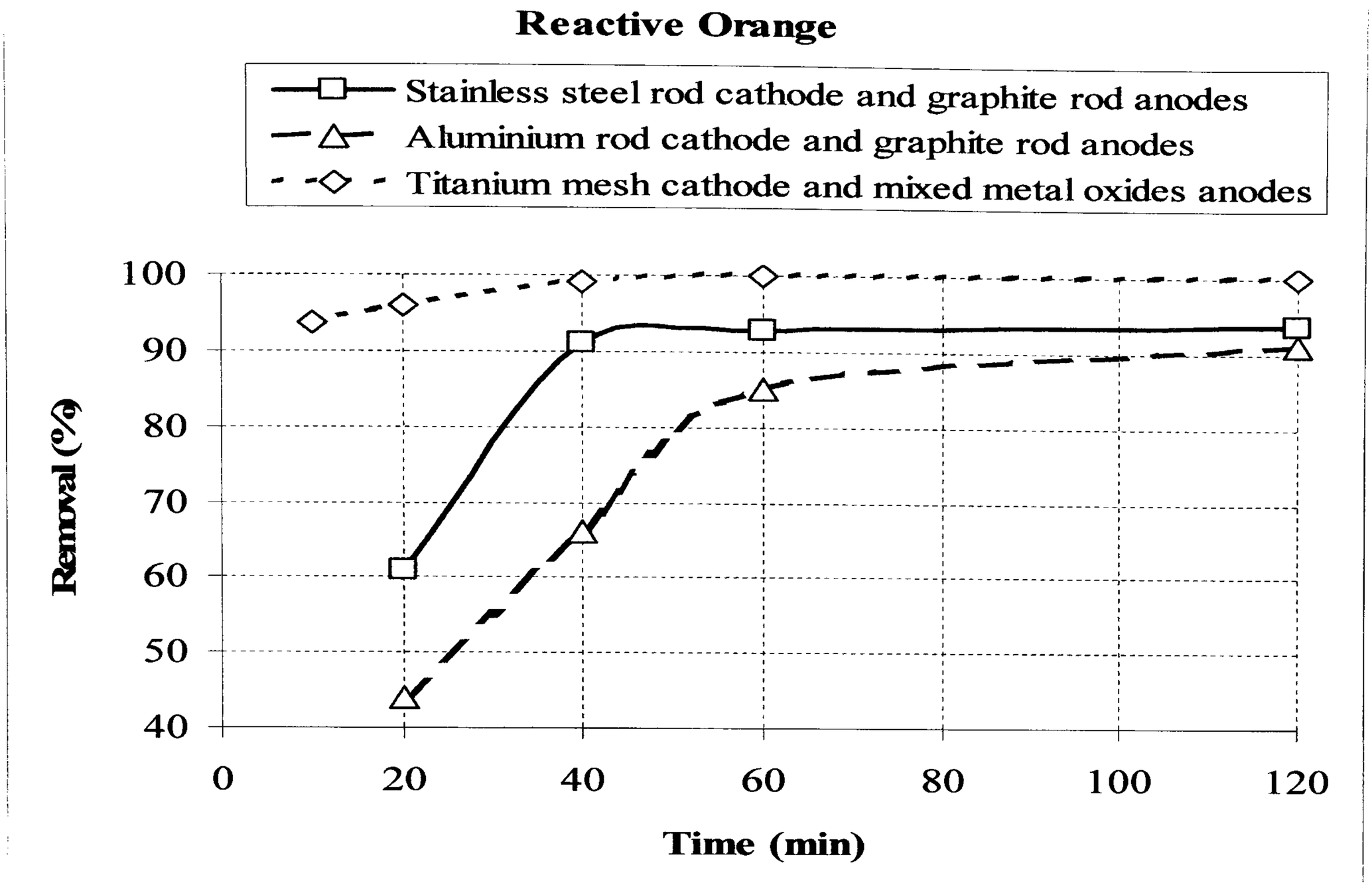


Figure 3.23: Percentage removal of disperse dyes using electro-precipitation process



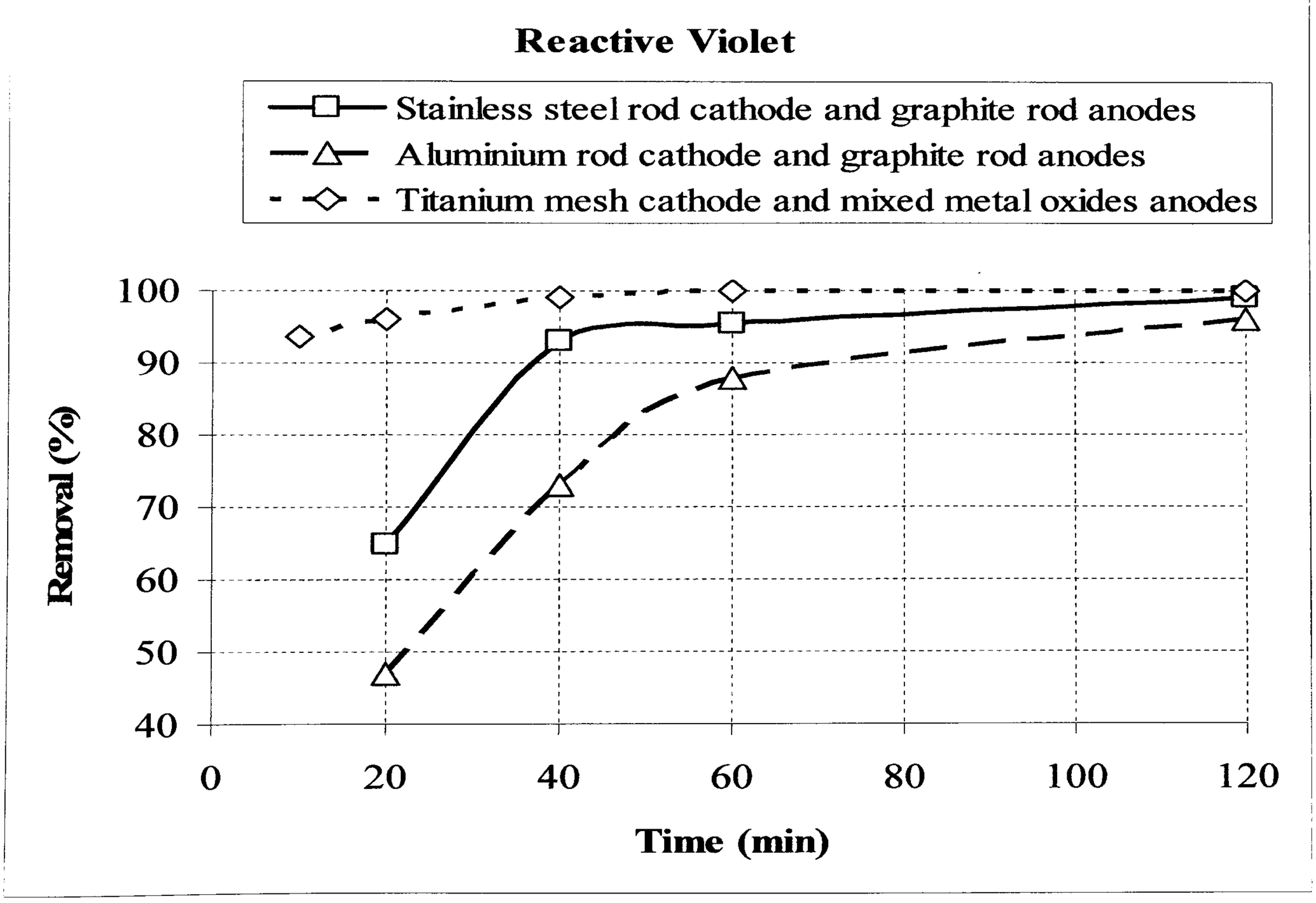
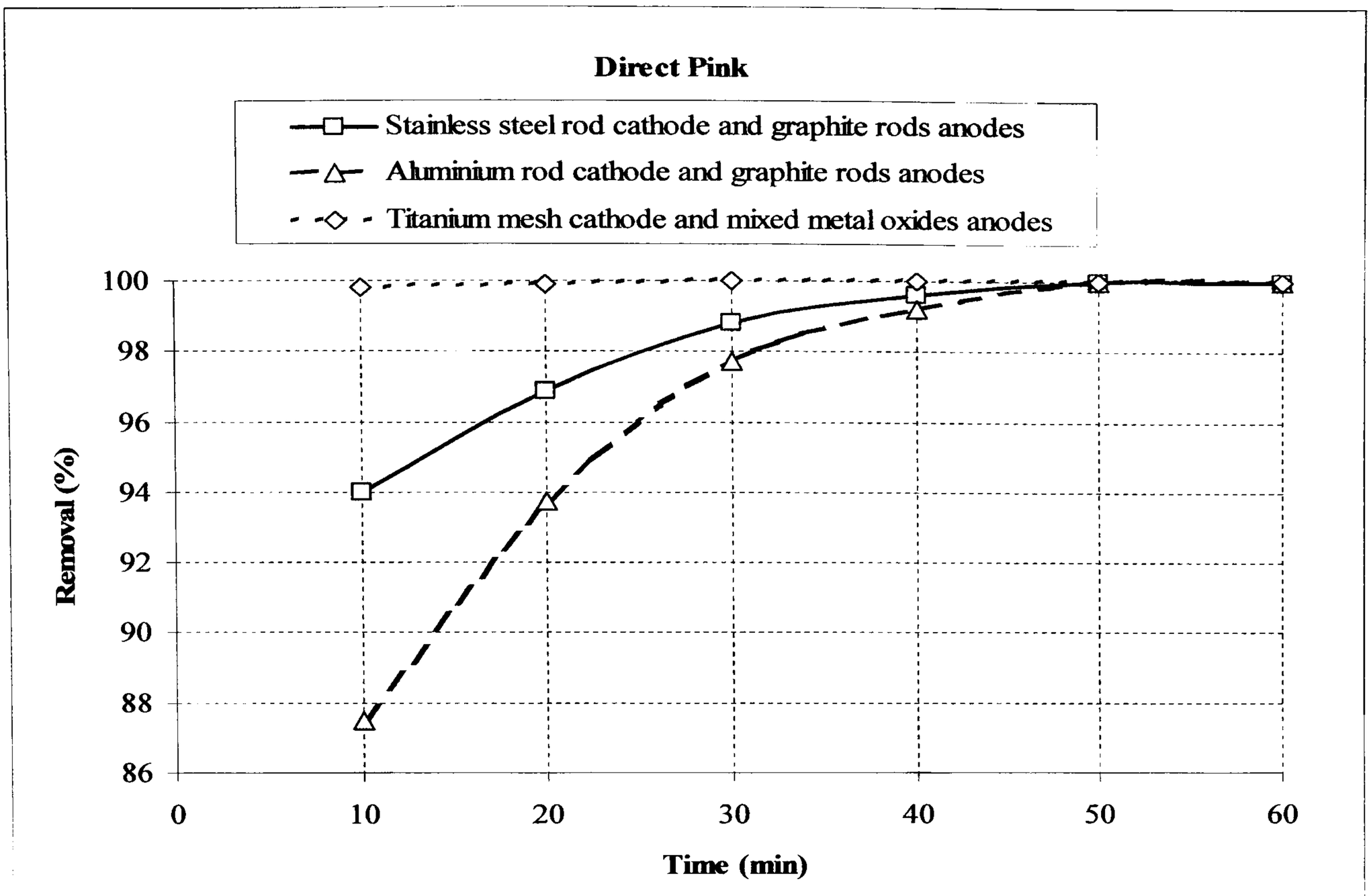


Figure 3.24: Percentage removal of reactive dyes using electro-oxidation process



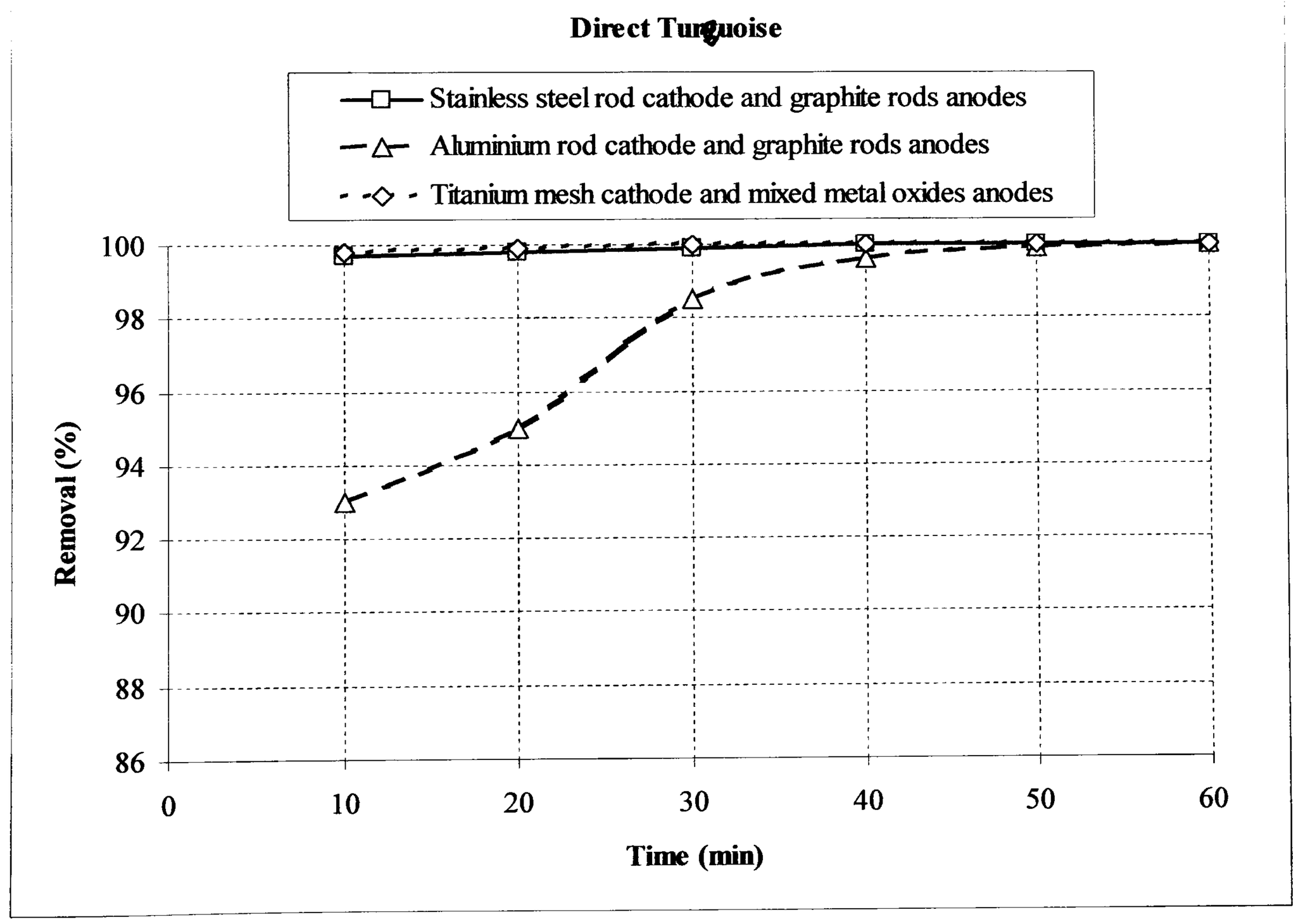


Figure 3.25: Percentage removal of direct dyes using electro-oxidation process

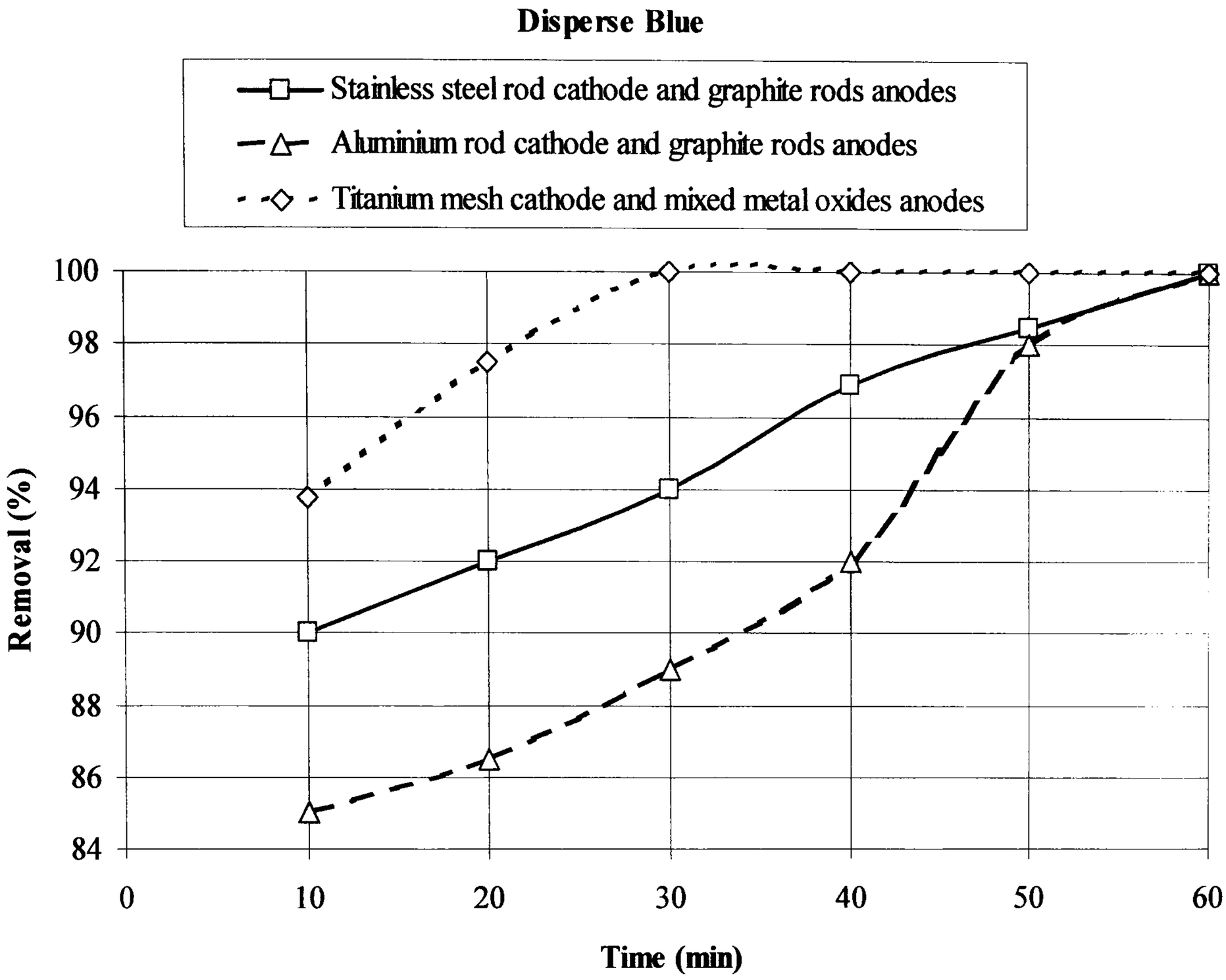


Figure 3.26: Percentage removal of disperse dyes using electro-oxidation process

The electro-precipitation process using either mild steel or aluminium anodes can be used for the complete removal of each dye and the process produce iron or aluminium hydroxide sludge which needs to be disposed of safely. On the other hand, the electro-oxidation processes do not produce any sludge because anodic oxidation actually destroys the structure of the dye molecule and the process may proceed through the formation of some intermediate species. These intermediate species, however, are completely destroyed along with the original dye molecule at the end of the reaction time.

3.2.5.2 Removal of dyes from industrial effluent streams

Three textile effluents *viz*: mixed effluent, printing effluent and dyeing effluent were supplied by a textile mill situated in Faisalabad, Pakistan. The optimised electrochemical processes, electro-precipitation and electro-oxidation, were used for the removal of dyes from these wastewater streams (Table 3.2). All experiments were conducted under the same conditions as described in the synthetic solutions in section 3.2.5.1.

Table 3.2: Optimum conditions for the electrochemical processes

Treatment Process	Treatment time (min)	Anodes	Cathodes
Electro-precipitation	30	Mild steel plate	Stainless steel plate
	30	Aluminium plate	Stainless steel plate
Electro-oxidation	60	Graphite rod	Stainless steel rod
	30	Mixed metal oxide	Titanium mesh

Electrochemical treatment of mixed stream effluent

Experiments were carried out using the electro-precipitation process, with both mild steel and aluminium anodes, and the results are given in Figure 3.27. The results show that after only 20 minutes treatment time the visible and the UV-portion of the spectrum fall to zero. The Ames tests show that the final effluent is non-mutagenic in nature. The results show an electro-precipitation process can be used to remove dyes from mixed effluent streams.

The results (Figure 3.28) from the electro-oxidation process with titanium mesh cathode and mixed metal oxide anodes show that this system leads to a complete mineralisation of dye molecules in 30 minutes. The electro-oxidation process with a stainless steel rod cathode and graphite rod anodes was unsuccessful and a complete degradation of dyes was not achieved even after 60 minutes of reaction time (Figure 3.29b).

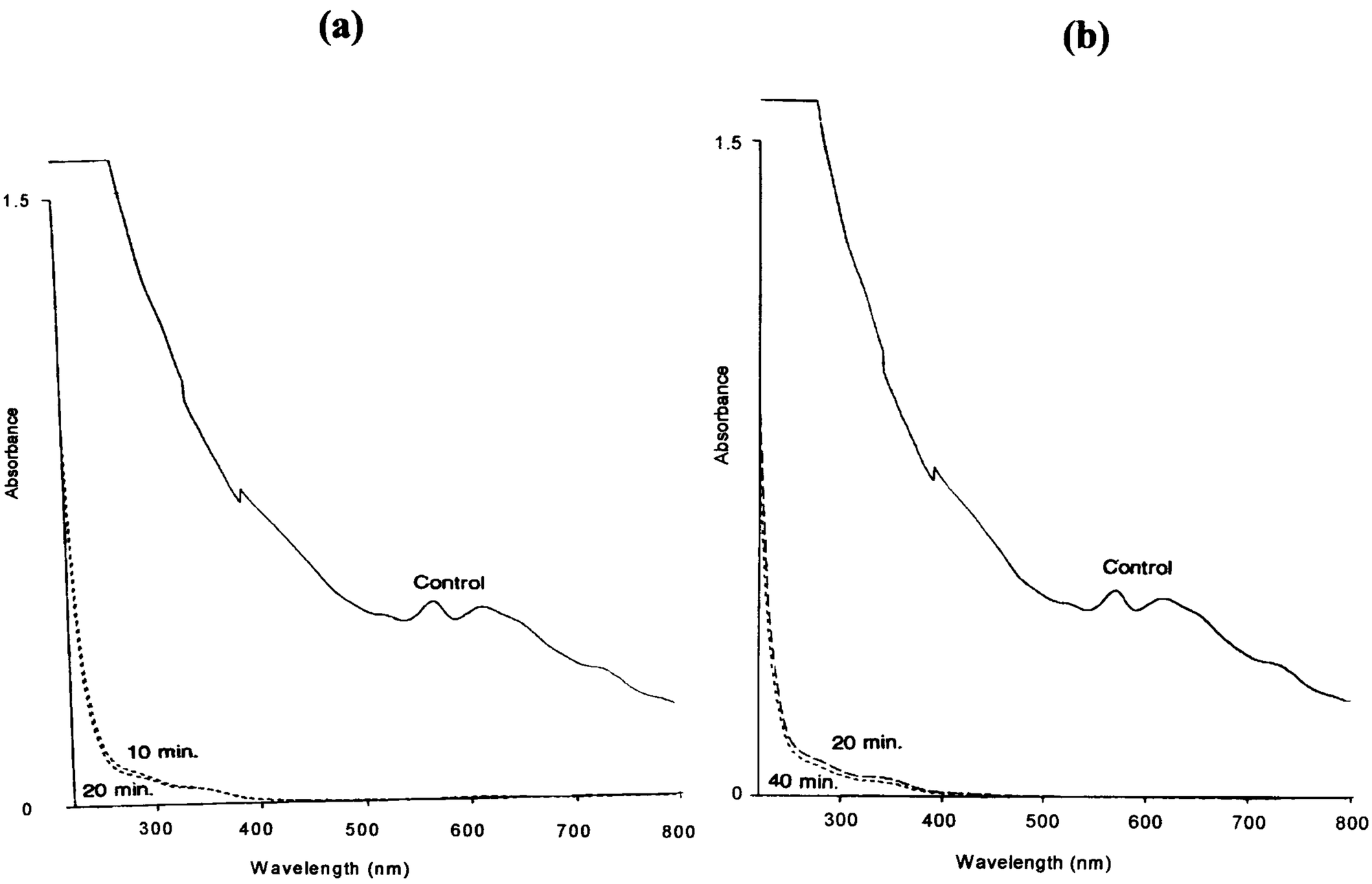


Figure 3.27: UV-visible spectra of mixed effluent before and after electro-precipitation process using a) mild steel anodes and b) aluminium anodes.

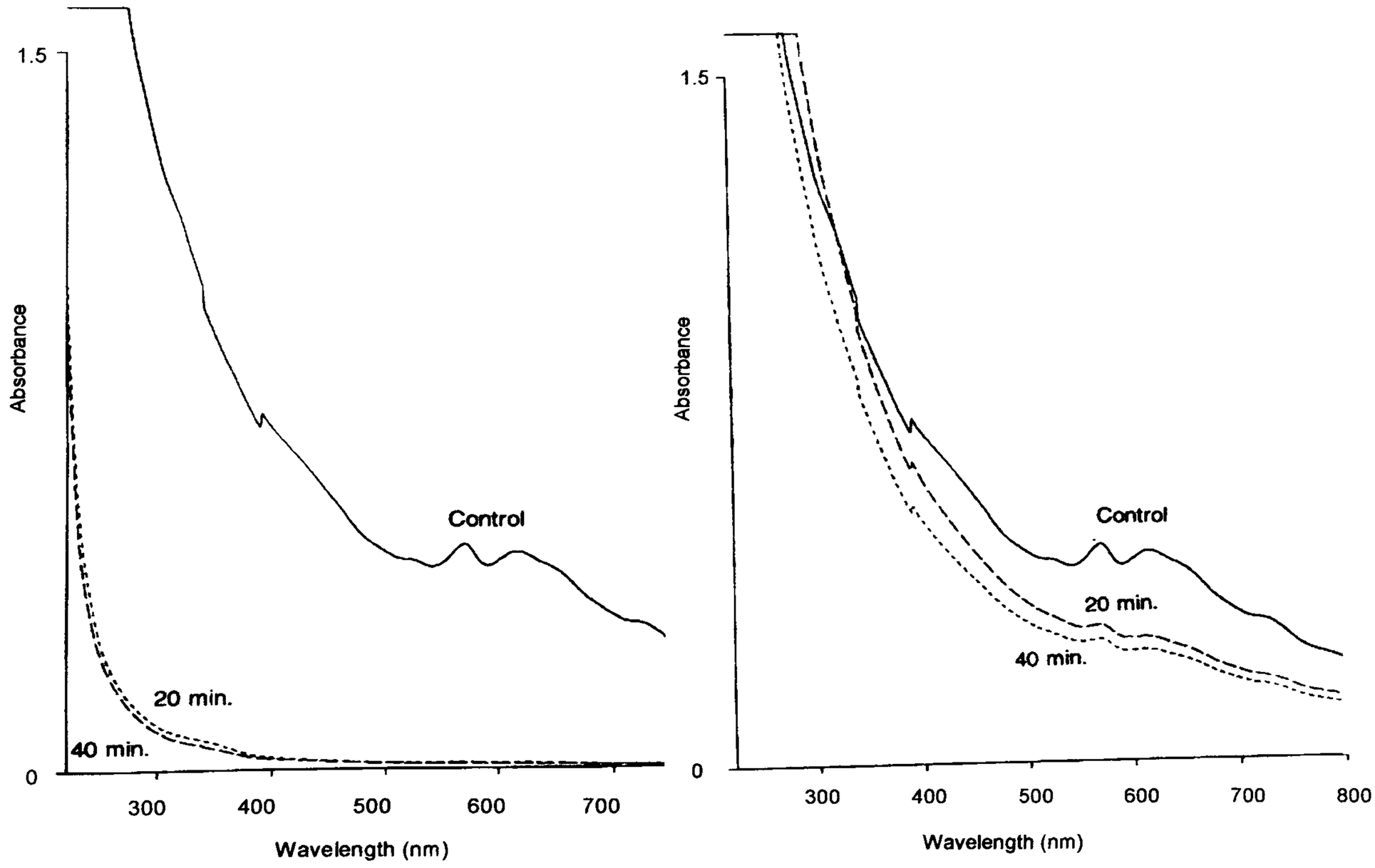
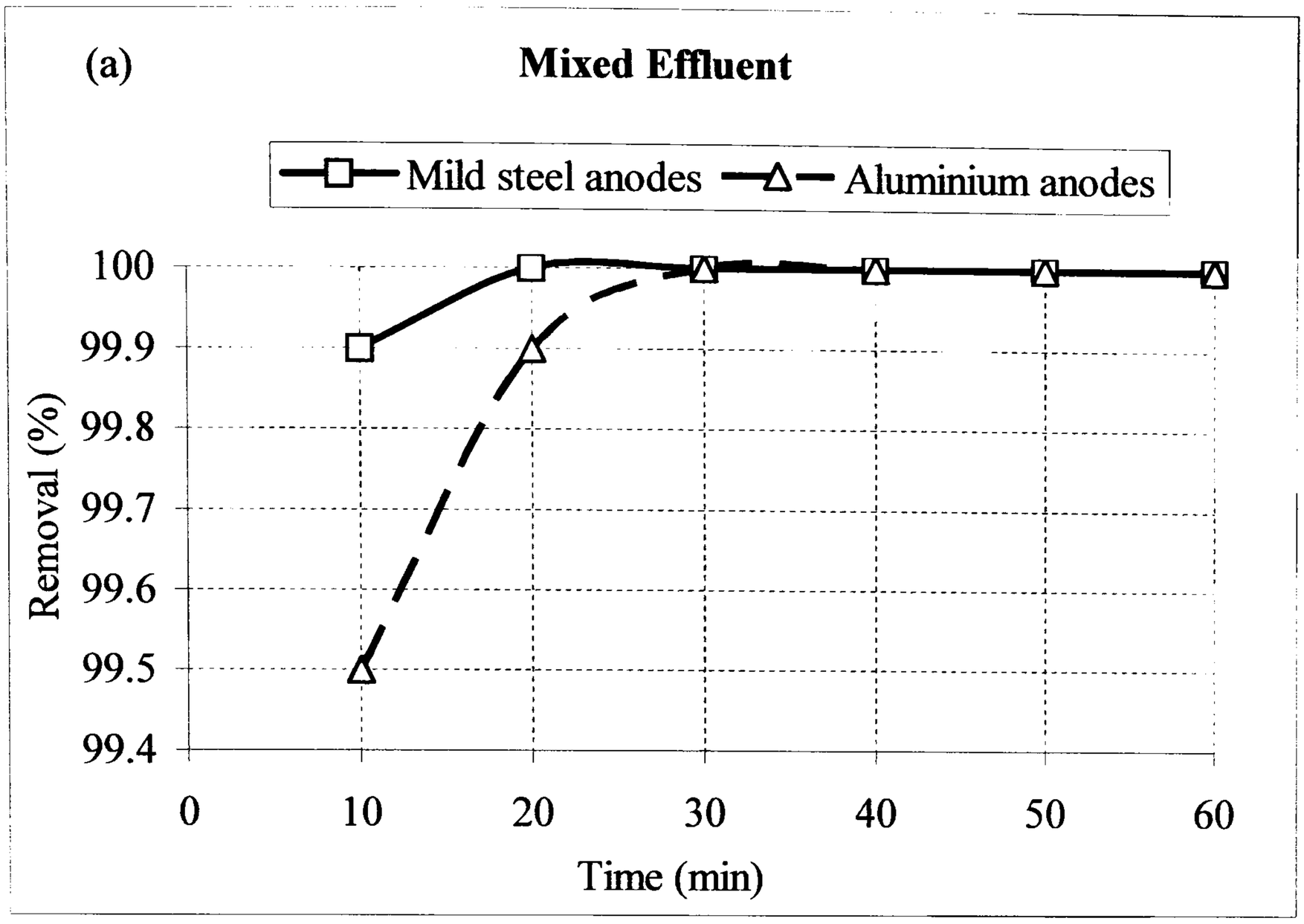


Figure 3.28: UV-visible spectra of mixed effluent before and after electro-oxidation process using a) titanium mesh cathode and mixed metal oxide anodes b) stainless steel rod cathode and graphite rods as anodes.



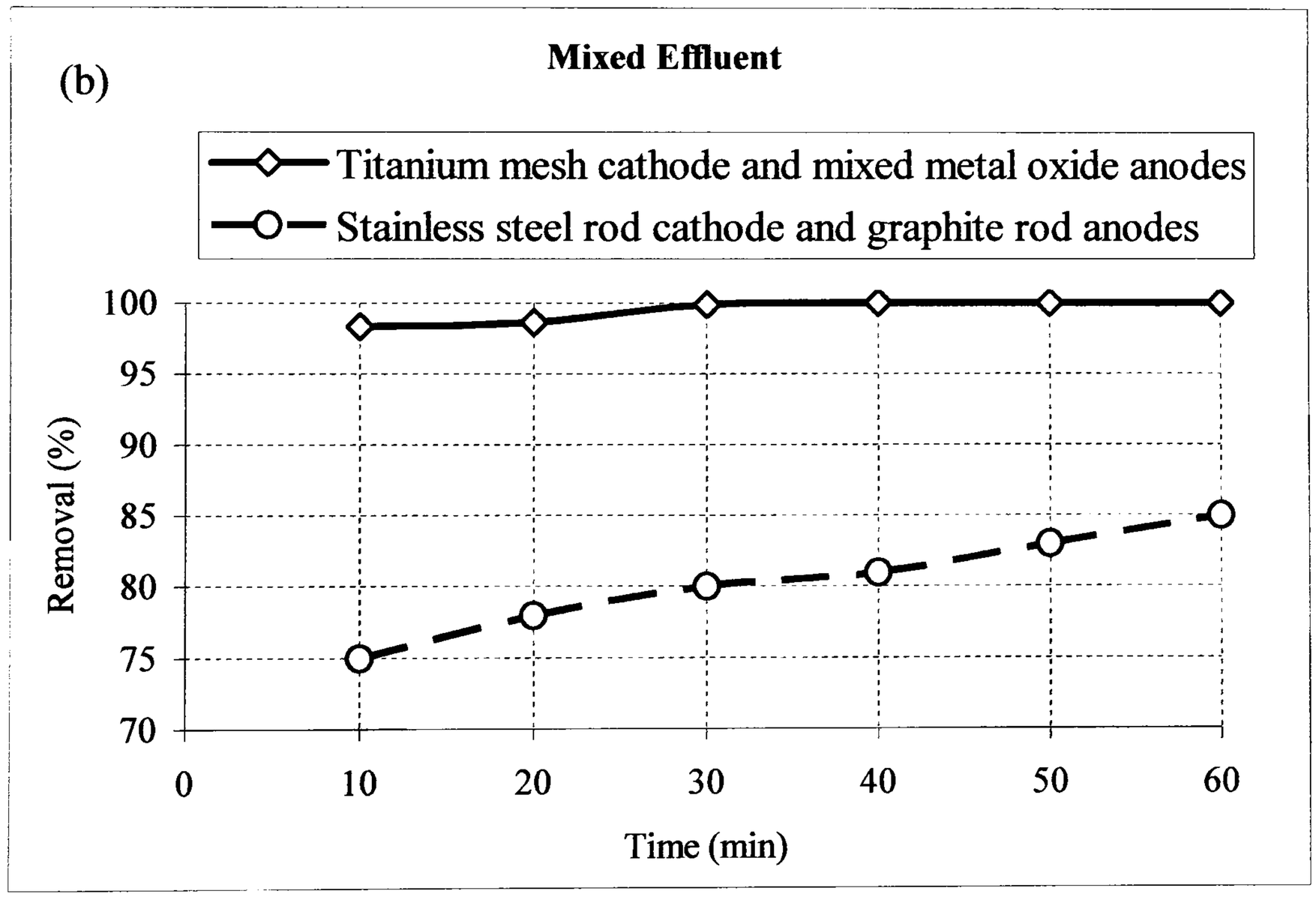


Figure 3.29: Treatment of mixed effluent using
a) electro-precipitation and b) electro-oxidation processes

Mixed effluent streams contain more than one dye and the treatment process may need to proceed through both oxidation and reduction at the anode and cathode surface. The results obtained show that changing the electrode types has a profound effect on the degradation of mixed effluent streams. Mixed metal oxide anodes are better than graphite rod anodes. Electro-oxidation process with titanium mesh cathode instead of stainless steel rod cathode may also be responsible for an increase in the degradation of mixed effluent streams. In some cases, a change in the cathode type can increase the reduction of dye molecules at the cathode surface; especially when different dye molecules are present in a mixed effluent streams. The main advantage of using the electro-oxidation process is that it does not lead to the production of sludge. The results in Table 3.3 show that final effluent obtained after treating the mixed effluent with the electro-oxidation process with graphite rod anodes is mutagenic. However, electro-oxidation process with mixed metal oxide can be used on an industrial scale for the treatment of mixed effluent as the final effluent is non- mutagenic in nature (Table 3.3).

Electrochemical treatment of printing stream effluent

The results in Figure 3.30 show that electro-precipitation process with the use of either mild steel anodes or aluminium anodes can be used for the complete removal of dye molecules from the printing effluent. A complete removal of dye was achieved after 30 minutes in both cases. Furthermore, the treated effluents are non-mutagenic. Although similar percentage removal is achieved in the both cases but mild steel electrodes are better for industrial application because the iron hydroxide sludge settling time is less compared to aluminium hydroxide sludge.

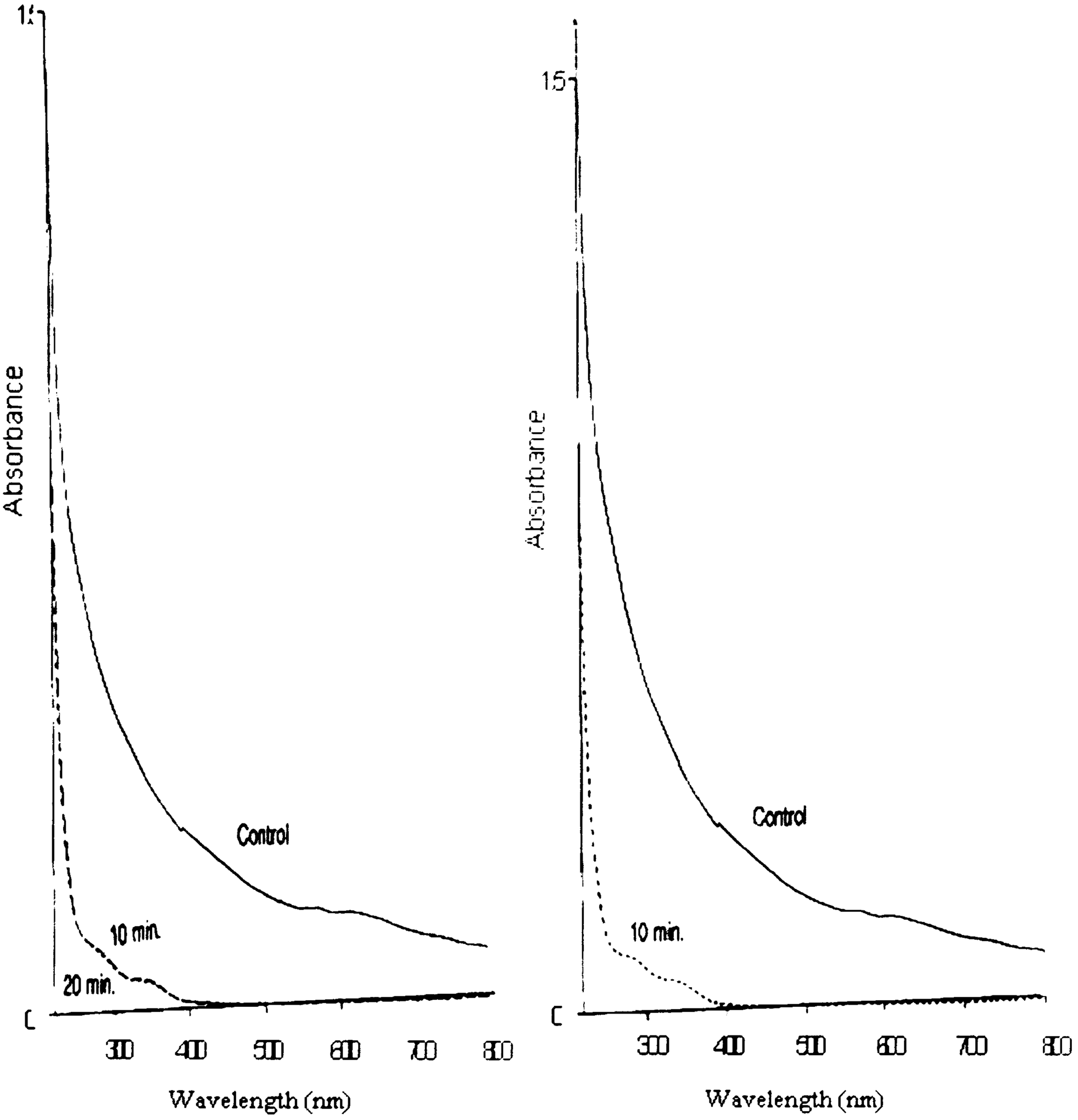


Figure 3.30: UV-visible spectra of printing effluent before and after electro-precipitation process a) mild steel anodes and b) aluminium anode.

The results in Figure 3.31 show that, an electro-oxidation process with a titanium mesh cathode and mixed metal oxide anodes can be used for the anodic oxidation of printing effluent and a complete removal of dye molecules was achieved in 20 minutes. The degradation process does not require the addition of sodium chloride and there is no chance for the formation of chloro-organic intermediate species.

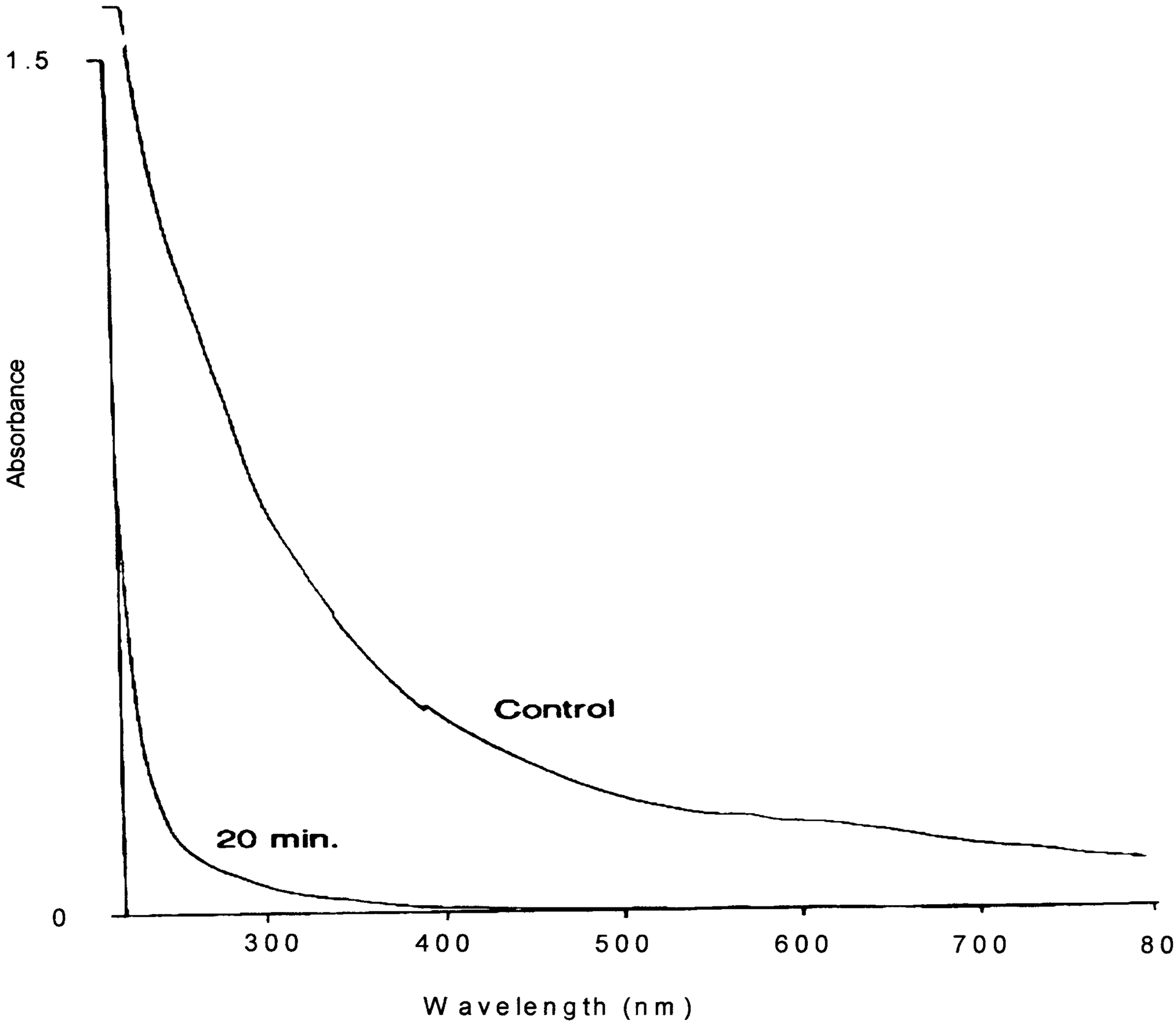


Figure 3.31: UV-visible spectra of printing effluent before and after electro-oxidation process using a titanium mesh cathode and mixed metal oxide anodes.

The results obtained show (Figure 3.32a) that an electro-oxidation process, with a stainless steel rod cathode and graphite rod anodes, cannot be used for the complete removal of dyes from printing effluent streams. Similar degradations were obtained after 20 and 40 minutes. It appears that the degradation stopped after 20 minutes and no increase in the degradation was achieved by increasing the treatment time from 20 to 40 minutes. The degradation of the printing effluent can be increase by using 2 g/L sodium chloride as a supporting electrolyte (Figure 3.32b) but the process was unable to achieve the same level of degradation as was achieved with the use of mixed metal oxide anodes (Figure 3.31)

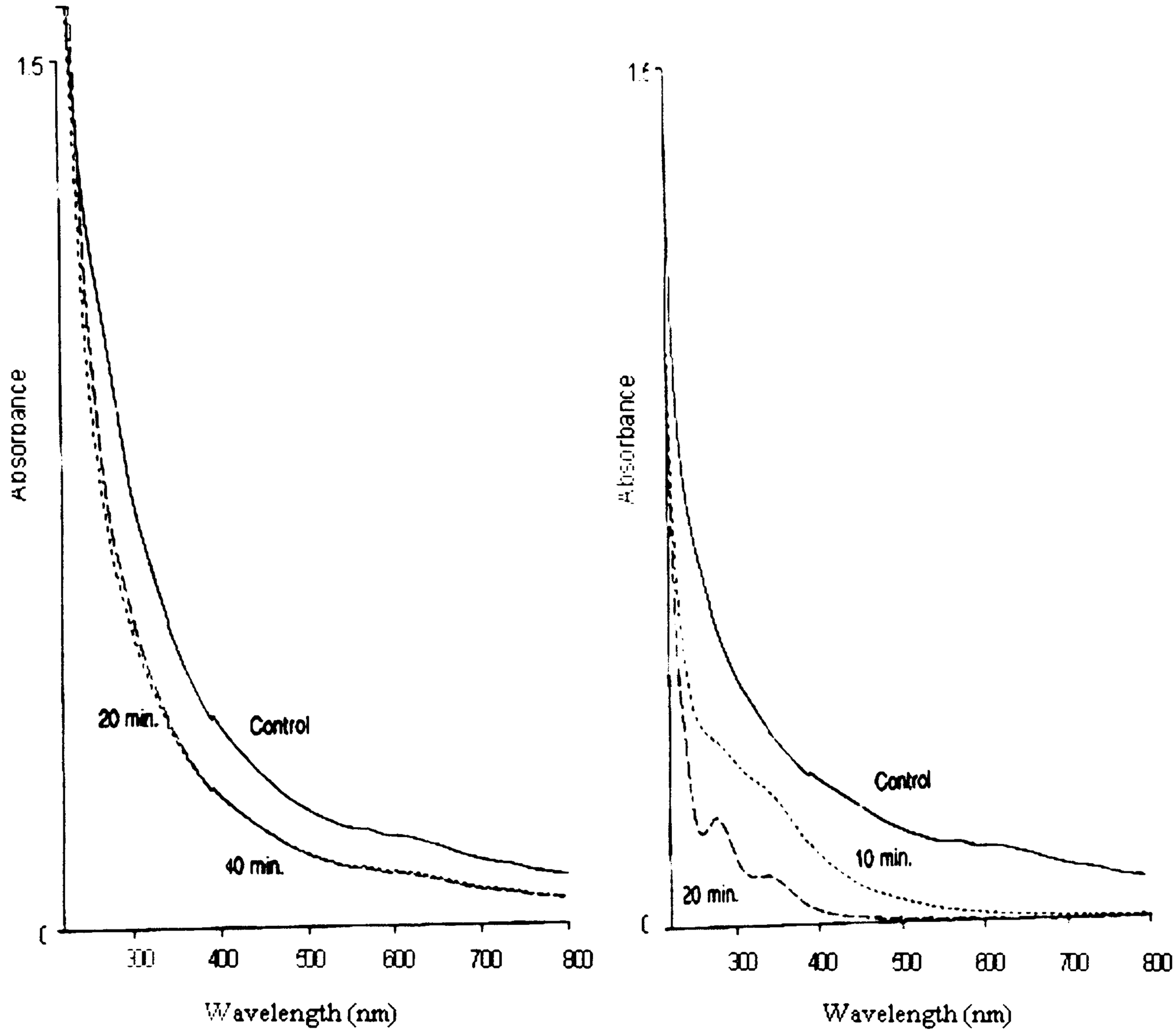
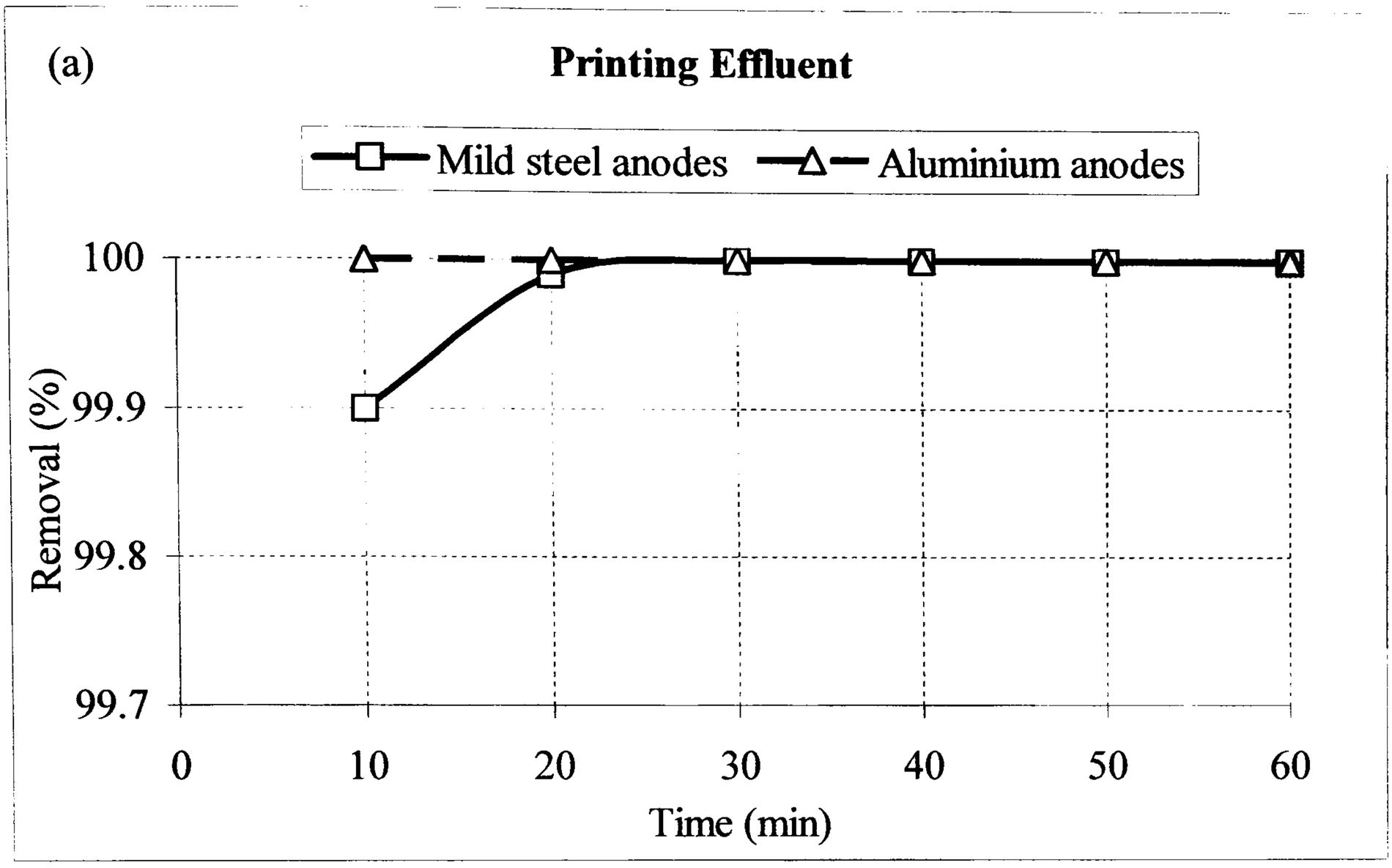


Figure 3.32: UV-visible spectra of printing effluent before and after electro-oxidation process using a stainless steel rod cathode and graphite rods as anodes a) in the absence of sodium chloride and b) in the presence of sodium chloride (2 g/L).

The results in Figure 3.33 and the data of Ames tests in Table 3.3 show that an electro-precipitation with either mild steel anodes or aluminium anodes can be used for the removal of dyes from printing effluent streams because the treated effluents are non-mutagenic. The electro-oxidation process, with a stainless steel rod cathode and graphite rods as anodes, does not lead to complete dye removal and moreover the treated effluent is mutagenic. However, the electro-oxidation process, with titanium mesh cathode and mixed metal oxides anodes, can be used for the removal of dyes from printing effluent streams, as the treated solutions are non-mutagenic.



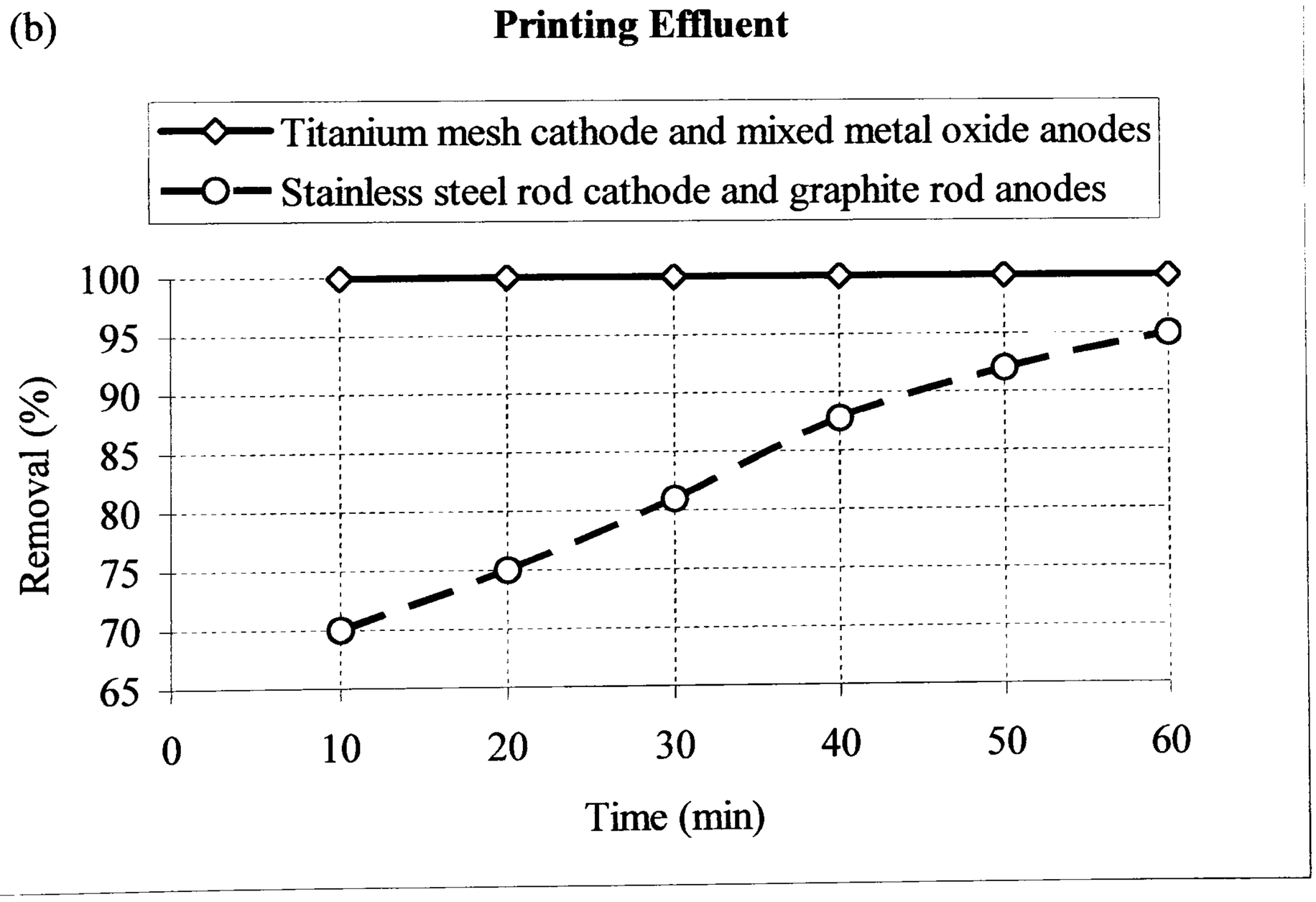


Figure 3.33: Treatment of printing effluent using
a) electro-precipitation and b) electro-oxidation processes

Electrochemical treatment of dyeing stream effluent

The treatment time (20-30 minutes) established for the synthetic and two real effluents is not sufficient to decolourize the dyeing effluent using an electro-precipitation process. The results show that mild steel anodes are better than aluminium anodes (Figures 3.34). This means that iron hydroxide precipitate is a better adsorbent than aluminium hydroxide.

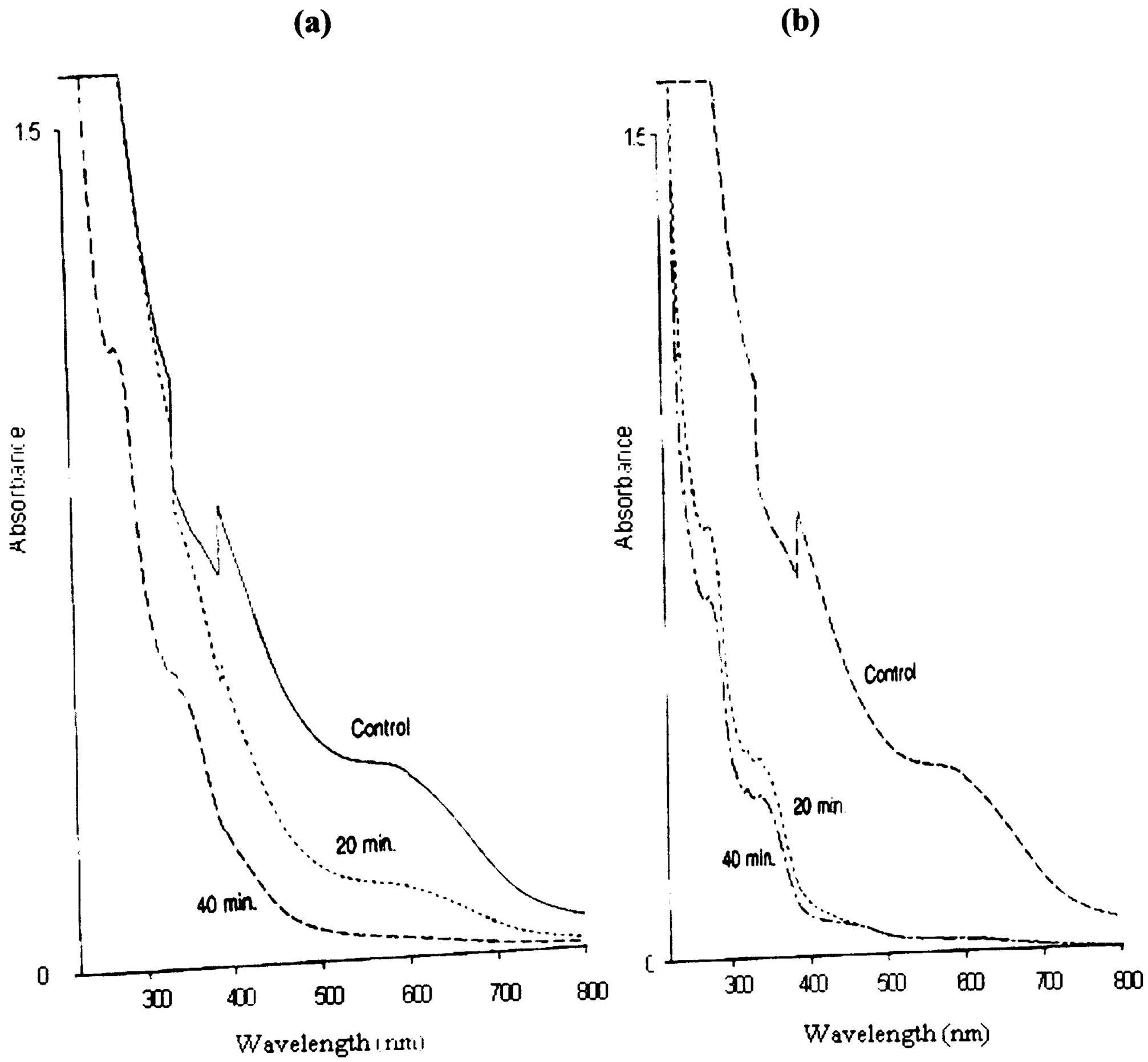


Figure 3.34: UV-visible spectra of dyeing effluent before and after electro-precipitation process using a) mild steel anodes and b) aluminium anodes.

The use of an electro-oxidation process, with titanium mesh cathode and mixed metal oxide anodes, leads to a complete degradation of dyes from the dyeing effluent streams (Figure 3.35a). However, an electro-oxidation process, with a stainless steel rod cathode and graphite rod anodes, was unable to achieve the same level of degradation but there is an evidence that the degradation is taking place (Figure 3.35b). The treated effluent is also non-mutagenic. The addition of sodium chloride to increase the oxidation of dyeing effluent was also not successful.

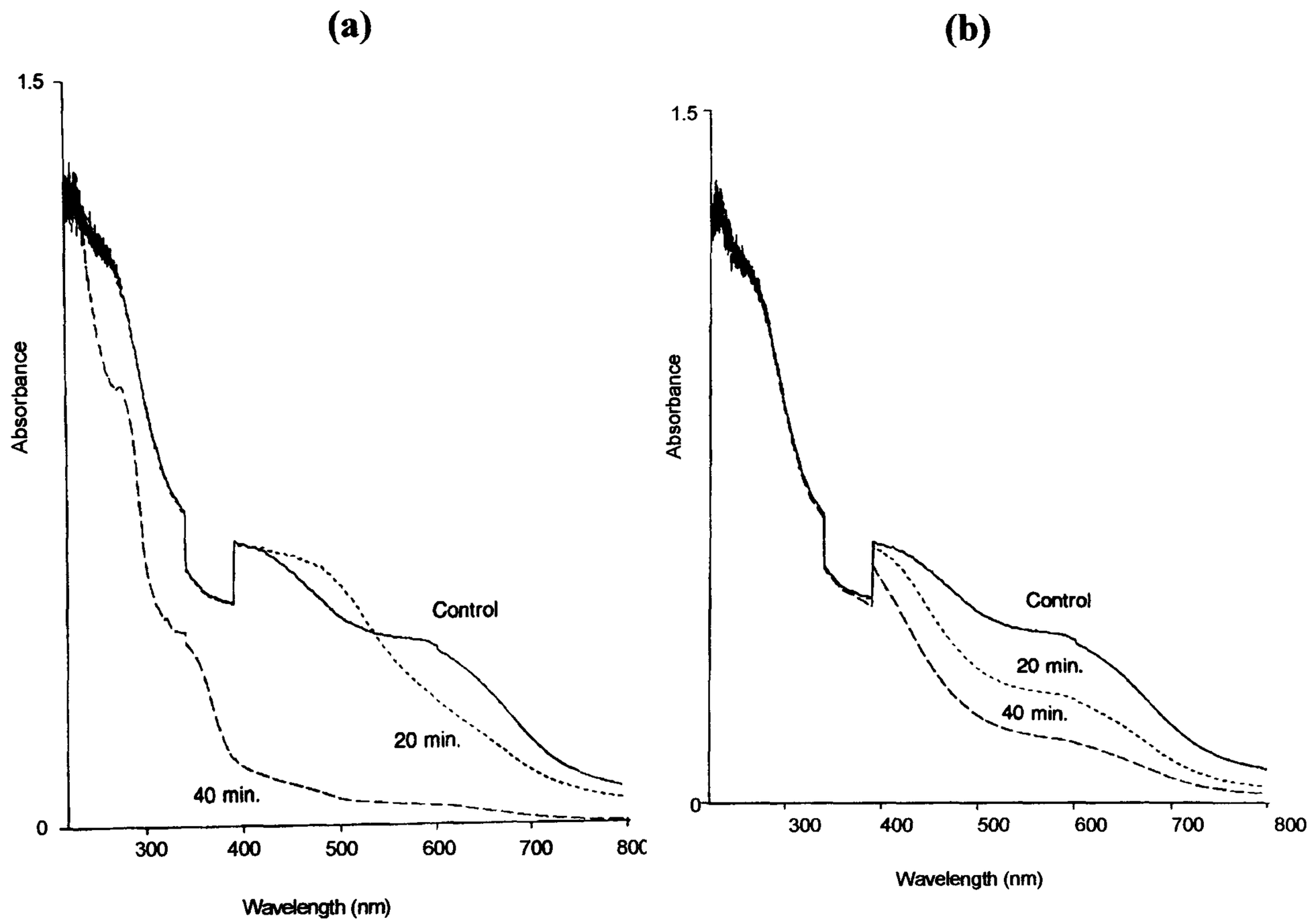
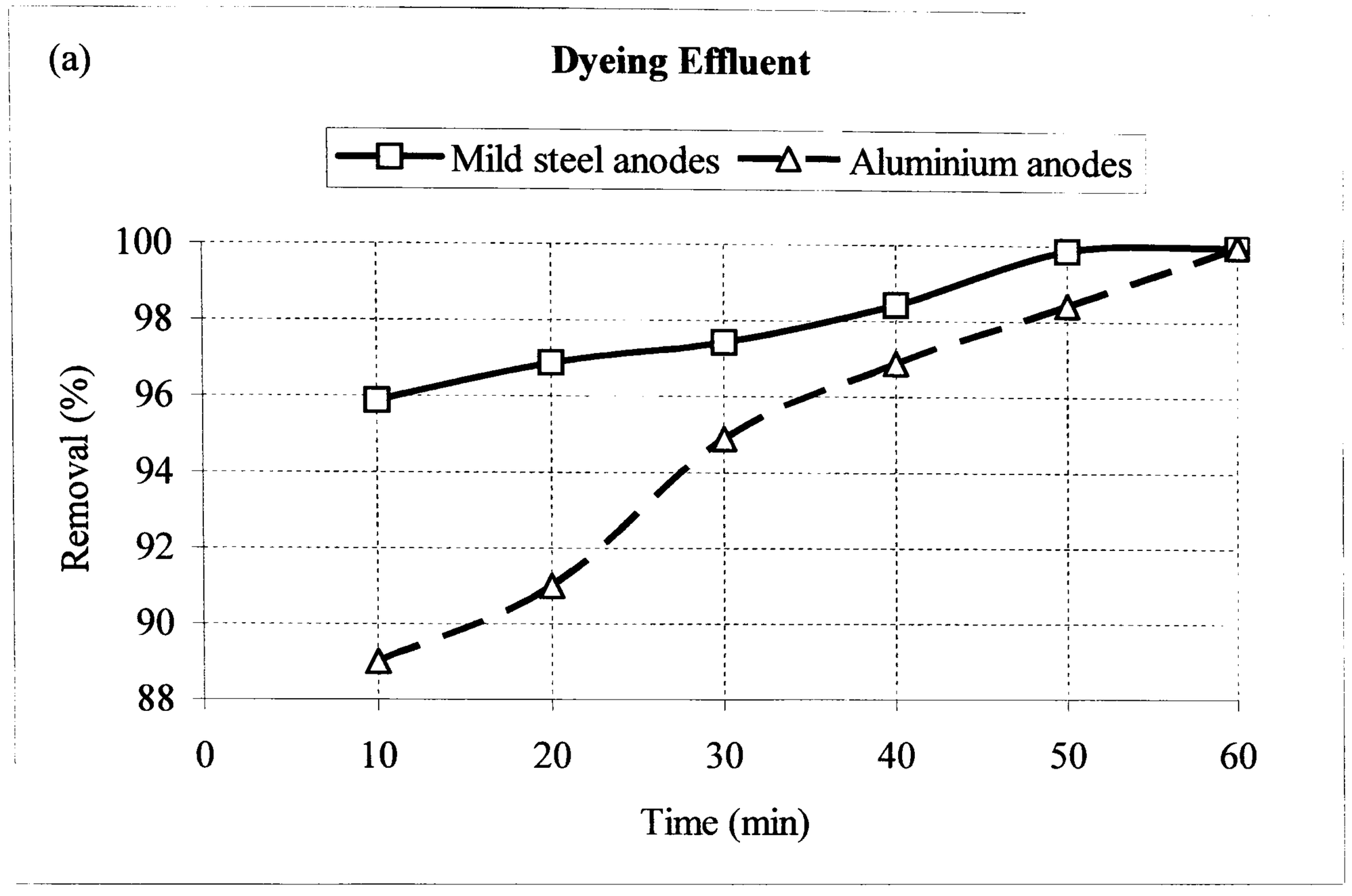


Figure 3.35: UV-visible spectra of dyeing effluent before and after electro-oxidation process using a) titanium mesh cathode and mixed metal oxide anodes b) stainless steel rod cathode and graphite rods as anodes.

The results in Figure 3.36 and the data of Ames tests in Table 3.3 show that, again, the electro-oxidation process with stainless steel rod cathode and graphite rods as anodes is not a suitable process for the treatment of dyeing effluent as the treated effluent is mutagenic. The remaining two electrochemical systems, an electro-precipitation process with both mild steel or aluminium anodes and an electro-oxidation process with mixed metal oxides anodes, can be used for the removal of dyes from dyeing effluent streams.



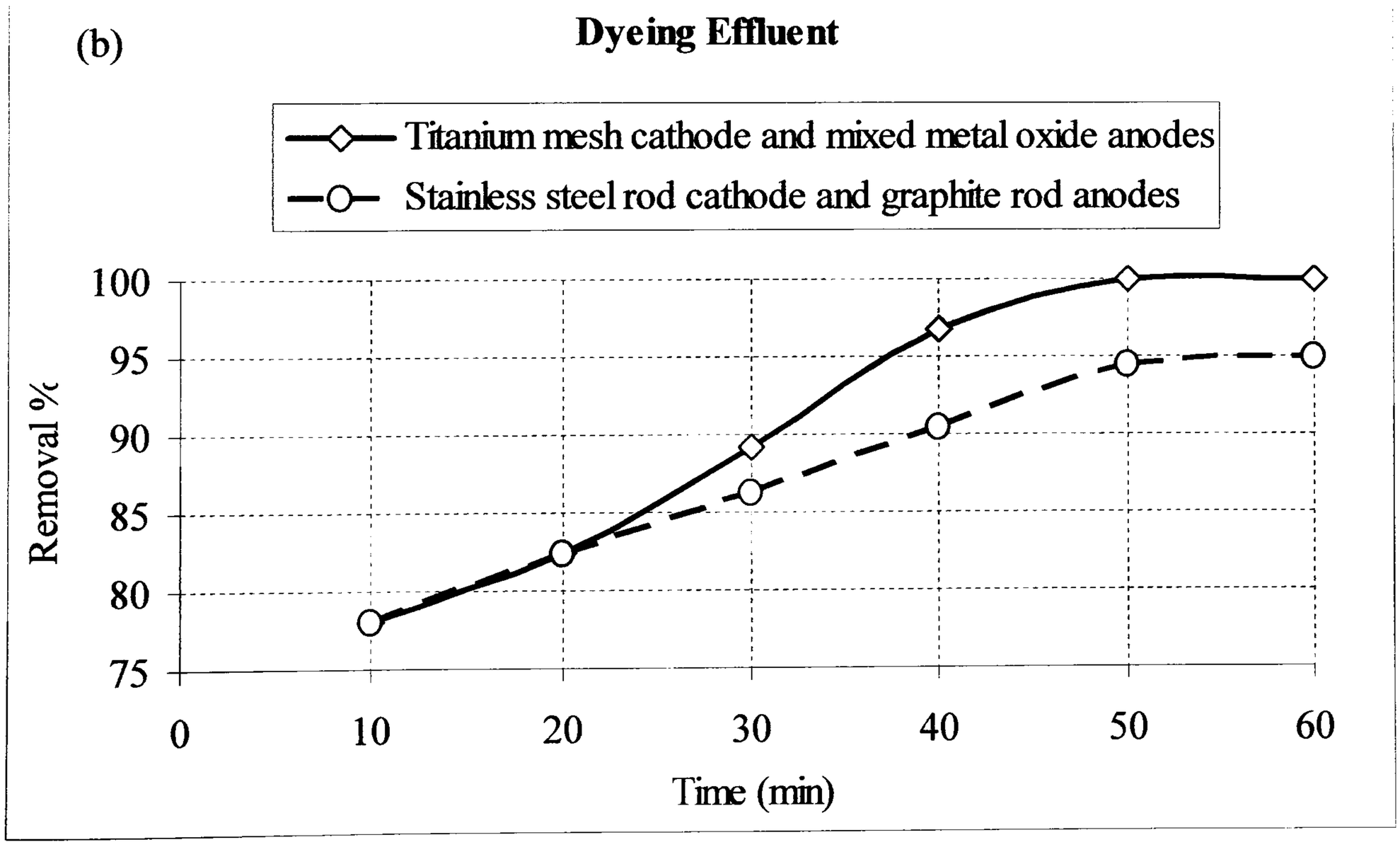


Figure 3.36: Treatment of dyeing effluent using
a) electro-precipitation and b) electro-oxidation processes

3.2.6 A Prototype Industrial Scale Unit

To test the results obtained in this work a prototype electro-precipitation cell of 75 litres capacity was designed and constructed by me with the help of industrial engineers of the textile mill. This unit was used for the removal of direct pink (100 ppm). At a constant current of 1.0 ampere it took almost 3 hours to bring the absorption value down to zero, which corresponds to above 99.9 % colour removal. The energy consumption was only 0.5 kWh/kg. These results confirmed that an electro-precipitation process could be used for the detoxification of textile effluent using mild steel electrodes.

Table 3.3: Analysis of mutagenicity of textile effluents using Ames tests strains *Salmonella Typhimurium* TA98 and TA100

No	Treatment methods	Industrial Sample	Time (min)	Mutagenesis Index TA 98	TA100	Result
1	No treatment	Mixed Effluent	0	2.47	0.93	M
2	Electro-precipitation (Al-anodes)		30	2.21	1.08	NM
3	Electro-precipitation (MS-anodes)		30	2.20	1.06	NM
4	Electro-oxidation (Gr-anodes)		60	2.48	0.97	M
5	Electro-oxidation (MM-anodes)		20	2.19	1.05	NM
6	No treatment	Printing Effluent	0	1.58	0.5	M
7	Electro-precipitation (Al-anodes)		30	1.22	1.7	NM
8	Electro-precipitation (MS-anodes)		30	1.19	1.5	NM
9	Electro-oxidation (G-anodes)		60	1.60	0.6	M
10	Electro-oxidation (MM-anodes)		30	1.20	1.5	NM
11	No Treatment	Dyeing Effluent	0	1.84	0.5	M
12	Electro-precipitation (Al-anodes)		60	1.5	1.2	NM
13	Electro-precipitation (MS-anodes)		60	1.6	1.1	NM
14	Electro-oxidation (Gr-anodes)		60	1.86	0.6	M
15	Electro-oxidation (MM-anodes)		60	1.3	1.5	NM

Mutagenesis index = number of revertants obtained in sample / number of revertants of the negative control

M = mutagenic; NM = non-mutagenic; nd = not determined

MS = mild steel; Al = Aluminium; MM = mixed metal; Gr = graphite rod
- Plate incorporation test was used
- Each value is an average of 3 experiments
- All the test were performed without S9 metabolic activation system

3.3 LEATHER EFFLUENT

3.3.1 Introduction

In south Asia, the leather industry encompasses more than 5000 tanneries scattered all over the region. The total production capacity increased by 2–3 times in the year 2005 to achieve 20 % world market share by the South Asian Leather Industries. Though this progress will be of great benefit to the Asian economy, it will also impose substantial threats to the environment and local communities living in close proximity to the tanneries [29].

The leather and the leather-based industries have acquired a significant position in Pakistan, over the last decade, as a main contributor to the national exchequer, earning foreign exchange, and becoming the third largest foreign exchange earner after cotton and textiles. The leather industry directly employees 2,000,000 workers and contributes about Pak Rs. 20 billion (650 million US$) to the national economy and approximately 4 % to the GDP. Pakistan is producing about 6 million hides and 42 million skins annually [30].

There are two main centres of leather processing in Pakistan one in Karachi and the other in Lahore and surrounding areas (Faisalabad, Kasur, Sheikhpure, Sialkot and Gujranwala). In Kasur, the effluent from 200 tanneries amounts to 7000 m^3/day containing 5-200 mg/L of chromium is being discharged into waterways without any treatment while in Karachi 937 tons of chromium per year is discharged to drain. In Pakistan, 10,000 tons of chromium is being used per year. Traditionally the preparation of leather involves extensive chemical treatment for softening, de-hairing, dying and removal of other proteins. Many of these treatment chemicals (such as Na_2S, NH_4SO_4, CaO, chromium, dyes etc.) result in an extensive environmental pollution problem [31].

Tanneries are mainly responsible for the release of a huge amount of chromium to the environment. Pentachlorophenol and related biocides used in the leather tanning processes are injurious to the growth of micro-organisms and also reduce the removal of chromium in tannery effluent. Chromium is widely used by the modern leather tanning,

electroplating and metal finishing industries. It is released to the environment when wastewater is discharged to surface waters without any treatment [29-36].

The hexavalent chromium present in the tanneries effluents is a known carcinogen. It is reported to cause skin dermatitis, nasal membrane inflammation and ulceration, liver damage and pulmonary congestion. It is also implicated in progressive pulmonary fibrosis, gastrointestinal afflictions, mutagenicity and carcinogenicity. Because of its high toxicity, it is imperative to achieve reductions in its discharge levels, and to promote of recycling and reuse [37-38].

3.3.2 Treatment Methods

Removal of metals from tanneries wastewater has been traditionally achieved by the application of processes such as adsorption, cementation, ion exchange, membrane separation, solvent extraction and electrochemical methods. Currently, chemical precipitation is the most widely used technique for the removal of metal ions from effluents because it is cheap and easy to operate.

Tannery chromium effluents are strictly regulated for their alleged environmental consequences. Discharge limits for trivalent chromium vary, ranging broadly from 1 to 5 mg/L in the case of direct discharge into water bodies and 1 to 20 mg/L in the case of discharge into the public sewer systems [39]. The level of chrome fixation on processed hides/skins is still low enough to result in high economic loss, with close to 70 % uptake achievable only in improved conventional tanning. The remaining 30 % of basic chromium sulfate applied is left in the spent chrome liquor and often wasted in effluent discharge [40].

Chromium in tannery solid by-products and effluent treatment sludges strongly militates against the use of tannery sludges as manure in agriculture. Chromium-containing tannery effluents are not acceptable for any beneficial reuse or discharge into the environment without full compliance with very stringent effluent limits.

Chromium (VI) is not removed by direct hydroxide precipitation. Various reducing agents such as sulfur dioxide, sodium bisulfate, ferrous sulfate and sodium metabisulfite in acidic media and hydrazine in alkaline medium are employed to reduce chromium

(VI) to its trivalent state. This has been followed by precipitation and filtration [38]. The following chemical reactions take place during the chemical precipitation process when a stoichiometric amount of Fe (II) ions as iron sulfate heptahydrate ($FeSO_4.7H_2O$) is added to reduce dichromate ion ($Cr_2O_7^{2-}$) to Cr (III).

$$6Fe^{2+} \rightarrow 6Fe^{3+} + 6\bar{e}$$

$$Cr_2O_7^{2-} + 7H^+ + 6\bar{e} \rightarrow 2Cr^{3+} + 7OH^-$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7OH^-$$

3.3.3 Aim of This Work

The main aim of the work described in this section is to extend the use of an electro-precipitation process to remove either Cr (VI) and or Cr (III) from leather tanning industry effluent. Electrochemical techniques are becoming increasingly attractive in dealing with environmental problems as the electrons (at least their point of source) provide clean, versatile and efficient reagents for many redox processes.

The electro-precipitation cell used in this work for the treatment of textile effluent was also used for the removal of Cr (III) and Cr (VI) from leather effluent. The following chemical reactions take place in the electro-precipitation of leather treatment process wastewaters.

$$Fe \rightarrow Fe^{2+} + 2\bar{e}$$

$$2H_2O + 2\bar{e} \rightarrow H_2 + 2OH^-$$

$$Fe + 2H_2O \rightarrow H_2 + Fe(OH)_2$$

$$Cr_2O_7^{2-} + 6Fe(OH)_2 + 7H_2O \rightarrow 2Cr(OH)_3 + 6Fe(OH)_3 + 2OH^-$$

The toxic Cr (VI) is reduced to Cr (III) by Fe (II), which is generated electrochemically. The Fe (III) and Cr (III) produced in the electrolyte solutions are precipitated by the production of $2OH^-$ ions on the cathode surface. This mixed Fe (III)/Cr (III) hydroxide sludge can be used in place of flocculants/adsorbents for the removal of dyes from wastewater streams originating from textile industries [41].

The research work described in this chapter extends the adsorption studies carried out by the Brunel University group [36] on the removal of dyes from textiles effluent using mixed Cr (III)/Fe(III) hydroxide sludge. This sludge is produced as a waste product during the treatment of etching solutions originating from electronic and electroplating industries. The authors have successfully used this surface-active metal hydroxide sludge as an adsorbent material for the removal of different types of dye molecules from aqueous solutions. The work described in this section focuses on the following four main points:

1. The use of electro-precipitation process for the treatment of leather effluent to produce mixed Cr (III)/Fe (III) hydroxide sludge
2. The use of dried Cr (III)/Fe (III) hydroxide sludge as an adsorbent material for the adsorption of dyes from textile effluent
3. The use of electro-precipitation process for the *in-situ* production of Cr (III)/Fe (III) hydroxide sludge to remove dyes and chromium from mixed textile/leather effluent
4. The use of a waste from one industry to treat the waste of another in order to achieve an overall waste minimisation objective set by the PEPA.

3.3.4 Experimental and Methodology

Both model and industrial solutions were used to produce mixed Cr (III)/Fe (III) hydroxide sludge. Model synthetic solutions, each containing 200 ppm of Cr (VI), were prepared by dissolving standard grade potassium dichromate supplied by Merck, in distilled water. These model solutions were used to optimise the conditions for the removal of Cr (VI) by electro-precipitation process with mild steel electrodes. These optimum conditions were then used to remove Cr (VI) from industrial solutions supplied by a local tanning industry in Pakistan. All experiments were carried out using 1.5 L solution at a constant current of 0.5 ampere. Five mild steel electrodes were used for each experiment. Samples were collected periodically and analysed using both UV-visible spectroscopy and atomic absorption spectroscopy. Mutagenicity tests were also carried out to investigate the effectiveness of the process studied in this work.

The mixed Cr (III)/Fe (III) hydroxide sludge obtained by treating the leather effluent was washed with tap water and then dried at 70°C for 5 hours. Four separate portions of 1.5 g of dried hydroxide sludge were added to four conical flasks each containing 50 ml of 100 ppm direct pink solution. The solution pH was adjusted in four experiments to 3, 5, 8.4 and 9.5 by using solid sodium hydroxide and sulfuric acid. The flasks were agitated using a shaker at room temperature and the solutions were filtered after 60 minutes. The colour removal was monitored using a UV-visible spectrophotometer. The leachability of metals was examined by AAS.

Model mixed leather/dye solutions were prepared by mixing one litre of leather effluent solution, supplied by the local tanning industry, with 500 ml of 100 ppm direct pink dye solution. These mixed solutions were used to investigate the possibility if chromium and dye molecules can be removed simultaneously by the *in-situ* production of iron hydroxide sludge during the elector-precipitation process with mild steel anodes. Other experimental conditions were exactly the same as described for the removal of chromium from both model and industrial leather solutions.

3.3.5 Results and Discussion

3.3.5.1 Treatment of leather effluent streams with electro-precipitation process to produce mixed Cr (III)/Fe (III) hydroxide sludge

The results in Figure 3.37 demonstrated that it takes 180 minutes to bring the concentration of Cr (VI) from 200 mg/L to below 1 mg/L from model solutions. The resultant solution is suitable for discharge to a sewer system. After process optimization the study was extended to use a real industrial effluent supplied by a local tanning industry. As supplied solution was filtered to remove suspended solid and the filtrate was analysed for chromium concentration. Preliminary analysis of a real tanning effluent indicated that the solution contained ~190 mg/L of chromium and most of this chromium is in oxidation state (III) and very little in Cr (VI) form. The results demonstrated that both chromium and suspended solid can be precipitated out electrochemically with minimum energy and Fe (II) consumption from the industrial effluent. A complete removal of chromium can be achieved in 90 minutes as most of the chromium is already in oxidation state (III). The treated effluent is also non-mutagenic. These results confirmed that the electro-precipitation process is suitable for the production of mixed Cr (III)/Fe (III) hydroxide sludge from tanneries effluent streams. This mixed Cr (III)/Fe (III) hydroxide sludge, however, contains fat and other organic impurities.

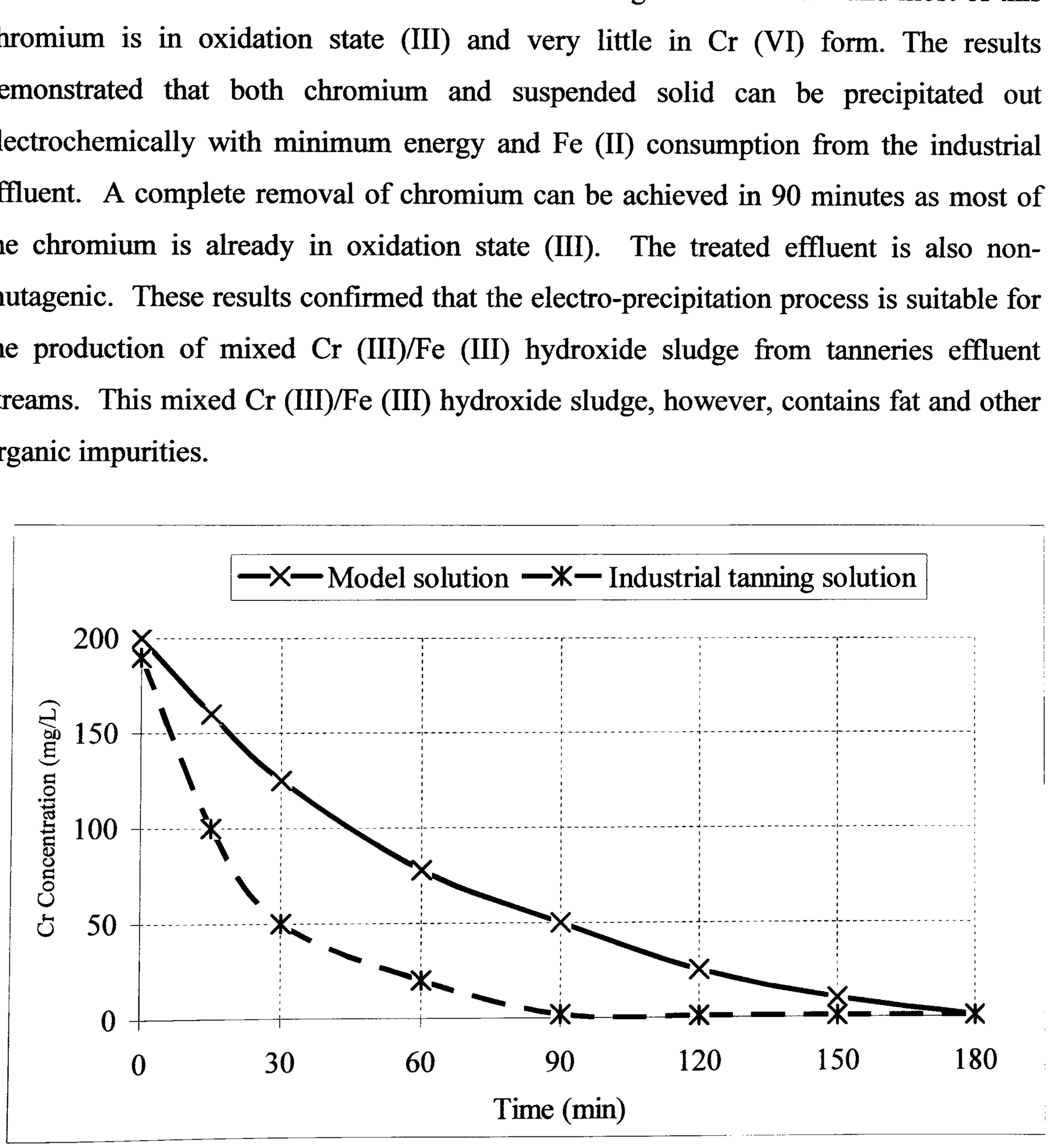


Figure 3.37: Removal of chromium from model and industrial tanning solution

3.3.5.2 Adsorption of dye molecules from textile effluent streams using mixed Cr (III)/Fe (III) hydroxide sludge as an adsorbent material

The adsorption studies carried out by the Brunel group [41] on the use of waste Cr (III)/Fe (III) chromium sludge as an adsorbent for the removal of cationic and anionic dyes show that the mixed chromium waste sludge is an excellent material for the removal of dye molecules. It has been shown that the surface charge on the sludge was positive at low pH, hence the adsorption of anionic dye species such as reactive blue and congo red. The surface charge at high pH was, however, negative and the cationic dye, such as methylene blue, was adsorbed. This surface-active chromium waste sludge was obtained by precipitating chromium from chromium etching solutions used in electronic industries to etch away the excess copper from printed circuit boards. This mixed sludge contained both oxides and hydroxides of Cr, Fe, Cu, Ni and was free from fat and other organic molecules.

The objective of the work described in this is to determine whether the waste Fe (III)/Cr (III) hydroxide sludge, obtained from leather effluent, can also be used as an adsorbent for the removal of dye molecules from textile effluent streams.

The results in Figure 3.38 show the effect of pH on the removal of direct pink from aqueous solutions at pH values 3, 5, 8.5 and 9.5 under otherwise identical conditions. The results show that the visible portion of the spectrum of direct pink fell to zero absorption at every pH value, but absorption in the UV- portion shifts slightly towards higher wavelength and the changes are pH dependent. Increasing the pH from 3 to 5 brings about a small decrease in the absorbance value at 285 nm but further increase in pH from 5 to 8.5 and 9.5 results in no change in the UV part of the spectra indicating that the mixed Cr (III)/Fe (III) hydroxide sludge is not a suitable adsorbent material for the removal of dyes from aqueous solutions.

The mixed Cr (III)/Fe (III) sludge, obtained after treating the leather effluent, contains fat and other organic impurities. The low efficiency of this mixed waste sludge in removing direct pink from aqueous solution is attributed to the reduction in the total surface area and the surface charges of this mixed sludge. During the drying process, the active sites on the mixed sludge were blocked with fat and other organic molecules and this ultimately reduces the uptake of dyes from the aqueous effluent streams.

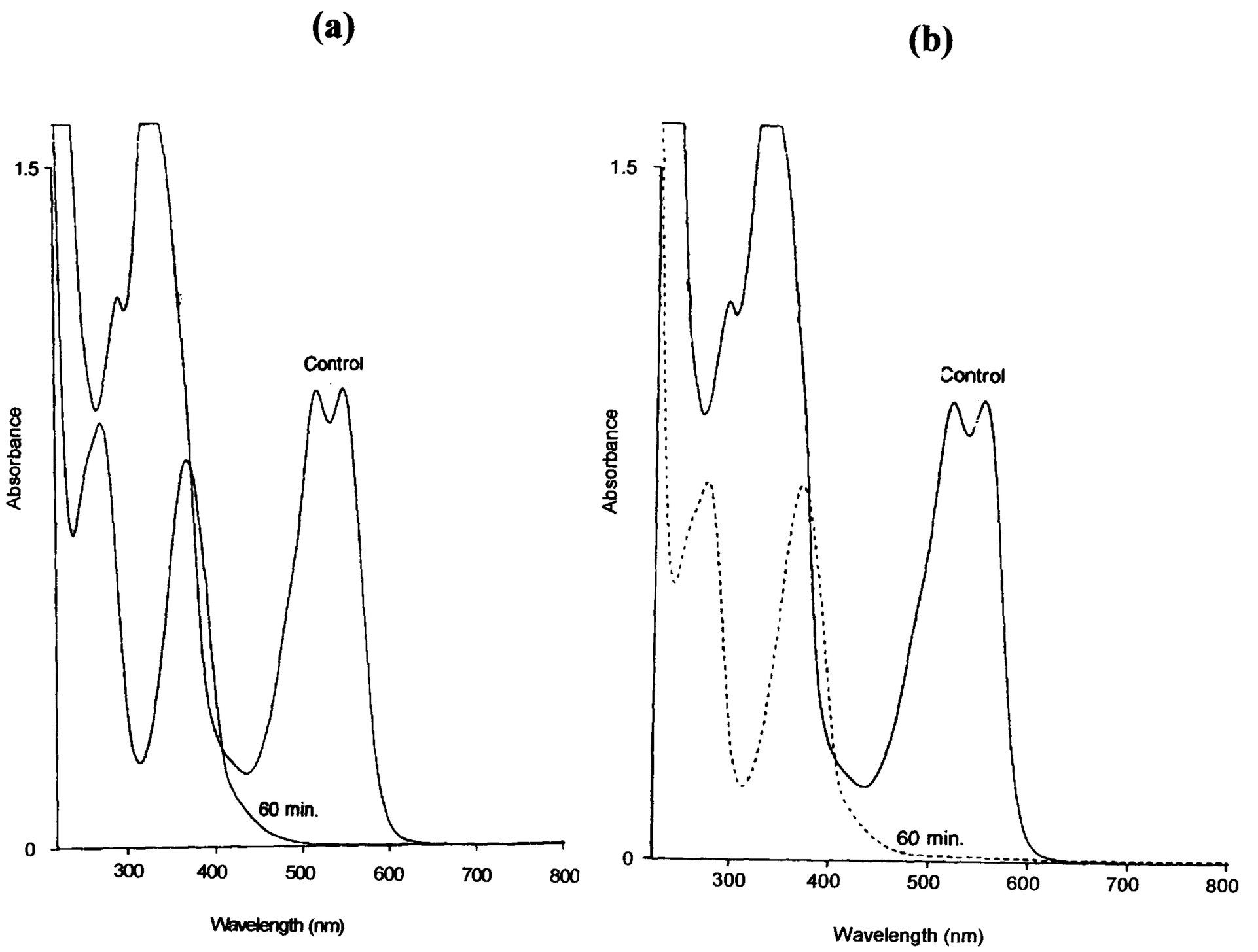


Figure 3.38: The effect of pH on the adsorption of direct pink using Cr (III)/ Fe (III) hydroxide sludge at pH a) 3.0, b) 5.0, c) 8.5, d) 9.5.

3.3.5.3 Simultaneous removal of dye (direct pink) and chromium from mixed textile/ leather effluent streams by the in-situ production of mixed Cr (III)/Fe (III) hydroxide sludge produced during the electro-precipitation process

The electro-precipitation with mild steel electrodes is an excellent process for the removal of direct pink from aqueous solutions (Figures 3.12a and 3.22). Aqueous solution containing direct pink dye was mixed with the leather effluent containing chromium and an electro-precipitation process with mild steel electrode was used for the simultaneous removal of dye and chromium from this mixed effluent stream. The objective of this part of the work was to determine whether the *in-situ* production of Fe (III)/ Cr(III) hydroxide sludge can be used for the simultaneous removal of chromium and dye molecules from mixed leather and textile effluent streams. The *in-situ* production of surface-active precipitates would eliminate the need to dry the resultant Fe (III)/Cr (III) hydroxide sludge and could be used for the treatment of mixed leather/textile effluent streams. The results in Figure 3.39 show that a complete removal of colour can be achieved from the mixed effluent streams. The higher removal efficiency is attributed to the combined electro-precipitation, cathodic reduction, anodic oxidation and adsorption processes occurring simultaneously in the system. These results confirmed that a combined treatment process can be used for the treatment of mixed effluent to achieve the overall waste minimisation objective set by the PEPA.

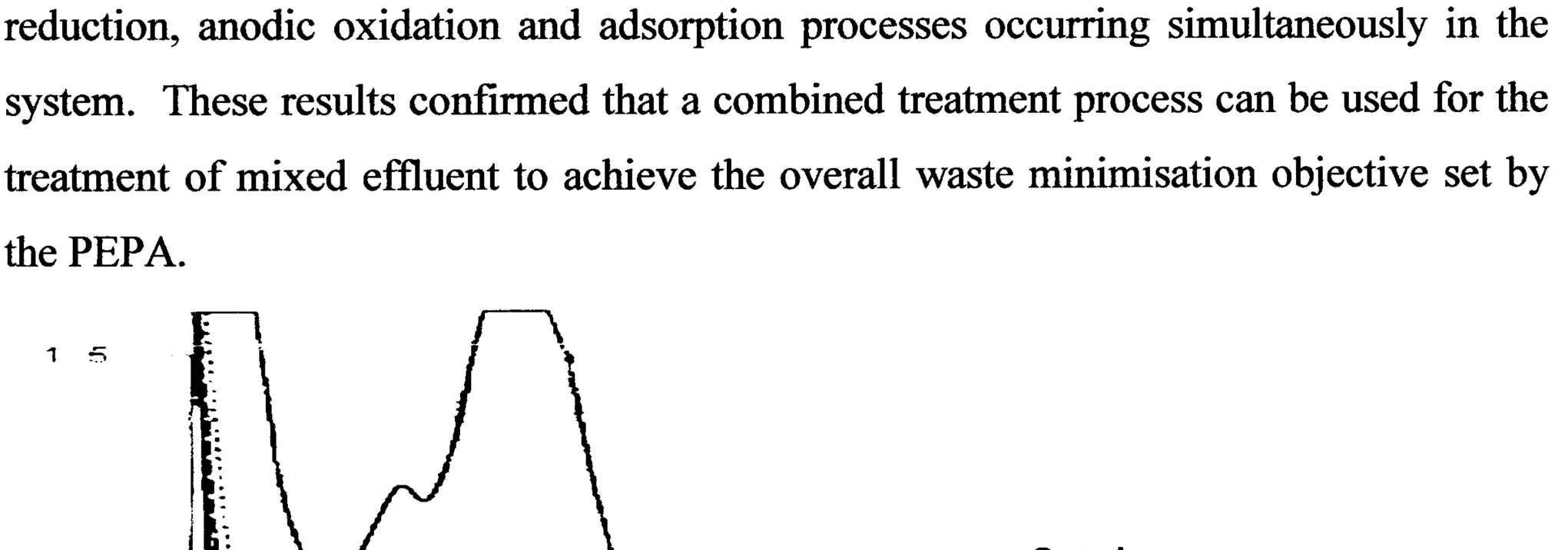


Figure 3.39: UV-visible spectra of mixed leather and textile effluent streams with time using an electro-precipitation process with mild steel anodes.

3.3.5.4 Mutagenicity testing

Microbial tests were performed to determine the potential mutagenicity nature of the treated effluent streams. Mutagenicity results of leather effluent (synthetic and real), direct pink and mixed leather and direct pink before and after treatment are given in Table 3.4.

Table 3.4: Analysis of Mutagenicity of tannery, textile (Direct Pink) and mixed leather/textile effluent streams using Ames test strains *Salmonella Typhimurium* TA 98 and TA 100

No	Treatment method	Sample	Time (h)	Mutagenesis Index		Results
				TA 98	TA100	
1	No treatment		0	2.0	nd	M
2	Electro-precipitation (MS-anode)	Cr (VI) 200 ppm	3	1.64	nd	NM
3	No treatment	Tan-effluent	0	1.9	0.7	M
4	Electro-precipitation (MS-anodes)	(190 ppm)	3	1.5	nd	NM
5	No treatment		0	1.23	nd	M
6	Electro-precipitation (MS-anodes)	Direct pink (100 ppm)	20 (min)	1.6	1.13	NM
7	Adsorption	Direct pink	1	1.95	nd	M
8		Mixed effluent	1	1.94	nd	M
9	Electro-precipitation (MS-anodes)	Mixed effluent	3	1.4	nd	NM

Mutagenesis index = number of revertants obtained in simple/number of revertants of the negative control

M = mutagenic NM = non-mutagenic, nd = not determined, MS = mild steel

- Plate incorporation test was used
- Each value is an average of 3 experiments
- All the test were performed without S9 metabolic activation system

The results in Table 3.4 show that an electro-precipitation process using mild steel electrodes can be used for the removal of chromium, as mixed Cr (III)/Fe (III) hydroxide sludge, from both model solutions and real industrial effluent streams as the

treated effluents are non-mutagenic. The mixed Cr (III)/Fe (III) hydroxide sludge obtained during the electro-precipitation process of leather effluent is not a suitable adsorbent for the adsorption of direct pink dye and mixed effluent streams as the treated effluents are also mutagenic.

The results demonstrated that the *in-situ* production of mixed Cr (III)/Fe (III) hydroxide sludge is an excellent process for the removal of chromium and dye molecules from mixed effluent streams. This process is suitable for developing countries like Pakistan where these two industries are located in close proximity and create effluent streams which are being discharged into waterways without any treatment. The results obtained from this research work were made available to the PEPA. Industrial trials on the use of these treatment technologies have been planned by the PEPA and the prototype units of different sizes are being prepared which will be used for the treatment of textile, leather and for the simultaneous removal of dye and chromium from mixed effluent streams.

3.4 SUMMARY

3.4.1 Textile Effluent

The electro-precipitation process, with mild steel or aluminium anodes, is an excellent treatment process for the removal of dyes from synthetic and industrial effluent streams. This treatment process does not degrade or oxidise the dye molecules and, therefore, the dye removal process is one of physical adsorption and not dye destruction. Increasing treatment time, corresponding to increasing release of aluminium or iron from the anodes, resulted in increased removal of colour from the textile wastewater. A treatment time of 30 minutes was found to be the optimum value for the complete removal of dyes from both synthetic solutions and industrial effluent streams (Tables 3.5 and 3.6). The overall water quality of the treated textile wastewater is suitable for recycling and also complies with the discharge consent level.

Table 3.5: Treatment of synthetic dye solutions using electro-precipitation process

Dye solution	Electrode type		Optimum time / min	Mutagenicity
	Cathode	Anode		
Reactive orange	SS	MS	30	NM
		Al	30	NM
Reactive violet	SS	MS	30	NM
		Al	30	NM
Direct pink	SS	MS	30	NM
		Al	30	NM
Direct turquoise	SS	MS	30	NM
		Al	30	NM
Dispersed blue	SS	MS	30	NM
		Al	30	NM
Dispersed violet	SS	MS	30	NM
		Al	30	NM

SS = Stainless steel; Ms = Mild steel; Al = Aluminium

Table 3.6: Treatment of industrial effluent streams using electro-precipitation process

Industrial effluent	Electrode type		Optimum time / min	Mutagenicity
	Cathode	Anode		
Mixed effluent	SS	MS	30	NM
		Al	30	NM
Printing effluent	SS	MS	30	NM
		Al	30	NM
Dyeing effluent	SS	MS	30	NM
		Al	30	NM

SS = Stainless steel; Ms = Mild steel; Al = Aluminium

During the electro-oxidation process the degradation or destruction of dye is responsible for colour removal from textile effluent. The data obtained suggest that electro-oxidation is a slow process compared to electro-precipitation. The one advantage of the electro-oxidation process is that there is no sludge formation and the treated water can easily be recycled within the manufacturing process. The electro-oxidation process, with titanium mesh cathode and mixed metal oxide anodes, is also a viable treatment method of cleaning up textile effluent streams (Table 3.7). However, the electro-oxidation process, with stainless steel rod cathode and graphite rods as anodes, cannot be used for the treatment of industrial effluent streams because a complete removal of dye molecules was not achieved and furthermore the treated effluents are mutagenic (Table 3.8).

Table 3.7: Treatment of synthetic dye solutions using electro-oxidation process

Dye	Electrode type		Optimum time / min	Mutagenicity
	Cathode	Anode		
Reactive orange	SS	Gr	120	NM
	Al	Gr	120	NM
	TM	MM	40	NM
Reactive violet	SS	Gr	120	NM
	Al	Gr	120	NM
	TM	MM	40	NM
Direct pink	SS	Gr	60	NM
	Al	Gr	60	NM
	TM	MM	20	NM
Direct turquoise	SS	Gr	40	NM
	Al	Gr	60	NM
	TM	MM	30	NM
Dispersed blue	SS	Gr	60	NM
	Al	Gr	60	NM
	TM	MM	30	NM
Dispersed violet	SS	Gr	60	NM
	Al	Gr	60	NM
	TM	MM	30	NM

SS = Stainless steel; TM = Titanium mesh; MM = Mixed metal; Al = Aluminium; Gr = Graphite

Table 3.8: Treatment of industrial effluent streams using electro-oxidation process

Industrial effluent	Electrode type		Optimum time / min	Mutagenicity
	Cathode	Anode		
Mixed effluent	SS	Gr	-	M
	TM	MM	20	NM
Printing effluent	SS	Gr	-	M
	TM	MM	20	NM
Dyeing effluent	SS	Gr	-	M
	TM	MM	40	NM

SS = Stainless steel; TM = Titanium mesh; MM = Mixed metal; Gr = Graphite

A prototype treatment unit, based on the electro-precipitation process, was successfully used for the removal of dyes from both synthetic solutions and industrial effluent streams.

The adsorption process using waste Cr (III)/Fe(III) hydroxide sludge, obtained electrochemically by treating leather effluent streams, as an adsorbent material cannot be used for the treatment of textile effluent steams. The results demonstrated that a complete removal of dye molecule was not achieved and furthermore the treated effluent was mutagenic in nature.

3.4.2 Leather Effluent

The treatment of leather effluent streams was carried by using an electro-precipitation process with mild steel anode to produce a Cr (III)/Fe (III) hydroxide sludge. The *in-situ* production of this hydroxide sludge is an excellent treatment method that can be used to remove chromium and other harmful organic species from leather effluent streams.

3.4.3 Mixed Textile and Leather Effluent

The *in-situ* production of mixed Cr (III)/Fe (III) hydroxide sludge is an excellent process for the removal of chromium and dye molecules from mixed effluent streams. This process is suitable for developing countries like Pakistan where these two industries are located in close proximity. These results support the idea that a single treatment process can be used for the removal of chromium and colour from a mixed

textile/leather effluent streams in order to achieve an overall waste minimisation objective. The use of final sludge obtained after the treatment of mixed effluent streams is also being investigated for different industrial applications such as the production of fire or concentrate bricks for pavement.

One of the technologies, electro-precipitation, developed in this chapter is based on the use of mild steel anodes which can be used for the treatment of both textile and leather effluent streams. I believe that this technology has a maximum chance of its adoption on industrial scale because it is simple, robust and operators require minimum training to carry out this process on industrial scale. Apart from the energy consumption the only other consumable is mild steel and this material is available in large quantities in Pakistan. Industrial trials on the use of this technology have been planned by the PEPA and prototype units are being prepared for the treatment of textile, leather and mixed leather/textile effluent streams.

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CHAPTER 4

DESTRUCTION OF VOLATILE ORGANIC COMPOUNDS (TOLUENE) USING CATALYTIC TECHNOLOGY

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CHAPTER 4

DESTRUCTION OF VOLATILE ORGANIC COMPOUNDS (TOLUENE) USING CATALYTIC TECHNOLOGY

4.1 INTRODUCTION

A toxic air contaminant is an air pollutant which may contribute to mortality or serious illness, or pose other potential hazards to human health. Most air toxics are volatile and are found primarily in the atmosphere in the gaseous form but some occur in atmospheric particles or liquid droplets.

There are a large number of industries that use a wide range of volatile organic compounds (VOCs) to manufacture products or chemicals which play an important part in modern human living. The wide spread use of these organic chemicals and the waste materials originating from the manufacturing processes emit a large number of VOCs to the environment which results in human exposure to these atmospheric toxins. The release of the toxins to the environment is due to the use of inappropriate manufacturing devices, old and faulty equipment, poor handling and most importantly lack of appropriate emission control technologies [1]. To protect the public, a number of national and international environmental regulations have been enacted to identify air pollutants, determine their sources, assess the amounts released to the environment, evaluate potential risk to the public and implement appropriate emission control strategies.

The accident in Bhopal, India, which claimed 4000 lives and injured tens of thousands more in December 1984, was an important event in the Indian subcontinent region which resulted in calling attention to the potentially devastating effects of massive releases of toxic chemicals. This event heightened concerns that protection measures were needed to reduce potential risk to the public from exposure to airborne toxic chemicals [2]. This event was also the turning point for most of the governments in the region and forced them to establish environmental protection agencies and to implement strict environmental regulations in order to protect public and the environment.

Although Pakistan is an agricultural country, and one of the five leading cotton-producing countries in the world, it also has an industrial base that services this sector. Cotton is cultivated largely in Punjab and Sindh provinces and it is the main cash crop of the country and a major contributor towards the nation's foreign exchange earnings [3]. The percentage share of cotton in total national exports was 58-64% during the decade of 1990s. Given the larger contribution of cotton towards the national economy, this crop enjoys priority over all other crops but wheat. Every possible step is taken to increase its production. Every year more and more area is brought under cotton cultivation. In addition, a large quantity of chemical pesticides is used to protect this vital cash crop from pest attack. A huge amount of pesticides and insecticides are specially being used to control cotton leaf curl virus, white fly and bollworms in order to increase cotton yield [4].

The increased use of these organic chemicals has, however, resulted in the production of pesticide active ingredients (PAIs) by a large number of chemical industries within the country. These active ingredients are usually used in the manufacture of pesticides, insecticides, herbicides, and fungicide products which are typically used in the agricultural industry. A variety of volatile organic compounds, including toluene, can be released to the atmosphere during the production of PAIs [5]. These chemical industries are being forced by the PEPA to meet emission limits for process vents by using either an add-on control device or a pollution-prevention alternative [6].

Most of the work carried out in the Centre for Environmental Research at Brunel University, on the degradation of organic pollutants, has been focused on the use of photolytic and photo-catalytic technologies [7]. These technologies are effective at destroying most of the organic compounds present in aqueous solution but cannot be installed in the process vent to reduce the level of VOCs emitting into the environment.

The aim of the work described in this chapter is to develop a catalytic technology in order to oxidise volatile organic compounds to produce harmless products such as carbon dioxide and water. Toluene was used as an indicator of volatile organic compounds during this study. The developed technology had to be capable of destroying VOCs at low temperature and can easily be installed in the process vents to

control the emissions of toluene and other toxic organic pollutants emitted during the production of PAIs.

4.2 TOLUENE

4.2.1 Sources and Emissions

Toluene is a clear, colourless, volatile and flammable liquid under standard conditions. It is a naturally occurring component of crude oil and petroleum. Its odour has been described as sweet and pungent. The primary use of toluene is in the production of benzene. It is also used as a feedstock or starting material in the synthesis of various organic chemicals. Toluene is widely used as a solvent in paints, varnishes, lacquers, gums, resins, pesticide formulations, printing inks, dyes, adhesives, sealants, cleaning agents, nail polish, and for chemical extractions. The major sectors that release toluene to air are the petroleum refineries and manufacturing of PAIs. For the majority of these facilities, fugitive emissions comprise the largest portion of toluene emissions to air, although stack emissions and releases during storage and handling can also contribute greatly to toluene air emissions, depending on the facility. Another source of toluene release to the environment is the production, transport, use and disposal of gasoline, and other industrial and consumer products that contain toluene [8]. Amino/phenolic resins are primarily used in the manufacture of plywood, particleboard, adhesives, wood furniture and plastic parts. A number of VOCs, including toluene, formaldehyde, phenol, methanol, and xylene are released during the resin manufacturing process [9]. So there is an urgent need to encourage the use of pollution prevention measures and develop suitable control devices that can be used to prevent the emissions of VOCs into the environment.

4.2.2 Environmental Fate

Toluene is released into the atmosphere principally from the volatilisation of petroleum fuels and toluene-based solvents and thinners and from a large number of VOCs that are being used in different industries [10]. Considerable amounts are discharged into waterways or spilled on land during the storage, transport and disposal of chemicals and fuel oils.

If toluene is released to soil, it will be lost by evaporation from near surface soil and microbial degradation. Above 94 % of toluene added to clay loam can be removed by

these processes. Since it is relatively mobile in soil, it is possible that it will get into the groundwater and remain there where microbial degradation will not occur [11].

When released into water, toluene will be lost by both volatilization to the atmosphere and biodegradation. The predominant process will depend on water temperature, mixing conditions and the existence of acclimated microorganisms at the site. The half-life will range from days to several weeks. It will not significantly hydrolyse, directly photolyse, adsorb to sediment or bioconcentrate in aquatic organisms [12].

If toluene is released to the atmosphere, it is exist predominantly in the vapour phase. It degrades moderately rapidly by reaction with photochemically produced hydroxyl radicals ($^{\bullet}OH$). Its half-life ranges from 3 hours to somewhat over a day [13]. It is very effectively washed out by rain. It is not subject to direct photolysis in sunlight, although a complex of toluene with molecular oxygen has been shown to absorb light at wavelengths >290 nm [13].

4.2.3 Health Effects

Occupational exposure to toluene may cause mild eye and respiratory tract irritation. The central nervous system (CNS) is the primary target organ for acute and chronic exposures. Toluene is a CNS depressant. A Short-term exposure may cause minor nervous system disorders such as fatigue, nausea, weakness, confusion and cardiac arrhythmias. Toluene has the potential to cause the following effects from a lifetime exposure at levels above the maximum contaminant level (MCL): more pronounced nervous disorders such as spasms, tremors, impairment of speech, hearing, vision, memory, coordination; liver and kidney damage [14].

Various epidemiological studies did not detect a statistically significant increased risk of cancer due to inhalation exposure to toluene. However, these studies were limited due to the size of the study population and lack of historical monitoring data. The U.S. EPA has placed toluene in Group D “not classifiable as a carcinogen” [15]. The International Agency for Research on Cancer has placed toluene in Group 3 “not classifiable as a carcinogen” [16].

The MCL for toluene has been set at 1 ppm because EPA believes, given present technology and resources, this is the lowest level to which water systems can reasonably be required to remove this contaminant should it occur in drinking water.

4.3 TREATMENT METHODS

Before beginning evaluations as to what treatment techniques will remove the contaminant(s) of concern, an effort should be first made to identify and abate the origin of the contamination. This can minimize the size of the treatment device and will shorten the period during which treatment will be necessary.

Different types of treatment methods have been shown to be effective in removing organic contaminants from various types of environmental samples. The description and the importance of some of the treatment methods used for the removal of toluene and reported in the literature are given in the following sub sections.

4.3.1 Aeration

Aeration treatment consists of passing large amounts of air through the contaminated soil or water samples. This method is also called air sparging, air stripping or air volatilisation and is usually used to reduce the concentration of volatile organic contaminants that are adsorbed on solids or dissolved in water. The goal is to allow the contaminants to volatilize into the air stream. Contaminant-free air is injected into the saturated zone, allowing a phase transfer of hydrocarbon from a dissolved phase to a vapour phase. This method generally works better at remediating the lighter organic contaminants, like benzene, toluene, ethylene and xylene (BTEX). For the treatment of water samples, the efficiency of the device is improved by breaking up the water flow into many small droplets. Aerator configurations include packed tower and low profile shallow tray styles. The three main problems associated with the aeration process are:

- The process does not remove or destroy organic contaminants but simply transfers VOCs from one environmental compartment to another
- During the process oxidation of metal impurities, like iron and manganese, may occur if these ions are present at elevated concentrations
- Bacterial slime may grow in aerators requiring continuous or periodic chlorination.

The advantage of aeration is that there is no disposal or regeneration of the treatment system necessary [18]. The organic pollutants can also be destroyed by passing the contaminant air through a system containing catalytic technologies.

4.3.2 Adsorption

Activated carbon has an enormous surface area and is often used as an adsorbent material for the removal of organic contaminants from a variety of different streams. Once the removal capacity of the carbon is used up, the carbon may be returned to the manufacturer for regeneration or can be disposed of appropriately. There are two main problems associated with the use of activated carbon as an adsorbent for the removal of organic contaminants:

- Activated carbon can foster the growth of bacteria by concentrating the food the bacteria need to live.
- The possible release of those contaminants, which are already adsorbed. This possibility is known as "dumping" and can occur when the carbon is nearly saturated with contaminants and a contaminant of high preference displaces another with lower preference.

To address exhaustion and dumping, the overall amount of carbon should be divided into two treatment tanks and the two tanks installed in "series" such that breakthrough in the first unit can be adsorbed by the newer carbon in the second unit [22].

4.3.3 Bioremediation

This process makes use of natural processes to reduce the concentration and amount of pollutants in environmental waste samples. This process is suitable for both solid and liquid waste streams. The environmental contaminants and microorganisms are left together in a reaction chamber to destroy or neutralise contamination. The bioremediation process, however, is not an acceptable option for all environmental samples because the rate of conversion is usually very slow. Long-term monitoring is necessary to demonstrate that contaminant concentrations are continually decreasing at a rate sufficient to ensure that they will not become a health threat [20].

4.3.4 Biofiltration

Biofiltration has been increasingly applied as an air pollution control technology to minimize or eliminate emissions of volatile organic compounds from industrial sources and environmental remediation activities. Atoche and Moe [21] have studied the efficiency of the biofiltration process by treating a model waste gas stream containing a two-component mixture of methyl ethyl ketone (MEK) and toluene. One biofilter was operated as a sequencing batch biofilter (SBB), and the other was operated as a conventional continuous-flow biofilter (CFB). The model waste stream contained MEK concentrations ranging from 80 to 89 ppmv and toluene concentrations ranging from 28 to 30 ppmv. Both operating strategies resulted in stable long-term performance with greater than 99 % contaminant removal during these loading conditions [21].

4.3.5 Thermal Oxidation

Thermal oxidation of VOCs and other air pollutants works by a simple reaction of the harmful air pollutants with oxygen and heat. In this environment the VOCs are converted to carbon dioxide gas, water vapour and usable heat. These harmless gaseous by-products are released to atmosphere and varying heat recovery technologies are incorporated into oxidiser designs to recover heat. Direct fired thermal oxidisers, recuperative thermal oxidisers, regenerative thermal oxidisers, and catalytic thermal oxidisers are all variations implemented to minimise heating requirements and operating costs [22].

The two main problems associated with this technology are: a) the formation of products of incomplete combustion which could be emitted to the atmosphere. These products are formed due to a variation in temperature and b) thermal oxidation requires large inputs of heat, typically through combustion of natural gas, which can be quite costly. The technology is more energy efficient when treating compounds that produce high temperatures during combustion (petroleum hydrocarbons) and the heat is re-circulated to enhance efficiency [22].

Thermal oxidation processes have been modified in order to minimise the production of products of incomplete combustion by changing the heating source from gas to a furnace. Temperatures in a thermal oxidiser are typically maintained at 1600°-1850°F and the process is called flameless thermal oxidation. The flameless thermal oxidiser is

a destructive technology for off-gas treatment of volatile organic compounds (VOCs) and semi-volatile organic compounds originating from many sources including petroleum hydrocarbons and methylene chloride emissions generated during pesticide production. The process converts aromatic and chlorinated VOCs to carbon dioxide, water, and hydrogen chloride without exposing the vapours to a flame. The technology achieves uniform thermal oxidation of VOCs using a heated packed-bed reactor filled with ceramic pieces. The vapours are oxidised when they come into contact with the heated bed of ceramic pieces. The flameless oxidiser provides a controllable uniform heating zone to control temperature variation and reduces the formation of products of incomplete combustions [22].

4.3.6 Chemical Oxidation

Certain organic contaminants will react chemically with oxygen and oxygen-like compounds. After this treatment, the resultant compounds may be either fully neutralized or will have a lower level of hazard. Further treatment may still be necessary for the complete removal of organic contaminants. Oxidizing chemicals could include: potassium permanganate, hydrogen peroxide and hypochlorite. Chemical oxidation treatment processes have limited applications [23].

4.3.7 Photocatalytic Oxidation

Different types of photocatalytic reactors have been used for the oxidation of toluene in the presence of various types of catalysts and a UV lamp. Dezhi et al. [29] have studied the photo-oxidation of toluene by using porous nickel sheets that were coated with a Fe-doped TiO_2 catalyst. The reactor was used to investigate the factors that affect toluene degradation. The results showed that inlet toluene concentration, relative humidity and gas flow rate significantly affect toluene decomposition. The conversion decreases as inlet concentration increases. Degradation efficiencies of more than 95% can be achieved provided that the toluene concentration is kept below 3200 mg/m^3.

The efficiency of TiO_2 and Pt/TiO_2 as photocatalysts, immobilized on to UV-transparent quartz support, has been evaluated for the photodegradation of 160 ppm toluene-laden air [25]. It was found that 50-70% of toluene was degraded within the first 5 min of UV illumination. Both TiO_2 and Pt/TiO_2 photocatalysts suffered from deactivation after 18 hours of continuous operation, and the activity of the photocatalyst

was significantly reduced. It is concluded that the de-activation of the photocatalyst was due to the accumulation of intermediates on the photocatalyst surface preventing the toluene being adsorbed on the photocatalyst surface for further degradation.

Photocatalytic degradation of acetonitrile and toluene was carried out both in gas-solid and in liquid-solid regimes using two commercial TiO_2 samples as photocatalysts (Merck and Degussa P25, United Kingdom). The investigation was mainly aimed to study the influence of water present in the reaction environment on the mechanism and degradation rates of these two molecules. In the presence of water vapour, the activity of TiO_2 Merck United Kingdom remained stable but was greatly reduced if water was absent. TiO_2 Degussa P25 continuously deactivated, even in the presence of water vapour. In the liquid-solid regime, the main intermediates of toluene photodegradation were p-cresol and benzaldehyde, however, traces of pyrogallol and benzyl alcohol were also found. Benzoic acid and hydroquinone were detected only when TiO_2 Merck, United Kingdom was used. The photodegradation products of acetonitrile were cyanide, cyanate, formate, nitrate and carbonate ions [26].

Photocatalytic activity of TiO_2 can be increased by washing it with water or HCl before using it as a semiconductor material in a phtocatalytic cell for the phtodegradation of organic compounds. Photocatalytic oxidations of toluene and benzene in air were carried out by using water and HCl pretreated TiO_2. The results show that the use of HCl pretreated TiO_2 enhances the toluene removal rate [27]. The main purpose of this work was to identify intermediate products. Benzoic acid, benzaldehyde and benzyl alcohol were the three major toluene intermediate products identified. The degradation of benzene proceeds through the formation of phenol which was accompanied by hydroquinone and 1,4-benzoquinone. Acetic and formic acids were also formed from both benzene and toluene [27].

4.3.8 Catalytic Oxidation

Catalytic oxidation has become an effective means of treating air streams containing a variety of volatile organic compounds and is a strongly favoured alternative to thermal oxidation. Examples of VOCs treated are methanol, acetone, amines, benzene, natural gas and toluene. Catalysts can oxidise a wide variety of VOCs to CO_2 and water vapour at lower temperatures and with less energy consumption and NO_x formation than

thermal methods. The presence of a catalyst allows virtually complete destruction of organic compounds in the feed without yielding products of incomplete combustion, which can be produced from thermal incineration. In the case of chlorinated VOCs, the products are HCl, CO_2 and H_2O where HCl is easy to remove from the effluent gas stream.

There have been several studies on the development of catalysts for deep oxidation of a broad range of VOCs [28-35]. These catalysts fall into two categories based on noble or on transition metal oxides. The supported transition metal oxides such as Cu, Cr and Mn, have low activity and most of them are subjected to catalyst deactivation, especially when halogenated VOCs are used.

A chromia/alumina spheres catalyst has been used in catalytic oxidation of halogenated VOCs in fluidized bed reactors. The surface of the spheres of this inexpensive catalyst is kept clean by the movement of the spheres in a fluidized bed. A feature of this catalyst is its ability to provide high oxidation efficiencies without deactivation by sulphur or chlorine compounds in the gas. The disadvantage of this process is the continuous loss of catalyst from the reactor and deleterious effects of possible chromium emissions.

Supported noble metal catalysts have shown their ability to form complete oxidation products, but the presence of halogenated VOCs deteriorate and temporarily poison the performance of precious metal catalysts. Herbert [36] developed a noble metal monolith catalyst that could tolerate and even destroy halogenated VOCs. Windawi et al. [37] and Noordally et al. [38] also developed a platinium metal washcoated monolith catalyst for deep oxidation of chlorinated VOCs. Agarwal et al. [39] studied the catalytic destruction of cyanogen chloride using a 2.15% Pt-Al_2O_3 catalyst. A combination of Pt, Pd, Mo and Fe as oxides supported on TiO_2 catalysts has been developed by an impregnation method to destroy a wide variety of VOCs [40]. Recently, Lago et al. [41] developed copper chloride based catalysts for deep oxidation of chlorinated VOCs in air at mild temperatures (350-500°C) and Ramachandran et al. [42] studied the decomposition of methylene chloride and carbon tetrachloride in air over H-, Co-, Na-Y zeolite catalysts at temperatures ranging between 180 and 350°C with a space velocity of 2400 h^{-1} at atmospheric pressure. Very recently, low

temperature catalytic combustion using bulk metal (e.g. Mo, Mn, and V) oxide catalysts was used to neutralize low-level mixed waste from nuclear weapons stations [43].

US Patent 4833114 [44] and its equivalent EP 0352 398 discloses a process for preparing a palladium catalyst which comprises dissolving dinitrodiammine palladium in nitric acid solution and aging the solution in the temperature range 60 to 100°C, applying the solution to a carrier, and reducing the palladium compound on the carrier to prepare the palladium catalyst. It is stated that the temperature range specified is essential to prepare a functional catalyst. In the specification the aging process is said to be followed by a colour change in which the solution turns from pale yellow to reddish brown and from reddish brown to thick reddish brown on aging at a temperature of 80°C for 9 to 15 hours. This process was found to be difficult to control and follow and, in practice, it was found very difficult to produce an active catalyst consistently.

The purpose of the work described in this chapter is to prepare catalysts using γ-Al_2O_3 spheres, γ-Al_2O_3 washcoated monolith and TiO_2 (anatase) washcoated monolith impregnated with platinum or palladium. This research work has two primary objectives: (1) to prepare and characterise new supported noble metal catalysts and (2) to study the activity of these new catalysts for VOCs emission control applications. Toluene was used as an indicator of volatile organic compounds during this study.

4.4 EXPERIMENTAL AND METHODOLOGY

The aim of this work was to prepare inexpensive transition metal support catalysts suitable for the destruction of VOCs. A number of transition metal support catalysts were prepared, including copper, cobalt, nickel, using simple impregnation technique at room temperature. The suitability of these catalysts were tested for the oxidation of toluene, as an indicator of VOCs, and the results obtained show that all these catalysts were ineffective up to a temperature of 300°C. For this reason the emphasis of this research was changed and the attention was then focussed on the preparation of noble metal support catalysts that could be used for the control of VOCs emissions from chemical manufacturing processes.

This section contains details of materials and methods adopted for synthesis, characterisation and application of noble metals (Pt and Pd) catalysts to control VOCs emissions into the environment. The effects of variations in the impregnation period and impregnation solution temperature on the catalyst metal loading were tested and the additions of different volumes of platinum solution relative to a fixed volume of the support were also studied.

A 50 ml batch of catalyst was prepared in each experiment. As supplied solutions (Degussa) United Kingdom of diammine dinitroplatinum (II) in nitric acid and diammine dinitropalladium (II) in nitric acid, (laboratory reagent, Fisher Scientific UK) 5 % Pt or Pd) were diluted with deionised water to produce solutions containing 0.2 % Pt or Pd. These diluted solutions were used to prepare the Pt or Pd impregnated catalysts using the following three substrates:

- γ-Al_2O_3 spheres
- γ-Al_2O_3 wascoated monoliths and
- TiO_2 (anatase) washcoated monoliths

4.4.1 Catalyst Preparation – Impregnation of γ-Al_2O_3 spheres with platinum

50 ml of γ-Al_2O_3 spheres (2-3 mm diameter, surface area = 80 m^2g^{-1}, supplied by Degussa UK) were transferred into a stainless steel sieve basket. The basket was dipped into a beaker containing 70 ml of 0.2 % Pt solution, which completely covered the γ-Al_2O_3 spheres. The basket was shaken from time to time during a 15-minute impregnation period. The impregnation was carried out at room temperature and after 15 minutes of impregnation, the basket was removed and the excess solution removed by shaking the basket. The wet catalysts samples were dried and calcined according to the procedure described in section 4.4.6. The volume of drain solution left behind in each experiment was around 20-25 ml and the metal analysis by AAS showed around 30-50 ppm of Pt was left in the drain solution.

4.4.2 Effect of Impregnation Period on the Catalyst Metal Loading

Three identical volumes (50 ml) of γ-Al_2O_3 spheres were poured into three stainless steel sieve baskets (numbered from 1 to 3). The three baskets were dipped into three

beakers (also numbered 1 to 3), each containing 70 ml solution of diammine dinitroplatinum (II) in nitric acid solution (0.2 % Pt) at room temperature (23°C). The baskets 1, 2 and 3 were removed from the impregnation solutions after 15, 30 and 60 minutes respectively. The wet catalysts samples were dried and calcined according to the procedure described in section 4.4.6. The volume of drain solution left behind in each experiment was around 20-25 ml.

4.4.3 Effect of Solution Temperature on the Catalyst Metal Loading

Three identical volumes of γ-Al_2O_3 spheres were poured into three stainless steel sieve baskets (numbered from 1 to 3). These baskets were dipped into three beakers also numbered from 1 to 3), each beaker containing 70 ml of diammine dinitroplatinum (II) in nitric acid solution (0.2 % Pt). The impregnation time was fixed at 15 minutes for all three samples. The samples 1, 2 and 3 were impregnated in Pt solutions at temperatures of 23, 50 and 75°C. The wet catalysts samples were dried and calcined according to the procedure described in section 4.4.6. The volume of drain solution left behind for each experiment was around 18-24 ml.

4.4.4 Effect of the Volume of Pt Solution Relative to Fixed Volume of γ-Al_2O_3 Spheres on the Metal Loading

Different volumes (50 and 70 ml) of 0.2 % Pt solution were added to the γ-Al_2O_3 spheres sample so that they completely covered the spheres. The spheres were impregnated by continuously shaking them with the solution for 15 minutes at room temperature, (23°C). The wet catalysts samples were dried and calcined according to the procedure described in section 4.4.6. The volume of drain solution left behind was about 12-18 ml.

4.4.5 Impregnation of γ-Al_2O_3 spheres, γ-Al_2O_3 washcoated monolith and TiO_2 (anatase) washcoated monolith with platinum or palladium

The above procedures were repeated to impregnate γ-Al_2O_3 and TiO_2 washcoated monoliths (surface area around 10 $m^2 g^{-1}$, ~ 200 cell per square inch (cpi) and supplied by Johnson Matthey, United Kingdom) with platinum or palladium. 50 g of washcoated monolith was used for each experiment. Experiments were also conducted to impregnate γ-Al_2O_3 spheres with palladium.

4.4.6 Drying/Calcination

The wet γ-Al_2O_3 spheres, impregnated with the catalyst, were transferred to a stainless steel sieve tray and stacked in a calcination oven. The catalyst was dried and calcined at 120°C for 2 hours and at 350°C for 2 hours. The finished catalyst is PtO_2/γ-Al_2O_3 spheres. The Pt contents were determined by atomic absorption spectroscopy (AAS) after leaching the catalyst in HCl/HNO_3. A similar drying and calcinations method was used for washcoated monolith catalysts impregnated with Pt or Pd.

4.4.7 Catalytic Performance

Spheres and monolith catalysts, prepared as above were tested for complete combustion of toluene in air. A fixed-bed bench-scale activity rig was used in this study (Figure 4.1).

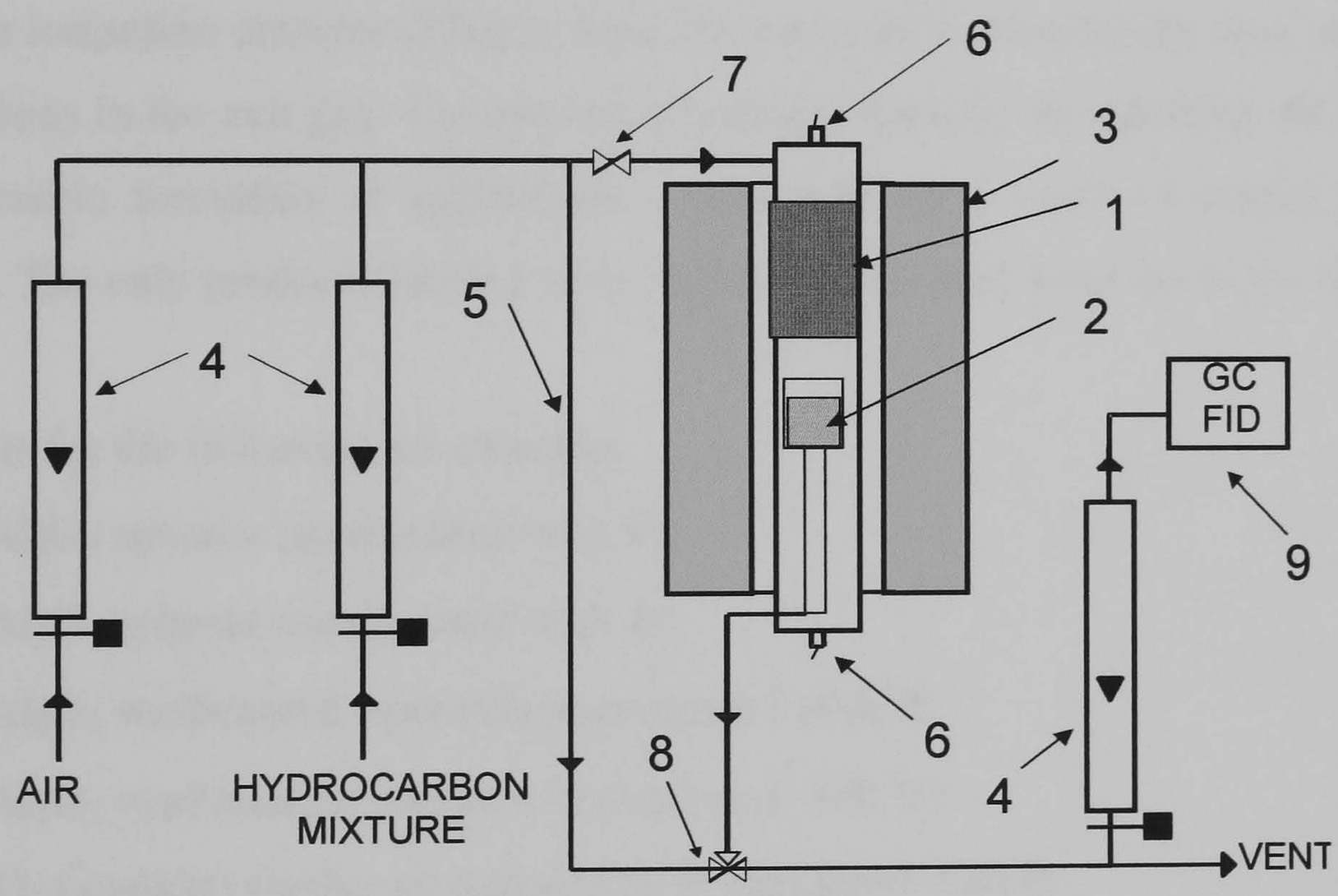

Figure 4.1: Activity Rig

1. Reactor 2. Catalyst holder 3. Furnace 4. Flow meter 5. Bypass
6. Thermocouples 7&8. Valves 9. Flame Ionisation Detector (FID)

The activity rig used (Figure 4.1) consisted of a quartz tube reactor (1), containing an inner quartz cup (2) to hold the catalyst. The reactor was housed in a furnace (3). The activity performance of each catalyst was investigated by increasing the furnace temperature at a rate of 10°C/min for up to a maximum temperature of 300°C. The flow of a continuous stream of the test gas mixture was controlled by a flow meter (4) and allowed to pass through the bypass (5) or through the reactor (1) at atmospheric

pressure. An additional standby air cylinder was also a part of this activity rig setup which could be used if a further dilution of the test gas was required for investigation. The test gas mixtures contained 1000 ppmv toluene in air. Thermocouples (6) monitored the inlet and outlet temperatures of the test gas mixture. Valves (7) and (8) were used to allow the test gas mixture to pass through the reactor or the bypass line. In control experiments, the test gas mixture was passed through the reactor, in the absence of the catalyst, and the product exiting the reactor were analysed. In separate test experiments, the test gas mixture was passed through the reactor, in the presence of the catalyst, and the products exiting the catalyst were also analysed. The reaction was carried out at a gas hourly space velocity between 20,000 and 40,000 h^{-1}. Different volumes of catalyst (monolith or spheres) were used in each test and the tests were carried out over a range of temperatures and the catalytic activities monitored. An on-line flame ionisation detector (FID) system (9) was used to monitor the total unoxidised hydrocarbons in the exit gas. The product selectivity data for the catalysts did not show any detectable formation of undesirable compounds as a result of partial oxidation reactions. The only products formed were carbon dioxide and water in all the tests.

The results for the following six catalysts

- γ-Al_2O_3 spheres impregnated with Pt
- γ-Al_2O_3 spheres impregnated with Pd
- γ-Al_2O_3 washcoated monolith impregnated with Pt
- γ-Al_2O_3 washcoated monolith impregnated with Pd
- TiO_2 (anatase) washcoated monolith impregnated with Pt
- TiO_2 (anatase) washcoated monolith impregnated with Pd

are given in Tables 4.4-4.9 and are compared in Figure 4.2.

4.5. RESULTS AND DISCUSSION

4.5.1 Effect of Impregnation Period on the Catalyst Metal Loading

The results in Table 4.1 show that the metal loading in the catalysts were similar. The impregnation period of around 15 minutes was a suitable time to achieve the removal of at least 93 % of the Pt metal from the Pt solution (0.2 % Pt) by the γ-Al_2O_3 spheres; 15 minutes as impregnation period was used for the rest of the experiments.

Table 4.1: Effect of impregnation period on the catalyst metal loading

	Impregnation	**Pt (%)**	**Pt (%)**
Catalyst No.	Period (minute)	Catalyst	Drain solution
1	15	0.20	0.008
2	30	0.20	0.009
3	60	0.21	0.008

4.5.2 Effect of Solution Temperature on the Catalyst Metal Loading

The results in Table 4.2 showed similar catalyst metal loading at differing temperatures during the impregnation of between 23 - 75°C. These results confirm that impregnation can be carried out at room temperature and no advantage in metal loading can be achieved by increasing the temperature to 75°C.

Table 4.2: Effect of solution temperature on the catalyst metal loading

	Pt (%)	
Solution temp. (°C)	Catalyst	Drain solution
23	0.20	0.008
50	0.19	0.010
75	0.20	0.009

4.5.3 Effect of the Volume of Pt Solution Relative to Fixed Volume of γ-Al_2O_3 Spheres on the Metal Loading

In both cases when the solution volume was 70 ml or 50 ml, the support picked up more than 90 % of the Pt metal from the solution, which was deposited on the surface of the support. These results show that Pt can be deposited on the γ-Al_2O_3 spheres, from an acidic solution, and provides an excellent method for a surface coating. This simple surface impregnation technique enables the amount of Pt deposit on the surface of the γ-Al_2O_3 spheres to be controlled and tailored to a particular application e.g. a particular VOC application.

Table 4.3: Effect the volume of Pt solution relative to fixed volume of γ-Al_2O_3 spheres on the metal loading

	Pt (%)	
Solution volume (ml)	Catalyst	Drain solution
70	0.20	0.007
50	0.14	0.01

4.5.4 Catalytic Performance

The activity of the prepared catalysts for the oxidation of toluene was determined by using the activity rig as described in section 4.4.7 and its schematic is given in Figure 4.1. The oxidation of toluene in presence of support and in the presence of a catalyst, support impregnated with Pt or Pd, were performed under similar conditions and up to a maximum temperature of 300°C. The results obtained show that no detectable degradation of toluene was observed when the oxidation was carried out under controlled conditions. These results confirmed that a suitable catalyst is required if the oxidation of toluene to be carried out at low temperatures. The oxidation of toluene, under controlled conditions, can be achieved at temperatures higher than 500°C but this system would not be an economically viable technology and would not be adopted by industry to control the emission of volatile organic compounds in the process vents.

4.5.4.1 γ-Al_2O_3 spheres impregnated with Pt

The results in Table 4.4 show that a complete oxidation of 1000 ppm toluene in air, space velocity = 20,000 h^{-1} at atmospheric pressure was achieved at 236°C.

Table 4.4: Activity measurement of γ-Al_2O_3 spheres (2-3 mm diameter) coated with Pt

Temperature °C	**Conversion Oxidation %**
201	40
207	70
212	88
220	94
227	97
236	100

4.5.4.2 γ-Al_2O_3 spheres impregnated with Pd

The results in Table 4.5 show that a complete oxidation of 1000 ppm toluene in air, space velocity = 20,000 h^{-1} at atmospheric pressure was achieved at 240°C. These results show that the γ-Al_2O_3 spheres impregnated with Pt is a better catalyst compared to the γ-Al_2O_3 spheres impregnated with Pd.

Table 4.5: Activity measurement of γ-Al_2O_3 spheres (2-3 mm diameter) coated with Pd

Temperature °C	**Conversion Oxidation %**
210	35
215	65
220	78
225	89
230	95
240	100

4.5.4.3 γ-Al_2O_3 washcoated monolith (200 cpi) impregnated with Pt

Results in Table 4.6 show that a complete oxidation of 1000 ppm toluene in air, space velocity = 40,000 h^{-1} at atmospheric pressure was achieved at 280°C.

Table 4.6: Activity measurement of γ-Al_2O_3 wascoated monolith impregnated with Pt

Temperature °C	Conversion Oxidation %
218	40
228	70
231	80
243	90
267	98
280	100

4.5.4.4 γ-Al_2O_3 washcoated monolith (200 cpi) impregnated with Pd

The results in Table 4.7 show that a complete oxidation of 1000 ppm toluene in air, space velocity = 40,000 h^{-1} at atmospheric pressure was achieved at 265°C. These results show that the γ-Al_2O_3 washcoated monolith impregnated with Pd is a better catalyst compared to the γ-Al_2O_3 washcoated monolith impregnated with Pt.

Table 4.7: Activity measurement of γ-Al_2O_3 wascoated monolith impregnated with Pd

Temperature °C	Conversion Oxidation %
215	45
223	81
241	93
254	98
259	99
265	100

4.5.4.5 TiO_2 (anatase)- washcoated monolith (200 cpi) impregnated with Pt

The results in Table 4.8 that a complete oxidation of 1000 ppm toluene in air, space velocity = 40,000 h^{-1} at atmospheric pressure was achieved at 268°C.

Table 4.8: Activity measurement of TiO_2 washcoated monolith impregnated with Pt

Temperature °C	**Conversion**
	Oxidation %
218	45
223	72
233	88
253	96
265	98
268	100

4.5.4.6 TiO_2 (anatase)- washcoated monolith (200 cpi) impregnated with Pd

The results in Table 4.9 that a complete oxidation of 1000 ppm toluene in air, space velocity = 40,000 h^{-1} at atmospheric pressure was achieved at 278°C. These results show that the TiO_2 washcoated monolith impregnated with Pt is a better catalyst compared to the TiO_2 washcoated monolith impregnated with Pd.

Table 4.9: Activity measurement of TiO_2 wascoated monolith impregnated with Pd

Temperature °C	**Conversion**
	Oxidation %
215	42
225	70
235	85
255	95
270	98
278	100

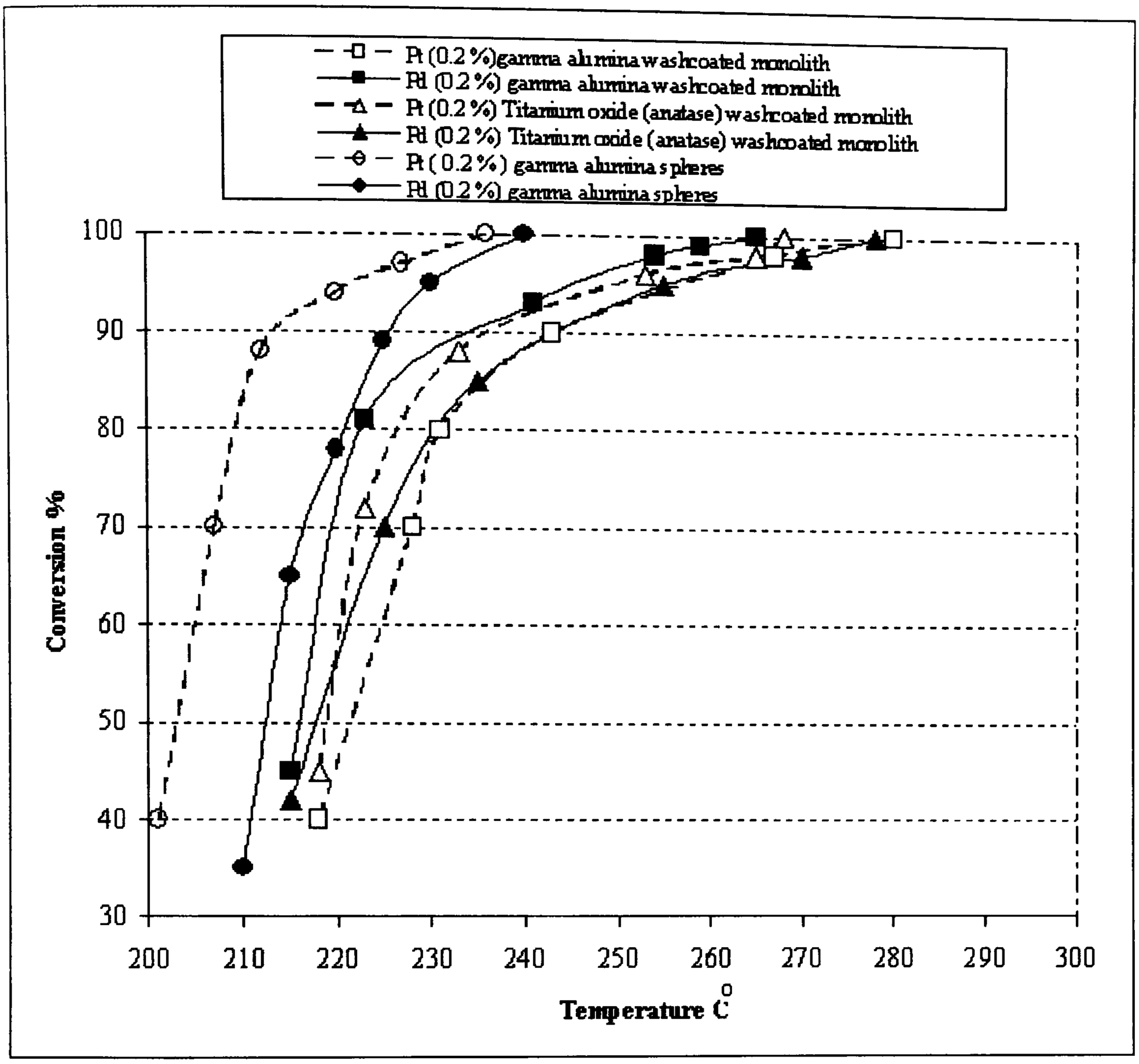

Figure 4.2: Comparison of the oxidation of 1000 ppm toluene in air using different catalysts.

4.6 CONCLUSION

The work described in this chapter has been focussed on the development of a method to prepare an improved platinum group metal catalyst. The investigation has provided a method of preparing platinum group metal catalysts by suitable carriers at room temperature.

The method used in the investigation enables the amount of active catalyst on the carrier to be controlled, as this is proportionate to the concentration of metal in the solution. The calcined catalyst on its support can be used as a VOC catalyst to oxidise toluene and other related waste hydrocarbons in the purification of waste gases.

During the preparation stage, the following parameters were studied to find out the optimum conditions:

- Effect of impregnation period on the catalyst metal loading
- Effect of solution temperature on the catalyst metal loading
- Effect of the volume of solution relative to fixed volume of carrier
- Effect of types and shapes of different carrier material

In the present research work, unlike the process disclosed in US Patent 4833114 [49], impregnation is achieved at room temperature or with slight heating e.g. 23 to 50°C and there is no need to carry out the prolonged aging process at temperatures above 60°C. Calcination is carried out in a conventional muffle furnace at elevated temperatures. Preferably, the calcination involves two stages with the first stage being a drying stage e.g. at above 100°C and the second stage taking place at a higher temperature e.g. above 300°C.

By using the surface impregnation technique of the present investigation it is possible to make very active catalysts with controlled metal loading on a suitable carrier or support such as a ceramic, zeolite, titanium dioxide, porous carbon etc. The preferred catalyst support is, however, γ-Al_2O_3 which can be in the form of spheres or washcoated monoliths as in conventional catalyst supports and carriers. All the catalysts, prepared in this work, were successfully used for the complete oxidation of toluene as an indicator of VOCs. The best results were achieved in the case γ-Al_2O_3 sphere impregnated with Pt where the complete oxidation of toluene was achieved at 236°C. This catalyst has the potential to be installed in the process-vent of chemical industries to control the emissions of toluene and other VOCs during the production of pesticide active ingredients (PAIs).

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CHAPTER 5

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CHAPTER 5

ROOM TEMPERATURE IONIC LIQUIDS AS GREEN SOLVENTS

This chapter describes the synthesis and characterisation of some selected room temperature ionic liquids (RTILs) and their potential use in the recovery of metals from industrial wastes and low grade primary sources.

5.1 ROOM TEMPERATURE IONIC LIQUIDS

5.1.1 Introduction

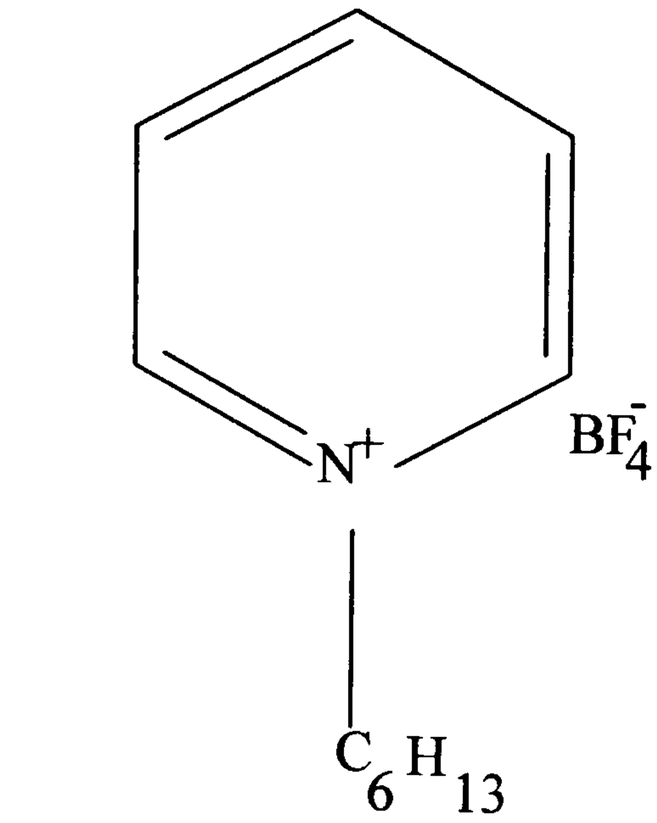
The world of chemistry is being transformed by the discovery of RTILs. In recent years, ionic liquids have emerged as "green" solvents. They are environmentally benign and have no measurable vapour pressure. These liquids are being studied for their use in chemical synthesis (particularly in catalyst reactions), separation technology, solar cells and recovery of metals and as electrolytes in batteries. The present research focuses on the development of different types of RTILs and their evaluation as alternative solvents for the extraction of metals [1]. RTILs are composed of a cation and an anion, whose forces of attraction are not sufficiently strong to hold them together as a solid at ambient temperature.

Normally ionic compounds are solids held together by strong electrostatic forces between anions and cations. These salts generally have a high melting point, (for example 801˚C for sodium chloride and 614˚C for lithium chloride), which greatly limits their use as molten solvents in most applications [2]. Ionic liquids are, however, as their name implies, salts that are liquid at low temperature [3]. The adopted upper temperature limit for the classification "ionic liquid" is 100°C, though some solidify to glasses on cooling. Higher melting ion systems are typically referred to as molten salts [4]. RTILs usually contain large nitrogen-based organic cations and inorganic anions. This composition allows them to dissolve both inorganic and organic compounds and serve as potential solvents for industrially important reactions.

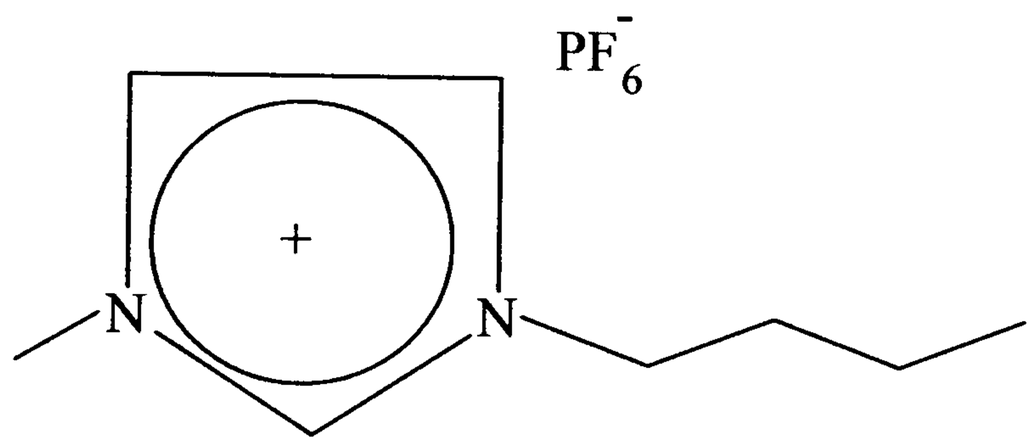
In the late 1940s Frank Hurley and Tom Weir [5], working at the Rice Institute in Texas, discovered that they could make some salts liquid at close to room temperature.

They mixed and gently warmed powdered alkylpyridinium chloride and aluminium chloride, and found that the two powders reacted together quickly and formed a clear, colourless liquid - an ionic liquid. Hurley and Weir's ionic liquid remained a chemical curiosity for decades until now, when the chemical industry is under pressure to find cleaner alternatives to the volatile, toxic and flammable organic solvents that are currently used in many processes. Later research has suggested that ionic liquids might have useful properties, such as being able to dissolve almost anything including coal, plastics, metals and even rock minerals. Other properties such as the fact that ionic liquids do not evaporate, do not burn and that they are fairly non-toxic and can be easily recycled, make them attractive as potential solvents. Another important aspect of this new chemistry is that reactions in ionic liquids are often carried out at lower temperatures than their current industrial counterparts using organic solvents. Lower temperatures mean less energy, which reduces costs and makes the processes more environmentally friendly. This applies to, for example, Diels-Alder reactions [6-22].

An ionic liquid generally consists of a large organic cation and a smaller inorganic anion. Examples of the most common ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate and N-hexylpyridinium tetrafluoroborate, are shown in Figure 5.1. The asymmetry of the large cations reduces the lattice energy of the crystalline structure and results in a low melting point salt. These simple liquid salts (single anion and cation) can be mixed with other salts (including inorganic salts) to form multi-component ionic liquids. There are estimated to be hundreds of thousands of simple ion combinations that could result in ionic liquids, and a near endless (10^{18}) number of potential ionic liquid mixtures. This implies that it should be possible to design an ionic liquid with the desired properties to suit any particular application by selecting anions, cations and mixture concentrations. Ionic liquids can be adjusted or tuned to provide a specific melting point, viscosity, density, hydrophobicity, miscibility, etc. for specific chemical systems.



N-hexylpyridinium tetrafluoroborate



1-butyl-3-methylimidazolium hexafluorophosphate

Figure 5.1: Common ionic liquids

The components of ionic liquids (ions) are constrained by high coulombic forces and thus exert practically no vapour pressure above the liquid surface. Importantly, the near-zero vapour pressure property of ionic liquids means they do not emit the types of potentially hazardous volatile organic compounds (VOCs) associated with many industrial solvents during their transportation, handling and use. It should be noted, however, that the decomposition products of ionic liquids at high temperatures could have measurable vapour pressures. In addition, ionic liquids are non-explosive, non-oxidizing and non-flammable. These characteristics provide significant environmental, safety and health benefits compared to existing solvents [6-20].

Each ionic liquid, however, is likely to be classified as a new chemical and may require significant environment, safety and health studies prior to widespread use. Structural similarities between certain ionic liquids, herbicides and plant growth regulators have been noted. These similarities raise potential safety and environmental concerns and give ionic liquids a potentially unknown risk factor. Development of rapid and efficient techniques for the analysis of ionic liquids is required to create ionic liquid property databases and quality control checks in industrial processes. Analysis of ionic liquids must be simple and reliable if they are to be used as an alternative to conventional organic solvents. Combinatorial chemistry methodology will be needed to conduct high-throughput synthesis and fast screening of ionic liquids. The data will be needed to determine the collective roles played by anions and cations for the formation of room-temperature ionic liquids, to study what structural factors make such polar and charged molecules hydrophobic, and to explore stability, reactivity and solvent properties. Investigation of these issues will lead to a better understanding of the ionic liquid phenomenon and, ultimately, to new classes of ionic liquids [6-20]. Some ionic liquids have particularly useful solubility properties, making them good solvents for transition metal compounds in, for example, spent catalysts. Such ionic liquid systems enable easy catalyst recycling and product isolation [6-16].

5.1.2 Properties

Ionic liquids are becoming widely recognised as solvents for 'green' synthesis because they show significant enhancements in reaction rate, yield and selectivity [17-19]. They do not occur naturally, and therefore have to be manufactured. Variations in cations and anions can produce literally millions of ionic liquids, including chiral, fluorinated, and antibacterial RTILs [4]. The large number of possibilities allows for fine-tuning ionic liquid properties for specific applications [7,20].

The physical properties of RTILs such as viscosity, density, water solubility etc are determined by the anion. Cations are typically big, bulky and asymmetric species accounting for the low melting points. The cations contribute more to the overall characteristics of the RTILs and determine their air and water stability. Melting points can be easily changed by structural variation of one of the ions or combining different ions. The low melting points are a result of the chemical composition of RTILs, which contain larger asymmetric organic cations compared to their inorganic counterparts of

molten salts. The asymmetry lowers the lattice energy, and hence the melting point, of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point [3].

The structure and physical properties of simple ionic liquids has been the subject of qualitative [22] and quantitative reviews [23]. Ambient temperature ionic liquids [24] are the subject of this thesis. Although it has been established for some time that these ionic liquids are suitable for preparative chemistry, it is only recently that there has been a large amount of literature available in this area, including reviews that demonstrate their use as solvents for synthesis and catalysis [25,26].

The physical properties of the ambient-temperature ionic liquids lead them to be highly advantageous over conventional solvents [1,19]. These advantages include the following:

- Ionic liquids are non-volatile therefore may be used in high vacuum systems.
- Many inorganic and organic reagents are soluble in these ionic liquids, which mean that it is possible to bring unusual combinations of compounds into the same phase.
- The ionic liquids are often composed of poorly coordinating ions; hence they have the ability to be highly polar non-coordinating solvents.
- They are immiscible with conventional inorganic as well as organic solvents; therefore ionic liquids can be used effectively in two-phase systems.

Some room temperature ionic liquids have advantages over high-temperature ionic liquids, as they are useful solvents for thermally unstable materials, as the necessity for high temperature is removed. This feature also alleviates the requirement for special high temperature apparatus [27]. At ambient temperatures, however, some ionic liquids are very viscous [28].

5.1.3 Applications

The applications of RTILs are numerous. RTILs have been used for various industrial purposes (Figure 5.2) [7-40]. In recovery processes, ionic liquids may enhance the activity and selectivity for transition metals and a method of dissolution of spent nuclear fuels in ionic liquids has been developed by the British Nuclear Fuels Laboratory in Sellafield, England.

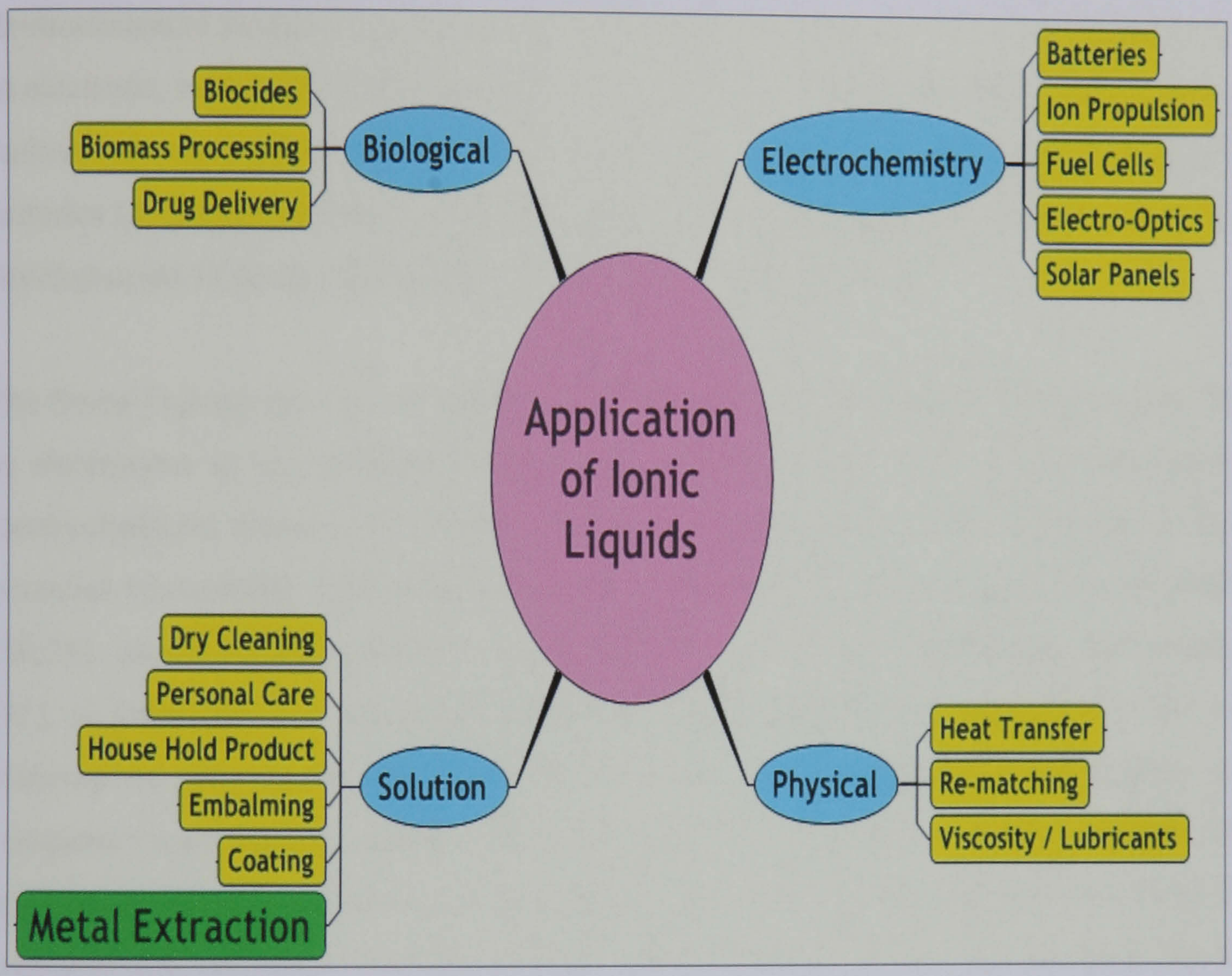


Figure 5.2: Industrial applications of RTILs

Research workers at the Institute of Chemistry at the Tallinn Technical University, Estonia, are looking into RTILs for their possible use in oil shale treatment. Oil shale is a sedimentary rock that contains organic matter known as kerogen, which is burned in power stations to generate electricity. Because of their unique solvent properties and large thermal stability, RTILs are good candidates for the development of efficient processes for the liquefaction, gasification or modification of oil shale kerogen [21]. Another group at the University of South Alabama, USA, is considering into the use of ionic liquids as sequestering agents to remove hydrogen sulfide and carbon dioxide from contaminated natural gas supplies, known as "sour gas". RTILs are also known to be good solvents for Friedel-Crafts alkylations, hydrogenations, olefin isomerisations,

Diels-Alder reactions, alkylations of heteroatoms and isomerisation of fatty acids and ethers [5-22].

Another good characteristic of ionic liquids is that they are excellent electrolytes that can be used in the battery industry. RTILs are inherently conductive and they can mitigate self-discharge. Moreover, the electrochemical window of RTILs, that is, the electrochemical potential range over which the electrolyte is not reduced or oxidized at an electrode, is usually much greater than for aqueous electrolytes. Batteries that contain molten salt electrolytes require high operating temperatures and are called thermal batteries [21]. Consequently, ionic liquids with low melting points promise to spur new developments of much higher performance in the battery industry.

The Swiss Federal Institute of Technology, Lausanne, has investigated the use of RTILs as electrolytes in dye-sensitised solar cells, electrochemical devices and other photo-electrochemical devices [21,33-36]. RTILs have also received attention due to their potential commercial applications in electrochemistry [37], heavy metal ion extraction [38,39], phase transfer catalysis and polymerization [40], solubilisation of materials [41], as substitutes for common VOCs [42] and enzymatic reactions [43,44]. The vast majority of these ionic salts are stable solvents for a wide range of organic and inorganic materials and provide polar alternatives to biphasic systems [45,46]. The application of ionic liquids to extract heavy metals from industrial wastes or end-of-life products has not been studied in detail. These novel solvents can be used for the selective extraction of heavy metal from a wide variety of environmental samples including low grade primary sources.

5.1.4 Why Consider RTILs?

Room temperature ionic liquids are regarded as green solvents in green chemistry, which is the use of chemistry for pollution prevention. More specifically, green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations. The twelve Principles of Green Chemistry, developed by Anastas and Warner in "Green Chemistry: Theory and Practice", provide a road map for chemists to implement green chemistry.

- It is better to prevent waste than to treat or clean up waste after it is formed.
- Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- Chemical products should be designed to preserve efficacy of function while reducing toxicity.
- The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and innocuous when used.
- Energy requirements should be recognised for their environmental and economic impact and should be minimised. Synthetic methods should be conducted at ambient temperature and pressure.
- A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.
- Unnecessary derivatisation (blocking group, protection/de-protection and temporary modification of physical/chemical processes) should be avoided whenever possible.
- Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
- Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
- Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.

In the light of this given background, the research work described in this thesis investigates the potential use of RTILs for leaching heavy metals from low-grade ores and solid industrial waste. The following statements were considered in the selection of the reagents used [6,7,18,40,41].

- RTILs are environmentally friendly alternatives to organic solvents for liquid/liquid extractions, catalysis, separations [3,4] and electrochemistry [15,16].
- RTILs reduce or eliminate the related costs, disposal requirements, and hazards associated with VOCs.
- RTILs have high thermal stability, high ionic conductivity, excellent solvating properties for a wide range of organic and polymeric materials and are non-volatile and non-flammable.
- RTILs are highly solvating.
- RTILs dissolve many different inorganic and organic materials.
- RTILs are highly polar
- RTILs consist of loosely co-ordinating bulky ions having no actual vapour pressure i.e. they do not evaporate.
- RTILs have a liquid window of up to 300°C, enabling wide kinetic control.
- RTILs are mostly thermally stable at >200°C.
- RTILs are immiscible with many organic solvents.
- RTILs are non-aqueous polar alternatives for phase transfer processes.
- RTILs give significant enhancements in reaction rate, yield and selectivity.
- RTILs are relatively inexpensive and easy to handle and store

The main aim of the work described in this chapter was to investigate whether RTILs can selectively dissolve metal from mixed industrial waste samples. The specific objectives were: 1) to synthesise some selective RTILs, 2) to characterise these RTILs using different analytical techniques and 3) to investigate the solubility of heavy metal, metal oxides and sulfides in these RTILs.

5.2 EXPERIMENTAL AND METHODLOGY

This section contains details of materials and methods adopted for synthesis, characterisation and application of RTILs used in this work.

5.2.1 Solvent Free Synthesis of RTILs

A series of eight RTILs was prepared, by a microwave-assisted (MW-assisted) method developed in this work. The series was constructed by increasing and decreasing the chain length of the cations and changing the position of the functional groups.

a. 1-(2-cyanoethyl)-3-methylimidazolium bromide
b. 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride
c. 1-methyl-3-propylimidazolium bromide
d. 1-cyanomethyl-3-methylimidazolium bromide
e. 1-(3-cyanopropyl)-3-methylimidazolium bromide
f. 1-(1-cyanoethyl)-3-methylimidazolium bromide
g. 1-cyano-1,1-bis(1-methylimidazolium)methane dibromide
h. 1-cyano-1,2-bis(1-methylimidazolium)ethane dibromide

5.2.1.1 Procedure and Chemicals

Reagents

Reagents used in this work were: 1-methylimidazole, 3-bromopropionitrile, 2-(2-chloroethoxyethanol), bromopropane, 1-bromoacetonitrile, 4-bromobutyronitrile, 2-bromopropionitrile, 2,2-dibromoacetonitrile, 2,3-dibromopropionitrile, acetonitrile, ether, isopropyl ether and methanol.

Procedure

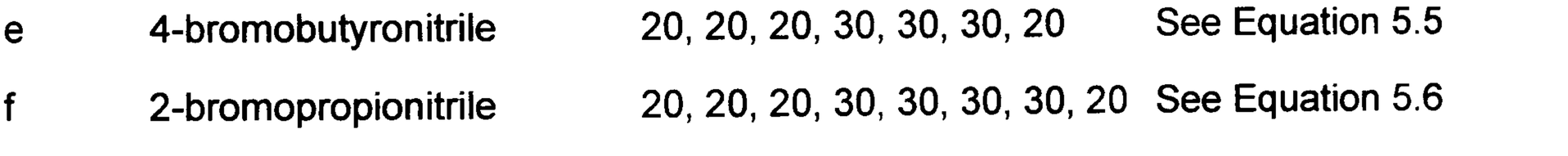
The RTILs were prepared using an organic imidazolium cation and different alkyl substituants e.g. 3-bromopropionitrile and 2-(2-chloroethoxyethanol). The physical and chemical properties of ionic liquids selected for this present work are dependent on the length of the alkyl groups and the insertion of metal-complexing groups. A Panasonic Microwave Oven (Model No. NW-T552WF) set on 270W (defrost mode) was used for the preparation of the RTILs because this is an efficient solventless protocol which exploits the microwave heating system to transfer energy directly to the reactants that results in the formation of pure products [47].

1-methylimidazolole (5g) and an anionic precursor (Table 5.1) in the mole ratio 1:1.25 were used in the preparation of the RTILs. Both components were mixed in a 150 ml round bottomed flask and heated in the microwave oven according to the sequential regime given in Table 5.1. The reaction was followed and was deemed to be complete when a golden viscous liquid had been formed. The bulk temperature recorded was in the range of 70 to 100°C. The ionic liquids were cooled to room temperature. The products were washed three times with ether to remove un-reacted starting materials then placed under vacuum for 10-20 minutes. The freshly prepared product was stored in a stoppered glass sample tube at room temperature.

Table 5.1: Preparation conditions for the preparation of the RTILs

RTIL	Anionic Precursor	Heating Regime (seconds)	Equation
a	3-bromopropionitrile	20, 20, 20, 30, 30, 20	See Equation 5.1
b	2-(2-chloroethoxyethanol)	20, 20, 30, 20	See Equation 5.2
c	Bromopropane	20, 20, 20, 30, 20	See Equation 5.3
d	1-bromoacetonitrile	Product formed without heating	See Equation 5.4
e	4-bromobutyronitrile	20, 20, 20, 30, 30, 30, 20	See Equation 5.5
f	2-bromopropionitrile	20, 20, 20, 30, 30, 30, 30, 20	See Equation 5.6
g	2,2-dibromoacetonitrile	20, 20	See Equation 5.7
h	2,3-dibromoacetonitrile	Product formed without heating	See Equation 5.8

The synthesis reactions leading to the formation of RTILs are summarised in equations 5.1-5.8.



1-Methylimidazole 3-bromopropionitrile 1-(2-cyanoethyl)-3-methylimidazoliumbromid

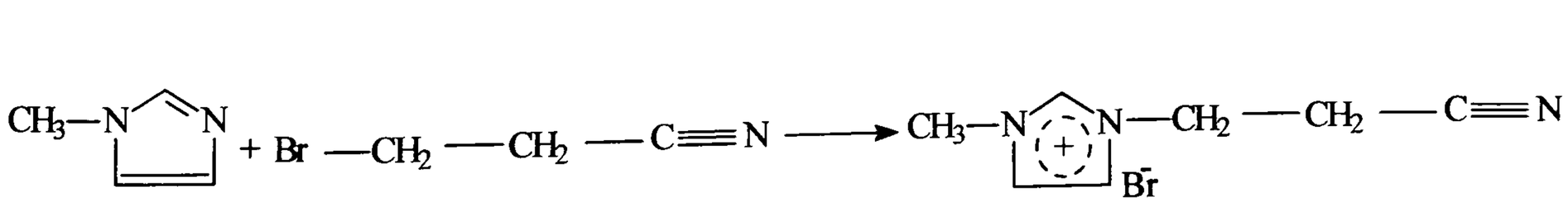
Equation 5.1: Synthesis of RTIL (a), 1-(2-cyanoethyl)-3-methylimidazolium bromide

1-methylimidazolole (5g) and an anionic precursor (Table 5.1) in the mole ratio 1:1.25 were used in the preparation of the RTILs. Both components were mixed in a 150 ml round bottomed flask and heated in the microwave oven according to the sequential regime given in Table 5.1. The reaction was followed and was deemed to be complete when a golden viscous liquid had been formed. The bulk temperature recorded was in the range of 70 to 100°C. The ionic liquids were cooled to room temperature. The products were washed three times with ether to remove un-reacted starting materials then placed under vacuum for 10-20 minutes. The freshly prepared product was stored in a stoppered glass sample tube at room temperature.

Table 5.1: Preparation conditions for the preparation of the RTILs

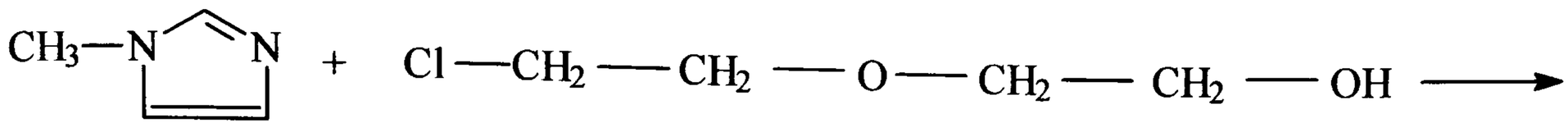
RTIL	Anionic Precursor	Heating Regime (seconds)	Equation
a	3-bromopropionitrile	20, 20, 20, 30, 30, 20	See Equation 5.1
b	2-(2-chloroethoxyethanol)	20, 20, 30, 20	See Equation 5.2
c	Bromopropane	20, 20, 20, 30, 20	See Equation 5.3
d	1-bromoacetonitrile	Product formed without heating	See Equation 5.4
e	4-bromobutyronitrile	20, 20, 20, 30, 30, 30, 20	See Equation 5.5
f	2-bromopropionitrile	20, 20, 20, 30, 30, 30, 30, 20	See Equation 5.6
g	2,2-dibromoacetonitrile	20, 20	See Equation 5.7
h	2,3-dibromoacetonitrile	Product formed without heating	See Equation 5.8

The synthesis reactions leading to the formation of RTILs are summarised in equations 5.1-5.8.



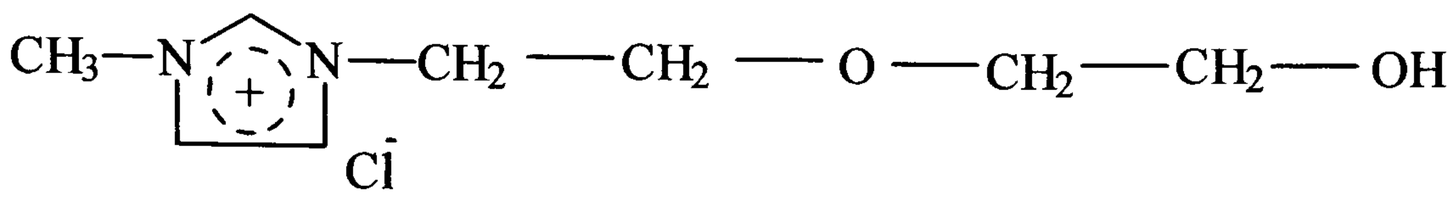
1-Methylimidazole 3-bromopropionitrile 1-(2-cyanoethyl)-3-methylimidazoliumbromid

Equation 5.1: Synthesis of RTIL (a), 1-(2-cyanoethyl)-3-methylimidazolium bromide



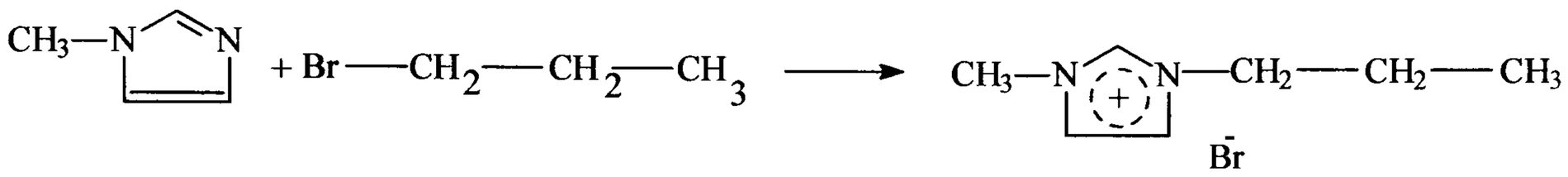
1-Methylimidazole

2-(2-choloroethoxyethanol)



1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride

Equation 5.2: Synthesis of RTIL (b), 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride

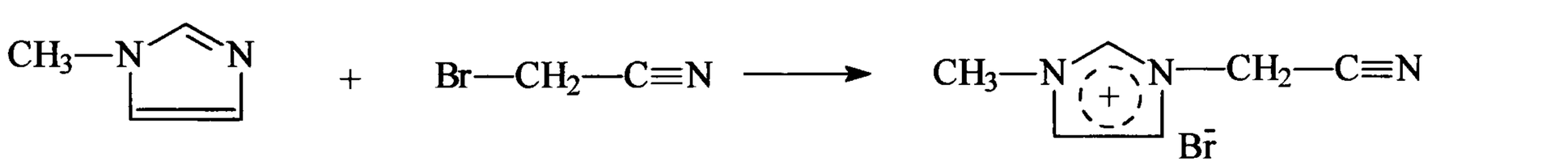


1-Methylimidazole

Bromopropane

1-methyl-3-propylimidazoliumbromide

Equation 5.3: Synthesis of RTIL (c), 1-methyl-3-propylimidazolium bromide

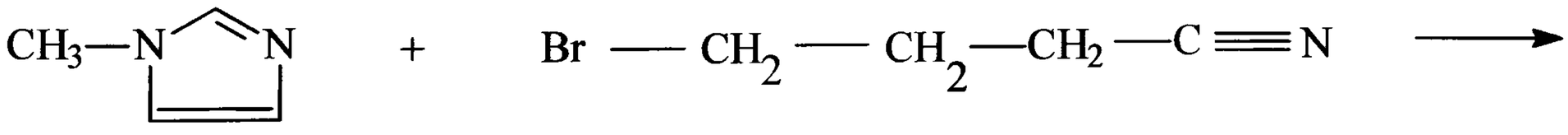


1-Methylimidazole

Bromoacetonitrile

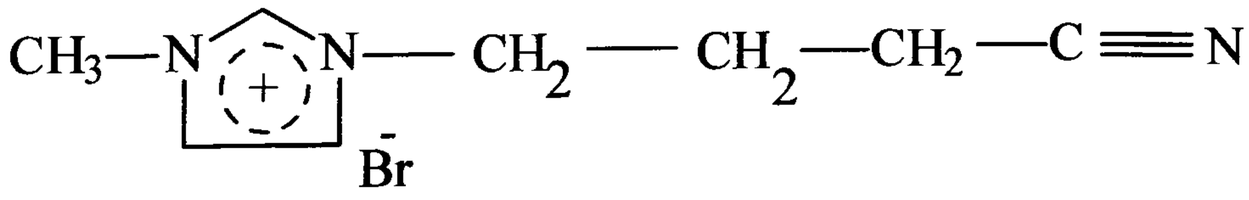
1-Cyanomethyl-3-methylimidazolium brom

Equation 5.4: Synthesis of RTIL (d), 1-cyanomethyl-3-methylimidazolium bromide



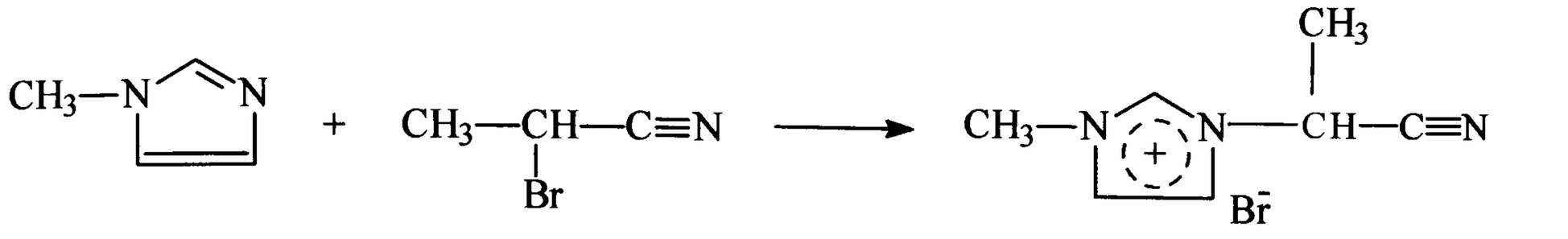
1-Methylimidazole

4-bromobutyronitrile



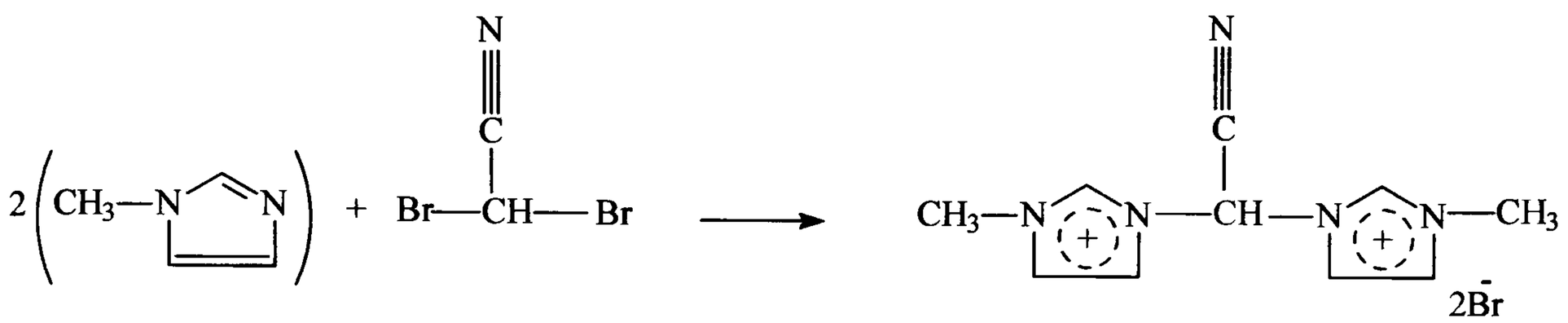
1-(3-cyanopropyl)-3-methylimidazoliumbromide

Equation 5.5: Synthesis of RTIL (e), 1-(3-cyanopropyl)-3-methylimidazolium bromide



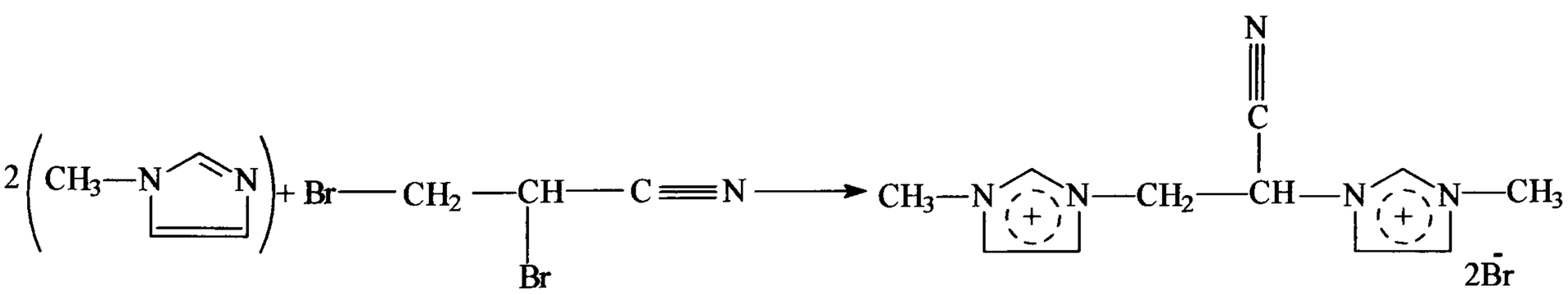
1-Methylimidazole 2,bromopropionitrile 1-(1-Cyanoethyl)-3-methylimidazolium brom

Equation 5.6: Synthesis of RTIL (f), 1-(1-cyanoethyl)-3-methylimidazolium bromide



1-Methylimidazole 2,2dibromoacetonitrile 1-Cyano-1,1-bis(1-methylimidazolium)methanedibromide

Equation 5.7: Synthesis of RTIL (g), 1-cyano-1,1-bis(1-methylimidazolium)methane dibromide.



1-Methylimidazole 2,3dibromopropionitrile 1-Cyano-1,2-bis(1-methylimidazolium)ethanedibromide

Equation 5.8: Synthesis of RTIL (h), 1-cyano-1,2-bis(1-methylimidazolium)ethane dibromide

5.2.2 Characterisation of RTILs

Before characterisation, the un-reacted starting materials were removed from the reaction flask using a washing solvent that dissolves un-reacted materials but not the ionic liquids. The type of solvent varies depending on the starting materials and hydrophobicity of the RTIL. All of the ionic liquids were washed three times with eather. The washed products were dried under vacuum before characterisation.

Two out of the eight synthesised RTILs were solids, 1-cyanomethyl-3-methyl-imidazolium bromide and 1-cyano-1,1-bis(1-methylimidazolium) methane di-bromide, and therefore could not be classed as room temperature ionic liquids. The ionic liquid (c), 1-methyl-3-propylimidazolium bromide, was insoluble in water and a homogeneous mixture was not obtained which is necessary for HPLC characterisation. The remaining five ionic liquids, 1-(2-cyanoethyl)-3-methylimidazolium bromide, 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride, 1-cyanomethyl-3-methylimidazolium bromide, 1-(3-cyanopropyl)-3-methylimidazolium bromide and 1-(1-cyanoethyl)-3-methylimidazolium bromide were characterised by high performance liquid chromatography (HPLC).

Two out of the five synthesised RTILs, 1-(2-cyanoethyl)-3-methylimidazolium bromide, 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride, were also characterised using the analytical techniques described in Chapter 2. These techniques are UV/visible spectroscopy (UV/vis), infrared spectroscopy (IR) and mass spectrometery (MS). The selection of these two ionic liquids were based on their structure and preliminary metal solubility data.

5.2.2.1 Procedures adopted for characterisation

The following procedures were adopted for the characterisation of the RTILs and the results used to show the differences that occur when transition metal ions are dissolved in these RTILs:

HPLC – 0.03 g liquid was diluted with 8 ml deionised water in a 10 ml glass sample tube. A homogeneous mixture was formed by shaking the fluid and this was used to obtain a HPLC trace. A mixture of 95 % acetonitrile and 5 % deionised water was used as eluent for all the RTILs except 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium

chloride where two eluents were used - acetonitrile and water in the ratio 85%:15 % and methanol and water in the ratio 85%:15 %.

The retention time for each of the starting materials and the ionic liquids is presented, on the x- axis, as distance (cm) from the starting mark to the centre of each peak.

UV/vis spectroscopy – UV/vis spectra of the two ionic liquids, 1-(2-cyanoethyl)-3-methylimidazolium bromide and 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride, and their starting materials were carried out by dissolving one drop of each material in a separate glass sample tube containing 10 ml deionised water. A solution was obtained by shaking the mixture which was added to a UV cell and the UV/vis spectrum obtained.

IR spectroscopy – IR spectra of the ionic liquid, 1-(2-cyanoethyl)-3-methylimidazolium bromide, and its starting materials were obtained by placing a small drop of each of the material on a clean sodium chloride plate and secure these plates in a sample holder.

Mass spectroscopy – Accurate mass measurements of 1-(2-cyanoethyl)-3-methylimidazolium bromide and 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride were carried out at the EPSRC National Centre, Swansea.

5.2.3 Application of RTILs

The solubility of heavy metals and their compounds in the synthesized RTILs and their recoveries from the solution were investigated. The experiments were carried out for single and for mixed metal systems. The resultant solutions were analysed by atomic absorption spectrophotometer and results are given in Tables 5.3-5.7. The solubility data obtained was compared with the solubility achieved with standard leaching solvents and the results are compared in Tables 5.8-5.11 and are summarised in Figures 5.15- 5.18.

5.2.3.1 Solubility of metals and metal oxides in ionic liquids

0.2 g and 0.5 g of pure metals, oxides and sulfides of Cu, Ni, Co, Zn and Cr (Laboratory reagent supplied by Fisher Scientific, United Kingdom) were mixed with 2 g and 5 g of each RTIL without water in a 200 ml of pyrex beaker. All the samples were then stirred for 10 minutes at 40°C. All of the RTILs used in this work are viscous at room temperature and 40°C is the minimum temperature at which the mixture could easily be stirred with a magnetic follower on a hot plate. During the dissolution period the colour of each mixture changed. 10 ml of deionised water were then added and the mixture stirred for a further three minutes at room temperature, the colour changing again. The mixtures were than filtered using whatman filter paper number 1, 18.5 cm diameter, diluted as required and analysed by AAS.

5.2.3.2 Solubility of metals and metal oxides in aqueous solution of ionic liquids

0.2 g and 0.5 g of pure metals, oxides and sulfides of Cu, Ni, Co, Zn and Cr (Laboratory reagent supplied by Fisher Scientific, United Kingdom) were mixed with 2 g and 5 g of each RTIL in the presence of 10 ml of deionised water in a 200 ml pyrex beaker. All samples were stirred for 4 hours at room temperature. After the stirring period, the mixtures were filtered using whatman filter paper number 1, 18.5 cm diameter. Thereafter, the filtrates were diluted as required and analysed by AAS.

5.2.3.3 Solubility of copper, oxide and sulfide in traditional solvents

In separate experiments for comparison purposes, 0.2g of copper metal powder, oxide and sulfide (Laboratory reagent supplied by Fisher Scientific, United Kingdom) were mixed with 20 ml of either 3 M hydrochloric, nitric and sulfuric acids or *aqua regia*, (laboratory reagent, grade Fisher Scientific) in flanged flasks. All samples were then stirred for 4 hours at room temperature and at 40°C and the mixture filtered and the filtrates, after suitable dilution with deionised water, were analysed by AAS. The selection of leaching temperature and leaching time was based on some preliminary experiments which showed maximum solubilities of copper metal powder, oxide and sulfide under these conditions.

5.2.3.4 Solubility of industrial waste sample containing copper and zinc

0.2 g and 0.5 g of the industrial waste sample (sample ID 1879) were mixed with 2 g and 5 g of each RTIL in a 200 ml of pyrex beaker. The solubility tests were carried out in the absence and presence of water using exactly the same methods as described in sections 5.2.3.1 and 5.2.3.2 respectively.

5.2.4 Characterisation of metal-RTIL complexes

The solubility of different metals, oxides and sulfides in various ionic liquids show that 1-(2-cyanoethyl)-3-methylimidazolium bromide can be used for the selective extraction of copper from industrial waste samples. 1-(2-cyanoethyl)-3-methylimidazolium bromide complexes with copper were characterised by their IR spectra of solidified products. These complexes were also characterised by comparing the UV/Vis spectra of pure ionic liquid and ionic liquid containing copper. X-ray diffraction of the solidified product of Cu-RTIL was also conducted to examine whether the product is crystalline or amorphous.

The following two methods were used to obtain the solidified products of 1-(2-cyanoethyl)-3-methylimidazolium bromide complexes with copper.

1. The dissolution of copper oxide in the RTIL produces a thick paste like material that was characterised by IR spectroscopy.
2. The dissolution of copper oxide in the aqueous solution of RTIL was carried out using the method as described in section 5.2.3.2. Dean and Stark method was used to remove water content in order to obtain a thick paste like material that was characterised by IR spectroscopy.

The Dean-Stark apparatus or Dean-Stark receiver is a piece of laboratory glassware normally used in synthetic chemistry to collect water (or occasionally other liquid) from a reactor. It is used in combination with a reflux condenser connected to a reactor for continuous removal of the water that is produced during a chemical reaction performed at reflux temperature. Two types of Dean-Stark traps exist – one for use with solvents with a density less than water and one for use with solvents with a density greater than water.

The Dean-Stark laboratory apparatus (Figure 5.3) typically consists of vertical cylindrical piece of glass (the trap), often with a volumetric graduation on its full length and a precision tap on the bottom very much like a burette. The top of the cylinder is a fit with the bottom of the reflux condenser. Protruding from the top the cylinder has a side-arm at less than right angle. At the end the side-arm makes a sharp turn so that the end of the side arm is vertical as well. This end connects with the reactor.

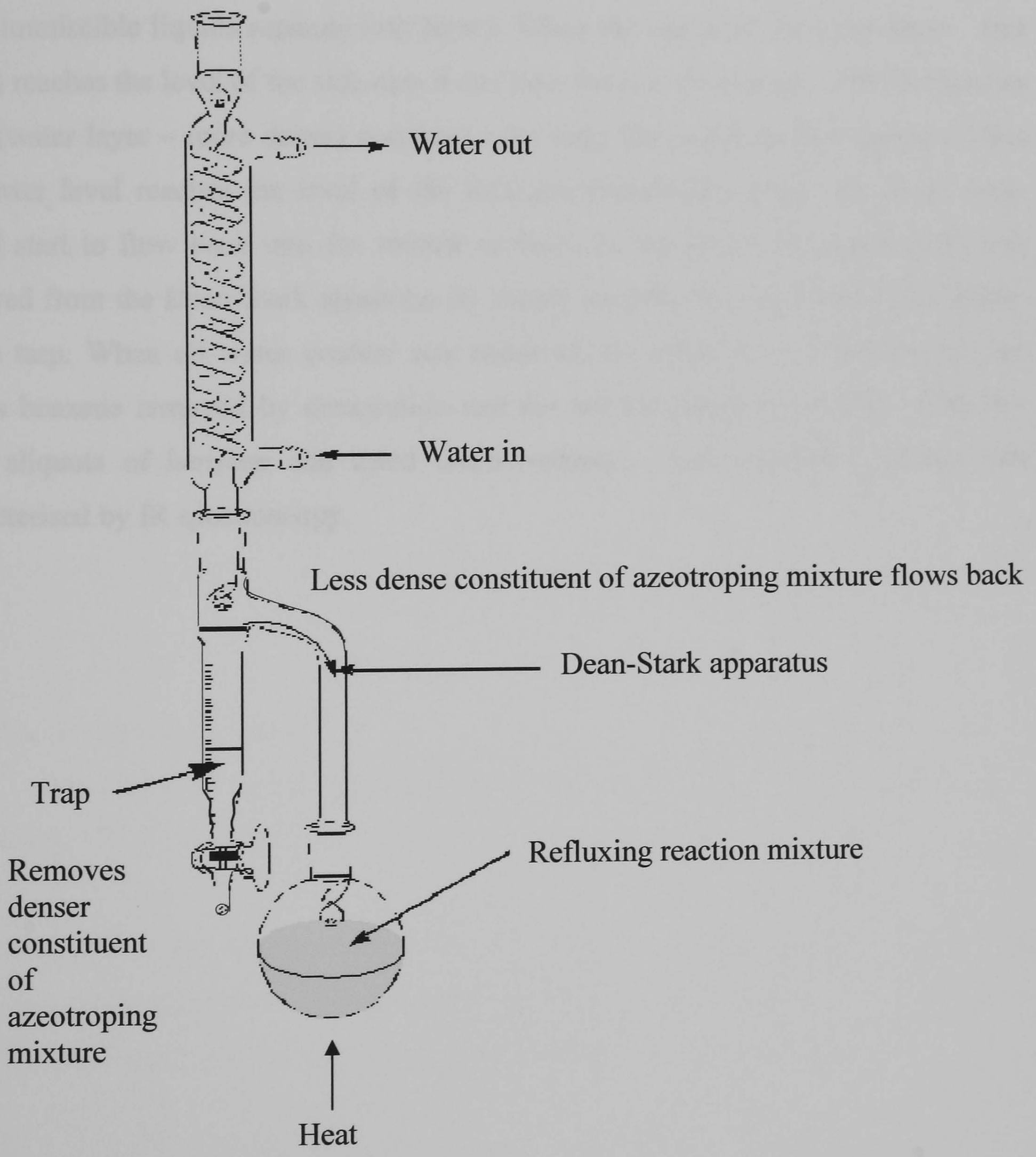


Figure 5.3: Dean – Stark apparatus

This piece of equipment is usually used in azeotropic distillations. A common example is the removal of water generated during a reaction in boiling benzene. An azeotropic mixture of benzene and water distil out of the reaction, but only the benzene (density = 0.8786 g/cm^3) returns. Water (density = 1 g/cm^3) collects in the trap and can be removed periodically.

A know volume (100 ml) of benzene was added into the reaction flask containing the aqueous solution of RTIL and copper. During the reaction, benzene and water vapours travel out of reaction flask up into the condenser, and then drip into the distilling trap. Here, immiscible liquids separate into layers. When the top layer (benzene layer - less dense) reaches the level of the side-arm it can flow back to the reactor, while the bottom layer (water layer – more dense) remains in the trap. The trap is at full capacity when the lower level reaches the level of the side-arm-beyond this point, the lower layer would start to flow back into the reactor as well. At this point, the lower layer was removed from the Dean-Stark apparatus by simply opening the tap fixed at the bottom of the tarp. When all water content was removed, the reaction was stopped and the excess benzene removed by decantation and the solid product was washed with two fresh aliquots of benzene and dried under vacuum. This solidified product was characterised by IR spectroscopy.

5.3 RESULTS AND DISCUSSION

5.3.1 Synthesis of RTILs

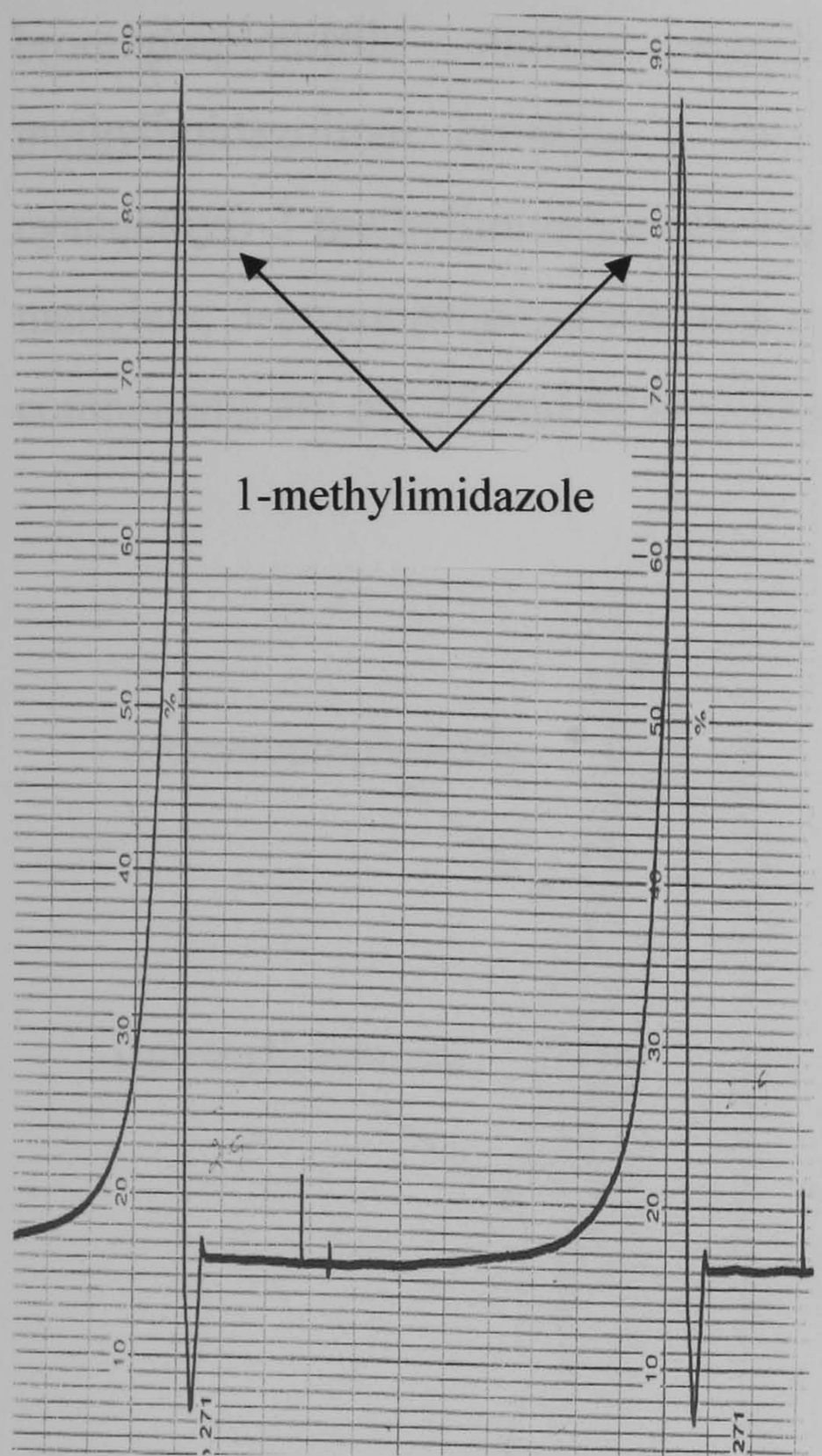
Preliminary experiments were carried out to prepare ionic liquids using a conventional synthesis method. Conventional synthesis of RTILs involved the use of a hot plate or liquids bath as heating source. The synthesis was carried out in a flask containing acetonitrile and the starting materials. A condenser was used to trap the vapours and condensed them back into solution. There were many problems associated with the conventional method, for example, longer reaction time (up to 72h) and the HPLC analysis showed that the products were not pure and contained some by-products.

In order to overcome these limitations, all of the ionic liquids used in this work were synthesised using a solvent-free microwave assisted method. This novel synthesis approach led to the formation of pure products because the starting materials were completely transformed into the final product without the formation of any by-products. In the microwave-assisted method the energy was transferred directly to the sample that resulted in a direct, rapid and uniform heating of the system without wasting the energy required to heat the heating bath. Therefore, the microwave assisted heating technique was considered as better, because it accelerated the reaction rate and improved the product purity under relatively mild conditions and lower energy consumption.

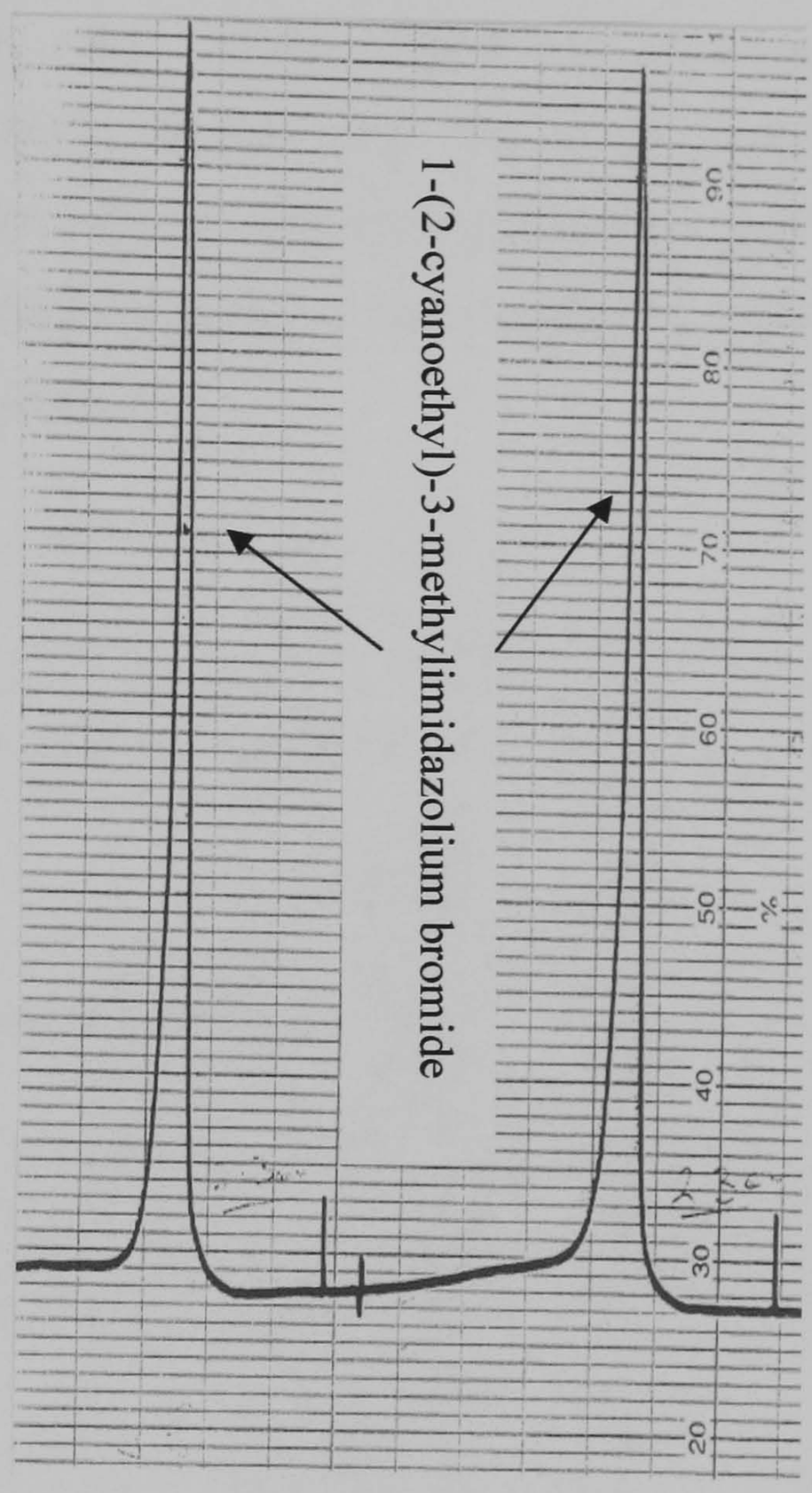
5.3.2 Characterisation of RTILs

HPLC - The traces and spectra of the characterisation procedures for each ionic liquid are illustrated in Figures 5.4-5.8.

Figure 5.4a shows the HPLC traces of 1-methylimidazole starting material and the ionic liquid 1-(2-cyanoethyl)-3-methylimidazolium bromide. The presence of a single peak confirms that the product is pure and free from the starting materials.



1-methylimidazole



1-(2-cyanoethyl)-3-methylimidazolium bromide

Retention times:

1-methylimidazole = 87 Sec. 1-(2-cyanoethyl)-3-methylimidazolium bromide = 69 Sec.

Conditions:

Eluent = acetonitrile (95%): water (5%)

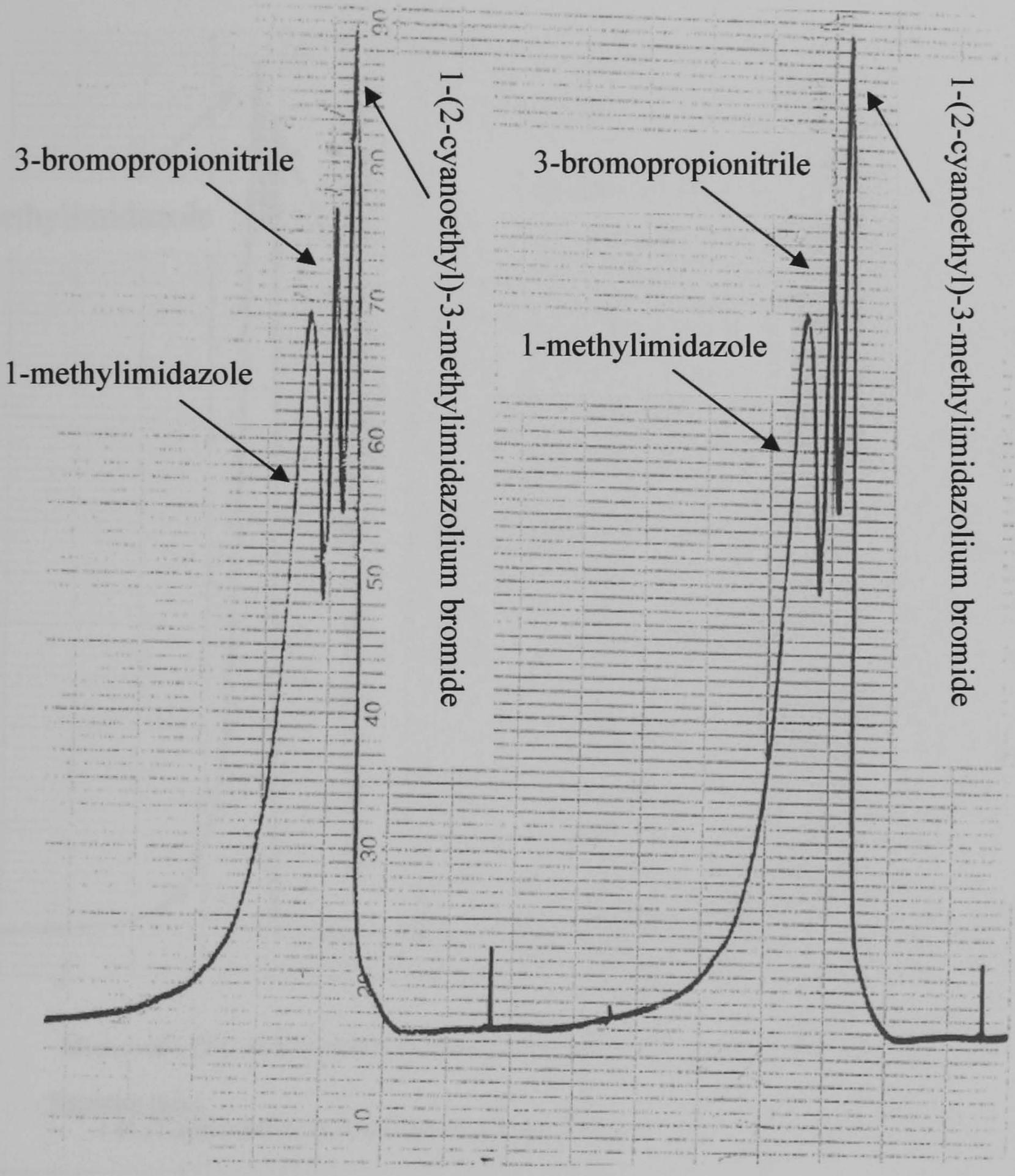
Absorbance = 0.1 Coarse absorbance = 7 Chart speed = 20mm/min Pressure = 5-6psi Flow rate = 1ml/min

Wavelength = 240nm Chart range = 50mv Detector = CECIL 1100 Series

Column = packed with Hichrome C18 packing material Diameter = 15cm Id= 4.5mm

Figure 5.4a: HPLC trace of 1-(2-cyanoethyl)-3-methylimidazolium bromide and 1-methylimidazole

Figure 5.4b shows the HPLC traces of a mixture of 1-methylimidazole, 3-bromopropionitrile starting materials and ionic liquid 1-(2-cyanoethyl)-3-methylimidazolium bromide. The results showed that the ionic liquid, 1-(2-cyanoethyl)-3-methylimidazolium bromide, eluted first followed by the two starting materials, 3-bromopropionitrile and 1-methylimidazole. The retention times for these components are 69, 78 and 87 second respectively.



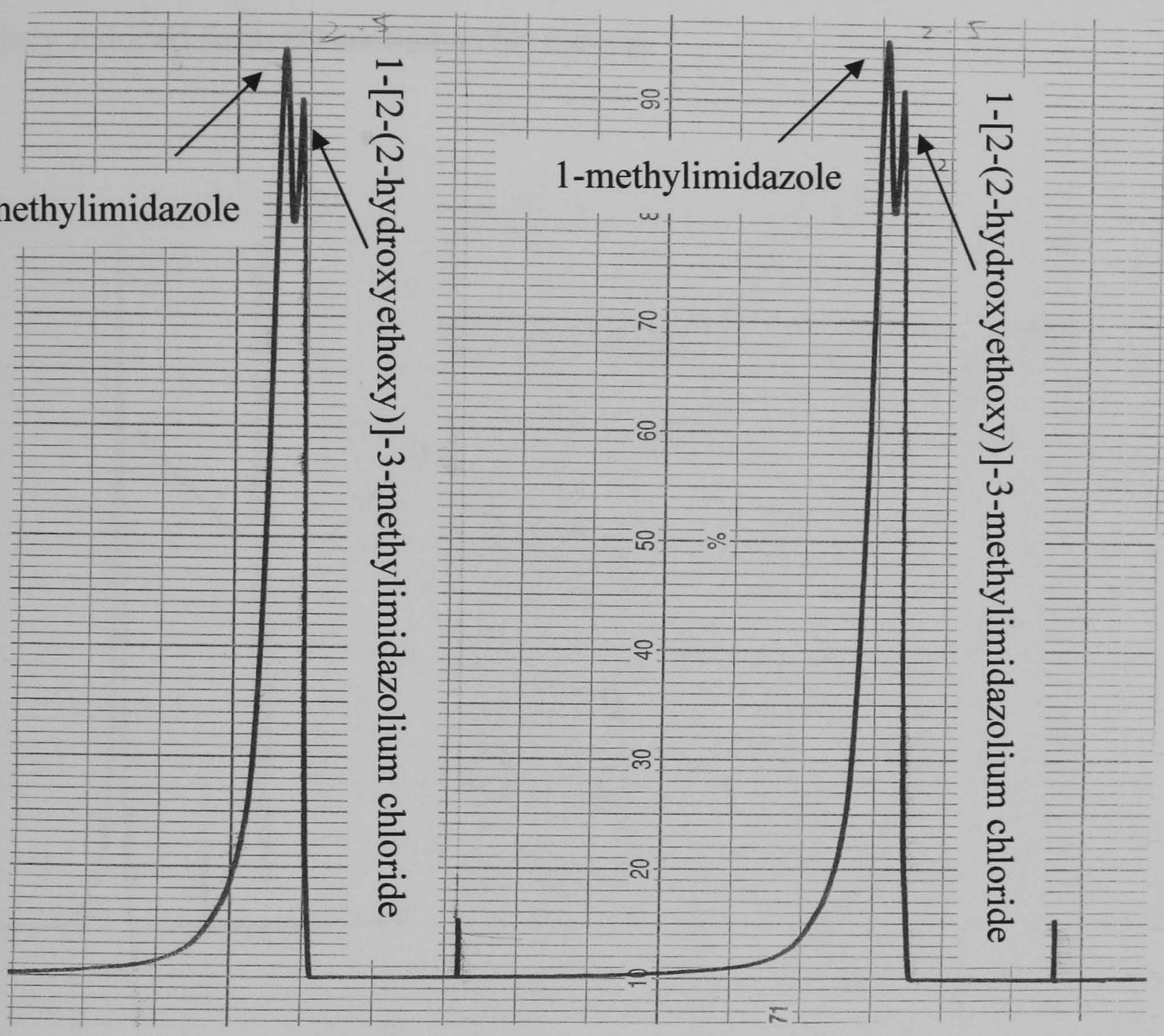
Mixture: 1-methylimidazole, 3-bromopropionitrile and 1-(2-cyanoethyl)-3-methylimidazolium bromide

Retention times: 87 Sec., 78 Sec. and 69 Sec. respectively

Conditions:
Eluent = acetonitrile (95%) : water (5%)
Absorbance = 0.1 Coarse absorbance = 7 Chart speed = 20mm/min Pressure = 5-6psi
Flow rate = 1ml/min Wavelength = 240nm Chart range = 50mv Detector = CECIL 1100 Series
Column = packed with Hichrome C18 packing material Diameter = 15cm Id = 4.5mm

Figure 5.4b: HPLC traces of a mixture of 1-methylimidazole, 3-bromopropionitrile and 1-(2-cyanoethyl)-3-methylimidazolium bromide

The HPLC analysis of a mixture of 1-methylimidazole starting material and ionic liquid 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride using a standard eleuent – mixture of acetonitrile and water (95 : 5) – was not able to separate the two peaks. Analyses were repeated using a mixture of acetonitrile and water (85 : 15) as an eluent. The results in Figure 5.5a shows that the peaks are still very close together and not fully separated from each other.



Mixture of 1-[2-(2-hydroxyethoxy)]-3-methylimidazoliumchloride and 1-methylimidazole

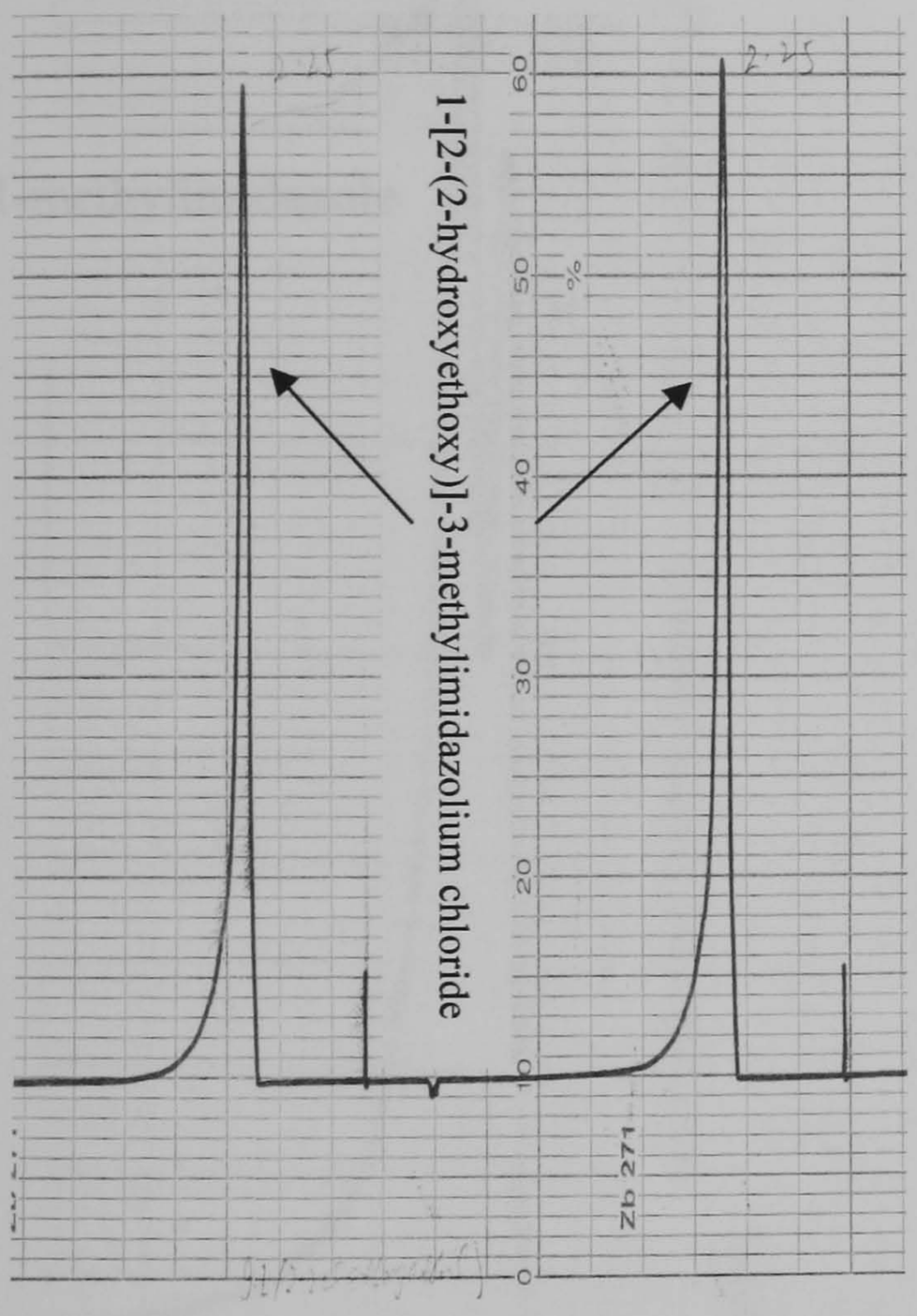
Retention times:

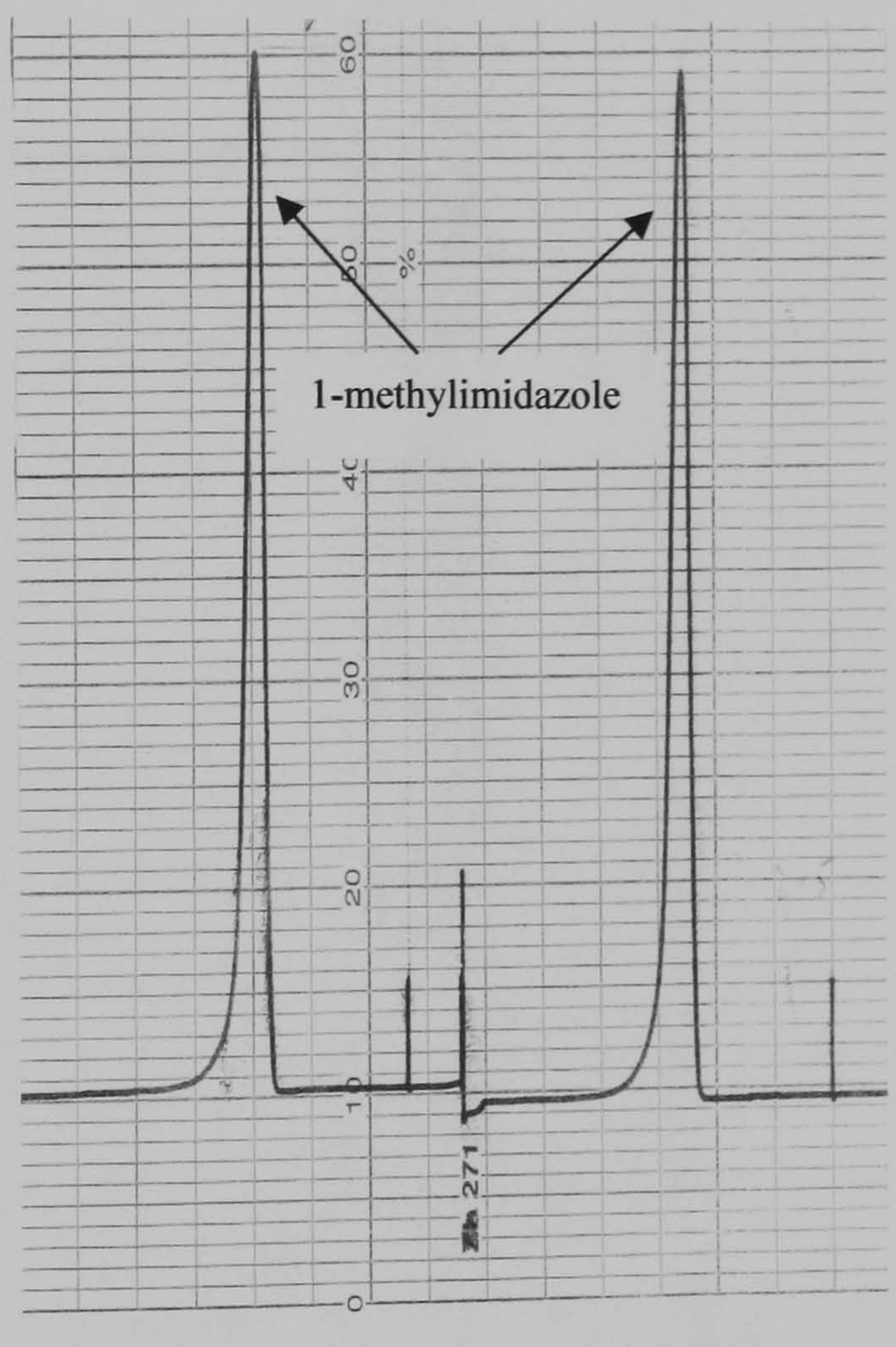
1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride = 69 Sec. 1-methylimidazole = 78 Sec.

Conditions:
Eluent = acetonitrile (85%): water (15%)
Absorbance = 0.2 Coarse absorbance = 7 Chart speed = 20mm/min
Pressure = 5-6psi Flow rate = 1ml/min Wavelength = 240nm
Chart range = 50mv Detector = CECIL 1100 Series
Column = packed with Hichrome C18 packing material Diameter = 15cm Id = 4.5mm

Figure 5.5a: HPLC traces of a mixture of 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride and 1-methylimidazole

The results in Figure 5.5a shows that the two peaks corresponding to 1-methylimidazole and 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride are very close together. An attempt was made to investigate if the two peaks can be separated from each other by changing the eluent from acetonitrile : water mixture to methanol : water mixture. The results in Figure 5.5b show the HPLC traces of 1-methylimidazole starting material and 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride using methanol : water mixture (85 : 15) as the eluent. The results show that the retention time for the ionic liquid is slightly reduced from 69 second to 66 second.





1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride

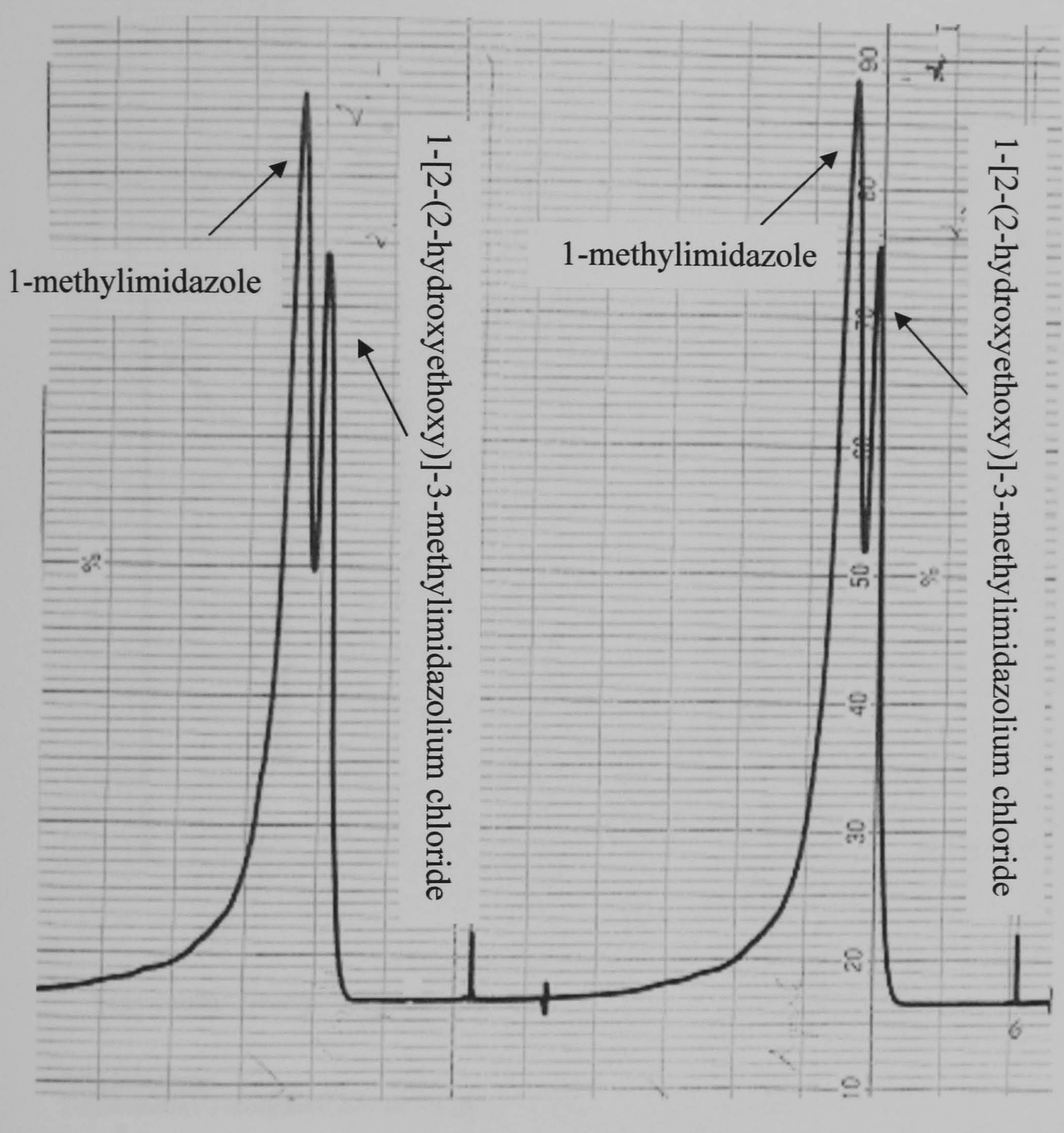
1-methylimidazole

Retention times:
1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride = 66 Sec. 1-methylimidazole = 75 Sec.

Conditions:
Eluent = methanol (85%) : water (15%)
Absorbance = 0.2 Coarse absorbance = 7 Chart speed = 20mm/min
Pressure = 5-6psi Flow rate = 1ml/min Wavelength = 240nm
Chart range = 50mv Detector = CECIL 1100 Series
Column = packed with Hichrome C18 packing material Diameter = 15cm Id = 45mm

Figure 5.5b: HPLC traces of 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride and 1-methylimidazole

Figures 5.5c shows the HPLC traces of a mixture of 1-methylimidazole starting material and ionic liquid 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride using methanol : water mixture (85 : 15) as an eluent. The comparison of this chromatogram with the chromatogram in Figure 5.5a shows that a slight improvement in peak separation can be achieved by changing the eluent from acetonitrile : water mixture to methanol : water mixture.



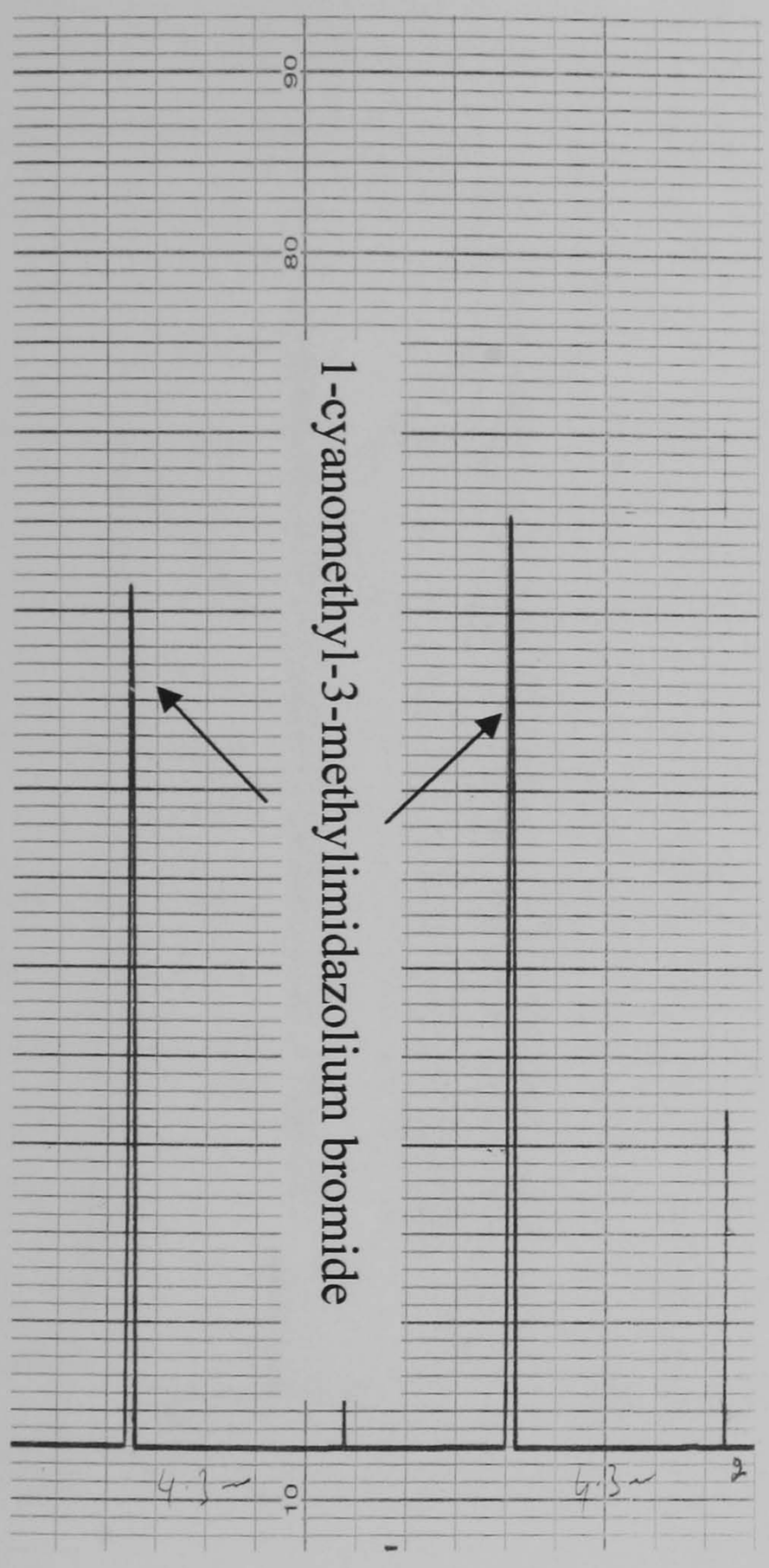
Mixture of 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride and 1-methylimidazole

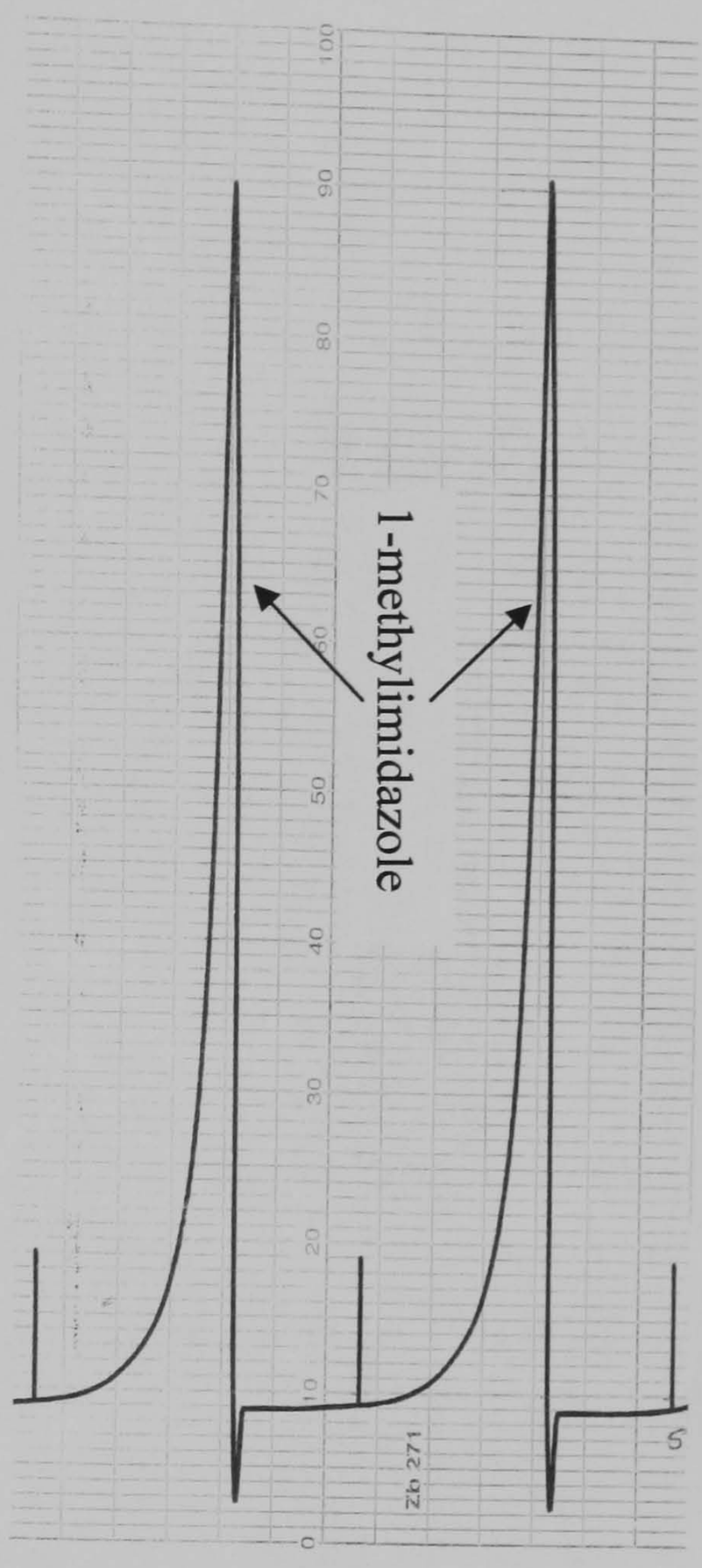
Retention times:
1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride = 66 Sec. 1-methylimidazole = 75 Sec.

Conditions:
Eluent = methanol (85%): water (15%)
Absorbance = 0.2 Coarse absorbance = 7 Chart speed = 20mm/min Pressure = 5-6psi
Flow rate = 1ml/min Wavelength = 240nm Chart range = 50mv Detector = CECIL 1100 Series
Column = packed with Hichrome C18 packing material Diameter = 15cm Id = 4.5mm

Figure 5.5c: HPLC traces of a mixture of 1-[2-(2-hydroxyethoxy)]-3-methylimidazoliumchloride and 1-methylimidazole

Figure 5.6 shows the HPLC traces of 1-methylimidazole starting material and ionic liquid 1-cyanomethyl-3-methylimidazolium bromide using a standard eluent – acetonitrile : water mixture (95 : 5). The presence of single peak ion the product HPLC traces confirms that the ionic liquid is pure and free from the starting materials.





1-cyanomethyl-3-methylimidazolium

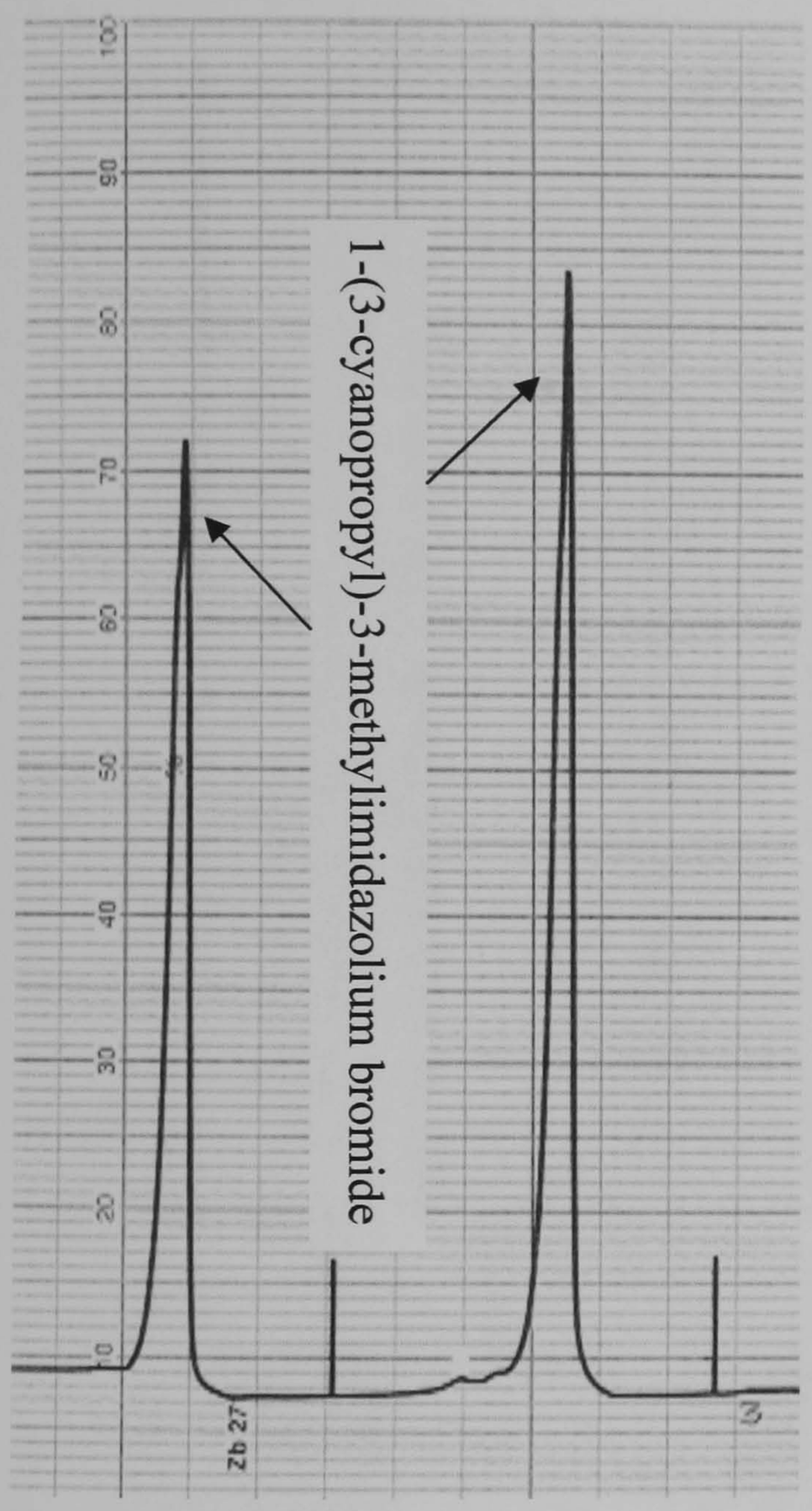
1-methylimidazole

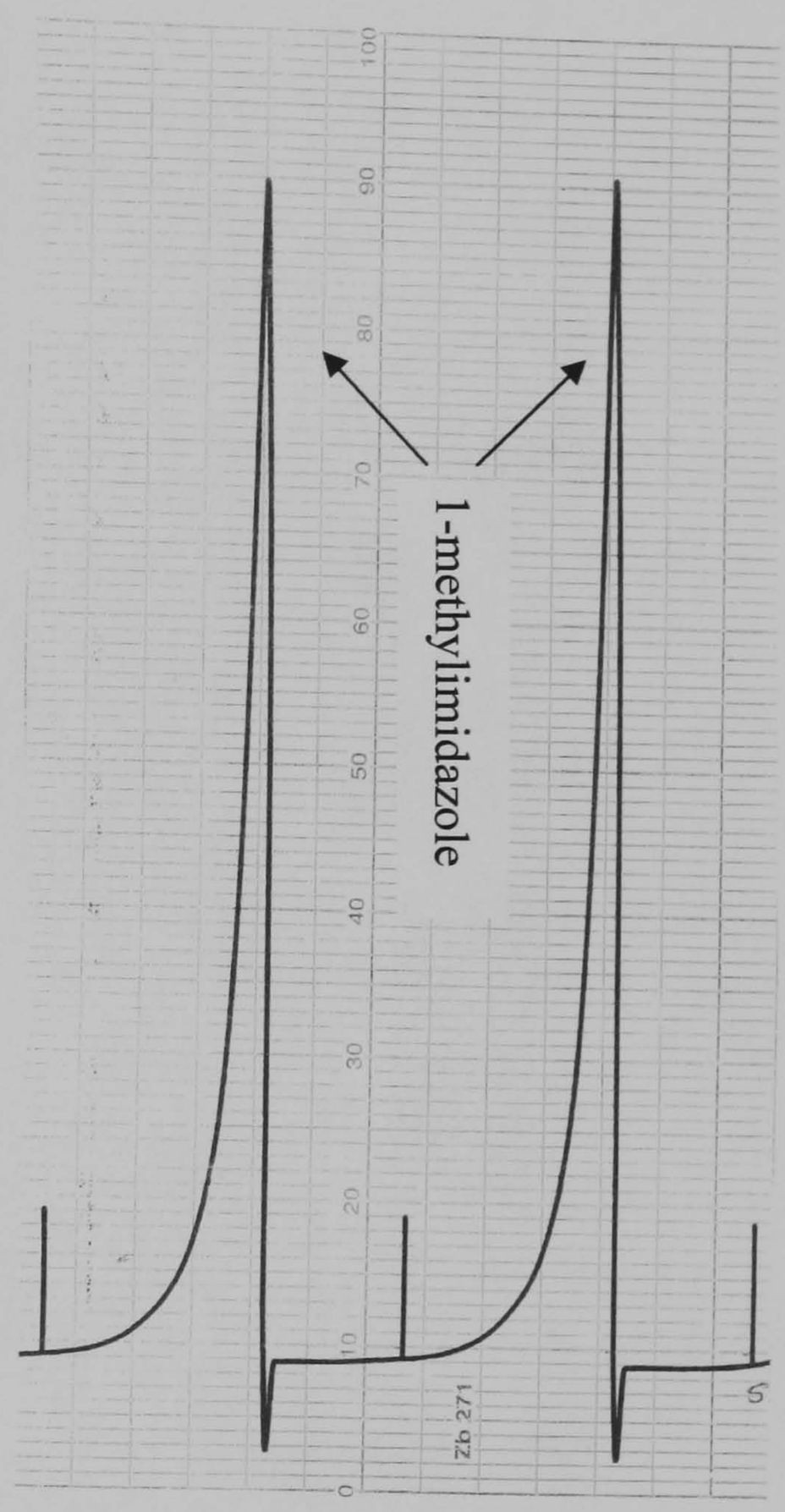
Retention times:
1-cyanomethyl-3-methylimidazolium bromide = 129 Sec. 1-methylimidazole = 87 Sec.

Conditions:
Eluent = acetonitrile (95%): water (5%)
Absorbance = 0.1 Coarse absorbance = 7 Chart speed = 20mm/min Pressure = 5-6psi
Flow rate = 1ml/min Wavelength = 240nm Chart range = 50mv Detector = CECIL 1100 Series
Column = packed with Hichrome C18 packing material Diameter = 15cm Id = 4.5mm

Figure 5.6: HPLC traces of 1-cyanomethyl-3-methylimidazolium bromide and 1-methylimidazole

Figure 5.7 shows the HPLC traces of 1-methylimidazole starting material and ionic liquid 1-(3-cyanopropyl)-3-methylimidazolium bromide. Again, the product is pure and free from the starting materials.





1-(3-cyanopropyl)-3-methylimidazolium bromide

1-methylimidazole

Retention times

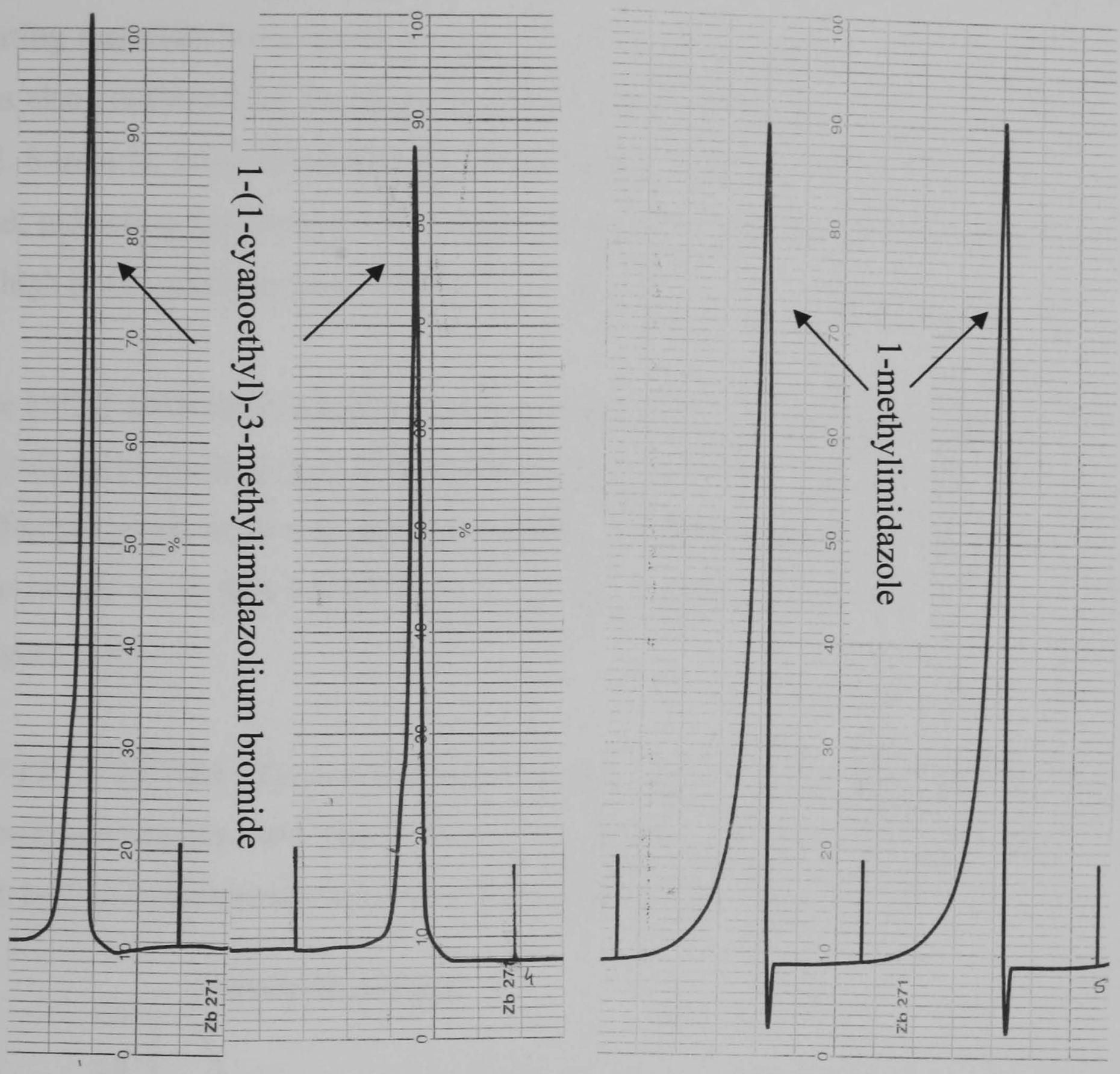
1-(3-cyanopropyl)-3-methylimidazolium bromide = 63 Sec.

1-methylimidazole = 87 Sec.

Conditions:
Eluent = acetonitrile (95%): water (5%)
Absorbance = 0.1 Coarse absorbance = 7 Chart speed = 20mm/min Pressure = 5-6psi
Flow rate = 1ml/min Wavelength = 240nm Chart range = 50mv Detector = CECIL 1100 Series
Column = packed with Hichrome C18 packing material Diameter = 15cm Id = 4.5mm

Figure 5.7: HPLC traces of 1-(3-cyanopropyl)-3-methylimidazolium bromide and 1-methylimidazole

Figure 5.8 shows the HPLC traces of 1-methylimidazole starting material and ionic liquid 1-(3-cyanoethyl)-3-methylimidazolium bromide. The ionic liquid is pure and free from the starting materials.



1-(1-cyanoethyl)-3-methylimidazolium bromide 1-methylimidazole

Retention times:
1-(1-cyanoethyl)-3-methylimidazolium bromide = 66 Sec. 1-methylimidazole = 87 Sec.

Conditions:
Eluent = acetonitrile (95%): water (5%)
Absorbance = 0.1 Coarse absorbance = 7 Chart speed = 20mm/min Pressure = 5-6psi
Flow rate = 1ml/min Wavelength = 240 nm Chart range = 50mv Detector = CECIL 1100 Series
Column = packed with Hichrome C18 packing material Diameter = 15cm Id = 4.5mm

Figure 5.8: HPLC traces of 1-(1-cyanoethyl)-3-methylimidazolium bromide and 1-methylimidazole

The HPLC analyses of a mixture of the two starting materials, 1-methylimidazole and 3-bromoproprionitrile, and the product, 1-(2-cyanoethyl)-3-methylimidazolium bromide produced three separate peaks (Figure 5.4b). The HPLC analysis of the product, 1-(2-cyanoethyl)-3-methylimidazolium bromide, showed the presence of a single peak which proved that the RTIL was of a high purity because the two peaks corresponding to the starting materials were absent in the product's HPLC trace. The purity of this RTIL was also confirmed by the accurate mass measurements and data is presented in Table 5.2. Similarly, all of the remaining ionic liquids, based on –CN group, produced single peak indicating the presence of a single materials and confirmed that the products were of high purity and free from the starting materials.

The HPLC analysis of a mixture of 1-methylimidazole, starting material, and the RTIL, 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride, was carried out using two different solvent mixtures, methanol : water, (85 : 15) and acetonitrile : water, (85 : 15). The results show that the RTIL is of a high purity and free from the starting material (Figure 5.5)

UV/VIS SPECTRA - Figures 5.9 and 5.10 show the UV/Vis spectra of starting material, 1-methylimidazole, and the RTILs - 1-(2-cyanoethyl)-3-methylimidazolium bromide and 1-[2-(2-hydroxyethoxy)]-3-ethylimidazolium chloride respectively.

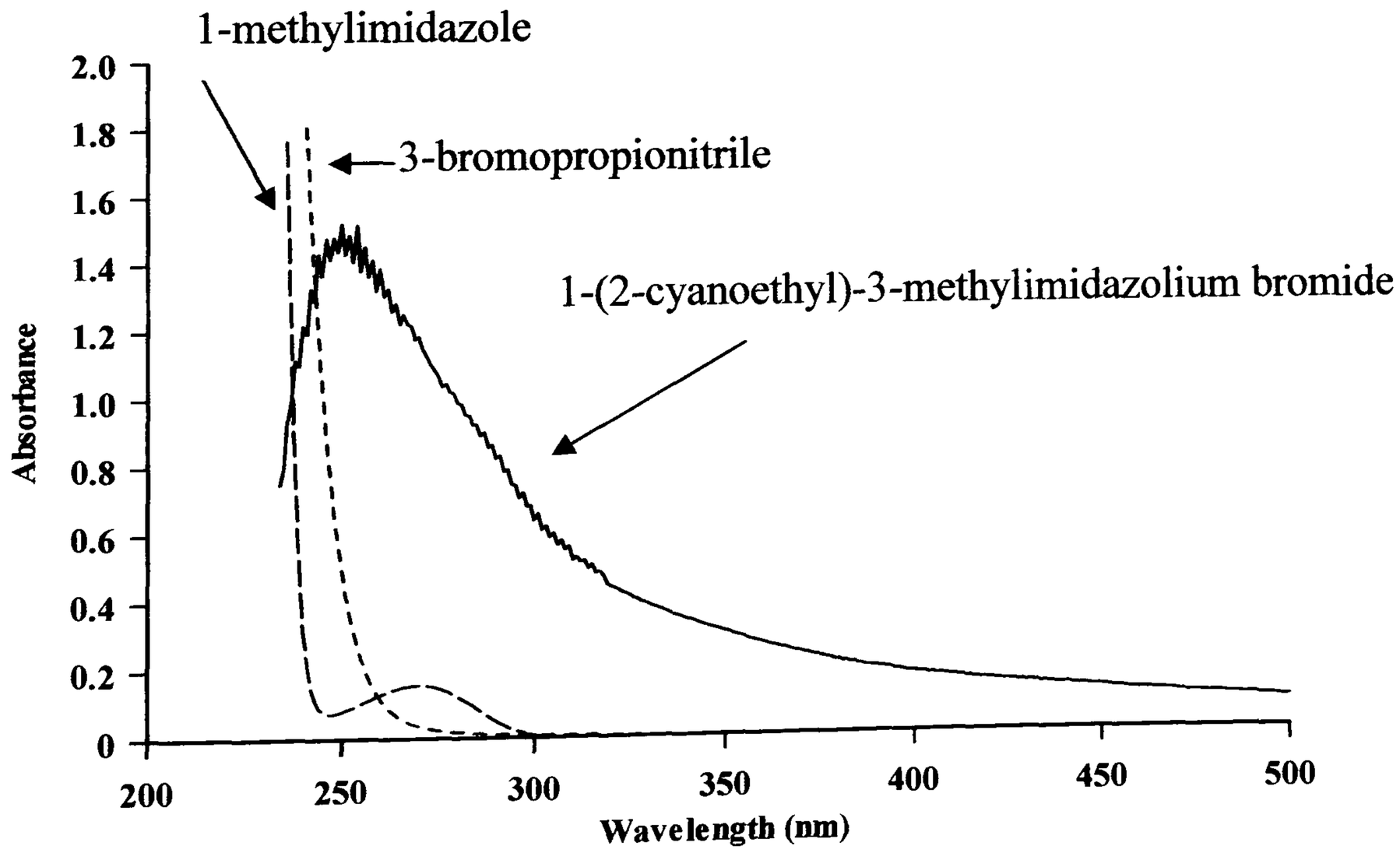


Figure 5.9: UV/vis spectra of 1-methylimidazol, 3-bromopropionitrile and 1-(2-cyanoethyl)-3-methylimidazolium bromide

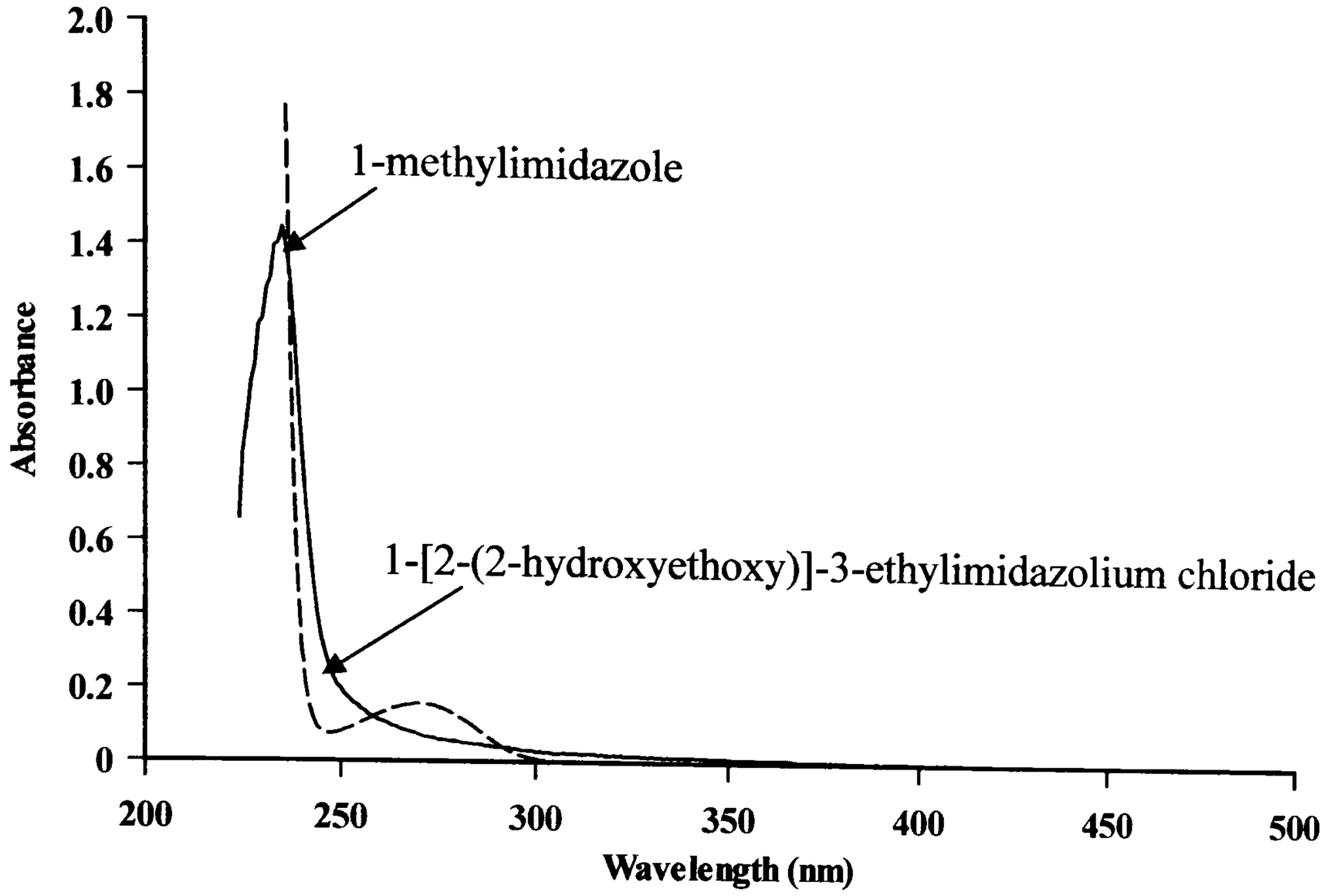


Figure 5.10: UV/vis spectra of 1-methylimidazol and 1-[2-(2-hydroxyethoxy)]-3-ethylimidazolium chloride

The presence of a single peak in each of the two products suggests that the prepared RTILs are of high purity and free from the starting materials. Again, the purity of this RTIL was confirmed by the accurate mass measurement (Table 5.2).

The UV/Visible spectra of all the remaining ionic liquids, based on –CN group, are similar and the existence of a single peak indicate the presence of a single material and confirm that the products are of high purity and are free from the starting materials.

Infrared spectra – Figure 5.11 – 5.14 show the infrared spectra of 1-methyle imidazole, 3-bromopropionitrile, 1-(2-cyanoethyl)-3-methylimidazolium bromide and the overlap spectra of 3-bromopropionitrile and 1-(2-cyanoethyl)-3-methylimidazolium bromide respectively. The interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of unknown compound with the known absorption frequencies for types of bonds. The absorption bands for different types of bonds and their corresponding wavenumbers are given in separate tables under each of the spectrum. Most of the observed absorption bands, excluding the fingerprint region, correspond to saturated C-H stretch, C≡N stretch and O-H stretch etc.

The infrared spectrum of 1-methylimidazole (Figure 5.11) shows a broad peak at 3400 cm^{-1} (possibly water), an intense peak at 3100 cm^{-1} (aromatic C-H stretching), a peak at

2950 cm^{-1} (C-H stretching of N-CH_3) and a peak at 1690 cm^{-1} (C=N stretch). Bands in the fingerprint region (wavenumber < 1500 cm^{-1}) correspond to stretching and vibration bands of different bonds.

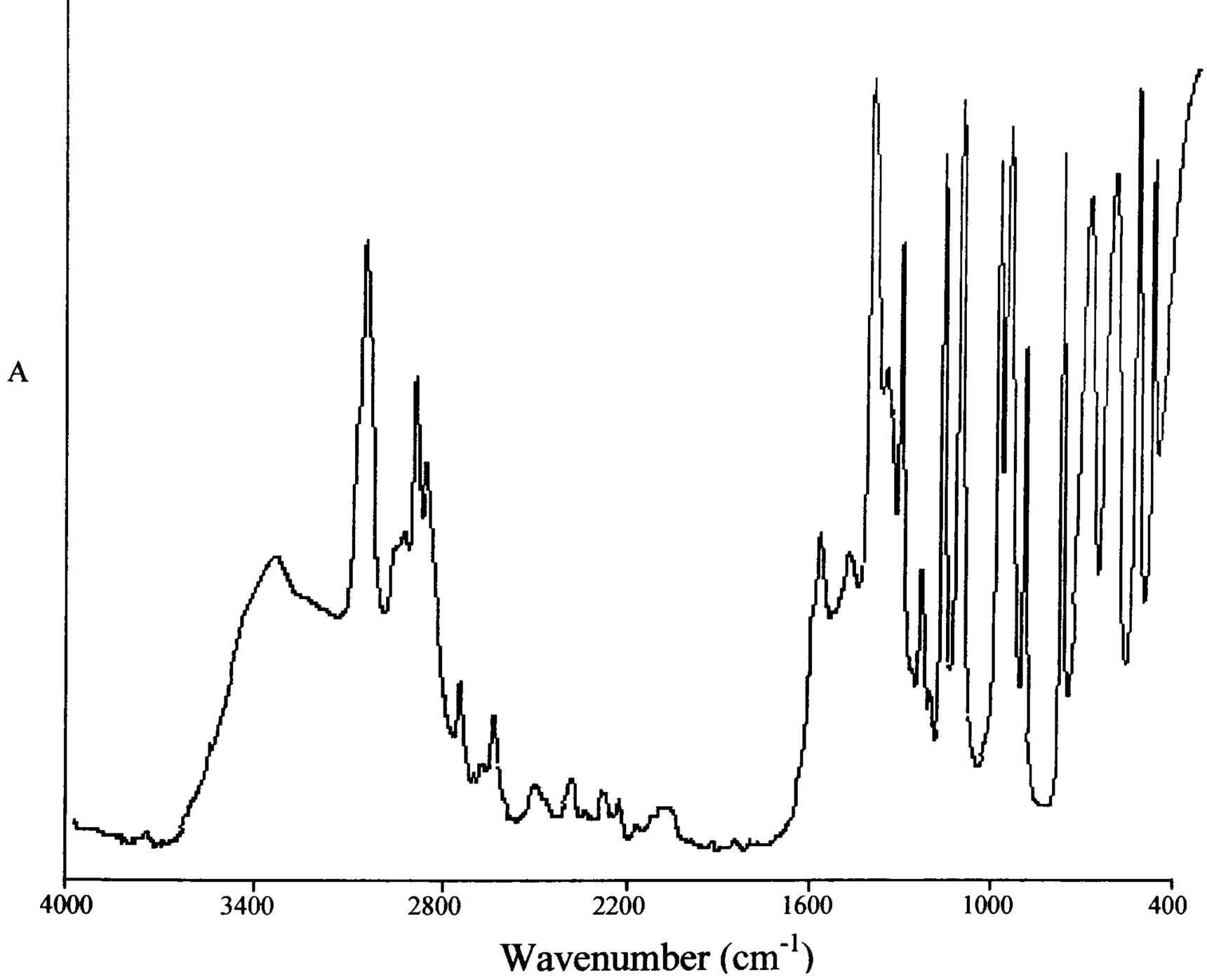
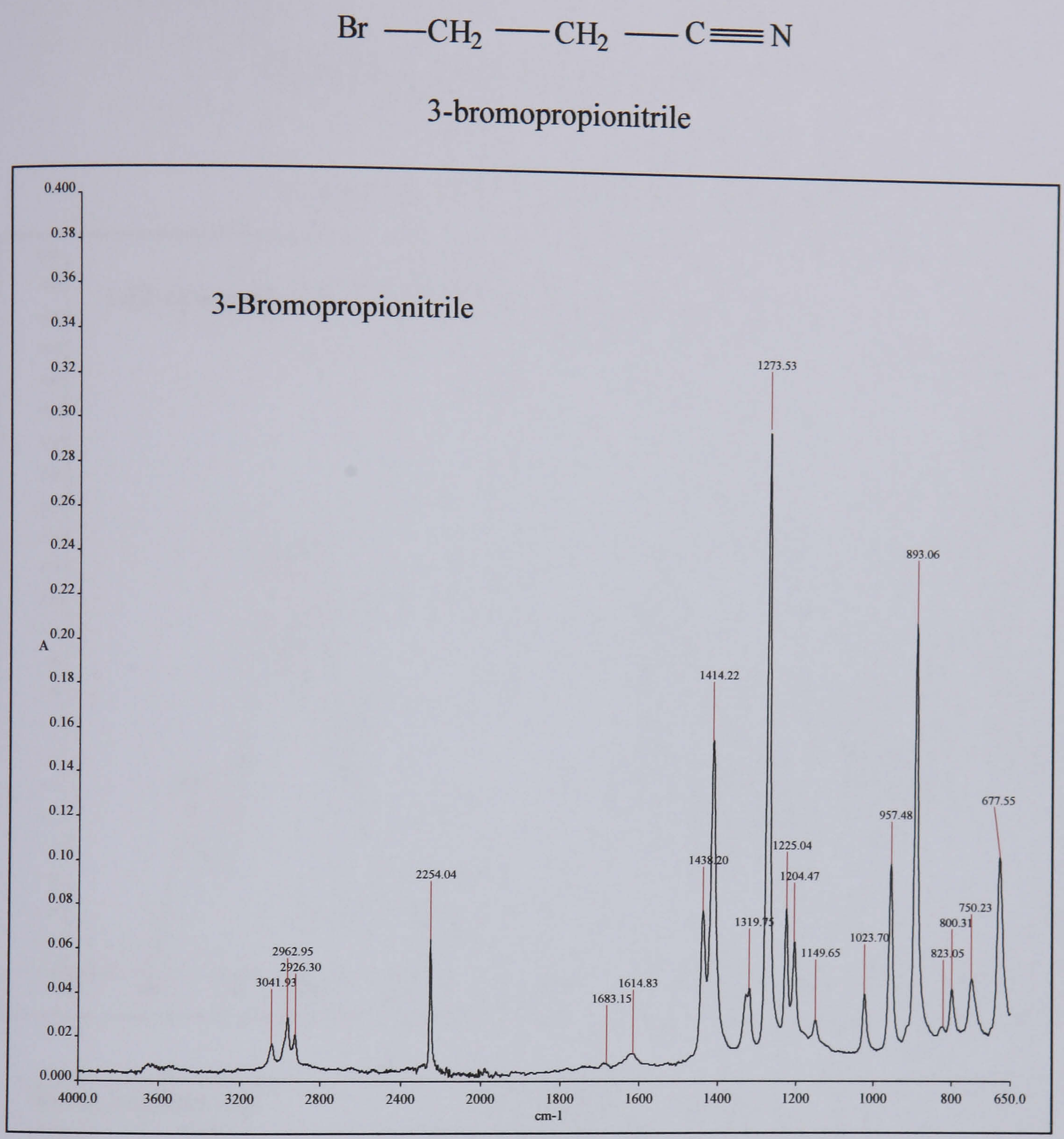
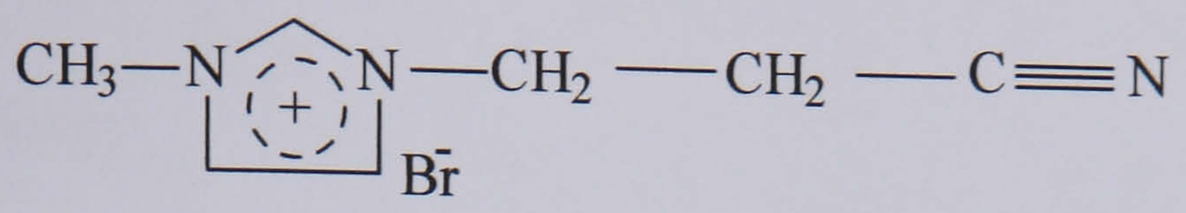


Figure 5.11: IR spectrum of 1-methylimidazole

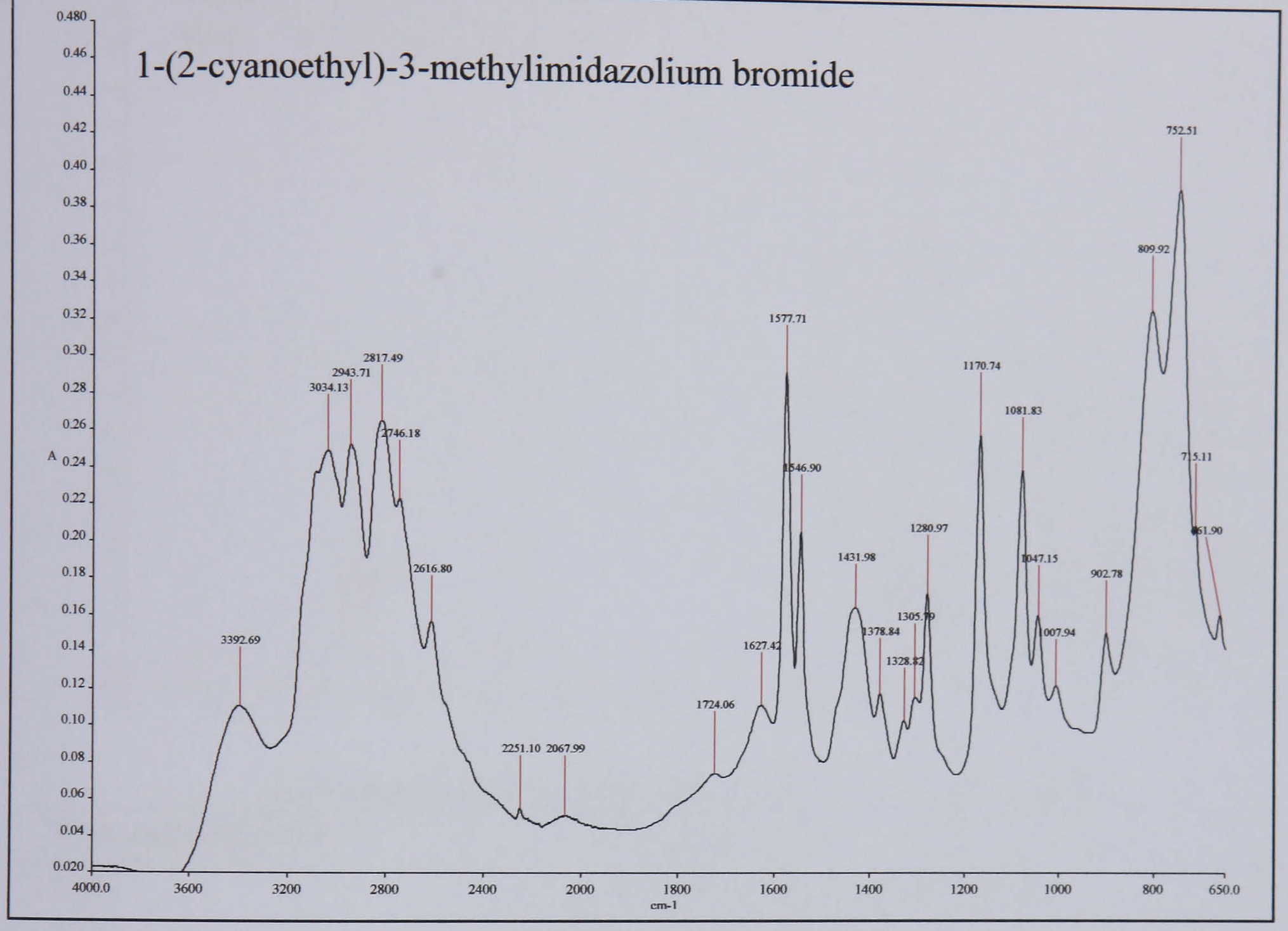


Wavenumbers /cm^{-1}	Vibration
3042	C-H Stretching (alkane symmetric)
2963	C-H Stretching (alkane antisymmetric)
2926	C-H Stretching (alkane, CH_3, antisymmetric)
2254	C≡N triple bond stretching (Nitriles)
1638 – 1683	C-C multiple bond Stretching (alkene)
1414	C-H bending (CH_3, antisymmetric)

Figure 5.12: IR spectrum of 3-bromopropionitrile

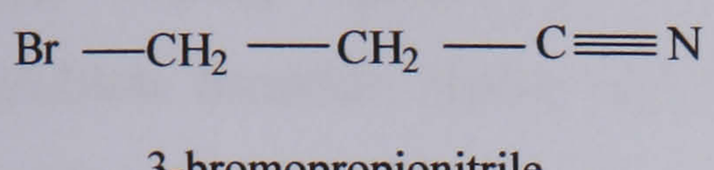


1-(2-cyanoethyl)-3-methylimidazoliumbromide

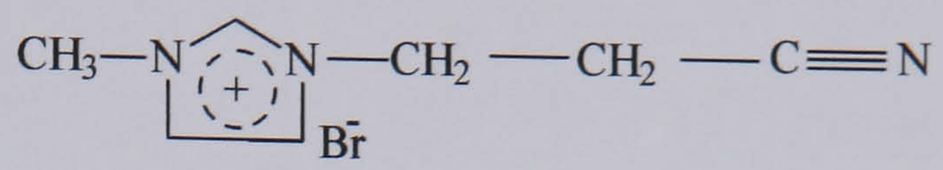


Wavenumbers /cm^{-1}	Vibration
3393	O-H Stretching (hydrogen bonded)
3034	C-H Stretching (alkene symmetric)
2944	C-H Stretching (alkane, CH_3, antisymmetric)
2818	N-CH_3 Stretching
2746	C-H Stretching (alkane, CH_2, symmetric)
2617	O-H Stretching (hydrogen bonded)
2251	C≡N Triple bond stretching (Nitriles)
1627	C-H Stretching (alkene, isolated)

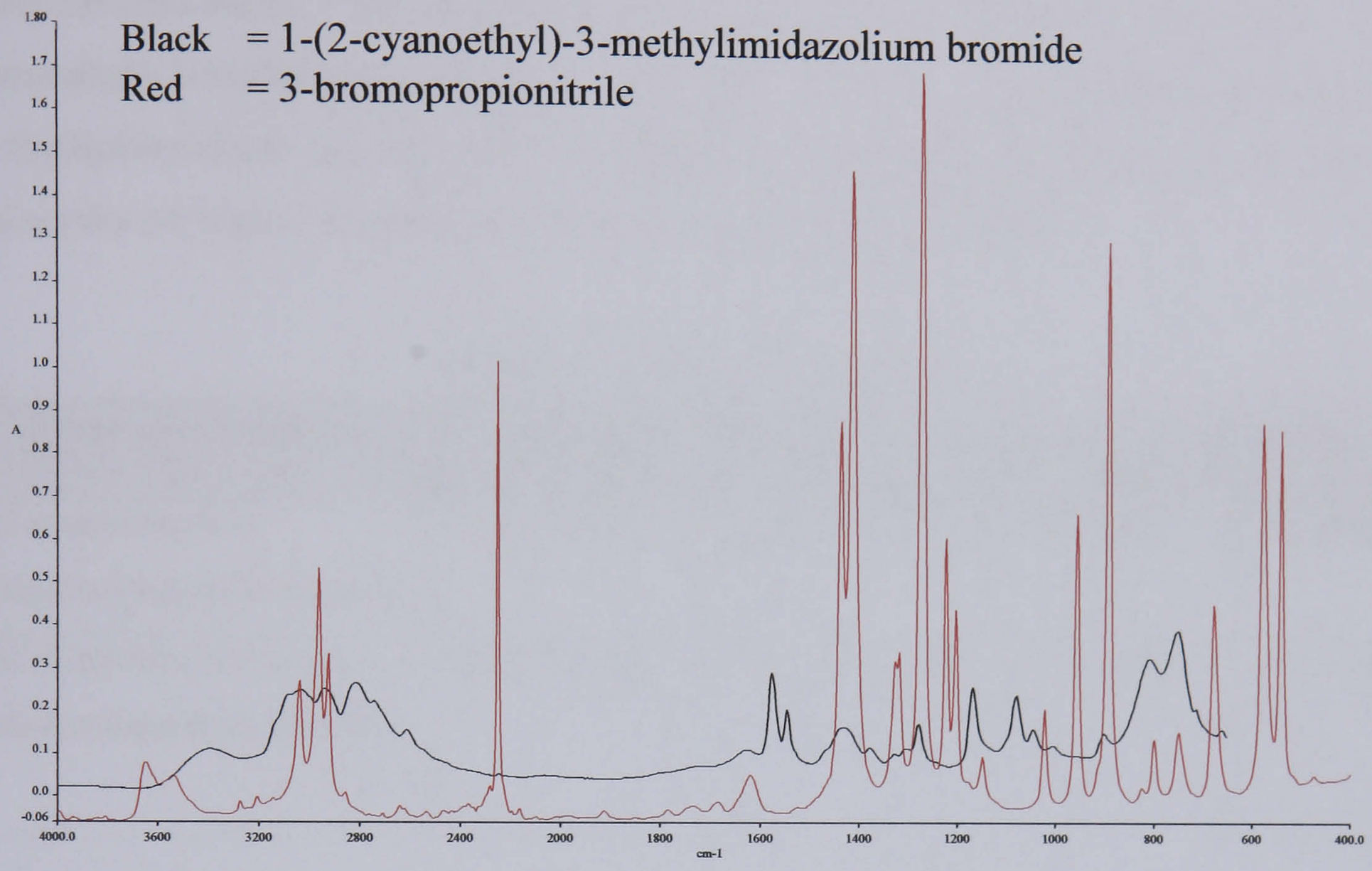
Figure 5.13: IR spectrum of 1-(2-cyanoethyl)-3-methylimidazolium bromide



3-bromopropionitrile



1-(2-cyanoethyl)-3-methylimidazoliumbromide



1-(2-cyanoethyl)-3-methylimidazolium bromide (black)

Wavenumbers /cm^{-1}	Vibration
3393	O-H Stretching (hydrogen bonded)
3034	C-H Stretching (alkene)
2944	C-H Stretching (alkane, CH_3, antisymmetric)
2818	C-H Stretching (alkane, CH_2, symmetric)
2617	O-H Stretching (hydrogen bonded)
2251	C≡N triple bond stretching (Nitriles)
1627	C-H Stretching (alkene, isolated)
1778	C-C multiple bond Stretching

3-Bromopropionitrile (Red)

Wavenumbers /cm^{-1}	Vibration
3042	C-H Stretching (alkene)
2963	C-H Stretching (alkane antisymmetric)
2926	C-H Stretching (alkane, CH_3, antisymmetric)
2254	C≡N triple bond stretching (Nitriles)
1638 – 1683	C-C multiple bond Stretching (alkene)
1414	C-H bending (CH_3, antisymmetric)

Figure 5.14: IR spectra of 1-(2-cyanoethyl)-3-methylimidazolium bromide (black) and 3-bromopropionitrile (red)

The overlap spectra of 3-bromopropionitrile and 1-(2-cyanoethyl)-3-methylimid-azolium bromide shows different absorption band for the starting material and the product again confirming the high purity of the RTIL (Figure 5.14).

Mass Measurements – Accurate mass measurements were carried on two RTILs, 1-(2-cyanoethyl)-3-methylimid-azolium bromide and 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride, at the EPSRC National Spectrometry Service Centre, University of Wales, Swansea and the data is presented in Table 5.2.

Table 5.2: Mass measurement data

Compounds name	Compound (Formula)	Molecular ion, $(M-X)^+$	Theoretical mass	Calculated mass
1-(2-cyanoethyl)-3-methylimid-azolium bromide	$C_7H_{11}N_3Br$	$[C_7H_{11}N_3\text{-}Br]^+$	136.0869	136.0868
1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride	$C_8H_{15}N_2O_2Cl$	$[C_8H_{15}N_2O_2\text{-}Cl]^+$	171.1128	171.1129

5.3.3 Application of RTILs

5.3.3.1 Solubility of metals and metal oxides in RTILs

The results in Table 5.3 show that the solubility of copper (II) oxide in the eight RTILs studied in this work does vary with the composition of the RTIL. The solubility varies from 12.2 % for 1-(3-cyanopropyl)-3-methylimidazolium bromide to 99.2 % for 1-(2-cyanoethyl)-3-methylimidazolium bromide. The fact that colours are formed in dissolving CuO, for example, green in the case of 1-(2-cyanoethyl)-3-methylimidazolium bromide, suggests that complexes are formed in the process. The change in colour to blue in the case of 1-(2-cyanoethyl)-3-methylimidazolium bromide identified when water is added to the system reflects the competition between the RTIL and water as a ligand for copper in solution.

The solubility data in Table 5.3 confirmed that the best results were achieved with the use of 1-(2-cyanoethyl)-3-methylimidazolium bromide which dissolved 99.2 % of CuO in less than 10 minutes. Further experiments were conducted to investigate the solubility of other heavy metal oxides in the same RTIL.

Table 5.3: Solubility of CuO with different ionic liquids

(Reaction between 2 g ionic liquid and 0.2 g CuO in the absence of water at 40°C)

Exp. No	RTILs	Colour without water	Colour after adding water	% Copper dissolved
1.	1-(2-cyanoethyl)-3-methylimidazolium bromide	Green	Blue	99.2
2.	1-[2-(2-hydroxyethoxy)]-3 methylimidazolium chloride	Light Green	Light Blue	21.9
3.	1-methyl-3-propylimidazolium bromide	No Change/ Brown	Brown	21.2
4.	1-cyanomethyl-3-methylimidazolium bromide	No Change/ Brown	Brown	16.8
5.	1-(3-cyanopropyl)-3-methylimidazolium bromide	No Change/ Brown	Brown	12.2
6.	1-(1-cyanoethyl)-3-methylimidazolium bromide	No Change/ Brown	Brown	18.6
7.	1-cyano-1, 1-bis (1-methylimidazoluim) methanedibromide	No Change/ Brown	Brown	14.4
8.	1-cyano-1, 2-bis (1-methylimidazolium) ethanedibromide	No Change/ Brown	Brown	17.6

The data in Table 5.4 provide a comparison of the solubility of copper (II) oxide in 1-(2-cyanoethyl)-3-methylimidazolium bromide with other metal oxides (CoO, NiO and ZnO) and metals (Cu, Co, Ni, and Zn). All of the oxides have greater than 90 % solubility in the RTIL and cobalt and nickel oxides form coloured solutions that change colour on the addition of water. The blue complex formed with cobalt oxide suggests, for example, the formation of a tetrahedral complex with Co(II) which changes to the

penta/octahedral $Co(H_2O)_6$ complex on the addition of water. Both copper and zinc metal powders are very soluble (>96 %) in the RTIL while 35.0 % and 26.9 % of the cobalt and nickel powders dissolve in 1-(2-cyanoethyl)-3-methylimidazolium bromide, respectively. Again coloured complexes are formed that change on addition of water. These results are shown graphically in Figure 5.15.

Table 5.4: Solubility of metals and metal oxides in 1-(2-cyanoethyl)-3-methylimidazolium bromide in the absence of water
(2 g ionic liquid, 0.2 g metal oxide, 40°C)

Exp. No	RTILs	Colour without water	Colour after adding water	% Metal dissolved
1.	CoO	Blue	Pink	92.2
2.	NiO	Blue	Green	95.4
3.	CuO	Green	Blue	99.2
4.	ZnO	Cream	Colourless	96.3
5.	Co (metal powder)	Blue	Pink	35.0
6.	Ni (metal powder)	Blue	Green	26.9
7.	Cu (metal powder)	Green	Blue	95.6
8.	Zn (metal powder)	Cream	Colourless	97.0

The data in Tables 5.5 show results for the solubilities of the oxides and metal in 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride. In this solvent even the solubility of CuO is less than in the 1-(2-cyanoethyl)-3-methylimidazolium system. The results are shown graphically in Figure 5.16.

The solubilities of the metal oxides and metals in 1-(2-cyanoethyl)-3-methylimidazolium bromide (RTIL 1) and 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride (RTIL 2) are compared in Figures 5.17. The data show that the solubilities are RTIL-solvent dependent.

Table 5.5: Solubility of metals and metal oxides in 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride in the absence of water
(2 g ionic liquid, 0.2 g metal oxide, 40°C)

Exp. No	RTILs	Colour without water	Colour after adding water	% Metal dissolved
1.	CoO	Blue	Pink	35.0
2.	NiO	Blue	Green	20.5
3.	CuO	Green	Blue	22.0
4.	ZnO	Cream	Colourless	46.9
5.	Co (metal powder)	Blue	Pink	18.9
6.	Ni (metal powder)	Blue	Green	6.05
7.	Cu (metal powder)	Green	Blue	70.0
8.	Zn (metal powder)	Cream	Colourless	32.5

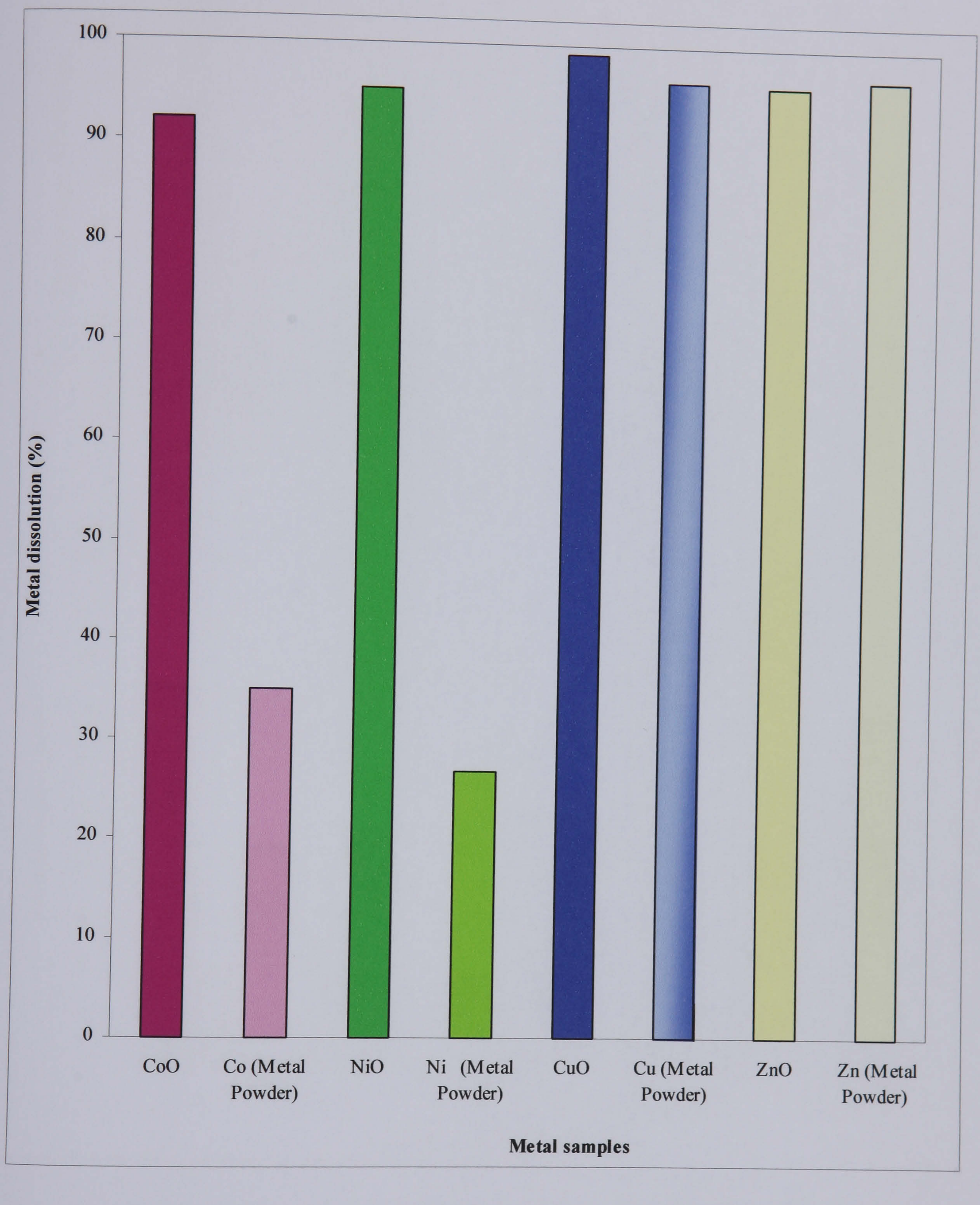


Figure 5.15: Solubility of pure metals and metal oxides in 1-(2-cyanoethyl)-3-methylimidazolium bromide and metal powder and oxides in the absence of water

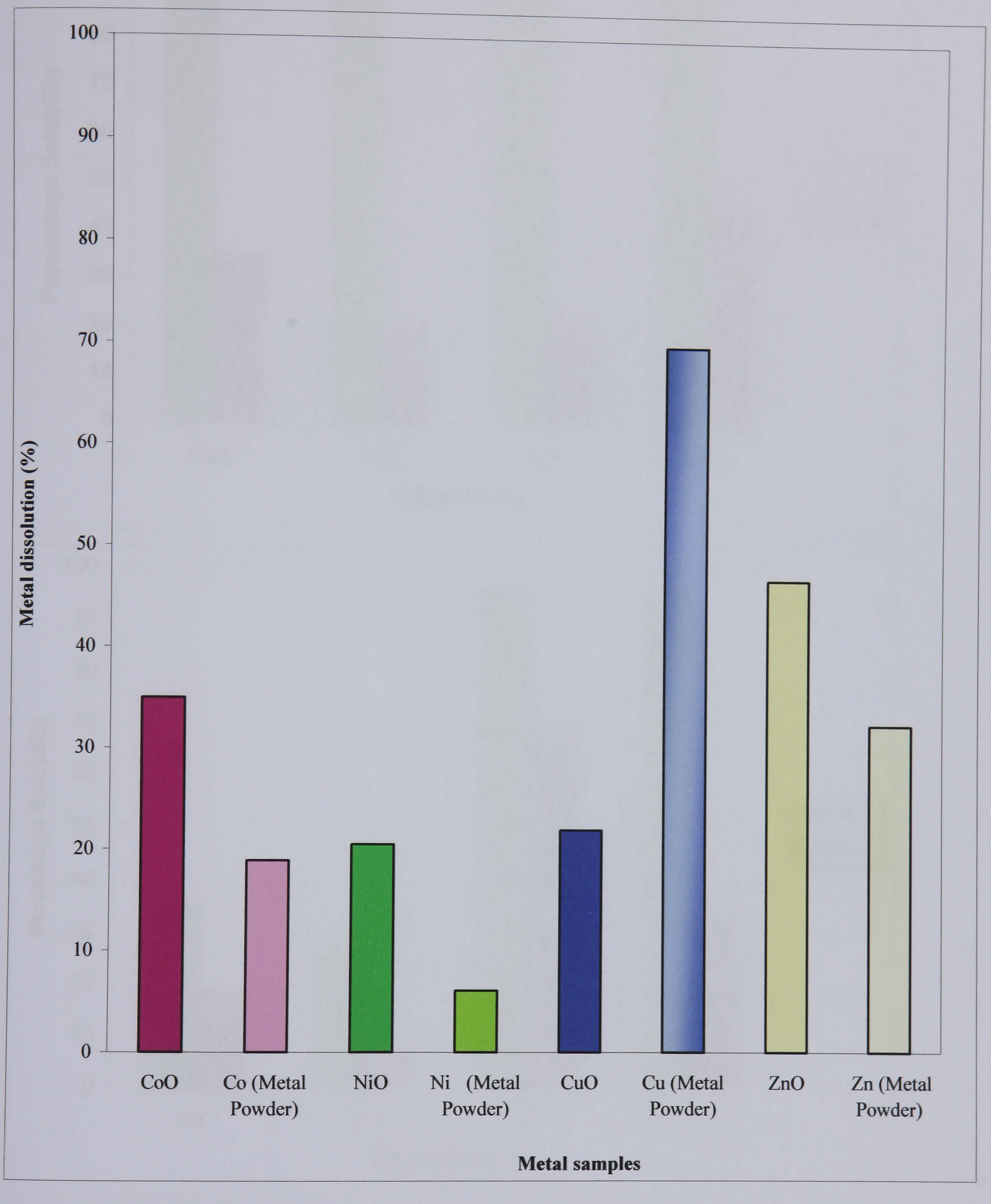
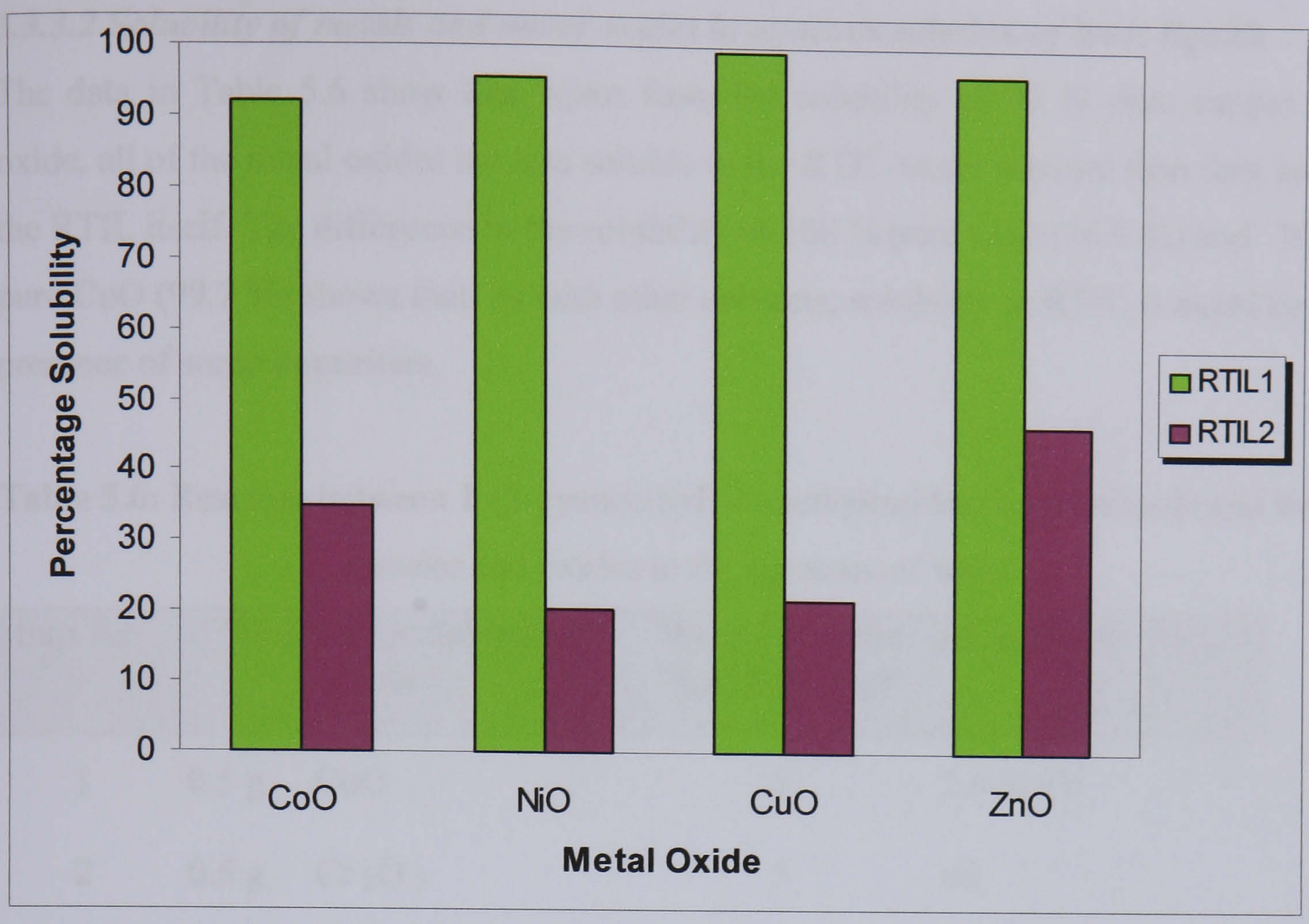


Figure 5.16: Solubility of metals and metal oxides in 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride in the absence of water



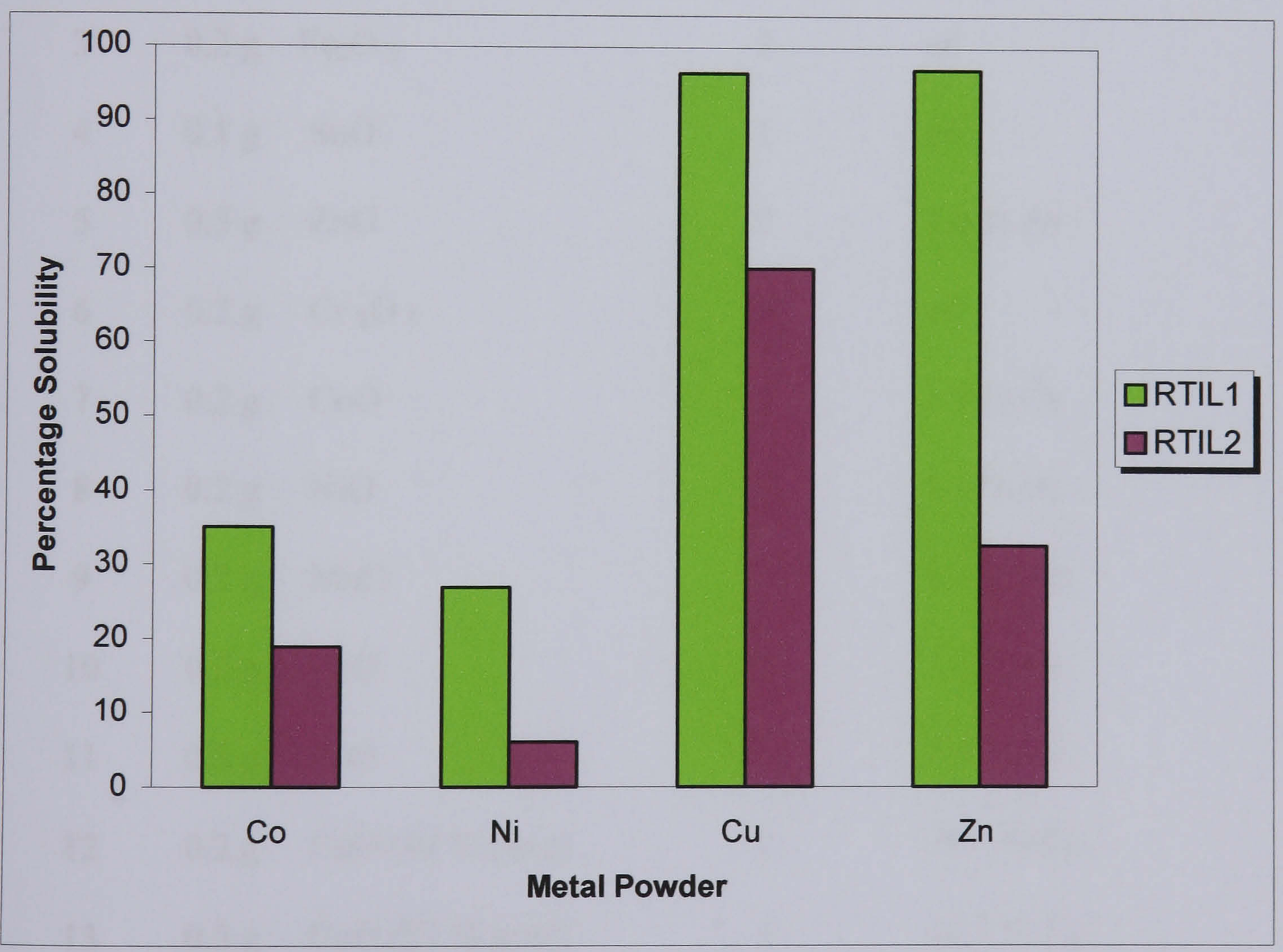


Figure 5.17: Comparison between 1-(2-cyanoethyl)-3-methylimidazolium bromide (RTIL No 1) and 1-[2-(2-hydroxyethoxy)]-3-methylimidazoliumchloride (RTIL No 2) on the basis of solubility of metal oxides and metal powders.

5.3.3.2 Solubility of metals and metal oxides in aqueous solution of ionic liquids

The data in Table 5.6 show that, apart from the solubility of 97 % pure copper (II) oxide, all of the metal oxides are less soluble in the RTIL-water mixture than they are in the RTIL itself. The difference in the solubility of 100 % pure CuO (14.9 %) and 97 % pure CuO (99.7 %) shows that, as with other solvents, solubility in RTIL is aided by the presence of some impurities.

Table 5.6: Reaction between 1-(2-cyanoethyl)-3-methylimidazolium bromide and metal powder and oxides in the presence of water

Exp. No	Weight of metal oxides used	Weight of ionic liquid used (g)	Metal dissolved
1	0.5 g CoO	5	2.6 % Co
2	0.5 g Cr_2O_3	5	nil
3	0.2 g Fe_2O_3	2	nil
4	0.1 g SnO	1	nil
5	0.5 g ZnO	5	3.0 % Zn
6	0.2 g Cr_2O_3	2	nil
7	0.2 g CoO	2	3.5 % Co
8	0.2 g NiO	2	1.1 % Ni
9	0.2 g MnO	2	1.3 % Mn
10	0.2 g ZnO	2	3.5 % Zn
11	0.5 g ZnO	5	2.9 % Zn
12	0.2 g CuO (97 % pure)	2	99.7 % Cu
13	0.5 g CuO (97 % pure)	5	86.7 % Cu
14	0.2 g CuO (100 % pure)	2	14.9 % Cu

The data in Table 5.6 and 5.7 show similar results for the solubilities of the oxides and metals in the aqueous solution of 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride. In this solution even the solubility of CuO is less than in the 1-(2-cyanoethyl)-3-methylimidazolium bromide system. These results again confirm that the solubilities are RTIL-solvent dependent.

Table 5.7: Reaction between 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride and metal oxides in the presence of water

Exp. No	Weight of metal oxides used	Weight of ionic liquid used (g)	Metal dissolved
1	0.5 g CoO	5	3.4 % Co
2	0.5 g Cr_2O_3	5	nil
3	0.2 g Fe_2O_3	2	nil
4	0.2 g SnO	1	0.3 % Sn
5	0.2 g ZnO	2	2.8 % Zn
6	0.2 g Cr_2O_3	2	nil
7	0.2 g CoO	2	3.5 % Co
8	0.2 g NiO	2	1.7 % Ni
9	0.2 g MnO	2	2.8 % Mn
10	0.2 g ZnO	2	7.3 % Zn
11	0.2 g ZnO	5	6.9 % Zn
12	0.2 g CuO (97 % pure)	2	29.0 % Cu
13	0.5 g CuO (97 % pure)	5	28.9 % Cu
14	0.2 g CuO (100 % pure)	2	13.9 % Cu

5.3.3.3 Solubility of copper, oxide and sulfide in traditional solvents

Table 5.8 contains data on the solubilities of copper powder, copper (II) oxide and copper (II) sulfide in the mineral acids, 3 M nitric acid, 3 M hydrochloric acid and 3 M sulfuric acid and *aqua regia*. These mineral acid solubilities are compared in Table 5.9 and Figure 5.18 with those for 1-(2-cyanoethyl)-3-methylimidazolium bromide. In all cases, the solubility in the RTIL is nearly equal to or greater than that achieved in the mineral acids. The solubility of copper sulfide in the RTIL is particularly interesting. CuS is the major copper mineral but recovery of copper by non-smelter techniques is not economic because of the low solubility in acids (apart from *aqua regia*, which would not be economically viable as a leaching material). The relatively high solubility in 1-(2-cyanoethyl)-3-methylimidazolium bromide, however, suggests that RTILs could provide a suitable leaching medium for the recovery of copper from, particularly, low-grade copper sulfide minerals.

Table 5.8: Solubility of copper metal, oxide and sulfide in traditional solvents

	Aqua-regia	3 M HNO_3	3 M HCl	3M H_2SO_4
Weight of sample	20 ml	20 ml	20 ml	20 ml
	Metal solubility / %			
0.2 g CuO 97 % Pure	99.8	99.8	99.6	99.7
0.2 g CuO 100 % Pure	85.8	88.0	88.2	89.1
0.2 g Cu-metal powder	81.9	95.0	88.1	76.3
0.2 g CuS	76.2	2.15	5.83	2.15

Table 5.9: Comparison of Cu metal dissolution between traditional solvents and 1-(2-cyanoethyl)-3-methylimidazolium bromide

Metal sample	*Aqua-regia* 20 ml	3M HNO_3 20 ml	3M HCl 20 ml	3M H_2SO_4 20 ml	Ionic liquid 2 g
	Metal solubility / %				
CuO 97 % pure	99.8	99.8	99.6	99.7	99.7
CuO 100 % pure	85.8	88.0	88.2	89.1	90.9
Cu metal powder	81.9	95.0	88.1	76.3	96.5
Cu-Sulfide	76.2	2.15	5.83	2.15	92.0

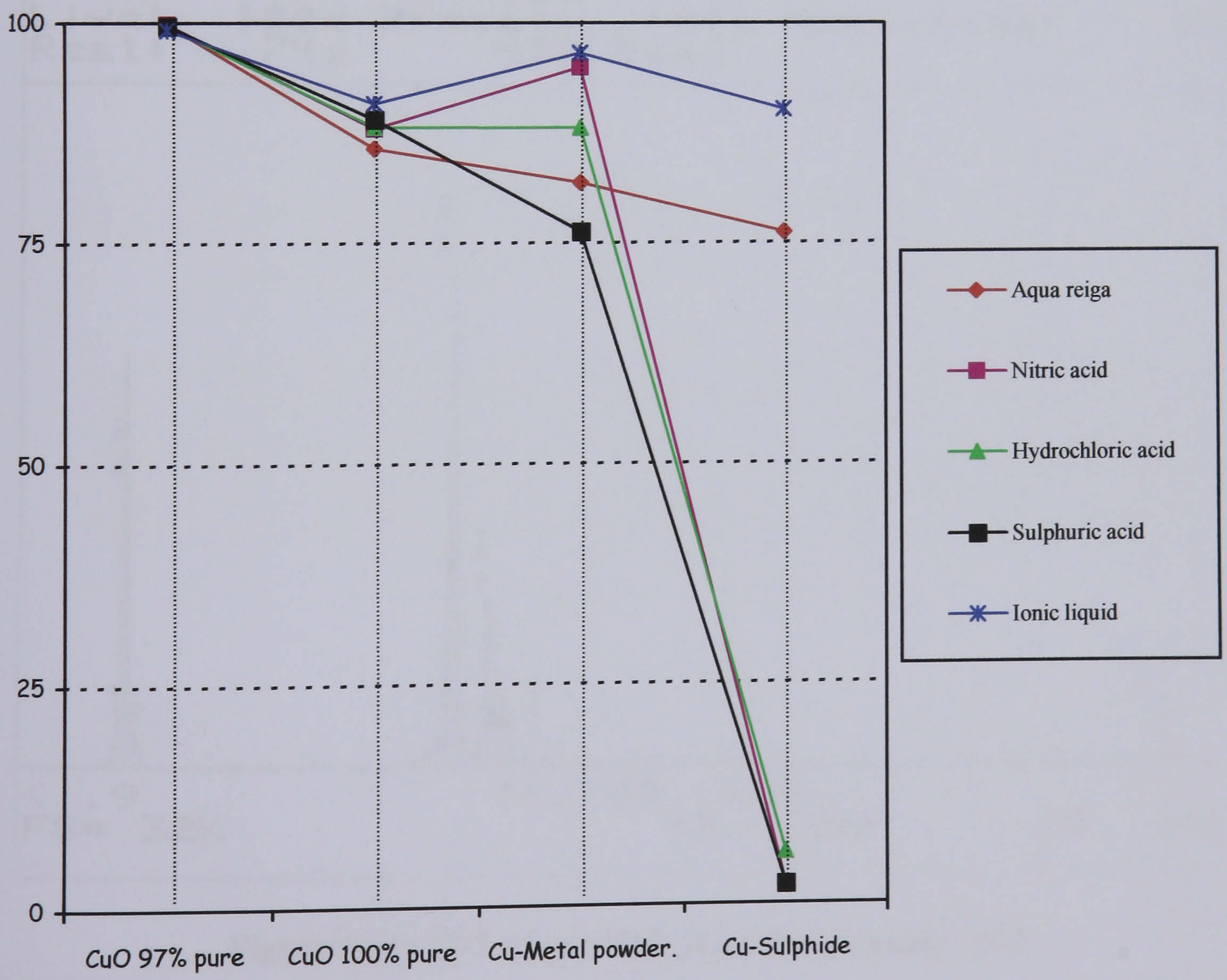


Figure 5.18: Comparison of copper metal and oxide solubility between traditional solvents and 1-(2-cyanoethyl)-3-methylimidazolium bromide

5.3.3.4 Solubility of industrial waste sample containing copper and zinc

A spent catalyst industrial sample, containing 45 % Cu and 22 % Zn, was used to investigate the leachibility of Cu and Zn. The presence of Cu and Zn, and the absence of other metals, in the catalyst was confirmed by XRF (Figure 5.19). A sample of this material was treated with the RTIL. The recovery data show that more than 99 % of the copper and more than 94 % of the zinc can be recovered by leaching with the RTIL, when water is added after the complexing reaction (Table 5.10). When the complexing reaction takes place in the presence of water (Table 5.11), the extraction of copper is 99 % but only 4 % of zinc was extracted. The data in Figure 5.20 suggest that this latter reaction can be used, as a near selective method, for the separation of copper from zinc and RTILs may be suitable solvents for metal recoveries from mixed metal industrial wastes.

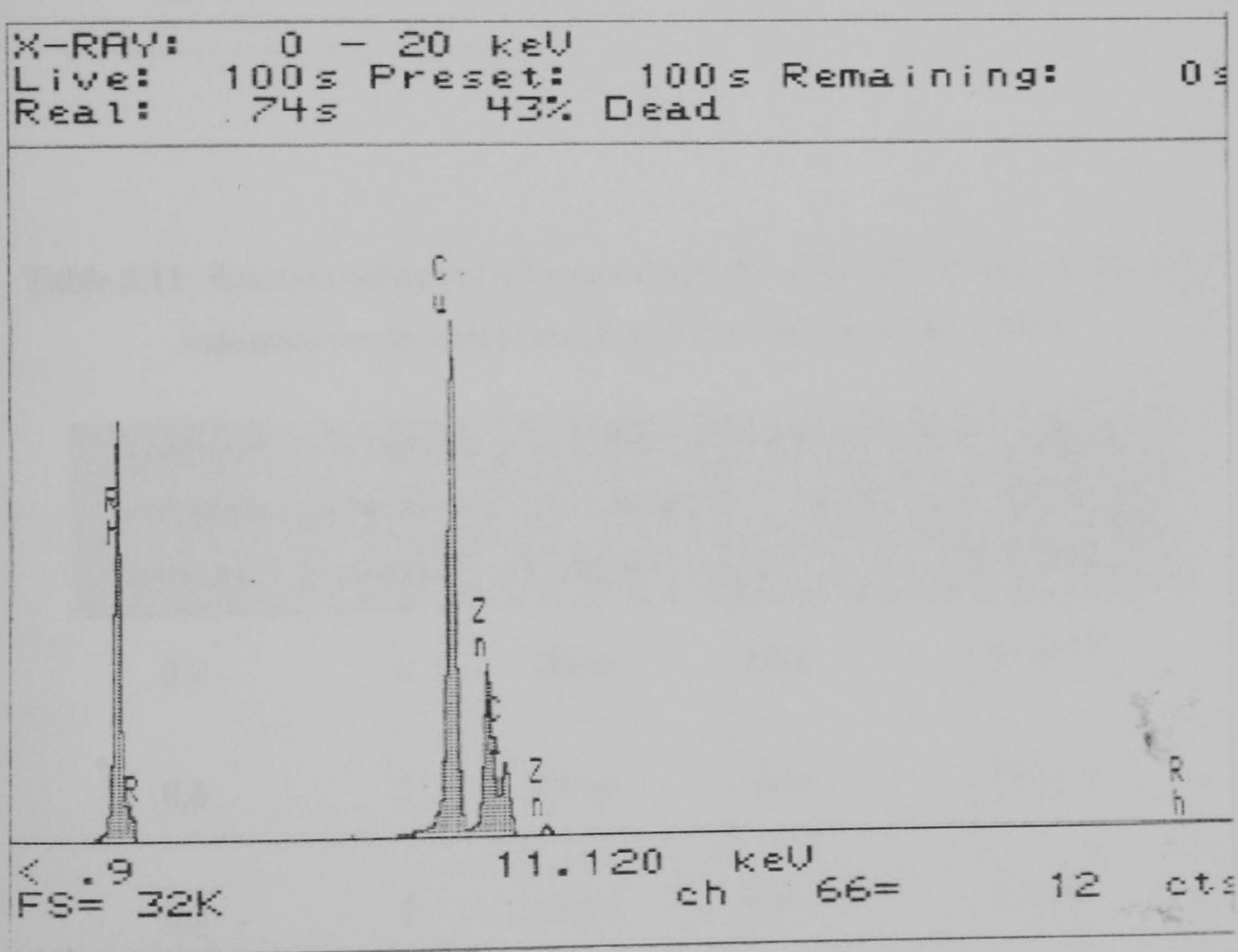


Figure 5.19: XRF trace of industrial waste sample 1879

Table 5.10: Reaction between 1-(2-cyanoethyl)-3-methylimidazolium bromide and industrial waste sample number 1879 in the absence of water

Weight of metal waste used (g)	Weight of ionic liquid used (g)	Colour without water	Colour with water	Metals dissolved (%)
0.2	2	Green	Blue	99.8 Cu
0.5	5	Green	Blue	99.0 Cu
0.2	2	Green	Blue	94.5 Zn
0.5	5	Green	Blue	92.1 Zn

Table 5.11: Reaction between 1-(2-cyanoethyl)-3-methylimidazolium bromide and industrial waste sample number 1879 in the presence of water

Weight of metal waste used (g)	Weight of ionic liquid used (g)	Colour without water	Colour of with water	Metals dissolved (%)
0.2	2	Green	Blue	99.8 Cu
0.5	5	Green	Blue	99.3 Cu
0.2	2	Green	Blue	3.8 Zn
0.5	5	Green	Blue	3.4 Zn

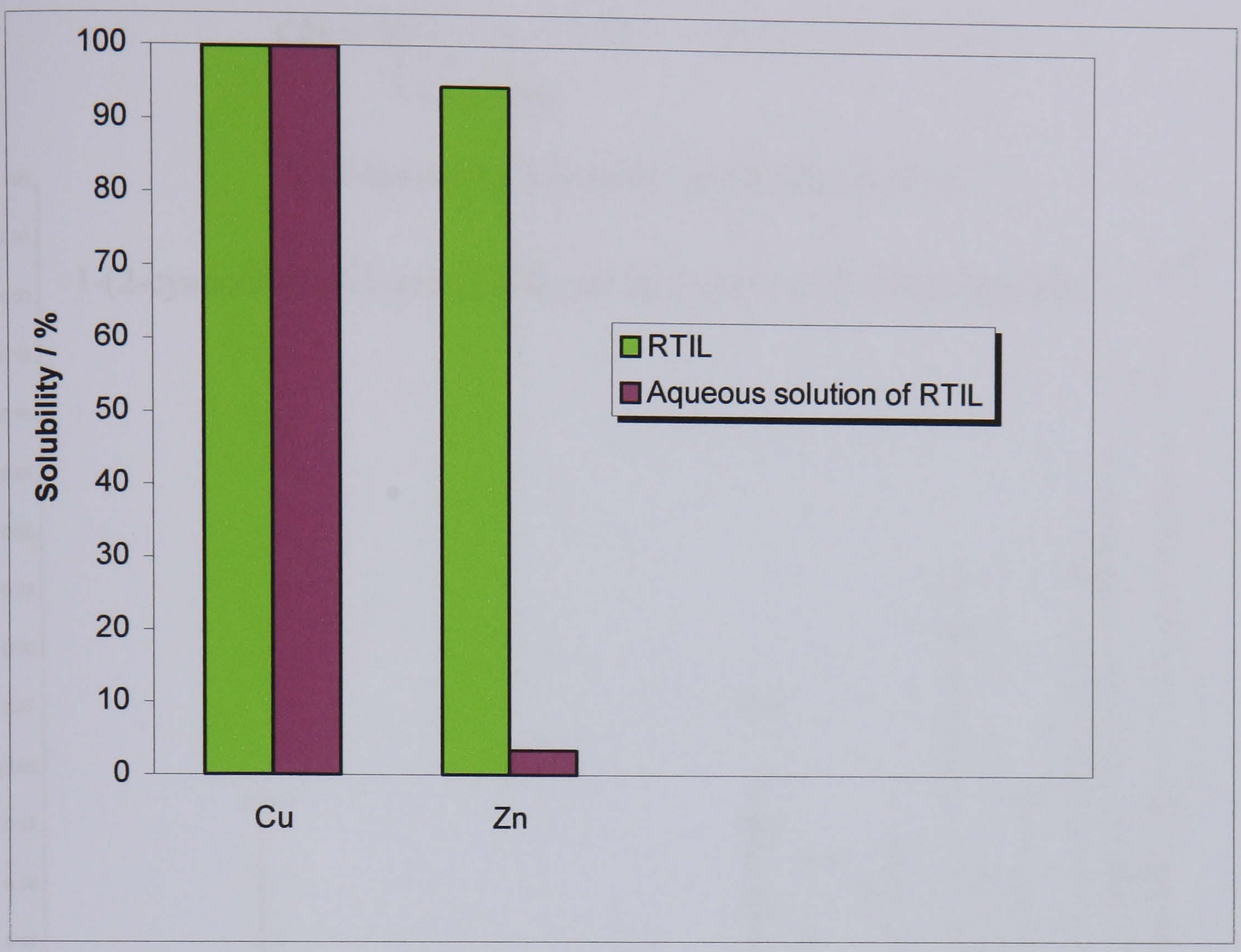


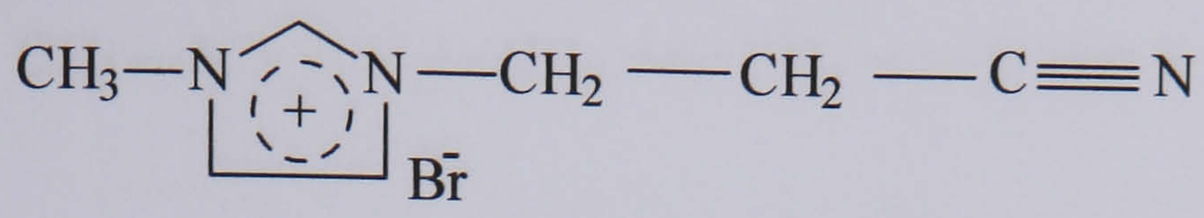
Figure 5.20: Leaching of copper and zinc from the industrial sample in 1-(2-cyanoethyl)-3-methylimidazolium bromide and in aqueous solution of the same ionic liquid.

5.3.4 Characterisation of metal-RTIL complexes

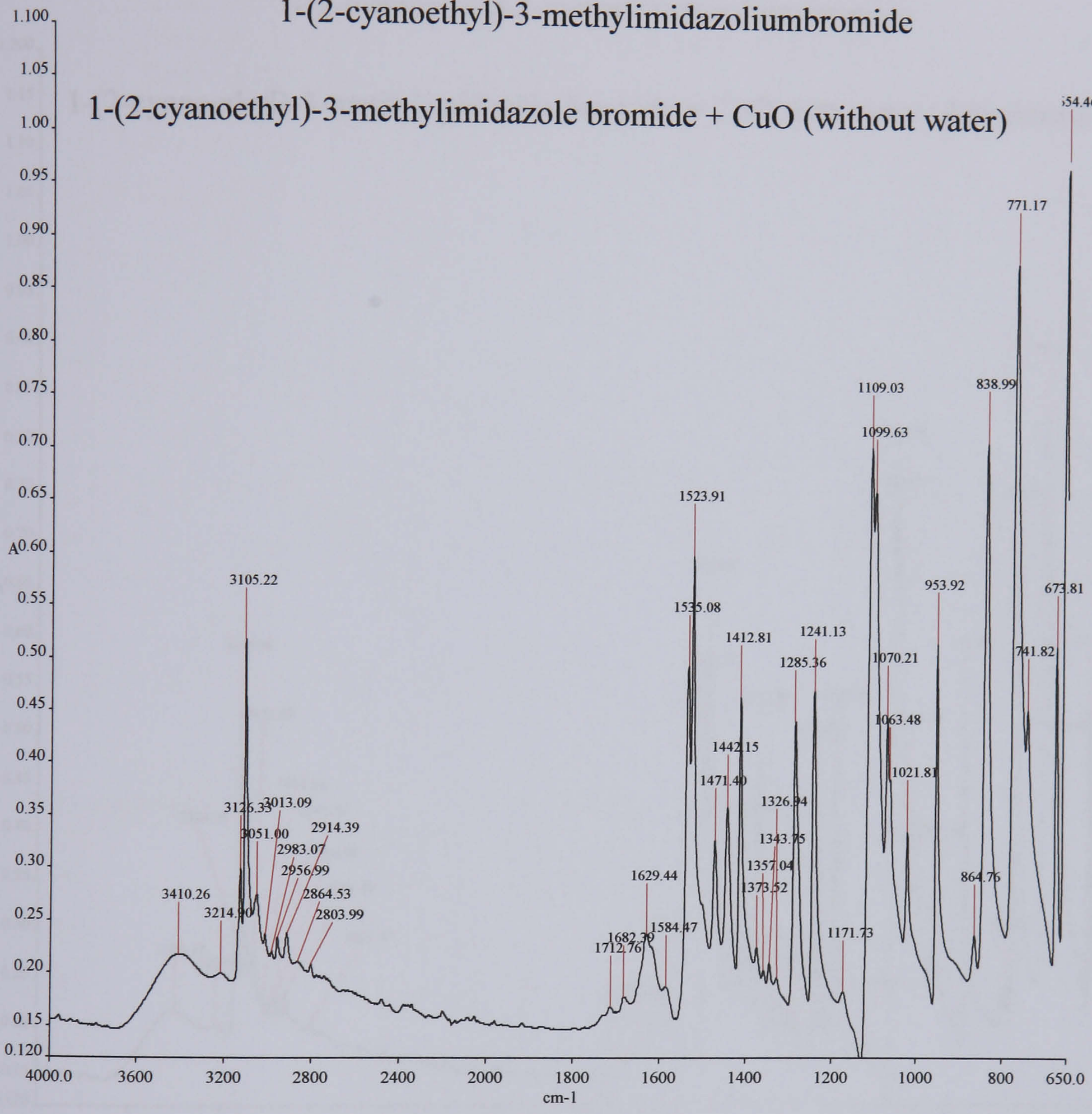
1-(2-cyanoethyl)-3-methylimidazolium bromide complexes with copper (II) were characterized by their infrared and UV-visible spectra and X-ray diffraction of solidified products.

5.3.4.1 Infrared Spectra

Figure 5.21 shows the infrared spectrum of 1-(2-cyanoethyl)-3-methylimidazolium bromide containing copper in the absence of water. Figure 5.22 shows the infrared spectrum of dehydrated Cu-RTIL complex. Dean - Stark method was used to remove water to obtain a solid product from the aqueous solution of RTIL containing copper. The comparison of these spectra shows that there is no significant difference between the absorption bands.

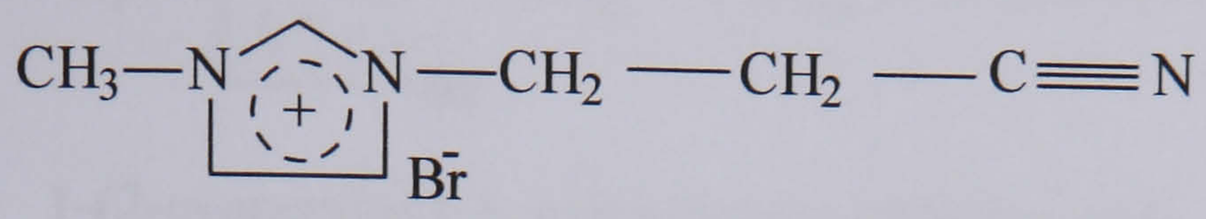


1-(2-cyanoethyl)-3-methylimidazoliumbromide



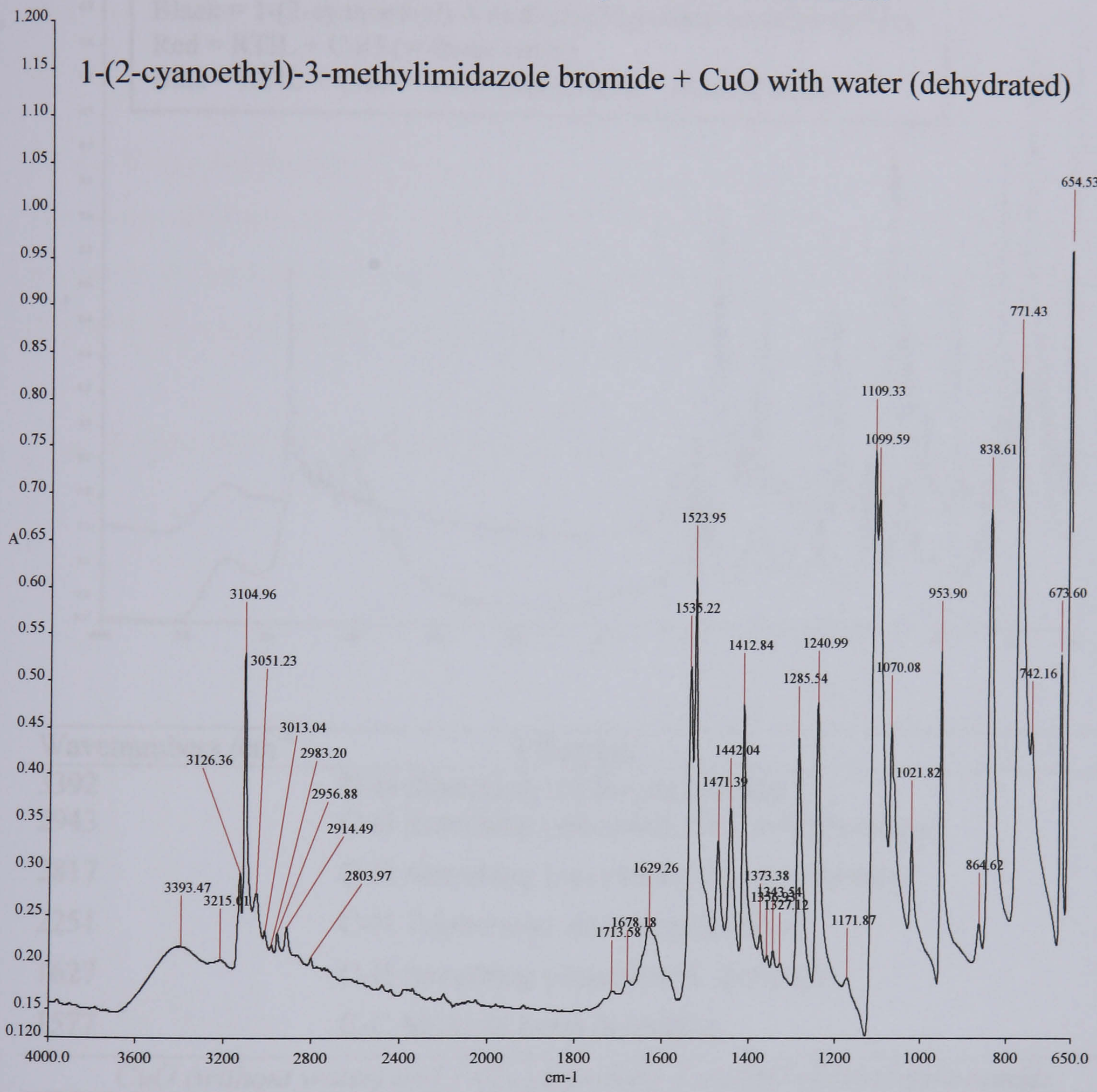
Wavenumbers /cm^{-1}	Vibration
3410	O-H Stretching (hydrogen bonded)
3104	C-H Stretching (saturated, CH_3, antisymmetric)
2864 – 2803	C-H Stretching (saturated, CH_2, symmetric)
2251	C-N Triple bond stretching (nitriles)
1682	C-C multiple bond Stretching (unsaturated, isolated)
1629 – 1584	C-C multiple bond Stretching (unsaturated, conjugated)

Figure 5.21: IR spectrum of mixture of 1-(2-cyanoethyl)-3-methylimidazolium bromide + CuO (without water)



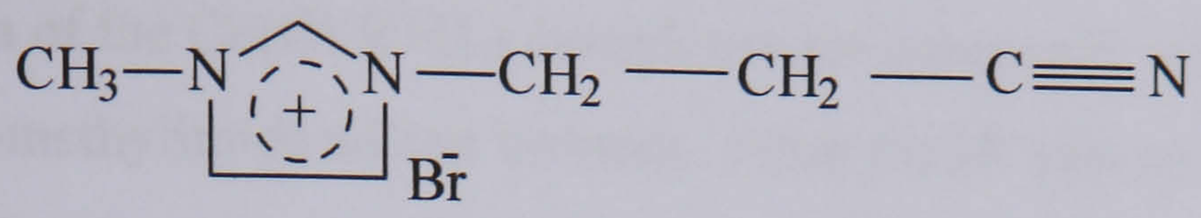
1-(2-cyanoethyl)-3-methylimidazoliumbromide

1-(2-cyanoethyl)-3-methylimidazole bromide + CuO with water (dehydrated)

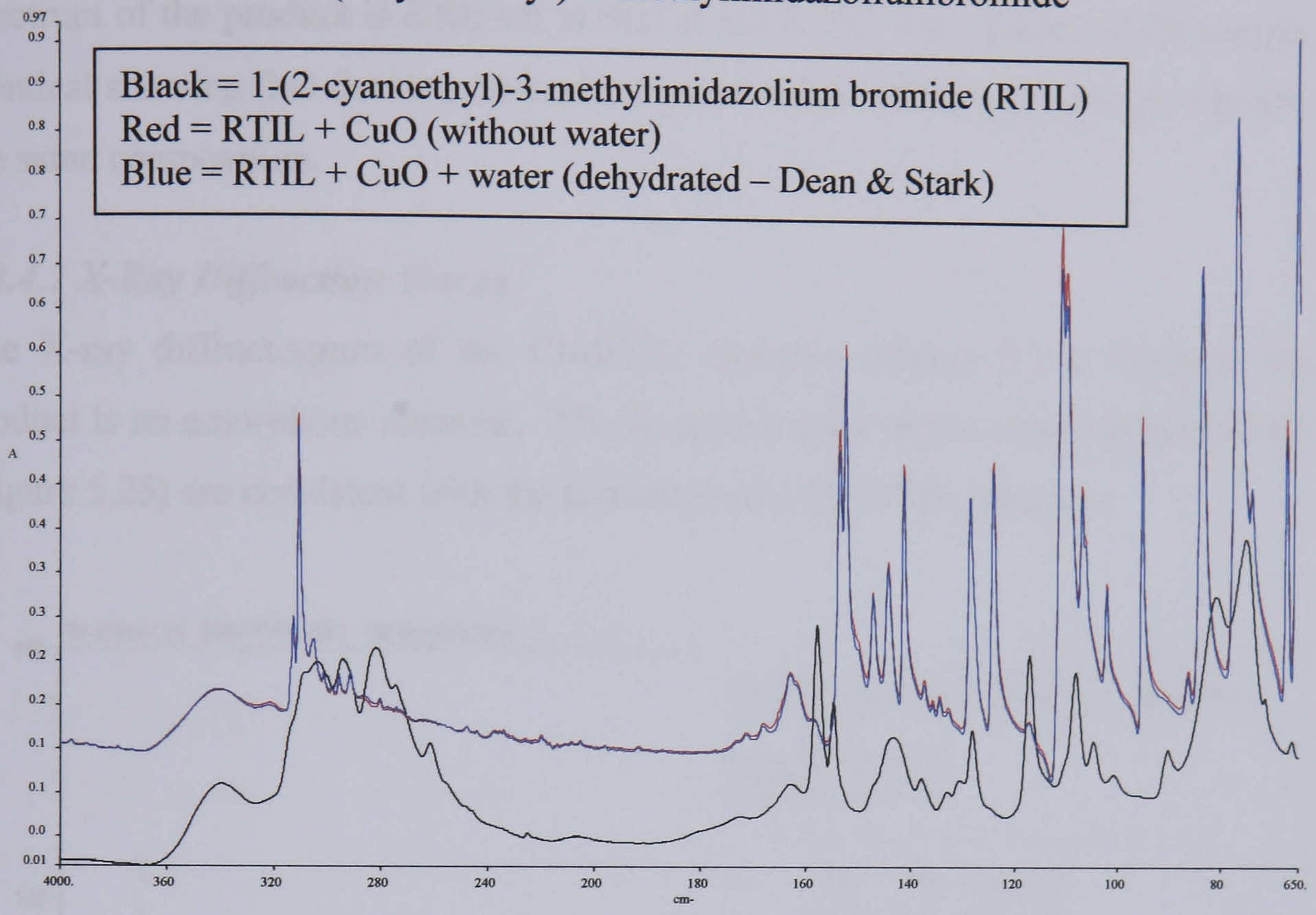


Wavenumbers /cm^{-1}	Vibration
3393	O-H Stretching (hydrogen bonded)
3104	C-H Stretching (saturated, CH_3, antisymmetric)
2818	C-H Stretching (saturated, CH_2, symmetric)
2251	C-N Triple bond stretching (nitriles)
1682	C-H Stretching (alkene, isolated)
1629	C-C Multiple bond Stretching

Figure 5.22: IR spectrum of mixture of 1-(2-cyanoethyl)-3-methylimidazolium bromide + CuO + water (dehydration – Dean - Stark)



1-(2-cyanoethyl)-3-methylimidazoliumbromide



Wavenumbers /cm^{-1}	Vibration
3392	O-H Stretching (hydrogen bonded)
2943	C-H Stretching (saturated, CH_3, antisymmetric)
2817	C-H Stretching (saturated, CH_2, symmetric)
2251	C-N Triple bond stretching (nitriles)
1627	C-H Stretching (unsaturated, isolated)
1577	C-C Multiple bond Stretching

CuO (without water) and 1-(2-cyanoethyl)-3-methylimidazolium bromide

Wavenumbers /cm^{-1}	Vibration
3410 – 3013	O-H Stretching (hydrogen bonded)
2983 – 2956	C-H Stretching (saturated, CH_3, antisymmetric)
2864 – 2803	C-H Stretching (saturated, CH_2, symmetric)
1682	C-C Multiple bond Stretching (unsaurated, isolated)
1629 – 15 84	C-C multiple bond Stretching (unsaturated, conjugated)

Figure 5.23: IR spectra of 1-(2-cyanoethyl)-3-methylimidazolium bromide, 1-(2-cyanoethyl)-3-methylimidazolium bromide + CuO (without water) and 1-(2-cyanoethyl)-3-methylimidazolium bromide + CuO with water (dehydrated)

The infrared spectra of the Cu(II) RTILs complexes are compared with the IR spectra of 1-(2-cyanoethyl)-3-methylimidazolium bromide. From the IR spectra in Figure 5.23 it is obvious that there has been a reaction between the copper oxide and the RTIL as the spectrum of the product is different to that of the RTIL. The spectra of the complex are identical showing that the two methods of preparations of the complex gave products of the same composition.

5.3.4.2 X-Ray Diffraction Traces

The X-ray diffractogram of the Cu-RTIL complex (Figure 5.24) confirms that the product is an amorphous material. The disappearances of the characteristics CuO lines (Figure 5.25) are consistent with the formation of a Cu-RTIL complex.

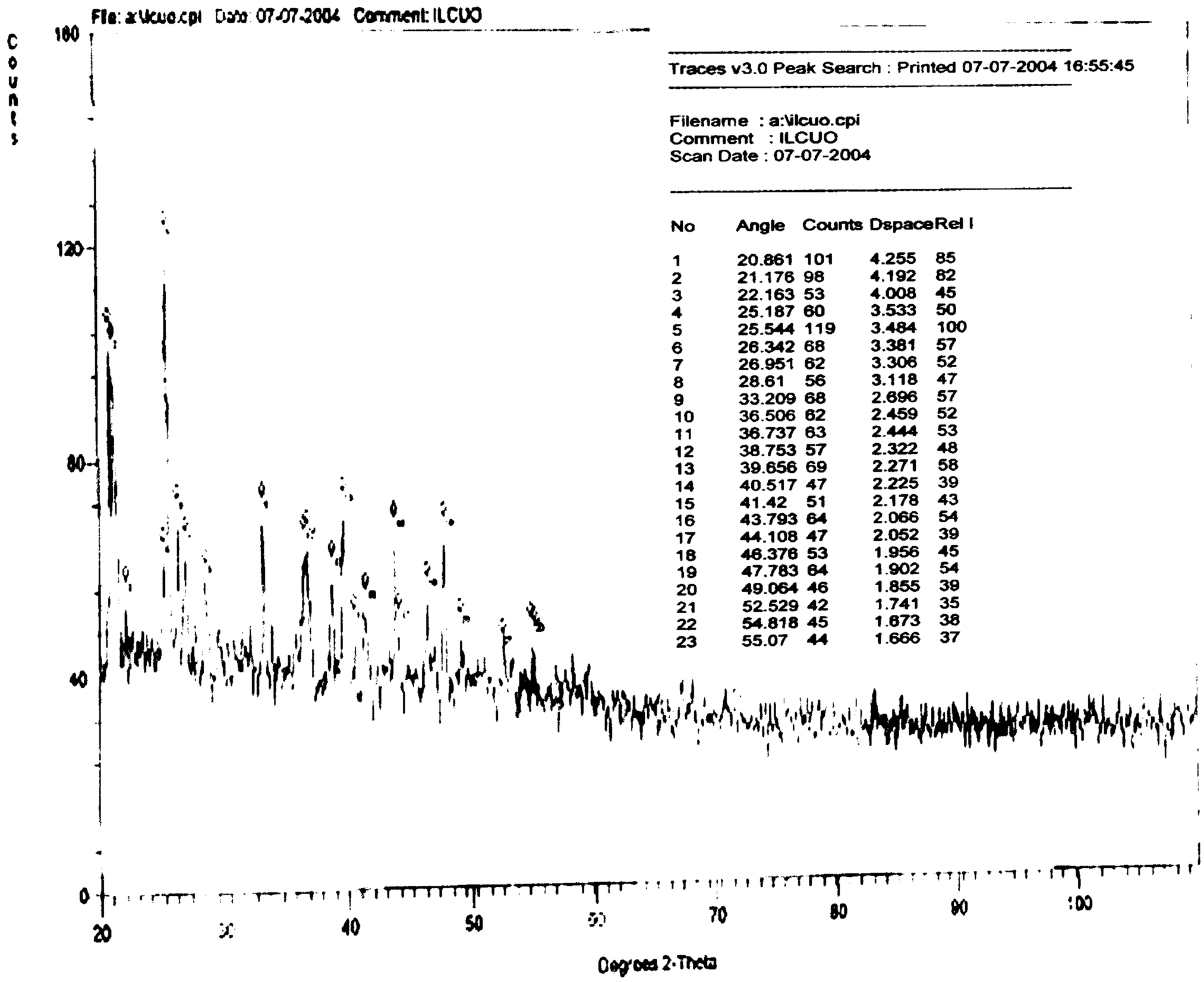


Figure 5.24: X-ray diffractogram of Cu-RTIL complex obtained after dissolving CuO powder in 1-(2-cyanoethyl)-3-methylimidazolium bromide

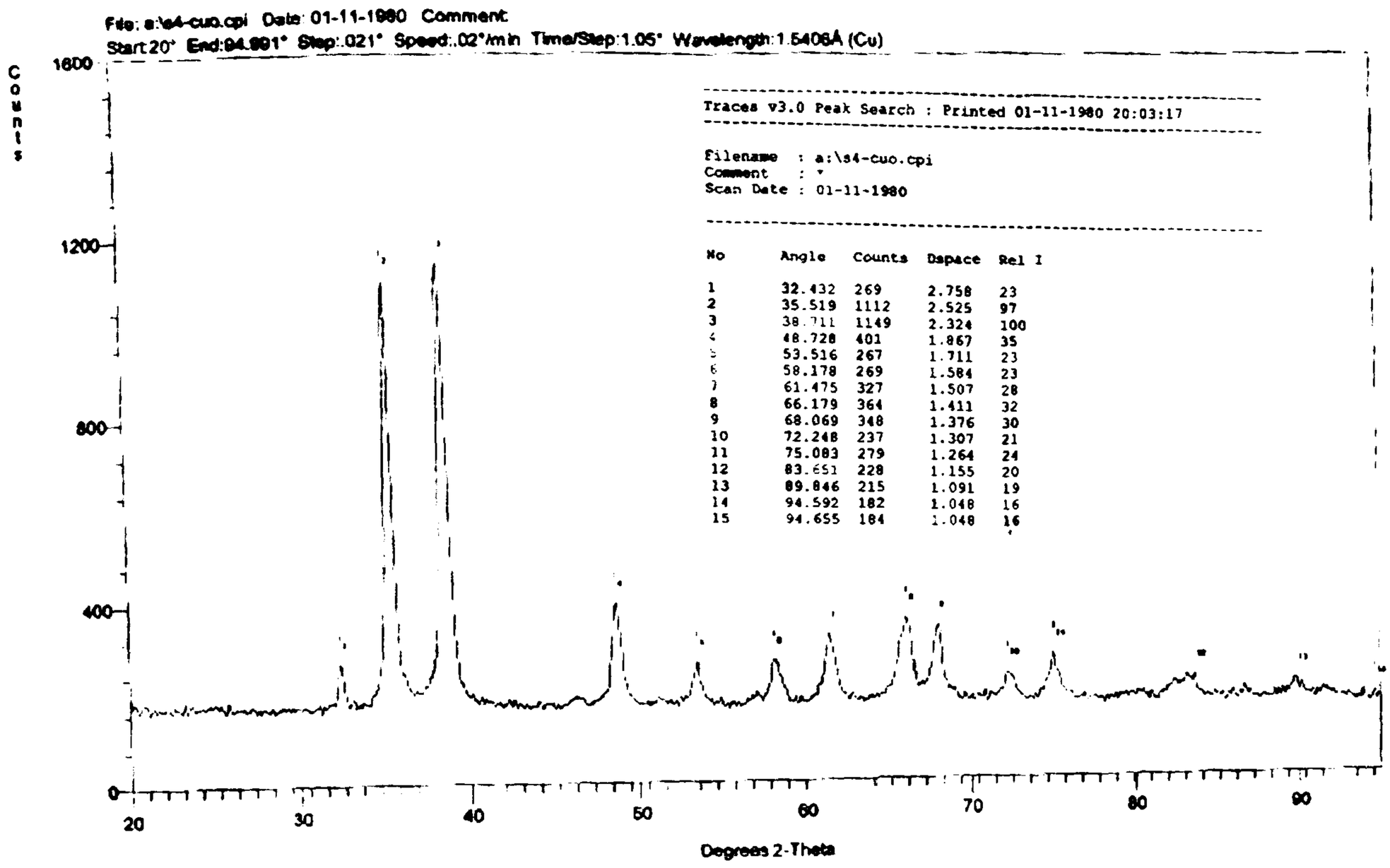


Figure 5.25 : X-Ray diffractogram of CuO powder

5.3.4.3 UV/visible Spectra

UV/visible spectra of the Cu (II) – RTIL complexes are compared with the UV/visible spectra of 1-(2-cyanoethyl)-3-methylimidazolium bromide and 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride in Figures 5.26 and 5.27 respectively.

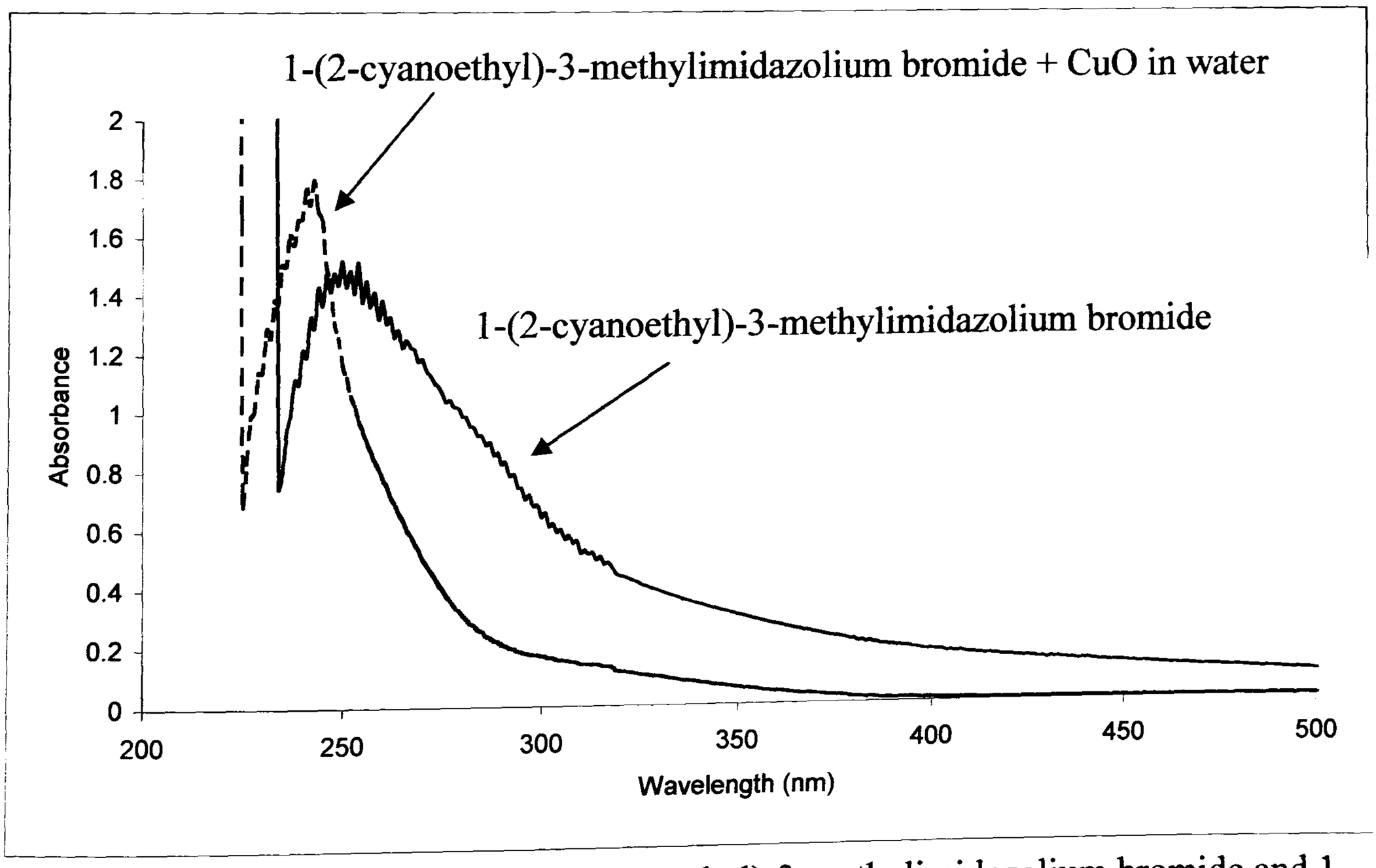


Figure 5.26: UV/vis spectra of 1-(2-cyanoethyl)-3-methylimidazolium bromide and 1-(2-cyanoethyl)-3-methylimidazolium bromide + CuO in water

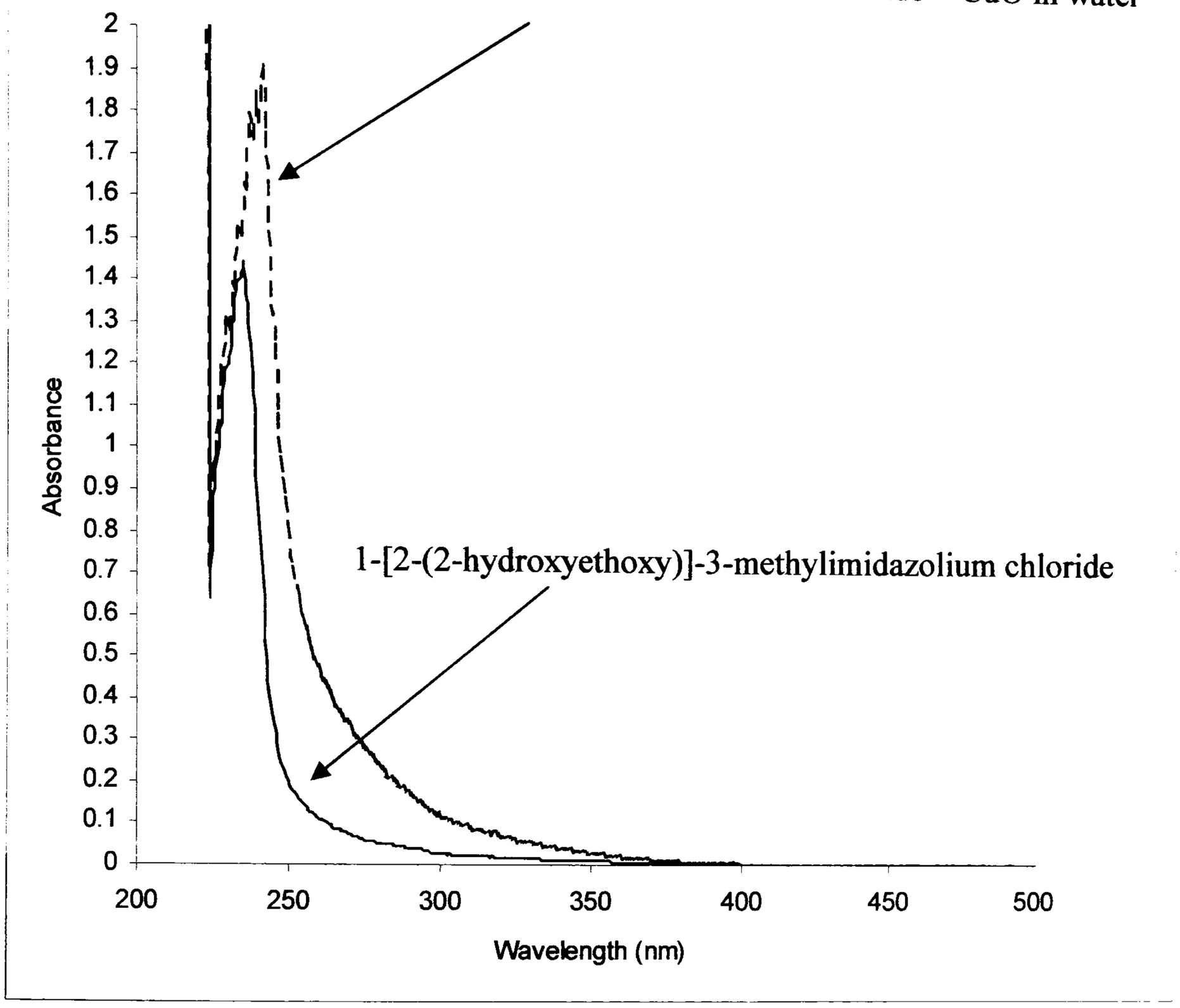


Figure 5.27: UV/vis spectra of 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride and 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride + CuO in water

A study of the UV spectra shows that all the peaks in the spectra occur in a small envelope of wavelength i.e, 225-250 nm. In the case of Cu (II) – 1-(2-cyanoethyl)-3-methylimidazolium bromide complex the peak has shifted towards lower wavelength and this corresponds to hypsochromic shift (Figure 5.26). In the case of Cu - 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride complex there is an increase in the absorption and this corresponds to hyperchromic effect (Figure 5.27). The observed changes in the UV spectra have lead to the conclusion that the copper is complexed with the RTILs.

5.4 CONCLUSIONS

Industrial solid wastes and secondary metal residues containing heavy metal content are significant for their ability to produce adverse effects on human, plants and, especially, the aquatic environment. These wastes can contain a variety of metals including cadmium, mercury, copper, nickel, zinc, chromium, manganese, cobalt, lead and arsenic. Traditionally, most metals from industrial solid wastes are extracted using standard leaching media such as hydrochloric, nitric and sulfuric acids. These leaching media are not generally selective and the resultant solutions after the leaching process usually contain more than one metal. The recovery and recycling of each individual metal from these mixed metal solutions generally requires an additional purification step. Most purification methods involve the use of traditional organic solvents that have low vapour pressures and evaporate easily at room temperature. The high concentrations of these volatile organic compounds can lead to environmental damage by producing secondary pollutants in the atmosphere. The aim of the work described in this chapter was to develop efficient techniques for the treatment and recovery of metal values especially from solid industrial waste or secondary metal residues, which could eliminate the use of volatile organic solvents.

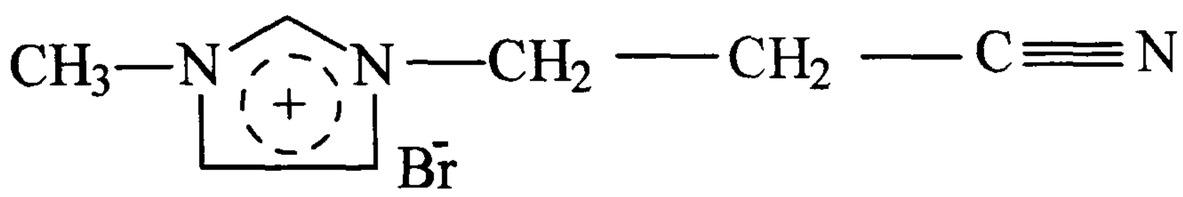
In order to improve the efficiency and viability of metal recovery and treatment, the use of alternative and novel technologies has been investigated in this work. The technology is based on the application of room temperature ionic liquids (RTILs) as selective solvents for the recovery and recycling of heavy metals. The work described in this chapter involved:

- The synthesis and characterisation of RTILs
- The measurement of the solubility of heavy metals and their compounds in selected RTILs
- The effects of the addition of water to metal-RTIL solutions
- The identification of complex formation in solutions of metal ions in RTILs
- Selective extraction of heavy metals from industrial waste samples using RTILs

The synthesis, characterization and application of eight ionic liquids (not previously reported in the chemical literature), were investigated in this work. The synthesis involved a novel microwave-assisted methodology.

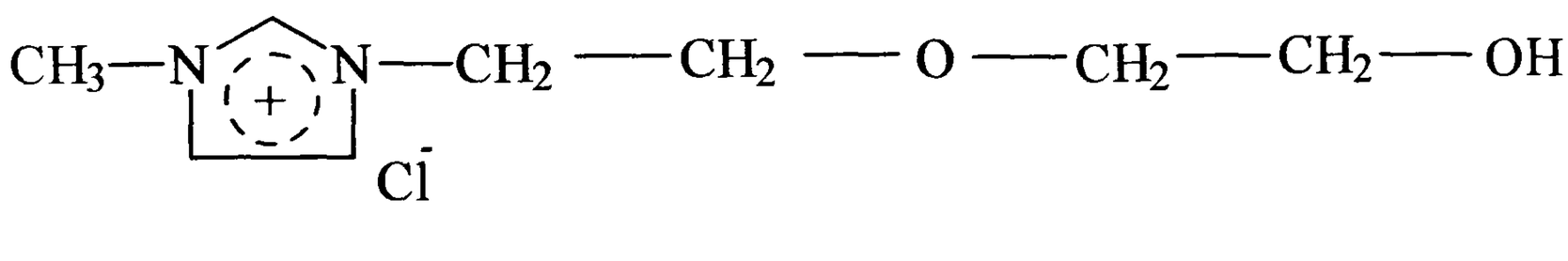
The RTILs synthesised differed by increasing and decreasing the chain length of the cation moiety in the RTIL and changing the position of the functional groups. The compounds prepared were:

a)



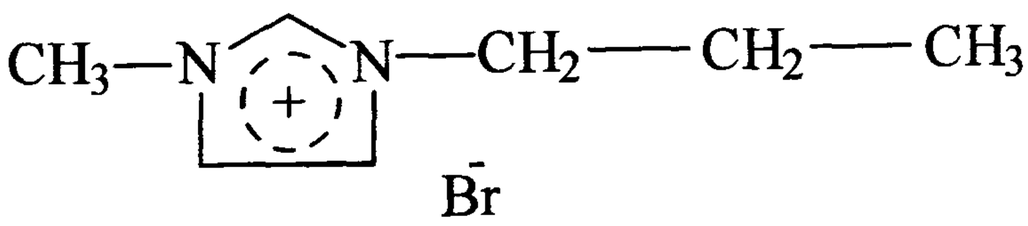
1-(2-cyanoethyl)-3-methylimidazoliumbromide

b)



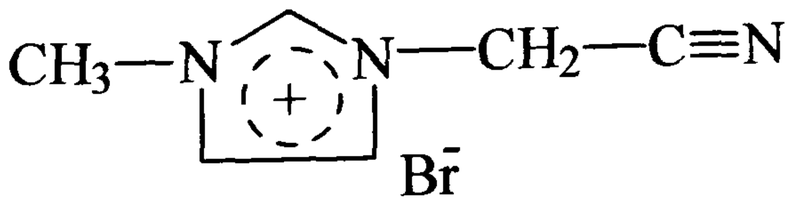
1-[2-(2-hydroxyethoxy)]-3-methylimidazoliumchloride

c)



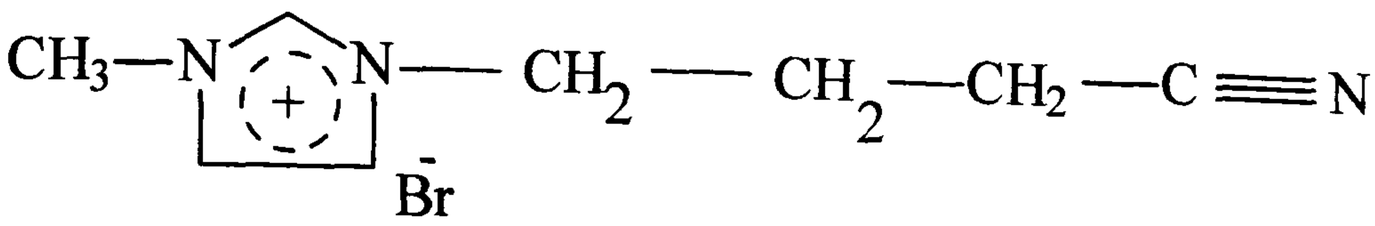
1-methyl-3-propylimidazoliumbromide

d)



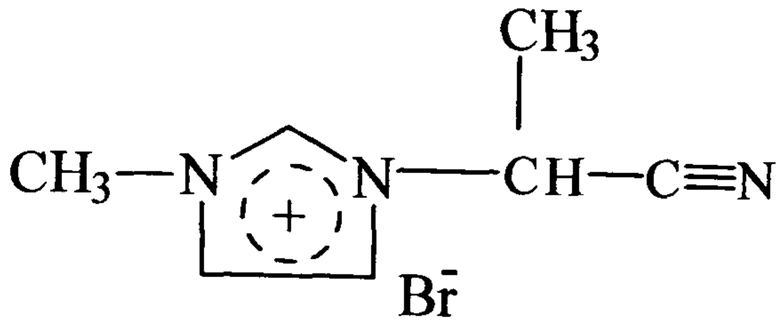
1-cyanomethyl-3-methylimidazolium bromide

e)



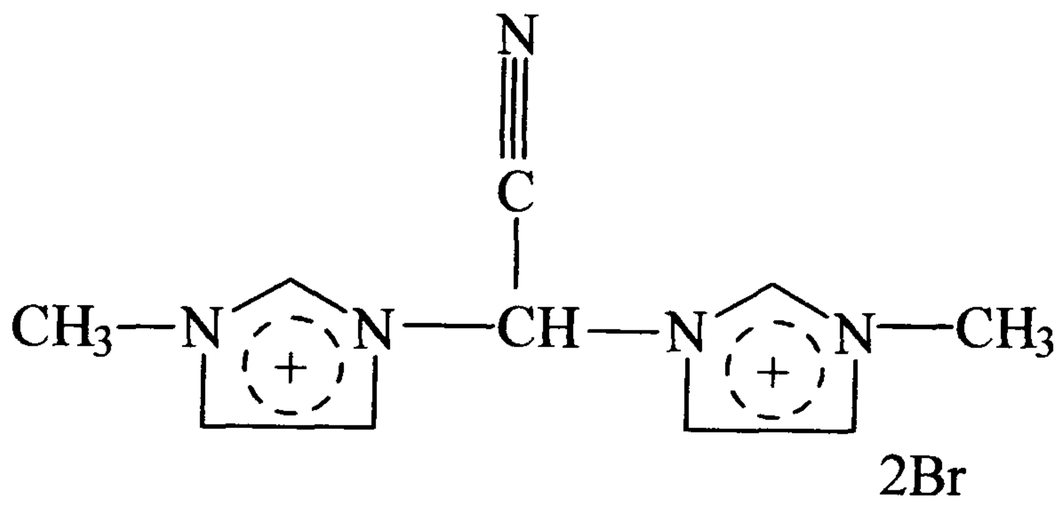
1-(3-cyanopropyl)-3-methylimidazoliumbromide

f)



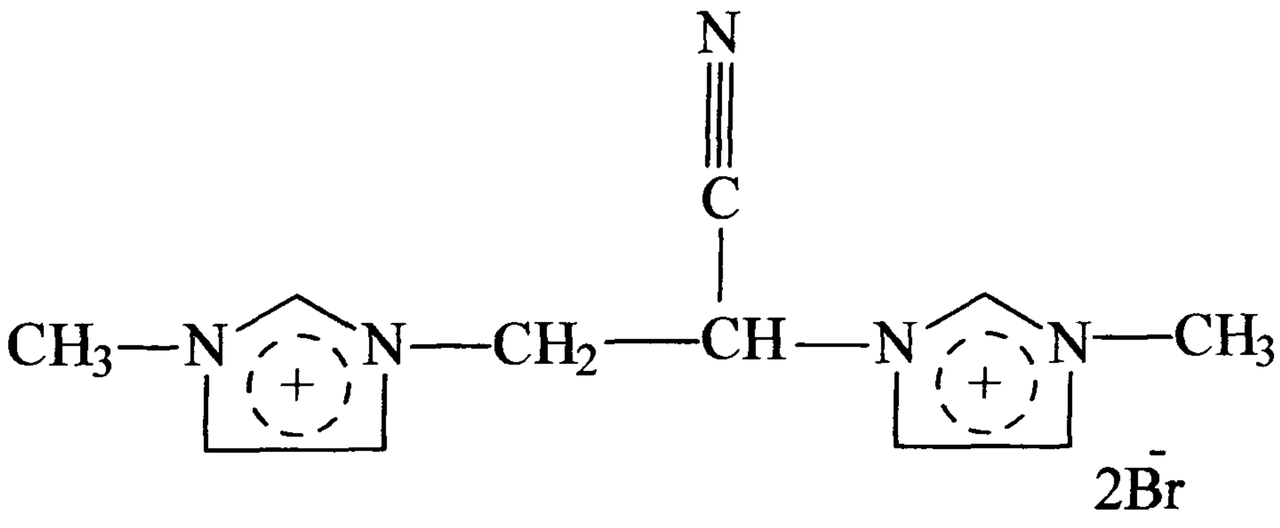
1-(1-cyanoethyl)-3-methylimidazolium bromide

g)



1-cyano-1,1-bis(1-methylimidazolium)methanedibromide

h)



1-Cyano-1,2-bis(1-methylimidazolium)ethanedibromi

Of the eight ionic liquids salts prepared, two were not liquids at room temperature.

- 1-cyanomethyl-3-methylimidazolium bromide was solid at room temperature but became liquid above 90^0C and, although soluble in water, this compound is not an ideal ionic liquid.

- 1-cyano-1,1-bis(1-methylimidazolium)methane dibromide was not useful as an ionic liquid as it is insoluble in organic solvents such as chloroform, dichloromethane and is only partially soluble in water. The remaining six RTILs were clear golden viscous liquids at room temperature.

The purity of the ionic liquids prepared in this work was confirmed using HPLC characterization. Different eluents were required for the different RTILs. The best results for 1-[2-(2-hydroxyethoxy)]-3 methylimidazolium chloride were obtained using methanol and water in the ratio 85:15 as eluent. The best results for the other RTILs were obtained by using acetonitrile and water in the ratio of 95:5 as eluent.

The purity of 1-(2-cyanoethyl)-3-methylimidazolium bromide and 1-[2-(2-hydroxyethoxy)]-3-methylimidazolium chloride was also confirmed by their UV/visible spectra and the 1-(2-cyanoethyl)-3-methylimidazolium bromide ionic liquid by its IR spectra and mass spectrum.

The results obtained in this work show that both metal powders and metal oxides dissolve in RTILs but that the extent of solubility depends upon:-

(1) the composition of the RTIL

(2) the metal or metal oxide studied.

The solubility of copper (II) oxide, for example, varies from 12.2 % in 1-(3-cyanopropyl)-3-methylimidazloium bromide to 99.2 % in 1-(2-cyanoethyl)-3-methylimidazolium bromide. The oxides of cobalt, nickel and zinc are also very soluble (>92 %) in this solvent. The metal powders, copper, zinc, cobalt and nickel, are also soluble in 1-(2-cyanoethyl)-3-methylimidazolium bromide, with copper and zinc being very soluble (>96 %), and with cobalt (35 %) and nickel (26.9 %) being less soluble (Table 5.4). The metal solutions in the solvent can be diluted with water without precipitating a metal compound. Mixtures of RTILs and water, however, do not, in general, lead to good solvent properties and, apart from copper (II) oxide which has a solubility of 99.7 % in the 1-(2-cyanoethyl)-3-methylimidazolium bromide-water mixture, all other oxides studied (CoO, Cr_2O_3, Fe_2O_3, SnO, ZnO, CoO, NiO and MnO) have low solubility (<4 %). There is evidence that the presence of impurities in copper (II) oxide does aid the dissolution of the metal with pure CuO being only 14.9 % soluble

in a RTIL-water mixture compared with 99.7 % solubility of a 97 % pure sample of CuO (Table 5.5). The low solubility of metals and metal oxides in 1-[2-(2-hydroxyethoxy)]-3-methylimidazoliumchloride confirm that the solubilities depend on the composition of the RTIL (Table 5.6).

The colours formed when transition metals are dissolved in RTILs are consistent with complex formation between the transition metal and the RTIL. The colour changes with the addition of water suggesting replacement of the RTIL donor with water molecules. The blue colour of solutions of cobalt(II) in RTILs suggests that a tetrahedral complex is formed with RTIL donor groups and the change in colour to pink on addition of water would be consistent with formation of the $Co(H_2O)_6^{2+}$ ion with only water co-ordinated to the metal.

The solubility of copper sulfide in the RTIL is particularly interesting. CuS is the major copper mineral but recovery of copper by non-smelter techniques is not economic because of the low solubility in acids (apart from *aqua regia*, which would not be economically viable as a leaching material). The relatively high solubility in 1-(2-cyanoethyl)-3-methylimidazolium bromide, however, suggests that RTILs could provide a suitable leach medium for the recovery of copper from, particularly, low-grade copper sulfide minerals.

Preliminary experiments have been carried out on mixed-metal wastes by studying an industrial waste arising containing both copper and zinc. The results show that greater than 99 % of the copper and greater than 92 % of the zinc can be recovered in solution in 1-(2-cyanoethyl)-3-methylimidazolium bromide, when water is added after the complexing reaction. In the case of RTIL-water mixtures, however, although the extraction of copper was 99 % only 4% of zinc was extracted. This suggests that RTILs can be used as a near selective leach material for the separation of copper from zinc.

The results obtained in this work show that RTILs can be prepared by low-energy microwave assisted methods. The data show that the solubilities of metals and their compounds do depend upon the RTIL used and that, once dissolved, the solvent can be diluted with water to facilitate metal recovery. The results also show that tailor-making

RTILs to achieve metal-specific dissolution properties should lead to the development of novel recovery and separation techniques to permit recycle of metals from single and mixed-metal wastes and low-grade primary materials.

5.5 REFERENCES

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CHAPTER 6

CONCLUSIONS

Both chemical and product manufacturing industries produce large quantities of waste and effluent streams containing low concentrations of heavy metal ions and organic pollutants that are difficult to recover by available treatment methods that usually involve the use of traditional solvents and generate secondary wastes. The traditional leaching media for the extraction of metal values from mixed solid industrial wastes are not selective and usually produce a solution containing mixed metals. The recovery of individual metals from such solutions usually involves the use of a purification step, for example, solvent extraction or ion exchange processes. These purification processes are expensive and produce secondary wastes that hinder the extension of developed methodologies to industrial scale due to environmental and economic reasons.

Pakistan is a developing country and has spent a huge amount of money and effort to encourage foreign investors and expatriate Pakistanis to invest in the following four main sectors: 1) textile industry, 2) leather industry, 3) pesticides and petrochemical industries, 4) extraction of metals from industrial wastes, end-of-life products and low-grade primary ores. The expansion of these industries has created huge environmental pollution problems associated with the management of their waste streams. These problems originated due to the lack of proper waste management systems and environmental legislation. The PEPA has now introduced and implemented some strict environmental legislation and forced these industries to combat the pollution problems associated with the management of their wastes.

The research work described in this thesis was partly funded by the PEPA and Azad Kashmir University, Pakistan. The overall aim of this research work was to develop sustainable and economically viable treatment technologies that can be applied on industrial scales to combat the environmental pollution problems associated with these four industries.

The specific objectives of this work to meet the requirements of pollution control in Pakistan were:

- To develop treatment technologies, based on electrochemical cell systems, to remove dyes from textile effluent streams.
- To develop treatment technologies, based on electrochemical cell systems, to remove chromium from leather effluent streams.
- To investigate the possibility of using a waste from one industry to treat the waste of another in order to achieve an overall waste minimisation objective.
- To investigate the possibility of developing treatment technologies that can be used for the treatment of mixed textile and leather effluent streams.
- To develop treatment technologies based on catalytic oxidation process to reduce volatile organic compounds VOCs emissions from pesticides and pesticides active ingredients manufacturing industries.
- To synthesise, characterise and investigate the potential use of room temperature ionic liquids (RTILs) for the selective extraction of heavy metal from low-grade ores and solid industrial wastes.

All these objectives have been achieved and the main findings of my research work are now discussed under the following three main headings:

1. Treatment technologies for the removal of dyes from textile and chromium from leather effluent streams.
2. Catalytic oxidation process to reduce the emission of volatile organic compounds.
3. Selective extraction of metal-values using RTILs.

6.1 REMOVAL OF DYES FROM TEXTILE AND CHROMIUM FROM LEATHER EFFLUENT STREAMS

6.1.1 Treatment of Textile Effluent Streams

The results obtained show that the use of both electro-precipitation and electro-oxidation processes can lead to the removal of dyes from textile effluent streams originating from various operations. The use of the electro-precipitation process,

however, produces sludge that needs to be disposed of safely. On the other hand, the use of electro-oxidation does not produce sludge but is unable to remove some of the organic impurities from the textile effluent. The UV/Visible spectra showed that the anodic oxidation of dyes during the electro-oxidation 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, no such intermediate species were formed during the electro-precipitation process.

The electo-precipitation process, with mild steel or aluminium anodes, is an excellent treatment process for the removal of dyes from textile effluent streams. This treatment process does not degrade or oxidise the dye molecules and, therefore, the dye removal process is one of physical adsorption and not dye destruction. Increasing treatment time, corresponding to increasing release of iron or aluminium from the anodes, caused increased removal of colour from the textile wastewater. A treatment time of 30 minutes was found to be the optimum value for the complete removal of dyes from both synthetic solutions and industrial effluent streams.

The use of electro-precipitation process with mild steel anodes has two advantages over the electro-precipitation process with aluminium anodes. The first advantage is that the *in-situ* production of hydroxide precipitate is a better adsorbent material for the removal of all the dye molecules studies in this work compared to aluminium hydroxide. Secondly, iron hydroxide precipitates loaded with dye molecules settled quickly and were easy to filter compared to the gelatinous aluminium hydroxide.

During the electro-oxidation process the degradation or destruction of dye is responsible for colour removal from textile effluent. The data obtained suggest that electro-oxidation is a slow process compared to electro-precipitation. The electro-oxidation process with titanium mesh cathode and mixed metal anodes takes between 30-40 minutes to achieve a complete mineralisation of each dye. It takes over 60 minutes to achieve the same level of degradation when anodic oxidation was carried out using an electro-oxidation process with the use of stainless steel rod cathode and graphite rod anodes. Replacing the stainless steel rod cathode with an aluminium rod can further increase the oxidation time and, in most cases, a complete mineralisation was only achieved after 120 minutes.

In conclusion, both electrochemical processes, electro-precipitation and electro-oxidation, are viable methods of cleaning up textile effluent streams and allow water to be discharged safely into rivers or canals (Figures 6.1 and 6.2). The Ames tests also confirm that the treated effluent streams, by electro-precipitation and or electro-oxidation processes, are also non-mutagenic.

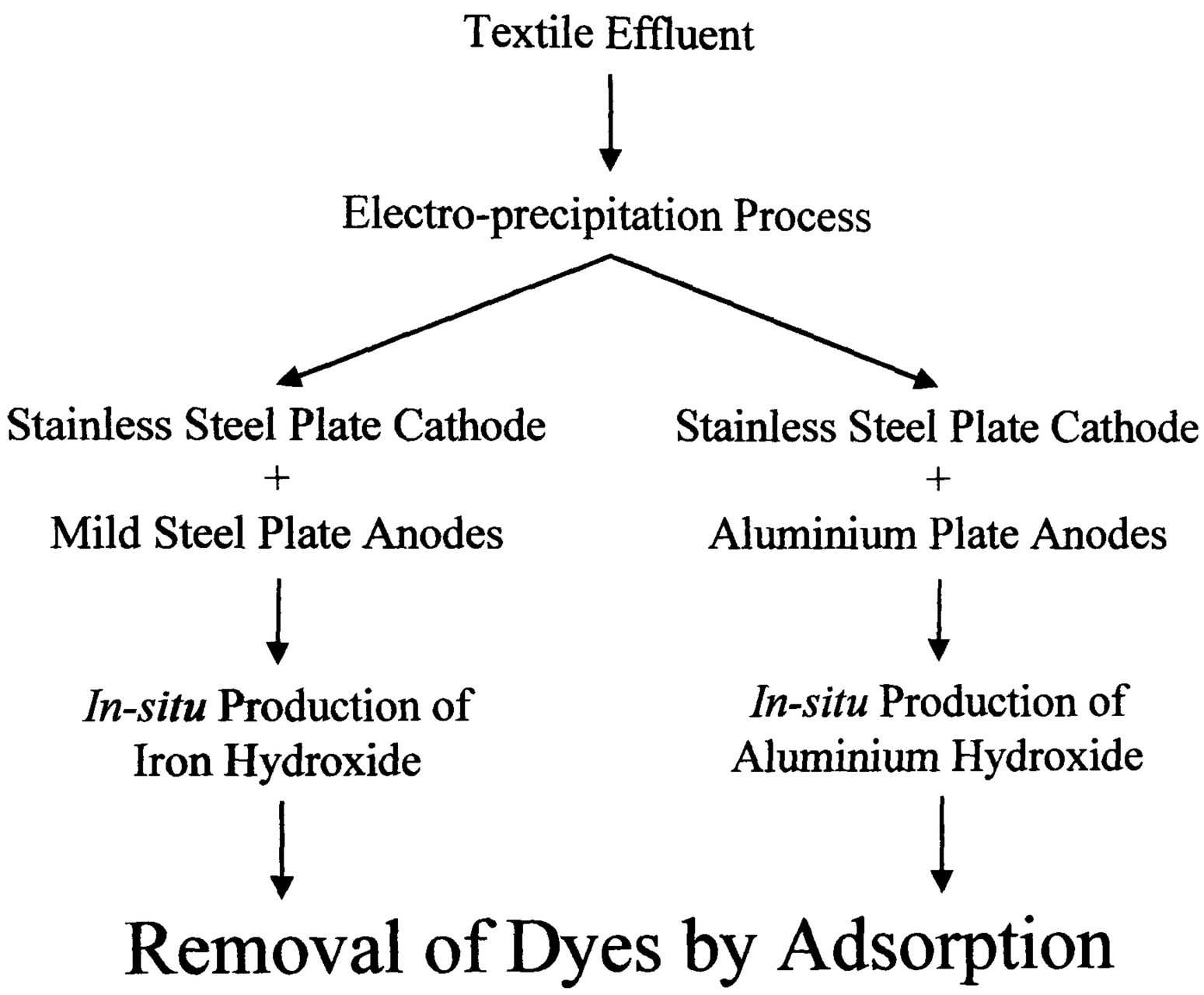

Figure 6.1: Electro-precipitation process for the treatment of textile effluent

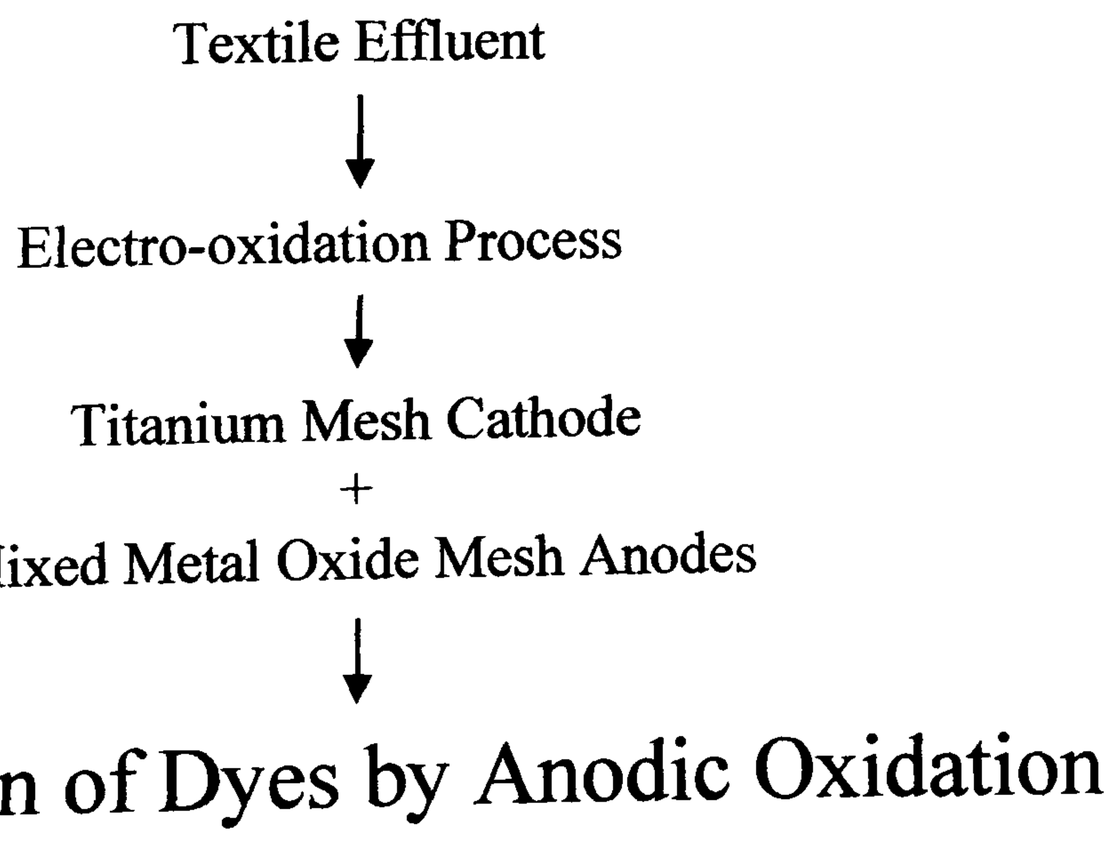

Figure 6.2: Electro-oxidation process for the treatment of textile effluent

6.1.2 Treatment of Leather Effluent Streams

After the successful application of the electro-precipitation process, with mild steel electrodes, for the removal of dyes from textile effluent, the use of this process was extended for the removal of chromium and other toxic inorganic and organic species from leather effluent streams. The treatment of leather effluent streams by the electro-precipitation process produces a mixed Cr (III)/Fe (III) hydroxide sludge consisting mainly of Cr, Fe, fats and other organic impurities. The *in-situ* production of this hydroxide sludge is a simple treatment method that can be used, in developing countries like Pakistan, to remove chromium and other harmful organic species from leather effluent streams (Figure 6.3).

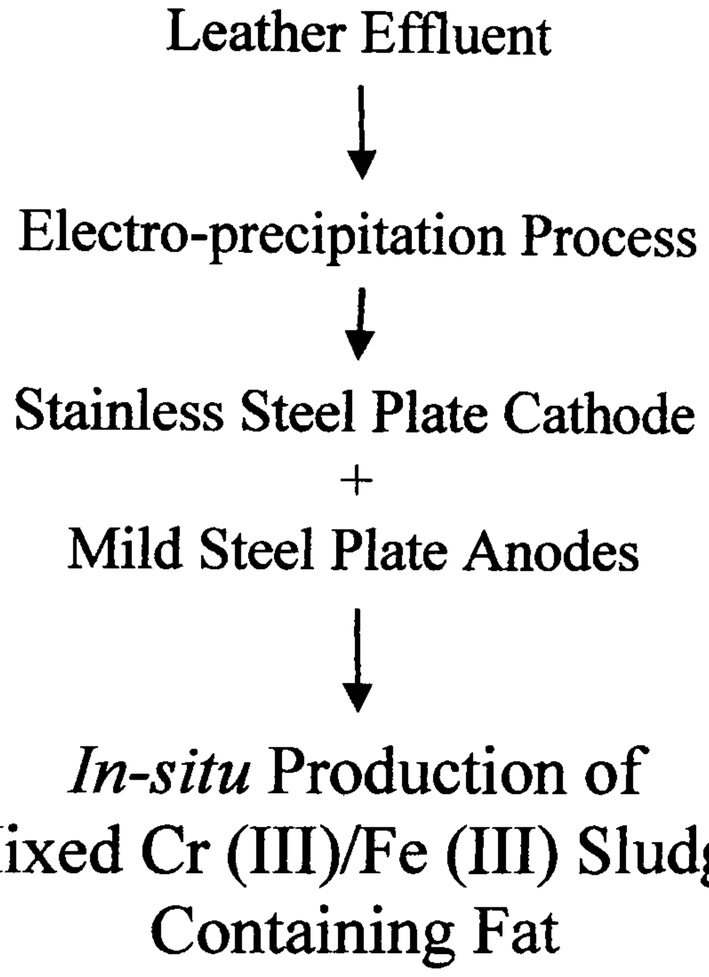

Figure 6.3: Electro-precipitation process for the treatment of leather effluent

The use of this dried mixed Cr (III)/Fe (III) sludge as a low cost adsorbent material for the removal of dyes from textile effluent streams was also investigated. The results obtained show that this mixed waste sludge is not a suitable adsorbent material for most of the dye molecules studied in this work and cannot be used for the complete removal of dyes from both synthetic and industrial effluent streams. The low efficiency of this mixed sludge in dye removal is attributed to the fact that the total available surface area and the active sites were reduced during the drying process. The presence of fats and other organic impurities also block the active sites and in doing so reduce the total surface area of the mixed sludge that resulted in low dye removal. Furthermore, the treated effluents were also mutagenic in nature.

6.1.3 Treatment of Mixed Textile and Leather Effluent Streams

Previous research work carried out at Brunel University proved that mixed Cr (III)/Fe (III) sludge is an ideal adsorbent material and can be used for the removal of methylene blue, reactive blue, congo red and disperse orange from aqueous media. This mixed sludge was obtained by precipitating chromium from etching solution, used to etch away excess copper from printed circuit board, consisting mainly of Cr, Cu, Ni and Fe oxides and hydroxides. The method is based on two steps: 1) preparation of chromium hydroxide from waste etching chromium solution using Fe (II) as a reducing agent and adjusting the pH by using solid sodium hydroxide and 2) using the resultant chromium hydroxide precipitates (washed with water and then dried) as an adsorbent material for dye removal.

The method used in this research work, and described in Chapter 3 of this thesis, is based on mixing the two effluent streams originating from textile and leather industries. This mixed solution was used for the *in-situ* production of mixed Cr (III)/Fe (III) hydroxide sludge using an electro-precipitation process with mild steel electrodes. The toxic Cr (VI) is reduced to Cr (III) by Fe (II), which is generated electrochemically due to the oxidation of mild steel anodes. The *in-situ* production of OH^- ions on the cathode surface initiates the production of mixed Cr (III) / Fe (III) sludge which acts as flocculants/adsorbents and are responsible for the removal of dyes from aqueous effluent streams (Figure 6.4). The results obtained show that the process was successful for the complete removal of chromium and dyes in a single step treatment process.

The *in-situ* production of mixed Cr (III)/Fe (III) hydroxide sludge is an excellent process for the removal of chromium and dye molecules from mixed effluent streams. This process is suitable for developing countries like Pakistan where these two industries are located in close proximity. These results support the idea that a single treatment technology can be used for the treatment of mixed textile/leather effluent streams in order to achieve an overall waste minimisation objective. Industrial trials on the use of this technology has been planned by the PEPA and the prototype units of different sizes are being prepared to be used for the simultaneous removal of chromium and dye molecules from mixed effluent streams. The use of final sludge obtained after the treatment of mixed effluent streams is also being investigated for different industrial applications such as the production of fire or concentrate bricks for pavement. The final

mixed Cr (III)/Fe (III) sludge loaded with dyes can also be landfilled along with other hazardous material.

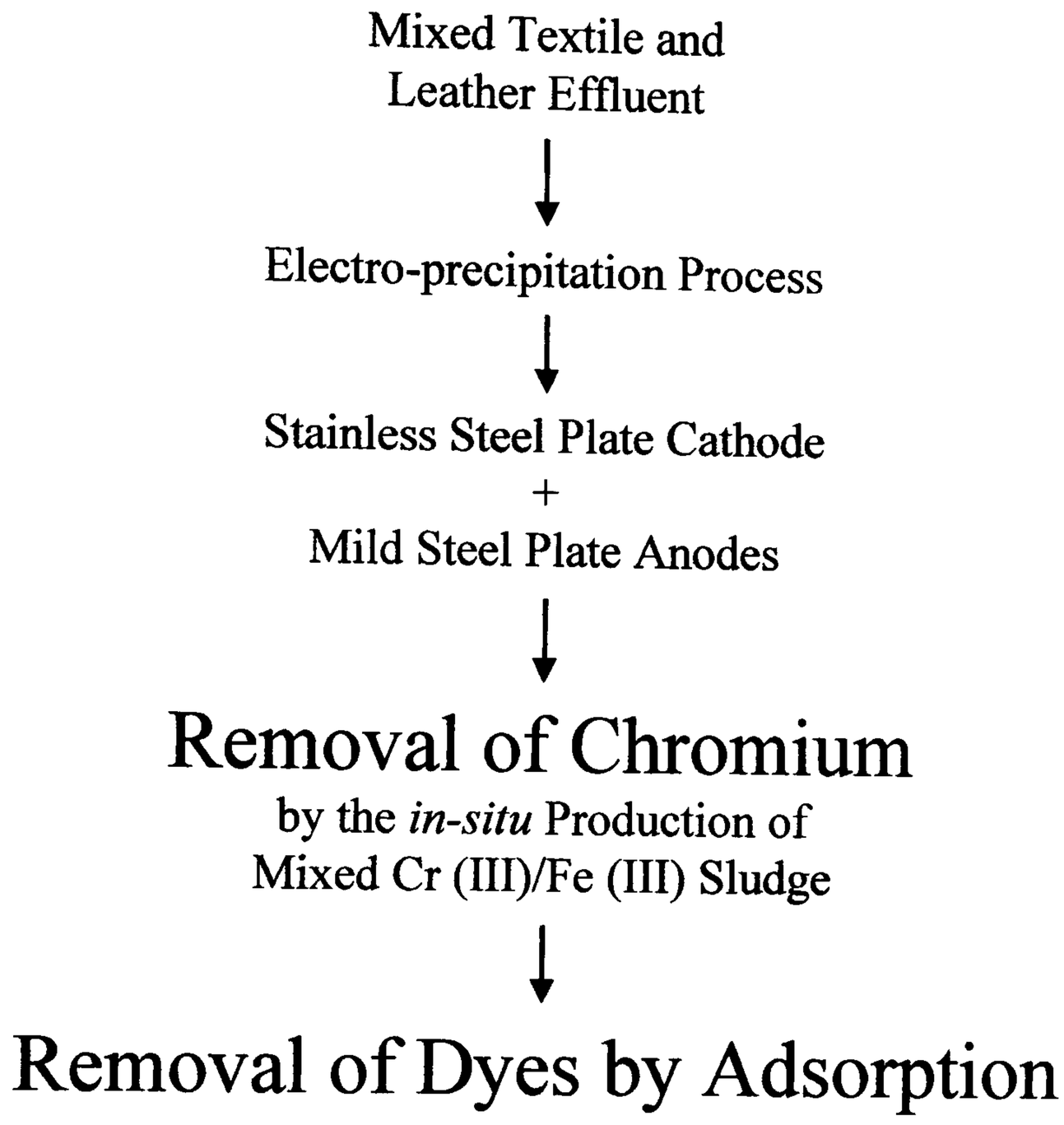

Figure 6.4: Electro-precipitation process for the treatment of mixed textile and leather effluent streams

6.2 CATALYTIC OXIDATION PROCESS TO REDUCE THE EMISSION OF VOLATILE ORGANIC COMPOUNDS

The aim of this work was to synthesise and optimise the use of inexpensive transition metal supported catalysts for the oxidation of volatile organic compounds. The results obtained demonstrated that these catalysts were ineffective in the oxidation of volatile organic compounds at low temperature. The emphasis of this research was then changed to prepare noble metal supported catalysts that could be synthesised and used for the oxidation of volatile organic compounds at low temperature. For this reason a simple method of preparing platinum group metal catalysts on inert supports at low temperatures was developed and used to oxidise toluene, as an indicator of volatile organic compounds. These noble metal catalysts have the capability to destroy toluene

at low temperature and could be installed in the process vents to control the emission of toluene and other volatile organic compounds into the environment.

Experiments were carried out to develop a method to prepare an improved platinum group metal catalyst. The investigation has provided a method of preparing a platinum group metal catalyst by applying the nitric acid solutions containing diammine dinitroplatinum (II) or diammine dinitropalladium (II) (0.2 % Pt or Pd) to carriers and drying and calcining the carriers containing the platinum group metals.

The method used in the investigation enables the amount of active metal on the carrier to be controlled, as this is proportionate to the concentration of metal in the solution. In the present research work, impregnation is achieved at room temperature or with slight heating e.g. 23 to 50°C and there is no need to carry out the prolonged aging process at temperatures above 60°C. Calcination is carried out in a conventional muffle furnace at elevated temperatures. Preferably, the calcination involves two stages with the first stage being a drying stage e.g. at above 100°C and the second stage taking place at a higher temperature e.g. above 300°C.

By using the surface impregnation technique of the present investigation it is possible to make very active catalysts with controlled metal loading on a carrier or support such as a ceramic, zeolite, titanium dioxide, porous carbon etc. The preferred catalyst support is γ-Al_2O_3 which can be in the form of spheres or washcoated monoliths as in conventional catalyst supports and carriers. These catalysts were successfully used for the oxidation of toluene as an indicator of VOCs. In the case of γ-Al_2O_3 spheres a complete oxidation of toluene was achieved at 236°C. However, the same level of oxidation was achieved at 268°C when the reaction was carried out in the presence of γ-Al_2O_3 washcoated monolith.

In conclusion, both these catalysts have the potential to be installed in the process-vent of chemical industries to control the emissions of toluene and other VOCs during the production of pesticides and pesticide active ingredients (PAIs).

6.3 SELECTIVE EXTRACTION OF METAL-VALUES USING RTILs

The main aim of this part of the research work was to prepare ionic liquids which are selective and can extract only one metal from a mixed industrial waste.

6.3.1 Synthesis and Characterisation of RTILs

To develop ionic liquid technology for metal recovery, a total of eight novel room temperature ionic liquids were prepared using microwave technology. Out of these eight, only five ionic liquids were characterised because the remaining three ionic liquids had a very high viscosity and were only partially soluble in water.

Characterisation was carried out by high performance chromatography (HPLC), infrared spectroscopy (IR), UV/Visible spectroscopy (UV/Vis) and mass spectrometry (MS). Characterisation results confirmed that the prepared RTILs were pure and free from the starting materials.

6.3.2 Application of RTILs for the Selective Extraction of Heavy Metals

In order to improve the efficiency and viability of metal recovery and treatment, the use of alternative and novel technologies has been investigated in this work. The technology is based on the application of RTILs as selective solvents for the recovery and recycling of heavy metals.

The results obtained in this work show that both metal powders and metal oxides dissolve in RTILs but that the extent of solubility depends upon:-

(1) the composition of the RTIL

(2) the metal or metal oxide studied.

The results in Figure 6.5 show that the solubility of copper (II) oxide, for example, varies from 12.2 % in 1-(3-cyanopropyl)-3-methylimidazloium bromide to 99.2 % in 1-(2-cyanoethyl)-3-methylimidazolium bromide. These results show that this ionic liquid may have the potential to be used as a selective solvent for the extraction of copper from industrial wastes and low-grade primary ores.

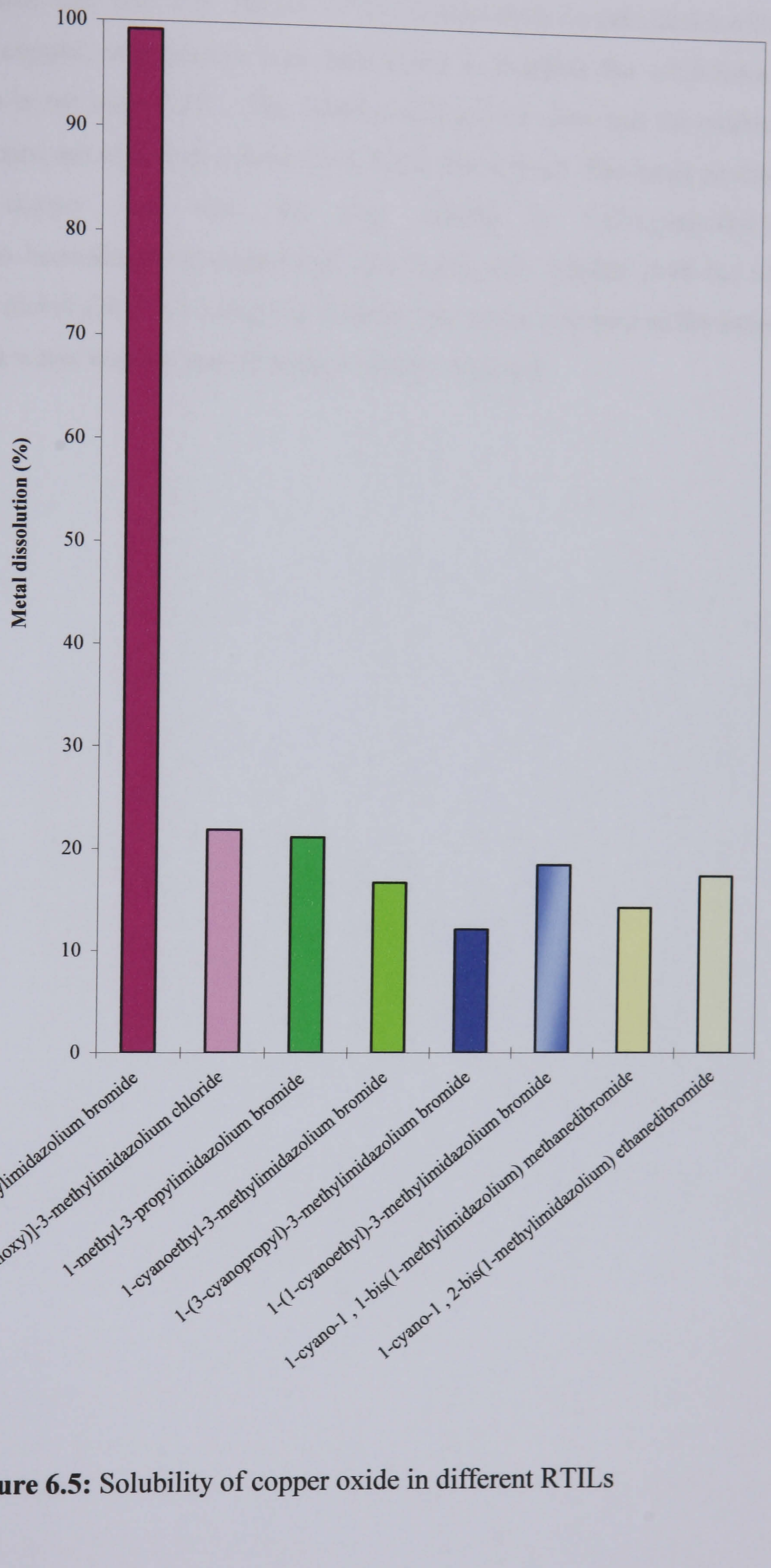

Figure 6.5: Solubility of copper oxide in different RTILs

In order to confirm the selective nature of 1-(2-cyanoethyl)-3-methylimidazolium bromide for only copper, experiments were carried out to examine the solubilities of other metal oxides in the same RTIL. The results in Figure 6.6 show that the oxides of cobalt, nickel and zinc are also very soluble (>92 %) in this solvent. The metal powders, cobalt, nickel, copper and zinc are also soluble in 1-(2-cyanoethyl)-3-methylimidazolium bromide, with copper and zinc being very soluble (>96 %) with cobalt (35 %) and nickel (26.9 %) being less soluble. The metal solutions in the solvent can be diluted with water without precipitating a metal compound.

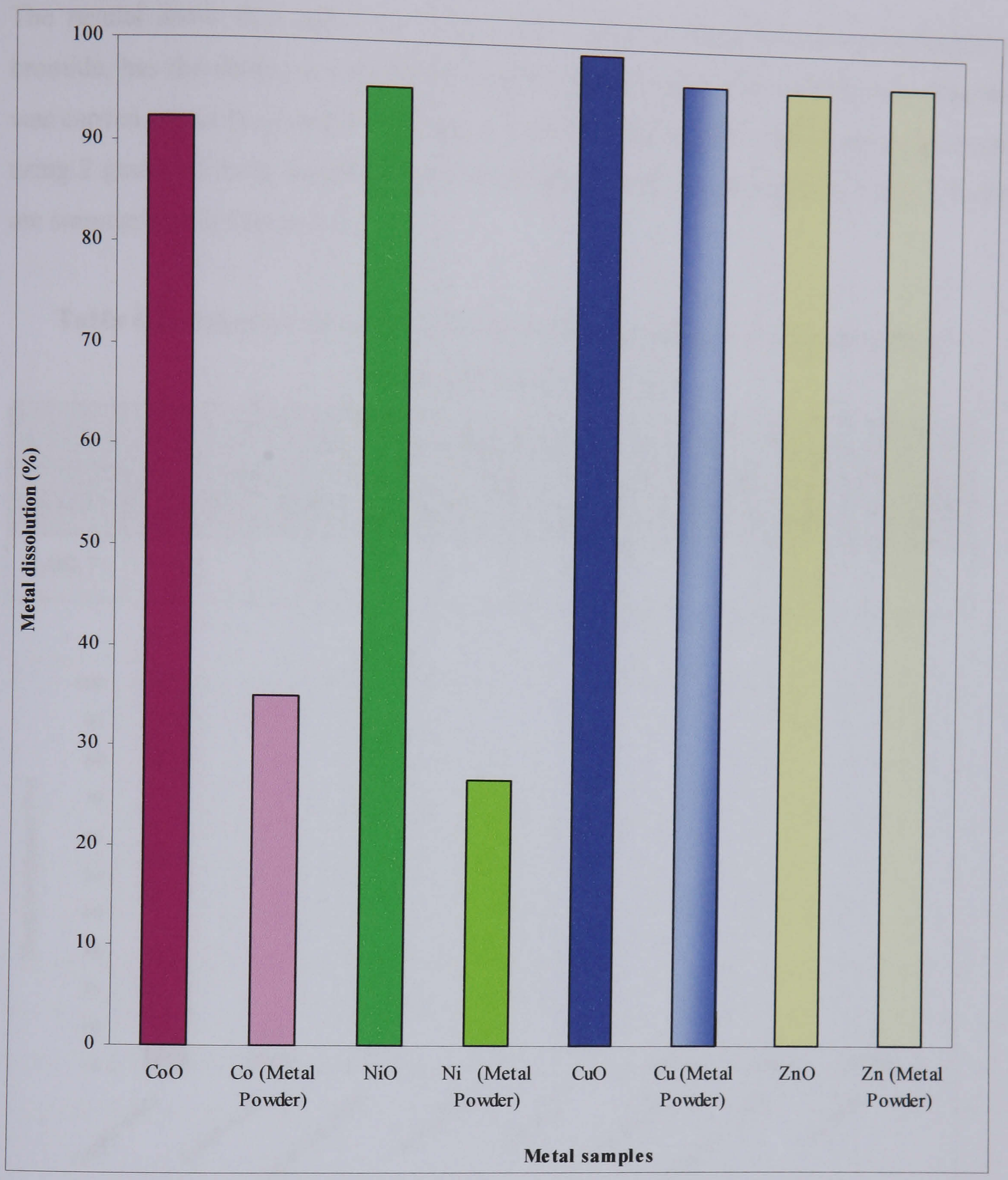

Figure 6.6: Solubility of pure metals and metal oxides in 1-(2-cyanoethyl)-3-methylimidazolium bromide

Aqueous solutions of RTILs, however, can enhance selectivity and, apart from copper (II) oxide with a solubility of 99.7 % in the 1-(2-cyanoethyl)-3-methylimidazolium bromide-water mixture, all other oxides studied (CoO, Cr_2O_3, Fe_2O_3, SnO, NiO, MnO and ZnO) have low solubility (<4 %). There is evidence that the presence of impurities in copper (II) oxide does aid the dissolution of the metal with pure CuO being only 14.9 % soluble in a RTIL-water compared with 99.7 % solubility of a 97 % pure sample of CuO.

The results show that only one ionic liquid, 1-(2-cyanoethyl)-3-methylimidazolium bromide, has the ability to selectively dissolve copper oxide and sulfide when reaction was carried out in the presence of water. The solubility results of different metal oxide using 2 grams of ionic liquid in 10 ml of distilled water are presented in Table 6.1 and are summarised in Figure 6.7.

Table 6.1: Solubility of metal oxides in aqueous solution of 1-(2-cyanoethyl)-3-methylimidazolium bromide

Metal dissolved / %							
CuO	CoO	Cr_2O_3	Fe_2O_3	SnO	NiO	MnO	ZnO
>99.7	3.5	0	0	0	1	1.3	3.0

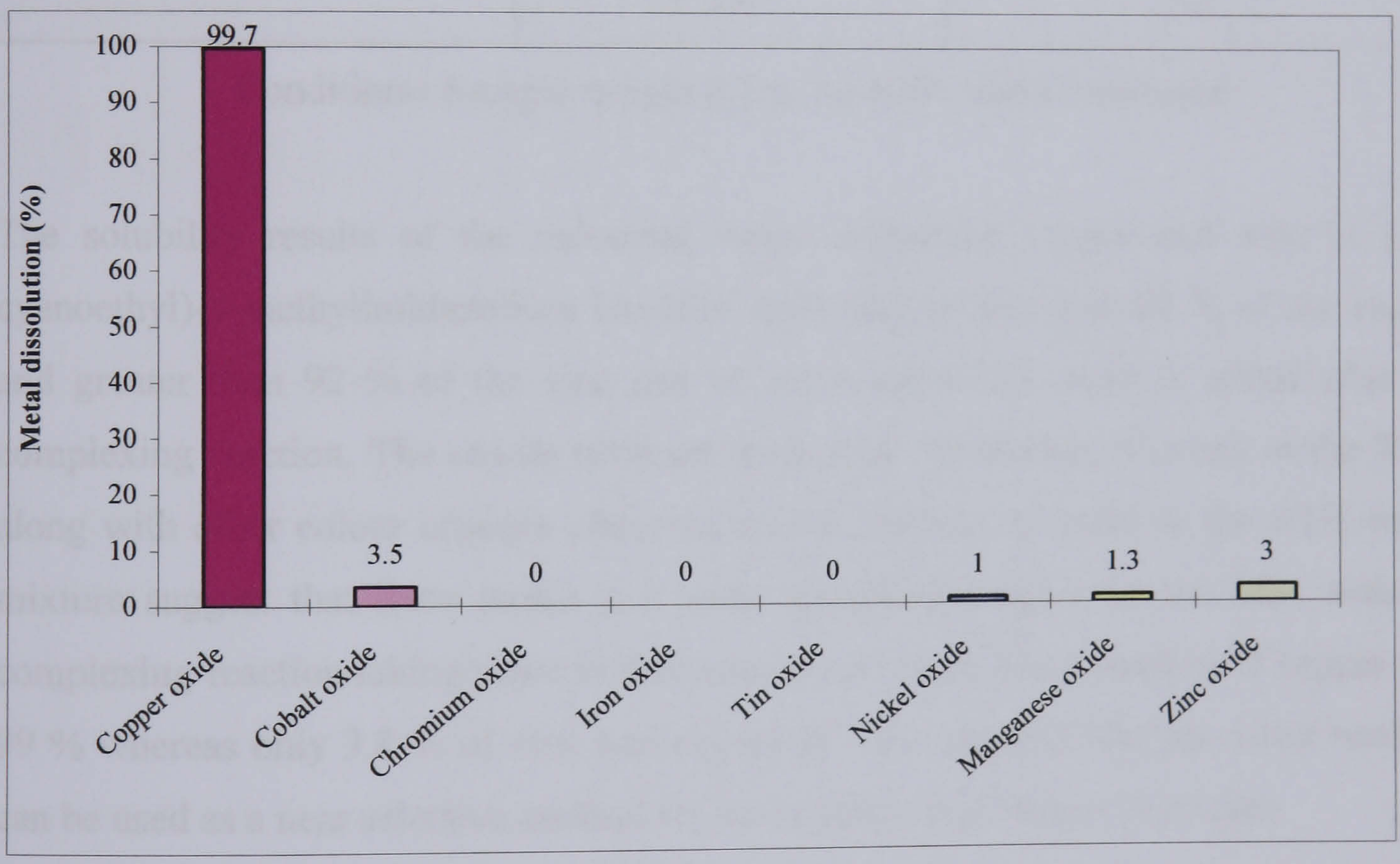

Figure 6.7: Solubility of metal oxides in aqueous solution of 1-(2-cyanoethyl)-3-methylimidazolium bromide

The solubility studies of different metals, metal oxides and sulfides have lead to the conclusion that 1-(2-cyanoethyl)-3-methylimidazolium bromide can be used for the selective extraction of copper from industrial waste samples containing other metal oxides. In order to confirm these results, an industrial sample containing copper and zinc oxides was supplied by industry and used for the selective extraction of copper.

The results show that the ionic liquid, 1-(2-cyanoethyl)-3-methylimidazolium bromide has the ability to selectively dissolve copper oxide in the presence of water. The solubility results of solid waste containing Cu and Zn using two grams of ionic liquid, in absence and presence of water are in Table 6.2.

Table 6.2: Solubility of Mixed metal oxides in 1-(2-cyanoethyl)-3-methylimidazolium bromide (in the absence and presence of water)

Solvent	Metal	Metal dissolved / %
RTIL	Cu	99.8
	Zn	92.1
Aqueous solution of RTIL	Cu	99.9
	Zn	3.8

Conditions: Sample weight 0.2 g, 2 g RTIL and 10 ml water

The solubility results of the industrial waste containing copper and zinc in 1-(2-cyanoethyl)-3-methylimidazolium bromide show that greater than 99 % of the copper and greater than 92 % of the zinc can be recovered when water is added after the complexing reaction. The results obtained during the dissolution of cobalt in the RTIL along with other colour changes observed on the addition of water to the RTIL-metal mixture suggest that ionic liquid is a weak complexing agent. In the case with the complexing-reaction taking place in the presence of water, the extraction of copper was 99 % whereas only 3.8 % of zinc was extracted. This suggests that this latter reaction can be used as a near selective method for the separation of copper from zinc.

A comparison of a traditional leaching approach with the selective RTIL leaching approach is given in Figure 6.8. The results obtained show that the RTIL leaching approach actually eliminates the need of a purification step that usually involved the use of volatile organic solvents. The release of VOCs into the environment interacts with other pollutants and lead to the formation of secondary pollutants which are responsible for the formation of photochemical smog.

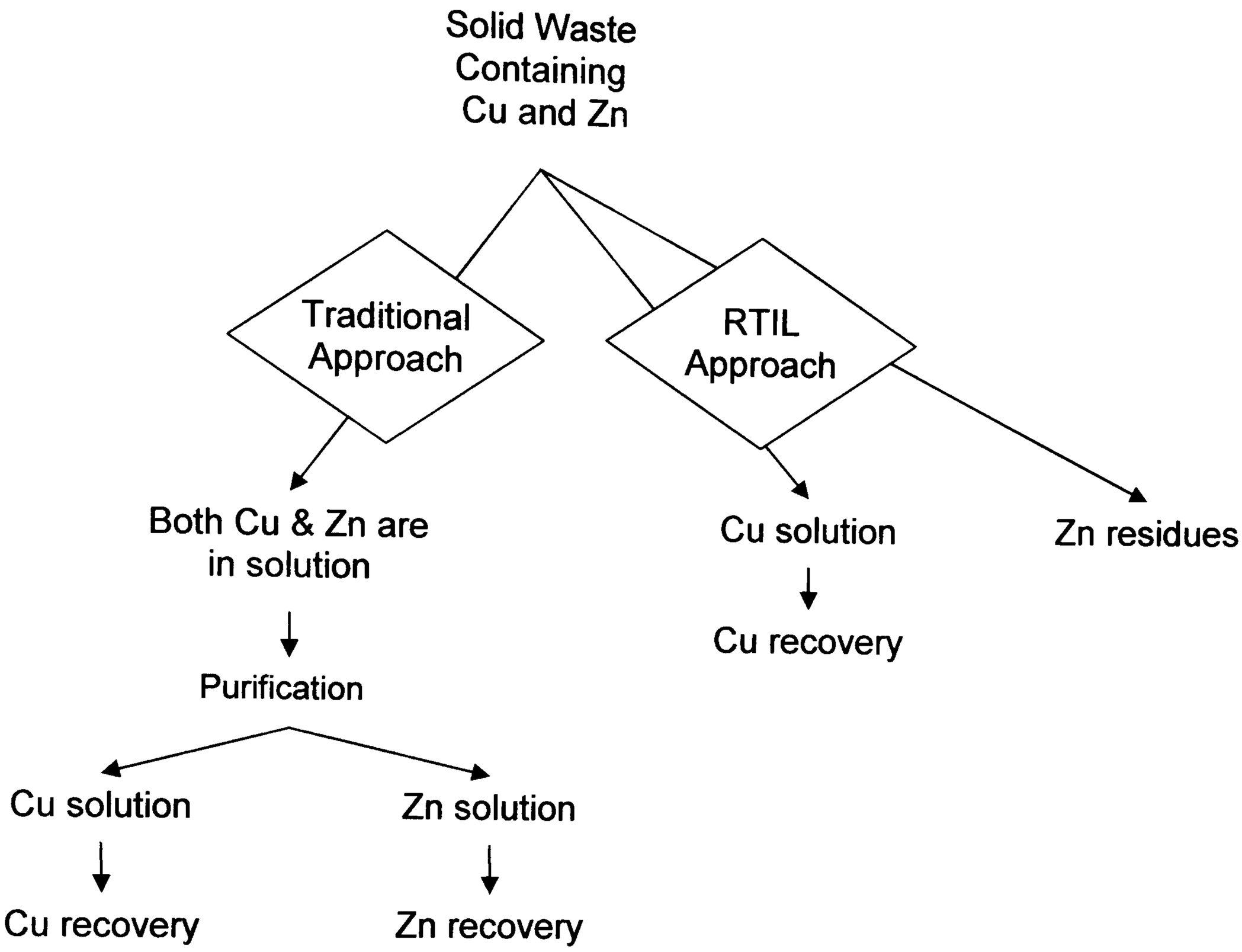

Figure 6.8: Selective leaching of copper using RTIL

6.4 APPLICATION OF TREATMENT METHODOLOGIES IN PAKISTAN

Pakistan's previous environmental record is poor, and the country has not yet been able to back up its commitment to environmental protection with action. The present national government, however, is determined to combat the environmental pollution problems associated with the management of industrial wastes and effluent streams. The PEPA has placed greater emphasis on environmental protection in order to stem the country's environmental degradation and safeguard citizens' health.

The present situation in Pakistan is that apart from a few large and export-oriented industries, which have to meet environmental standards, most of the small to medium size industrial units have no effluent treatment facilities. The situation is, however, changing due to the introduction of Pakistan Environmental Protection Act in 1997. All local governments and regulatory authorities are helping small and medium size industrial units to develop and install appropriate treatment technologies to comply with

the stringent environmental quality standards (EQS) as set out in the Environmental Protection Act of 1997.

The Federation of Pakistan Chambers of Commerce and Industry (FPCCI) believe that most of the small and medium size industrial units need sympathetic rather than harsh treatment because they do not have the expertise and resources to develop and install treatment units. If these units are forced to develop and install treatment units to meet the environmental requirements then their first option would be to close down their activities and this would be a disaster for the local economy and the job market. For this reason the PEPA has sponsored a number of projects under the Environmental Technology Programme for Industry (ETPI) to develop inexpensive methodologies to help these units.

The methodologies developed for the treatment of textile, leather and chemical industries have the potential to be adopted by the small and medium size units. One of the methodologies, electro-precipitation process, developed for the treatment of textile, leather and mixed textile/leather effluent streams has been tested successfully on a pilot scale. As most textile and leather units are located in close proximity in industrial estates and the adoption of this methodology by these units would be the first step to combat environmental pollution problems in Pakistan. The PEPA has also planned to test the suitability of other technologies developed in this work. One of the advantages of these developed methodologies is that treatment units of different sizes can be manufactured to handle the varied amount of wastes and effluent streams.