

**DEVELOPMENTS OF ELECTROCHEMISTRY IN ENVIRONMENTAL  
TECHNOLOGY**

A thesis submitted for the degree of Doctor of Philosophy

by

Nael Gergi Yasri

The Centre for the Environmental Research, Brunel University.

June 2001

BRUNEL UNIVERSITY

PUBLICATION OF THESES

Please complete in block capitals

NAME: MAEL YASRI

DEPARTMENT: CER

TITLE OF THESIS: Developments of Electrochemistry in Environmental Technology

PLEASE COMPLETE EITHER PART A OR PART B

A. I agree that the abstract of my thesis may be published by the University without further reference to me.

In accordance with the University's Handbook of Procedures, the Head of Library Services may allow my thesis to be copied in whole or in part without further reference to me. Such Authority shall apply only to single copies made for study purposes and shall be subject to normal conditions of acknowledgement.

(See notes overleaf)

Signature: [Signature]

Date: 3107/2001

B. I request that my thesis be held under confidential cover in the Library for a period of \_\_\_\_\_ years for the following reasons:

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Once the period of confidentiality has expired, I agree that the conditions set down in Part A will apply without further reference to me

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

Please pass this form to your supervisor who should sign below indicating his/her agreement to the retention of the thesis under confidential cover.

Signature of Supervisor: \_\_\_\_\_

Additional comments \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

If you have completed Part A please return this form direct to the Library.

Part B, when complete, should be returned to the Assistant Registrar.

To my lovely family.

To Jamill's spirit.

## ACKNOWLEDGEMENTS

I would like to thank my supervisors Professor J. Donaldson and Dr S. M Grimes for their encouragement, continued interest, constant help and guidance throughout my time at Brunel.

Great thanks also to Aleppo University for their financial support and full sponsorship to carry out this research. Many thanks are due to Dr S. El Kadri (Chemistry Department, Aleppo University) who has always been a source of inspiration and encouragement during the whole period of my research work.

In addition I would like to thank Dr Douglas Dick for his assistance in the preparation of this thesis, Dr H. Lateef, Dr J. Parrick, for their organic chemistry advice, Mr B. Wheals for his help in the HPLC preparation and analysis and Dr A.J Chaudhary for his advice.

Thanks to all my friends and colleagues and the international group in the CER for providing a friendly and most stimulating atmosphere. A special thanks go to Maggie for her co-operation.

Finally, and the most important thanks are due to my parents, brothers and sister, for their constant encouragement and showing me a lot of thought throughout my time in England. Dad; you can call me *Doctor*.

## ABSTRACT

Uses of electrochemical systems in environmental control technology are described for the removal and separation of metals from solution and the destruction of dye molecules in effluents.

A novel concentrator cell system for the removal of lead and cadmium from solution is developed. The operation of this system permits the pH-independent recovery of metals from solution by electrodeposition.

The formation of complexes with suitable ligands is exploited to achieve the separation of metals by electrochemical methods. The separations of tin, lead and indium from each other, the separation of nickel from cobalt and the separation of copper and palladium from cobalt are used to illustrate the benefits of complex formation.

A three-compartment electro dialysis cell for removal of nickel from cobalt exploiting the greater stability of the nickel-EDTA complex compared with the Co-EDTA complex is described. Efficient removal of nickel from cobalt can be achieved but there is a compromise between cobalt purity and the percentage of cobalt transferred to the catholyte chamber for recovery.

The anodic oxidation of a number of dye molecules including methylene blue, acid blue 25, reactive blue 2 and reactive blue 15 in chloride solution has been studied. The anodic oxidation of methylene blue results in the formation of seven neutral and two charged intermediates. The main intermediate is identified by X-ray diffraction crystal structure determination and accurate mass spectrometry as the novel compound 4,6-dichloro-7-dimethylamino-3*H*-phenothiazin-3-one, (C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>OS) formed by replacement of one of the dimethylamino groups of methylene blue with oxygen accompanied by regiospecific chlorination of the carbocyclic system. The mass spectra of other intermediates formed are interpreted in terms of this structure.

An electroadsorption system combining adsorption and electrolytic processes to achieve the elimination of the chlorinated compounds that are formed during the electro-oxidation of methylene blue is also reported.

# DEVELOPMENTS OF ELECTROCHEMISTRY IN ENVIRONMENTAL TECHNOLOGY

## CONTENTS

ABSTRACT.....	i
TABLE OF CONTENTS.....	ii
PUBLICATION.....	iii
CHAPTER 1: INTRODUCTION.....	1
CHAPTER 2: A NOVEL COMBINATION OF ADSORPTION AND ELECTROLYTIC PROCESSES FOR THE REMOVAL OF LEAD AND CADMIUM FROM DILUTE SOLUTION.....	37
CHAPTER 3: APPLYING THE ELECTROCHEMICAL TECHNIQUE FOR THE REMOVAL AND NOVEL SEPARATION PROCESSES OF LEAD, TIN, AND INDIUM IN MIXED METALS SOLUTION.....	103
CHAPTER 4: PROCESS OPTIMISATION FOR THE SEPARATION OF NICKEL FROM COBALT USING ELECTRODIALYSIS SYSTEMS IN THE PRESENCE OF EDTA AS A COMPLEXING AGENT.....	142
CHAPTER 5: A NOVEL COMBINATION OF ADSORPTION AND ELECTROLYTIC PROCESSES FOR THE REMOVAL OF DYE FROM AQUEOUS SOLUTION.....	205
CHAPTER 6: CONCLUSION.....	295
APPENDIX.....	300

## **Publication**

1. **Separation of nickel from cobalt using electro dialysis in the presence of EDTA.** *Journal of Applied Electrochemistry*, **30**, 439-445, 2000.
2. A conference paper accepted for presentation on 8 November, 2000, The Supreme Council of Science, Latakia, Syria.

**A Novel Combination of Adsorption and Electrolytic Processes for the Removal of Lead and Cadmium from Dilute Solution.**

# CHAPTER ONE

## INTRODUCTION

<b>1.1</b>	<b>BACKGROUND TO PRESENT WORK .....</b>	<b>2</b>
<b>1.2</b>	<b>THE NEED TO REMOVE HEAVY METALS.....</b>	<b>3</b>
<b>1.3</b>	<b>THE NEED FOR DYE REMOVAL .....</b>	<b>4</b>
<b>1.4</b>	<b>METHODS FOR WASTE MATERIAL REDUCTION AND MINIMISATION.....</b>	<b>5</b>
<b>1.4.1</b>	<b><i>Physical Treatment</i>.....</b>	<b>5</b>
<b>1.4.2</b>	<b><i>Biological Treatment</i>.....</b>	<b>8</b>
<b>1.4.3</b>	<b><i>Photolytic Treatment</i> .....</b>	<b>8</b>
<b>1.4.4</b>	<b><i>Chemical Treatment</i>.....</b>	<b>8</b>
<b>1.5</b>	<b>ELECTROCHEMICAL BACKGROUND.....</b>	<b>10</b>
<b>1.5.1</b>	<b><i>What is Electrochemical Science?</i> .....</b>	<b>10</b>
<b>1.5.2</b>	<b><i>Mechanism of Electrolysis and the Transport of Ions</i>.....</b>	<b>11</b>
<b>1.5.3</b>	<b><i>Transport of Ions in Dilute Solutions</i> .....</b>	<b>12</b>
<b>1.5.4</b>	<b><i>General Aspects of the Deposition Process</i> .....</b>	<b>14</b>
<b>1.5.5</b>	<b><i>General Aspects of Electrochemical Theory</i> .....</b>	<b>15</b>
<b>1.6</b>	<b>THEORY OF ADSORPTION.....</b>	<b>18</b>
<b>1.7</b>	<b>ANALYTICAL METHODS.....</b>	<b>19</b>
<b>1.7.1</b>	<b><i>Atomic Absorption Spectroscopy</i>.....</b>	<b>20</b>
<b>1.7.2</b>	<b><i>Scanning Electron Microscopy</i>.....</b>	<b>21</b>
<b>1.7.3</b>	<b><i>High Performance Liquid Chromatography</i>.....</b>	<b>22</b>
<b>1.7.4</b>	<b><i>Ultra Violet / Visible Spectroscopy</i>.....</b>	<b>23</b>
<b>1.7.5</b>	<b><i>Total Organic Carbon</i>.....</b>	<b>23</b>
<b>1.7.6</b>	<b><i>Other Techniques</i> .....</b>	<b>24</b>
<b>1.8</b>	<b>THE SCOPE OF THIS WORK .....</b>	<b>24</b>
<b>1.9</b>	<b>REFERENCES .....</b>	<b>26</b>



## 1.1 BACKGROUND TO PRESENT WORK

An increase in technology and consumer demand this century has resulted in increased amounts of pollution and has highlighted the need for public health protection. The reduction and control of water pollution and contamination has always been an important priority in the European Union's (EU) environmental programme<sup>1</sup>. The European Commission's Fifth Action Programme, "Towards Sustainability", building on current EU policies to 2000, has a number of aims including securing sufficient water supplies and maintaining and improving quality. The EU has issued the 76/464/EEC directive dividing pollutants that have been discharged to receiving water into List I and List II<sup>1</sup>. List I, often referred to as the "Black List", contains a total of 129 substances which are considered to be so toxic, persistent or bioaccumulative in the environment, that steps must be taken to eliminate pollution by them. They include organohalogen, organophosphorus and organotin compounds and cadmium, mercury and their compounds. List II, on the other hand, is referred to as the "Grey List". This covers those substances considered less harmful when discharged into water. Some of the materials included in this list are: zinc, nickel, chromium, lead, arsenic, copper, various biocides, cyanide and ammonia.

Implementation of this directive has resulted in lower discharge consent levels for heavy metals as well as for organic pollutants in aqueous effluent, and has created an increased awareness for the need for maximum recycle and minimum discharge. Many hazardous waste problems, however, can be avoided in the early stages by waste reduction (cutting down quantities of wastes at their sources) and waste minimization (utilization of treatment processes which reduce the quantities of wastes requiring ultimate disposal)<sup>2</sup>. It is now important to ensure that waste is recovered or disposed of without endangering human health and without using processes or methods that could harm the environment by using best available technology<sup>3</sup>. This places greater emphasis on the prevention, reduction, re-use and recycling of waste, and on the use of waste as a source of energy (NSCA, 1997).

Many different methods have been used for pollution treatment. Electrolytic techniques, however, can often provide an elegant solution to environmental problems

related to industrial effluent<sup>4</sup>. The work described in this thesis is an investigation of the use of electrochemical methods as clean techniques for effluent treatment including the removal, recovery and separation of dissolved metals and the destruction of dissolved dyes.

## **1.2 THE NEED TO REMOVE HEAVY METALS**

The concentrations of some metals in the environment above the 'natural levels' are a cause for concern due to their toxicological effects on humans and other living creatures<sup>5</sup>. It has been estimated that more than 12,000 tons of heavy metals are discharged to sewers each year in the UK alone<sup>6</sup>. Therefore, with increasing environmental awareness, the need to recover heavy metals from effluent streams is becoming more and more urgent for several reasons<sup>7</sup>:

1- From a legislative standpoint, more stringent limits for the discharge of trade effluents (mandatory limits outlined in the Surface Waters, Dangerous Substances Regulations 1989, amended 1990, 1992) are being set.

2- From an environmental standpoint the recovery of metals not only prevents pollution of the water course and a requirement for subsequent clean up, but also can achieve recovery of raw materials.

3- From a business standpoint, a reduction in waste and subsequent discharges results in savings in raw materials, discharge costs and water rates, so leading to simultaneous economic and environmental advantage.

Some of the metals, such as zinc, are essential to human and plant life, and others, such as lead, are not. However, regardless of being essential or not, all of these elements can be toxic if present in excessive levels.

Metals can be released into soils and become available to biological systems through the natural process of weathering. Once in soil, if the metals are mobile they can be leached into aqueous systems including groundwater and ultimately into the drinking water supplies. Heavy metals in the environment can also derive from human activity.

Sewage sludge spread on agricultural land, for either disposal or fertilisation, can contain high concentrations of heavy metals. Other anthropogenic sources include scrap yards and heavy industry, which can generate airborne pollutants that are subsequently deposited to land, as well as soil waste. Waste dumps present a problem with the potential risk of a cocktail of chemical compounds leaching into ground water.

### **1.3 THE NEED FOR DYE REMOVAL**

Effluent from the textile, dyeing and paper printing industries contains a wide variety of pollutants. These range from high molecular weight carbohydrate and aromatic compounds to smaller molecular weight solvents. These are complex chemical solutions which generally contain dyes at concentrations of 10 to 200 mg/l, depending on the dye process in operation. There is much evidence and research to show that underestimating the aggregation of such materials in aqueous systems can cause serious damage to human health and the environment. Governments have been sufficiently concerned to enforce regulation on the release of dye materials into the environment. Careful control of dye effluent sources is needed to minimize the problem, so enabling recycling to the water system.

Conventional treatment processes presently in use, at waste water treatment works, do not usually achieve satisfactory colour removal and result in coloured effluent being discharged from the treatment works. Consequently, downstream use of the treated water is limited, and the highly visible nature of the pollution source often gives rise to public concern.

Solutions to treatment problems are being sought through exploration of chemical, physical and biological options<sup>8</sup>. Chemical treatment processes such as reduction or oxidation, and physical treatment such as adsorption and filtration (reverse osmosis, crossflow microfiltration) can be used in removing colour. Specialised biological treatment of dye-containing wastewater has shown potential for a complete treatment system ie. mineralisation of organic dye compounds to breakdown products such as carbon dioxide, methane and water. From the disposal point, however, of view, the resulting chemical, adsorbent or biological product has to be considered.

Very little consideration has been given to the use of electrochemical methods for the destruction and decolourisation of dissolved dye molecules. There has been much interest in the use of electro-oxidation. But it is unlikely that the method will lead to complete mineralisation without going through a series of organic intermediates. The degradation of dye molecules can result in the formation of non-coloured dye fragments. Although this satisfies the requirement of decolourisation, it can result in the formation of environmentally unfriendly degradation products, such as aromatic amines and chloro-organic compounds.

The aim of the research described in this thesis is to investigate electro-oxidation as a method for dye decolourisation, and to identify the degradation products formed in the process. The aim of this part of the work is to develop a new electrochemical method for dye removal, whilst minimising unwanted intermediate compounds.

## **1.4 METHODS FOR WASTE MATERIAL REDUCTION AND MINIMISATION**

The appropriate treatment technology for hazardous wastes depends upon the nature of the wastes. The main methods for waste water treatment divide into four different categories: physical, biological, photolytic and chemical. Most waste treatment measures, however, have both physical and chemical aspects<sup>9</sup>.

### **1.4.1 Physical Treatment**

These operations include phase separation, transition, transfer and membrane separation.

#### ***1.4.1.1 Phase Separation***

This method involves the separation of the components of a mixture that are already in two different phases. The techniques used include sedimentation, decantation, filtration, centrifugation and flotation or dissolved air flotation<sup>10</sup>.

#### ***1.4.1.2 Phase Transition***

In this process the material changes from one phase to another. The most common drawback of these techniques is the necessary treatment or disposal of any

contaminated residual material. These methods include:

### Distillation

Used for recycling solvents, waste oil or aqueous phenolic waste. The residual distillation bottoms (still bottoms)<sup>11</sup> are hazardous and polluting and the landfill disposal of these distillation bottoms is limited.

### Evaporation

Usually used for concentrating waste from aqueous systems, e.g., by thin film evaporation in which the volatile constituents are removed by heating a thin layer of sludge on a heated surface<sup>12</sup>.

### Drying

Drying is used to reduce the waste quantity by removing any solvent which may interfere with subsequent treatment processes<sup>13, 14</sup>. Examples are the removal of the volatile phase or solvent from a solid, semisolid, liquid or suspension by processes such as freeze drying.

### Stripping (air or steam stripping)

The main application of this technique is the separation of volatile components from less volatile ones in a liquid mixture. The process includes partitioning the more volatile materials to the gas phase (air or steam) in a stripping tower equipped with trays or packed to provide maximum turbulence and contact between the liquid and gas phases. The two major products are condensed vapour and stripped bottom residue<sup>15 - 18</sup>.

### Physical precipitation

In this method, the solid is deposited from a solute in a solution as a result of a physical change in the solution. This can be achieved by cooling the solution, evaporation of the solvent, alteration of solvent composition, e.g., by ion exchange or by salting out with an organic solvent<sup>19</sup>. The last process can be achieved by adding, for example, a water miscible organic solvent to an aqueous solution.

### ***1.4.1.3 Phase Transfer***

This method utilizes the transfer of a solute in a mixture from one phase to another and includes the techniques of solvent extraction and sorption.

In solvent extraction, a substance is transferred from one solvent (usually water) to another (usually an organic solvent). It has been used recently for selective extraction of metals from wastewater<sup>20, 21</sup>.

Sorption processes include the transfer of a substance from solution to a solid phase (sorber). The most common sorber is activated carbon, which is used widely in wastewater effluent treatment. Activated carbon is very effective for removing poorly water soluble and high molecular weight materials, such as xylene, naphthalene, cyclohexane, chlorinated hydrocarbon, phenol, aniline, dyes and surfactants<sup>9</sup>.

### ***1.4.1.4 Membrane Separation***

This method<sup>22</sup> is based on passing dissolved contaminants or solvents under pressure through a size-selective membrane. A pure solvent phase (usually water) passes through the membrane leaving the concentrated impurity behind. The type of membrane used determines the types and size of the enriched species filtered through the membrane. The physical techniques covered by this methodology include hyperfiltration, ultrafiltration, reverse osmosis and electrodialysis.

Species of molecular masses between 100-500 can be filtered out by hyperfiltration, whereas, ultrafiltration allows the passage of species with molecular masses of 500 - 1,000,000 and is used with hyperfiltration in the removal of suspended oil, grease and fine solid particles from water.

Reverse osmosis is the most widely used of the membrane techniques. The principle is that the membrane is selectively permeable to water, while excluding ionic solutes. High pressures are used to move the solvent across the membrane. This process results in a highly concentrated salt stream on one side of the membrane and a highly purified solvent stream on the other. The reverse osmosis technique is metal ion selective and although tolerant to limited pH changes, it is easily fouled by suspended salts and organic materials.

Electrodialysis is discussed in detail in chapter 4. Along with other electrochemical techniques, the driving force for the separation is electrolysis with direct current between two electrodes. Membranes alternately permeable to cations and to anions are used to produce a purified stream, which can be discharged or reused, and a concentrated electrolyte stream which can be disposed of or processed for reclamation of the dissolved salt.

### **1.4.2 Biological Treatment**

Biological treatment can aid the removal of toxic organic and inorganic substances, such as heavy metal ions. This treatment is influenced by its physical characteristics (solubility and vapour pressure) and by its chemical properties (molecular weight, structure and the presence of various types of functional groups). Some toxic materials are resistant to the biological treatment (**recalcitrant** or **biorefractory**) i.e. resistant to the organism's metabolic attack. Chemical pretreatment, however, can make recalcitrant wastes much more biologically treatable. These treatment methods have a very limited pH tolerance, but can display high metal selectivity. The metal ion working range is from 0.1 to 100.0mg dm<sup>-3</sup> (23).

### **1.4.3 Photolytic Treatment**

Dye photolytic reaction is discussed in detail in chapter 5 of this thesis. The application of photolysis is in breaking down and destroying a number of hazardous wastes. In principle, the most important part in these reactions is the generation of a reactive intermediate (such as OH<sup>•</sup>), which participates in chain reactions that lead to the destruction of organic compounds. The addition of sensitizers (such as peroxide or titanium oxide) helps in absorbing radiation and generating reactive species which destroy wastes.

### **1.4.4 Chemical Treatment**

Chemical treatment methods make use of the chemical properties of wastewaters. The treatments include acid / base neutralization, chemical extraction and leaching, ion

exchange, chemical precipitation, electrolysis and redox reactions.

Neutralization is simple in principle; the waste is treated with the appropriate acid or base. Neutralization can present some problems such as evolution of volatile contaminants, excessive heat and apparatus corrosion, but can sometimes be used as a pH adjustment treatment prior to the use of other methods.

Chemical extraction and leaching include the removal of poorly soluble salts (usually heavy metal salts) by chemical extraction into a solution. This treatment method is usually followed by other treatments such as electrolysis. Caution is required when the material for acid leaching is chosen because, in some cases, toxic gases can be formed. For example, hydrogen cyanide or hydrogen sulfide can form when acid leaching is applied to cyanide or sulfide salts respectively.

The term ion exchange is generally understood to mean the exchange of ions of like sign between a solution and a solid highly insoluble body in contact with it. The solid (ion exchanger) must contain replaceable ions, and for the exchange to proceed sufficiently to be of practical value, the solid must have an open, permeable molecular structure so that ions and solvent molecules can move freely in and out. The ion exchanger is a polymer that carries an electric charge which is exactly neutralised by the charges on a counter-ion. These active counter-ions are cations in a cation exchanger and anions in an anion exchanger. Thus a cation exchanger consists of a polymeric anion with active cations, while an anion exchanger is a polymeric cation with active anions<sup>24</sup>.

The primary application of chemical precipitation is in heavy metal treatment, usually the deposition of metal hydroxides that are insoluble in aqueous solution. The chemical precipitation method has the disadvantage of being nonselective to heavy metal ions. Some metals can be precipitated from solution in the elemental form by the action of a reducing agent or with more active metals. Such a process is called **cementation**<sup>25</sup>.

The processes by which particles aggregate and precipitate from colloidal suspension is called **coagulation** or **flocculation**. Coagulation involves the reduction of



electrostatic repulsion forces between the colloidal particles in the solution, whereas, flocculation depends upon the presence of bridging compounds, which form chemical bonded links between the colloidal particles and enmesh the particles in relatively large masses called floc networks<sup>26</sup>.

Electrolysis can be used for wastewater treatment exploiting the oxidation / reduction reactions at the electrodes<sup>4</sup>. Reduction takes place at the cathode surface (for example metal deposited on the cathode surface) while at the same time oxidation of another species takes place at the anode surface. One of the advantages in using electrochemistry is the extra process control possible through the applied potential which can lead to the promotion of automatic control and increased safety.

## **1.5 ELECTROCHEMICAL BACKGROUND**

Electrochemistry is a science which is used, directly or indirectly, in many industrial applications. The wide range of electrochemical applications includes sensors, metal and organic analysis, corrosion protection, surface technology, energy generation, materials and chemical manufacture, recycling and effluent treatment.

The applications of electrochemical technology for industrial recycling and effluent treatment include the removal, recovery and separation of dissolved metals, the destruction of dissolved organic materials, and the treatment of waste gases. The main emphasis of this thesis is in the two areas of removal, recovery and separation of dissolved metals and the destruction of dissolved dyes. These are discussed in detail in chapters 2, 3, 4 and 5.

In order to develop effective electrochemical effluent treatment methods, it is important to understand the basic principles involved.

### **1.5.1 What is Electrochemical Science?**

Electrochemistry is the science which deals with the consequences of the transfer of electric charges from one phase to another. In particular, electrochemical science deals with surface situations and the electrical properties at interfaces. For example,

when two phases (a metal electrode and an electrolyte solution containing ions) are brought into contact, some of the ions in the original phases tend to transfer to the other, carrying their electrical charges. This creates, across the region between two phases a potential difference. This region is called an interface (electrode interface) and the potential is called the interface potential (electrode potential).

In an electrochemical cell, at one electrode-electrolyte interface, electrons leave the electrode (electron source, cathode) and the particles (cations) of the solution are reduced. At the second interface, the electrode (electron sink, anode) takes electrons from the particles, and oxidation take place. External control of the electron transfer rates across the interfaces causes the electrons to obtain specific energy.

### **1.5.2 Mechanism of Electrolysis and the Transport of Ions**

The ability of the solvent, especially water, to ionize substances dissolved in it makes electrolysis possible. However, the demand for electric charge at the interface cannot be met by ions which remain stationary in the solution, or just move about at random. Different ions move at different rates from the bulk solution to the interface between solution and electrode, and this is accompanied by electron transfer processes. An example is the case of using metal salt as an electrolyte in normal electroplating solutions. As the metal is deposited at a cathode, the solution in its immediate vicinity is depleted in metal ions. If plating is to continue, these ions must be replenished. There are three possible ways in which ions reach the electrode, diffusion (the movement of chemical species, either ionic or uncharged through the solution as a result of the concentration gradient), convection (the effect of hydrodynamic flow) and migration (the effect of the applied electric field)<sup>27</sup>.

#### **1.5.2.1 Diffusion**

Diffusion occurs as a result of concentration gradients being set up at the electrode interface in the electrolyte. A difference in the concentration can arise when an electrode takes ions out of a solution by electron transfer, so reducing the concentration of ions near the electrode compared with the concentration a few thousand angstroms further into the liquid. This gives rise to the movement of the species from the higher to the lower concentration<sup>28</sup>.

### **1.5.2.2 Convection**

There are two types of convection: forced or natural. Forced convection occurs when the solution is stirred. Natural convection, on the other hand, occurs whether a solution is stirred or not. When a difference in pressure, density or temperature exists in various parts of the electrolyte, then the liquid begins to move as a whole or parts of it move relative to other parts. For example, when ions are deposited on the electrode, the density of the solution at the electrode-solution interface is reduced. This density change causes an influx of ions from the surrounding part of the solution towards the electrode, independently of that caused by diffusion. Lower density solution at the vicinity of the electrode surface flow-upwards whilst the higher density solutions flows down into the bulk solution creating a movement by convection. The difference between diffusion and convection, therefore, is that diffusion occurs because of changes in concentration of ions and convection occurs because of density changes.

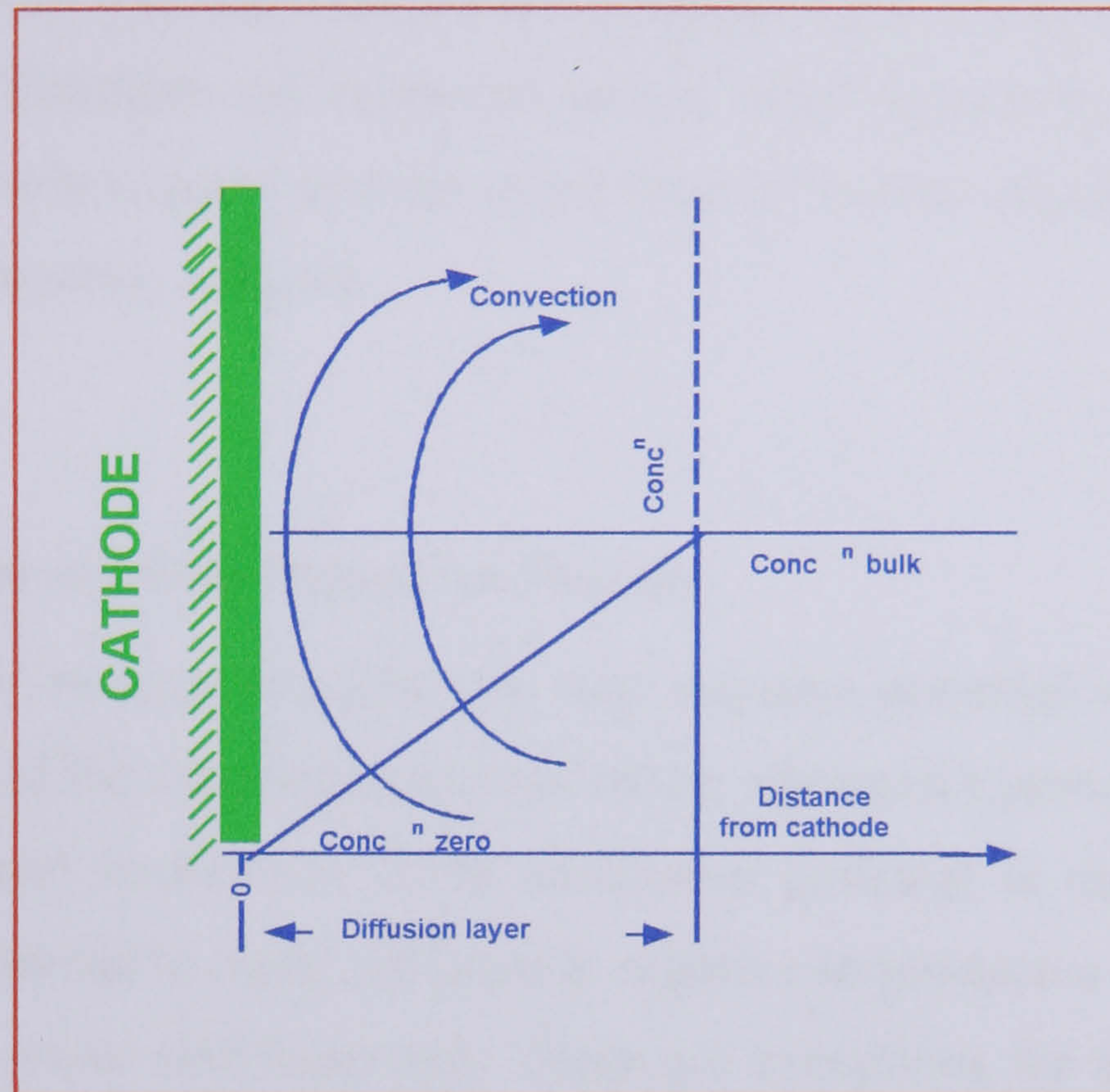
### **1.5.2.3 Migration**

This involves the movement of cations and anions through a solution under the influence of an applied potential between electrodes placed in the solution. The potential gradient will act upon the ions to push the positive ions towards the negative electrode and the negative ions towards the positive electrode. If the concentration of ions reacting at the electrode is small compared to the concentration of other ions in the solution, the effect of ionic migration is negligible compared to diffusion.

## **1.5.3 Transport of Ions in Dilute Solutions**

During the electrolysis processes of dilute solution, less than 1000 mg dm<sup>-3</sup> metal, transportation of ions cause several problems. In dilute solutions there is an ionic concentration gradient from the bulk of the electrolyte to the surface of the electrode where the value at the electrode is zero at limiting current density creating a diffusion layer (or boundary layer) of thickness  $\delta \cong 0.5\text{mm}$  (unstirred solution) depicted simplistically in Figure [1.1]. In order for metal ions to be removed from dilute solutions, the ions must cross this diffusion layer, and for this to be achieved the thickness of the layer must be reduced. If the thickness of the boundary layer is not

reduced and the current density is increased beyond that which brings the ion concentration to zero at the electrode surface, then other competing reactions such as the evolution of hydrogen will take place thus reducing the current efficiency of the process.



**Figure [1.1]:** Diffusion layer setup between a cathode surface and the solution.

In the case of dilute solutions, the most effective way to transport the ion across the boundary layer up to the electrodes is by diffusion. There is a gradient of ionic concentration in the boundary layer, from that of the bulk electrolyte to that at the electrode, which is zero at limiting current density. Fick's Laws<sup>30</sup> are the laws that govern the diffusion of ions in the electrolysis processes. In the Fick's First Law the study-state diffusion flux has been theoretically shown to be proportional to the gradient of concentration. And Fick's Second Law is the basis for the treatment of most time-dependent diffusion problems in electrochemistry. In Fick's First law the rate of diffusion in an electrolyte is directly proportional to the concentration of the dissolved substances. And the rate of diffusion in any given direction is directly proportional to the rate at which the concentration diminishes in that direction this law is written in the following equation:

$$dQ / dt = -D (C_b - C_e) / dx$$

where:  $dQ / dt$  is the flux of the material per second per unit area,  $D$  is the diffusion coefficient,  $C_b$  the concentration of ion studied in the bulk,  $C_e$  the concentration of ion

studied at the electrode,  $dx$  the distance over which the concentration change occurs and  $(C_b - C_e) / dx$  the concentration gradient.

When the ionic concentration is reduced, the forces diffusing the ions to the electrode become progressively less effective and the diffusion layer becomes more and more depleted of ions. Therefore the maximum rate at which deposition can be made to occur is progressively reduced and the upper limit of current density, which can be used, is also progressively reduced.

#### **1.5.4 General Aspects of the Deposition Process**

At the cathode, the reaction requiring the least negative potential will initially take place; exclusively, if the deposition potential of any alternative process is much more negative, and almost exclusively if the alternative potential is only a little more negative. If the potential is made sufficiently negative to produce a second reaction, that reaction may occur simultaneously. There are exceptions for some metals that cannot be deposited from aqueous solution at all. The metal ion with association ligands (water or ligands) attaches itself at certain preferred sites (irregular surfaces). At the same time the metal ion bonds to the electrode surface with partially neutralising its charge and the associated ligands dissociated and return into the solution. Monoatomic growth layers are produced. This lateral growth proceeds until several neighboring lattices meet to form a coating on the electrode.

At the anode, the reaction requiring the least positive potential occurs, unless the potential becomes so positive that a second reaction is possible. Under some conditions, the anode becomes coated with species such as metal oxides. This coated film in some cases may be an insulator, which prevents the current flowing throughout the solution.

#### **1.5.5 General Aspects of Electrochemical Theory**

##### ***1.5.5.1 Faraday's Law***

The basic law of electrochemical theory - Faraday's Law - states:

1. *The amount of chemical change produced by an electric current is directly proportional to the quantity of electricity that passes during a period of time.*
2. *The amounts of different substances liberated by a given quantity of electricity are proportional to their chemical equivalent weights.*

This law expressed mathematically in term of the weight of metal deposited at the electrode:

$$w = ItA / zF$$

where: (A) the atomic weight of metal deposited, (z) the metal valency, (I) current in amperes, (t) time in seconds and (F) is the Faraday and equal to 96487 coulombs/mol.

The Faraday constant is the quantity of electricity required to deposit the equivalent weight in grams of a metal (atomic weight = equivalent weight  $\times$  valency). This means that:

- 1- By measuring the quantity of electricity that passes, one has a measure of the chemical change that will be produced.
- 2- Knowing the chemical equivalent weight of a substance, one can predict the amount of that substance that will be reacted by a given quantity of electricity.

#### ***1.5.5.2 Current Density and Limiting Current Density***

The current density is defined as the current per unit area of electrode. This factor is very important in electrodeposition operations. The character of the deposit, the distribution and the current efficiency all depend on the current density. Limiting current density can be defined as the current density at which depositing ions are reduced as rapidly as they can diffuse to the electrode surface. The limiting current density of any electrolyte increases with the concentration of ions. In this way the current efficiencies obtainable are also increased. The limiting current density is also related to the thickness of the diffusion layer by the following expression:

$$i_L = k/d$$

Where:( $i_L$ ) limiting current density, (d) thickness of the diffusion layer and (k) can be defined as:

$$k = DnFc / (1-t)$$

Where: (n) ion valency (D) diffusion coefficient, (t) transport number, (c) concentration of ionic species and (F) Faraday's constant.

Under these conditions (of low ions concentration) the transport number of ions is normally zero thus;

$$i_L = DnFc / d$$

If the diffusion layer thickness is constant a decrease in ionic concentration will produce a proportional decrease in limiting current density. Similarly, by decreasing the diffusion layer thickness, it is possible to increase the limiting current density, thereby increasing reaction rates.

To obtain electrodeposition of metals from solution containing low concentration at high current efficiencies, current densities lower than the limiting current density have to be applied. This is a time-consuming process to deplete all metal ions in the bulk solution. The alternative is to increase the limiting current density by reducing the thickness of the diffusion layer. This can be achieved by increasing the mass transfer of ions obtained either by increasing the movement of the metal ions through agitation of the solution or by creation of a concentration of ions in the area close to the electrode surface. Agitation can be achieved by applying ultrasound, rotating the electrode or by using a specially designed cell<sup>29, 31</sup> such as the *Chemelec* cell that is a fluidized bed cell with inert beads as the fluidizing medium. Recent research performed using this technique at Brunel University has given good results for metal ion removal from dilute solution<sup>32</sup>. Increasing the metal ion concentration in the vicinity of the electrode surface, however, using a concentrator material is a potential method of dealing with the dilute solution case and is the subject of work described in this thesis.

#### ***1.5.5.3 Overvoltage***

There are number of types of overvoltage; the source and the way in which they influence the course of an electrochemical reaction are described briefly:

*1- Concentration overvoltage:* when the current is passed through the cell, the activity (concentration) near the electrode changes. At the cathode, the metal ions are deposited. The replenishment of these ions from the bulk solution is not as fast as the

deposition, so causing a difference in the concentration which lowers the equilibrium potential.

2- Activation overvoltage: for any reaction to take place there is an energy barrier that must be overcome. In an electrochemical reaction the portion of the total electrode overvoltage that produces the energy barrier is the activation overvoltage. This portion can be explained by the fact that most metal ions are hydrated in solution, and the coordination sphere of the ions must be distorted and the water molecules freed from their association with the metal ion for deposition to take place. For most metals depositing on a cathode, activation overvoltage is fairly small and can usually be neglected, unless the current density is very large. However, certain metals, and all gases, show evidence of considerable activation overvoltage.

The relation between the current and activation overvoltage is a logarithmic function described by the Tafel equation for the cathodic process as:

$$\eta_{\text{act}} = a + b \log i$$

where a, b are constants dependent on the mechanism of the reaction, and i is the current density.

3- Resistance overvoltage: the most common form of resistance overvoltage arises from the passage of electric current through an electrolyte solution surrounding the electrode. Such a solution is not of infinite conductivity and shows resistance to the current flow, with the result that an ohmic (*IR*) drop in potential occurs between the working electrodes. A less common form of ohmic overvoltage is caused by the formation of a surface-adherent film that in itself possesses substantial resistance. In some cases, one electrode or both is covered with a film having a resistance different from that of the bath.

The evolution of hydrogen and oxygen at the electrode surfaces are well-known phenomena during electrolysis of dilute aqueous solutions of acid and bases<sup>33</sup>. Hydrogen overvoltage is of great importance in the electrolysis process of solution containing metal ions; in fact, if there was no hydrogen overvoltage, many metals could not be deposited from aqueous solution, and because of hydrogen overvoltage,



some metals cannot be deposited at all from aqueous solution. Hydrogen overvoltage depends strictly on the cathode (material, and surface). Some cathodes cause a large hydrogen overvoltage value, which will allow some metal ions to deposit on the surface without the evolution of hydrogen gas or allow metal deposition and hydrogen evolution to take place at the same time. The hydrogen overvoltage is higher on smooth surfaces than on rough ones, and has a value that varies from negligible on platinum black and quite low on graphite to perhaps as much as 1 volt on mercury.

## 1.6 THEORY OF ADSORPTION

Since the 1960s, an increased awareness of the occurrence of many synthetic and natural organic substances in natural waters has led to the emergence of adsorption by activated carbon, as one of the most effective methods of removing these substances from drinking and wastewater. Adsorption is defined as the phenomenon in which a particular substance concentrates on the surface or the interface of a solid or liquid phase. The substance thus attracted to a surface is said to be the adsorbate, while the substance to which it is attached is the adsorbent. The adsorbent phase comprises so called active sites, which can bind the adsorptive to form the adsorbed phase. Two types of adsorption are generally recognized, viz, **physical** or van der Waals adsorption, which involves only relatively weak intermolecular forces, and **chemical** or activated adsorption (chemisorption) where there is the formation of a chemical bond between the adsorbed molecule and the surface of the adsorbent.

Physical adsorption is characterised by low heat evolution, adsorption equilibrium is reversible (established rapidly), and it is not site-specific i.e. the adsorbed molecules are free to cover the entire surface. In contrast, chemisorption is accompanied by much higher heat changes, leads to a much firmer attachment of the adsorbed phase with adsorbent, involves chemical bonding, is irreversible, and site-specific<sup>34</sup>. In many adsorption cases the processes are neither physical nor chemical, but a combination of both.

If the reaction is reversible, as it is for many compounds adsorbed on activated

carbon, molecules will continue to accumulate on the surface until the rate of the forward reaction (adsorption) equals the rate of the reversible reaction (desorption). When this condition is reached no further accumulation will occur<sup>35</sup>.

## **1.7 ANALYTICAL METHODS**

The main analytical techniques used throughout the work described in this thesis are:

- 1) Atomic Absorption Spectroscopy
- 2) Scanning Electron Microscopy
- 3) High Performance Liquid Chromatography
- 4) Ultra Violet / Visible Spectroscopy
- 5) Total Organic Carbon Analysis
- 6) Other Techniques

A brief description of these analytical techniques is given in the following subsections and analytical data obtained using these techniques are given where appropriate.

### **1.7.1 Atomic Absorption Spectroscopy**

Atomic absorption spectrometry (AAS) is the measurement of absorption of radiation by free atoms. The total amount of absorption depends on the number of free atoms present and the degree to which the free atoms absorb the radiation. When atoms of an element in the ground state are irradiated with electromagnetic radiation of appropriate wavelength, they will absorb radiation and be raised to an excited state. The wavelength of absorption and the amount of radiation absorbed provide qualitative and quantitative parameters for the determination of the element present, regardless of how these atoms are combined<sup>36</sup>.

The spectrometer used was a Perkin Elmer 2380. This instrument is capable of determining most elements. Sensitivities of atomic methods lie typically in the parts per million to parts per billion range. A key feature of this instrument is the sharpness of the absorption line (resonance line) when an atom is raised from its ground state to

its first excited state. In general the functions required in this method are<sup>37</sup>:

- 1- Delivery of the analyte to the flame, so that the element is introduced to the radiation beam.
- 2- Inducing the spectral transitions (absorption) by the radiation beam generated by a hollow cathode lamp, which has the wavelength characteristic of the element being determined.
- 3- Isolating the spectral lines required for the analysis.
- 4- Detecting the increase or decrease in intensity of radiation of the isolated lines.
- 5- Recording this intensity data.

A satisfactory flame source must provide the temperature and fuel/oxidant ratio required for a given analysis, with no spectral interference arising from the flame itself.

Atomisation in the spectrometer used in this work was achieved using a flame atomiser with an air-acetylene gas and in some cases N<sub>2</sub>O-acetylene gas was used.

Since atoms absorb light at very specific wavelengths, it is necessary to use a narrow-line source which emits the narrow-line spectra of the element of interest. Two types of lamps are used in atomic absorption instruments: hollow cathode lamps and electrodeless discharge lamps. The lamps used in this research work were hollow cathode lamps, with a different lamp being used for each metal.

### **1.7.2 Scanning Electron Microscopy**

The scanning electron microscope<sup>38, 39</sup> (SEM) is an extremely versatile tool, initially constructed by Knoll and Hruska in 1929, designed for the direct study of the surface of solid objects by scanning them with electrons. There are three types of electron microscope available:

1. Transmission Electron Microscope (TEM).
2. Scanning Electron Microscope (SEM).
3. Scanning Transmission Electron Microscope (STEM).

The electron microscope used in this work was an SEM, JXA-840A, instrument. The essential features of SEM are:

1. An electron source, using conventional tungsten filaments, LaB<sub>6</sub> or field emission tips.
2. A condenser lens system to focus a fine beam of electrons onto the specimen surface.
3. A scanning system to translate the electron beam over a selected area of the specimen.
4. A detection facility to collect the emitted signals from the specimen and to control image contrast.
5. A display and recording system to view the image and store information for later presentation.

### **1.7.3 High Performance Liquid Chromatography**

High Performance Liquid Chromatography (HPLC) is a technique which is able to separate macromolecules and ionic species, labile natural products, polymeric materials, and a wide variety of other high molecular weight polyfunctional groups. The mechanism involved in separation arises because of differences in the equilibrium distribution of sample components between two different phases, where one of these phases is a moving or mobile phase and the other is a stationary phase. The essential feature of this technique is the nature of the partitioning process which occurs between a solid stationary phase (column) and a mobile liquid phase. Separation is therefore achieved by the affinity of the analyte of interest for the stationary phase; the higher the affinity the greater the amount of analyte retained by the stationary phase and this results in different velocities of analyte migration due to differences in equilibrium distribution and mass transfer effects<sup>40</sup>.

The mobile phase is pumped through the chromatographic system using a CECIL 1100 pump, engineered to conform to the requirements of HPLC i.e. high pressures to force the mobile phase through the tightly packed column and delivery of a steady and pulse-free flow. The flow rate of the pump can be varied over the range of 1 to 10 cm<sup>3</sup> min<sup>-1</sup> in steps of 1 cm<sup>3</sup> min<sup>-1</sup>, and can be operated with a maximum pressure of

several thousand pascal. In practice a flow rate of  $1 \text{ cm}^3 \text{ min}^{-1}$  is normally used for analytical work. The sample solution is introduced into the mobile phase between the pump and the column by an injection loop of fixed volume (5-20 $\mu$ l).

The most important part of the chromatograph is the analytical column, through which the mobile phase is transported. The column is made of a stainless steel tube packed with a suitable packing material. Columns vary in size but are typically 10-20cm long with a 5mm internal diameter. Analyte species migrate at different rates down the column and thus separate before entering the detector. In this present study two types of detector system were used: (1) a CECIL 1200 detector a Variable Wavelength Absorbance Monitor operating in the ultraviolet-visible region and (2) mass spectrometry using an LS-MS instrument, Finnegan MATP SSQ7000.

#### **1.7.4 Ultra Violet / Visible Spectroscopy**

A UV/Visible spectrometer consists of a suitable source of electromagnetic radiation, an analysis system for the radiation used and an appropriate detector to determine the wavelength of the radiation absorbed.

The extent to which radiation is absorbed by a substance depends on the concentration of the substance, the distance the radiation travels in passing through the sample (the path length) and on the particular wavelength. For a fixed wavelength absorbed, it is found that dilute solutions obey the Beer-Lambert law<sup>41</sup>. This law is expressed as:

$$e = \epsilon c t = \log_{10} I_0 / I$$

where: (c) the concentration of the substance ( $\text{mol m}^{-3}$ ), (t) the path length (cm), ( $I_0$ ) intensity of incident radiation, (I) intensity of transmitted radiation and ( $\epsilon$ ) the molar absorption coefficients. The value  $\log_{10} (I_0 / I)$  is known as the optical density or absorbance (e) and it is this quantity which appears along the y-axis of recorded visible and ultra-violet spectra.

A Perkin-Elmer Lambda 9 UV/ VIS / NIR Spectrophotometer was used in this work. The cells used were two quartz cells of 1 cm thickness, one as the reference cell and

the other as the sample cell. The reference cell was filled with the solvent and the sample cell with the solution. This arrangement compensates for solvent absorption and also for losses of radiation by scattering and reflection.

### **1.7.5 Total Organic Carbon**

The measurement of total organic carbon (TOC) is now recognized as the best process of assessing the organic content of a water sample. This technique was originally developed by the Dow Chemical Company<sup>42</sup>. TOC is generally defined as that carbon in organic compounds which is converted to carbon dioxide by oxidation. In this work TOC was determined using an O.I. Corporation Model 700 instrument. The method involves:

1- eliminating inorganic carbon dissolved in the sample by acidification using phosphoric acid, to convert carbonate and bicarbonate ions to dissolved carbon dioxide which is purged with nitrogen and measured by infrared detector, to provide a value for total inorganic carbon.

2- determining TOC by adding a dissolved oxidizing agent, potassium persulfate ( $K_2S_2O_8$ ), at 90-100°C to oxidise all organic carbon present. The  $CO_2$  formed is purged from the system and concentrated by trapping then desorbed and carried into a non-dispersive infrared analyzer (NDIR) which has been calibrated to directly display the mass of carbon dioxide detected. The resulting carbon mass, in the form of carbon dioxide, is equivalent to the mass of organic carbon originally in the sample, which is calculated by the integrating system in the instrument using the concentration unit ppm (parts per million). The range of TOC detected using this instrument is 4 ppb (parts per billion) C to 10,000 ppm C with no sample pre-treatment<sup>43</sup>.

### **1.7.6 Other Techniques**

The other techniques used in the core of this work are Hydrogen Nuclear Magnetic Resonance ( $^1H$  NMR), Accurate Mass, Low Resolution Electron Impact Mass Spectroscopy and X-ray Crystallography.

## 1.8 THE SCOPE OF THIS WORK

Following this introduction chapter, which sets the background to the work described in this thesis and the analytical techniques used, chapter 2 describes the recovery of cadmium and lead from dilute aqueous solution using an electrochemical system in combination with concentrator techniques of carbon cloth and ion exchange resin. Chapter 3 describes the use of the electrochemical system to improve the ability of recovery and separation of lead, tin and indium from a mixed metal ion solution in the presence of the complexing reagent potassium thiocyanate. In chapter 4, the use of an electrodialysis technique for the separation of nickel from cobalt using sulfuric acid media in the presence of EDTA as a complexing agent is investigated. This work was extended to the separation and purification of cobalt from other impurities such as  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  or  $\text{Pd}^{2+}$ . The identification of the intermediate compounds formed during the electro-oxidation of methylene blue is reported in chapter 5. In this chapter, the results of using activated carbon granules in combination with an electrolytic system for the destruction of different dye materials is presented. Discussions and further recommended work are presented in chapter 6.

## 1.9 REFERENCES

- [1] NSCA (National Society for Clean Air and Environmental Protection) "1998 Pollution Handbook", 1998, Great Britain.
- [2] P. N. Cheremisinoff, "Encyclopedia of Environmental Control Technology", Vol. 5: Waste Minimization and Recycling, Houston, TX: Gulf Publishing, 1992.
- [3] N. Haigh, "EEC Environmental Policy and Britain", 2nd Revised Edition, Longman, 1990.
- [4] Keith Scott. "Electrochemical Processes for Clean Technology". The Royal Society of Chemistry, 1995, UK.
- [5] R.A. Goyer, C.D. Klaassen and M.P. Waalkes, "Metal Toxicology", Academic Press, INC, 1995.
- [6] E. Berman, "Toxic Metals and their Analysis", Heyden, London, 1980.
- [7] J. Arundel, "Sewage and Industrial Effluent Treatment", Blackwell Science. UK. 1995.
- [8] P. Vandevivere, R. Bianchi and W. Verstraete, *Journal of Chemical Technology and Biotechnology*, 1998, **72** (4), 289-302.
- [9] S. E. Manahan, "Environmental Chemistry", 6th edition, Lewis Publishers, 1994.
- [10] H. W. Gehm and J. I. Bregman, "Handbook of Water Resources and Pollution Control" Van Nostrand Reinhold, New York, 1976.
- [11] D. McCabe and M. Vivona, *Environmental Progress*, 1999, **18** (1), 30-33.
- [12] W. Hyde and W. Glover, *Chemical Processing*, 1997, **60** (2), 59- 64.
- [13] K. Tscheschlok and J. Czuberny, "Drying Plant waste", *Atw-Internationale Zeitschrift fur Kernenergie*, 1995, **40** (11), 685-688.
- [14] H. Gruter, M. Matter, K. Oehlmann, M. Hicks, *Water Science and Technology*, 1990, **22** (12), 57-63.
- [15] S. Kutzer, H. Wintrich and A. Mersmann, *Chemical Engineering & Technology*, 1995, **18** (3), 149-155.
- [16] B. Lamarre and D. Shearouse, *Pollution Engineering*, 1994, **26** (9), 46-48.
- [17] N. Kolev, R. Darakchiev and K. Semkov, *Industrial & Engineering Chemistry Research*, 1997, **36** (1), 238-240.
- [18] J. Phillips, *Journal of Environmental Science and Health Part A-*



- Environmental Science and Engineering & Toxic and Hazardous Substance Control*, 1995, **30** (5), 1075-1090.
- [19] D. De, A. Hrymak and R. Pelton, *AIChE Journal*, 1997, **43** (10), 2415-2423.
- [20] M. Cerna, *Environmental Monitoring and Assessment*, 1995, **34** (2), 151-162.
- [21] T.C. Lo, M.H.I. Baird and C. Hanson, "Handbook of Solvent Extraction", John Wiley & Sons, New York, 1983.
- [22] J. A. Howell, *The Membrane Alternative: Energy Implications for Industry*, Report number 21, Elsevier Applied Science, 1990.
- [23] N. F. Gray, "Biology of Wastewater Treatment", Oxford Science Publication, 1989.
- [24] G. H. Jeffery, J. Bassett, J. Mendham and R. C. Denney, in "Vogel's: Textbook of Quantitative Chemical Analysis", Fifth Edition, Longman Scientific & Technical, 1989.
- [25] O. Sohnel and J. Garside, *Precipitation: "Basic Principles and Industrial Applications"*, Butterworth-Heinemann Ltd, 1992.
- [26] Metcalf and Eddy, "Wastewater Engineering, Treatment, Disposal and Reuse", McGraw-Hill, Inc, Third Edition, 1991.
- [27] D. Pletcher and F. C. Walsh, "Industrial Electrochemistry", Second Edition, Blackie Academic & Professional. 1993.
- [28] D. R. Crow, "Principles and Application of Electrochemistry", Blackie Academic Professional, an imprint of Chapman & Hall, 1994.
- [29] F. Walsh and G. Mills, *Chemistry and Industry*, 1993, **2 August**, 576-580.
- [30] J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry, Volume 1, Ionics", Second Edition, Plenum Press, 1998.
- [31] S. Dando, Ph. D. Thesis, Brunel University, London, UK, 1995.
- [32] M. A. Jan, Ph. D. Thesis, Brunel University, London, UK, 1996.
- [33] P. A. Christensen and A. Hamnett, "Techniques and Mechanisms in Electrochemistry", 1st Edition, Blackie Academic & Professional, 1994.
- [34] S. D. Faust and O. M. Aly, "Adsorption Processes for Water Treatment", Butterworth Publishers 1987.
- [35] R. A. Alberty and R. J. Sibley, "Physical Chemistry", 1st Edition, John Wiley and Sons, New York, 1992.
- [36] J. E. Cantle, "Techniques and Instrumentation in Analytical Chemistry", Volume (5), Atomic Absorption Spectrometry, Elsevier Scientific, 1982.

- [37] "Atomic Absorption Spectrometric Handbook", Perkin-Elmer.
- [38] Reimern and Ludwig, "Scanning Electron Microscopy: physics of image formation and microanalysis", Berlin; London: Springer-Verlag, 1998.
- [39] "Handbook of the JXA-840A Scanning Electron Microscope".
- [40] H. Engelhardt, "Practice of High Performance Liquid Chromatography", Springer Verlag, Berlin, Heidelberg, 1986.
- [41] C. N. R. Rao, "Ultra-Violet and Visible Spectroscopy", 3rd Edition, Butterworths, London, 1975.
- [42] M. B. Hocking, "Handbook of Chemical Technology and Pollution Control", Academic Press, 1998.
- [43] O. I. Corporation, "Model 700, User Handbook Total Organic Carbon Analyzer Operating Procedures and Service Manual".

J

**CHAPTER TWO**  
**A NOVEL COMBINATION OF ADSORPTION AND ELECTROLYTIC**  
**PROCESSES FOR THE REMOVAL OF LEAD AND CADMIUM FROM**  
**DILUTE SOLUTION.**

<b>2.1</b>	<b>INTRODUCTION .....</b>	<b>29</b>
<b>2.2</b>	<b>LEAD.....</b>	<b>30</b>
<b>2.2.1</b>	<b><i>Electrochemistry of Lead and Lead Electrowinning .....</i></b>	<b><i>31</i></b>
<b>2.3</b>	<b>CADMIUM.....</b>	<b>33</b>
<b>2.3.1</b>	<b><i>The Electrochemistry of Cadmium and Cadmium Electrowinning.....</i></b>	<b><i>35</i></b>
<b>2.4</b>	<b>CONCENTRATOR ELECTROCHEMICAL TECHNOLOGY.....</b>	<b>37</b>
<b>2.5</b>	<b>EXPERIMENTAL.....</b>	<b>38</b>
<b>2.5.1</b>	<b><i>The Ion Exchange Resin Concentrator Cathode.....</i></b>	<b><i>39</i></b>
<b>2.5.1.1</b>	<b><u>In-situ</u> Regeneration of the Ion-exchange Concentrator .....</b>	<b>41</b>
<b>2.5.2</b>	<b><i>The Activated Carbon Cloth Concentrator Cathode.....</i></b>	<b><i>44</i></b>
<b>2.5.3</b>	<b><i>Lead and cadmium removal and recovery studies .....</i></b>	<b><i>46</i></b>
<b>2.6</b>	<b>RESULTS .....</b>	<b>48</b>
<b>2.6.1</b>	<b><i>Lead Recovery .....</i></b>	<b><i>49</i></b>
<b>2.6.1.1</b>	<b>Lead Recovery from Nitric Acid Media .....</b>	<b>49</b>
<b>2.6.1.2</b>	<b>The Effect of pH on Lead Removal .....</b>	<b>52</b>
<b>2.6.1.3</b>	<b>Lead Recovery from Acetic Acid Media.....</b>	<b>55</b>
<b>2.6.1.4</b>	<b>Successive Lead Recovery.....</b>	<b>58</b>
<b>2.6.2</b>	<b><i>Cadmium Recovery.....</i></b>	<b><i>60</i></b>
<b>2.6.2.1</b>	<b>Cadmium Recovery from Sulphuric Acid Media.....</b>	<b>60</b>
<b>2.6.2.2</b>	<b>Cadmium Recovery from Nitric Acid Media .....</b>	<b>66</b>
<b>2.6.2.3</b>	<b>The Effect of pH on Cadmium Recovery.....</b>	<b>69</b>
<b>2.6.2.4</b>	<b>Cadmium Recovery from Acetic Acid Media.....</b>	<b>71</b>
<b>2.6.2.5</b>	<b>Successive Cadmium Recovery.....</b>	<b>74</b>
<b>2.6.3</b>	<b><i>Lead and Cadmium Recovery in a Combined System .....</i></b>	<b><i>84</i></b>
<b>2.6.3.1</b>	<b>The Effect of Nitric Acid Concentration on the Recovery of Cd and Pb.....</b>	<b>84</b>
<b>2.6.3.2</b>	<b>The Effect of pH on the Recovery of Cd and Pb from Nitric Acid Solution.....</b>	<b>87</b>
<b>2.7</b>	<b>CONCLUSION.....</b>	<b>89</b>
<b>2.8</b>	<b>REFERENCES .....</b>	<b>90</b>

## 2.1 INTRODUCTION

A number of industrial operations produce large quantities of dilute effluent streams containing low concentrations of metal ions. Industries for which this type of effluent occurs include electroplating, metal finishing, acid treatment of alloys and leach liquors and effluent solutions from the manufacture of chemicals. This kind of effluent presents two main problems (1) loss of metals and (2) adverse environmental impact. The work described in this chapter is concerned with the removal of lead and cadmium from aqueous solution using novel concentrator electrochemical cell technology. Lead and cadmium were chosen for this study because of the major environmental impact that they have in aqueous systems.

Any recovery method must take into account economic interests and should have low energy and labour costs. A considerable effort has been devoted to the development of technologies that can be used, e.g. chemical precipitation, cementation, ion exchange, reverse osmosis, solvent extraction and electrolysis. There are, however, practical limitations in using these techniques, which arise from the failure to achieve low metal levels, high costs, or the need to use additional chemicals, which increases the contaminants in both solid and liquid discharges, complicating the problem of ultimate disposal.

Electrolysis is an important and effective method for recovery and recycling of the metal from effluent streams because it results in a directly re-usable metal that can be returned to the commercial cycle by melting or dissolving or as an anode in electroplating. The electrodeposition of metals from a dilute stream, (less than 1g/l) can, however, present several major problems. This is often due to a low mass transfer. The methods of enhancing mass transfer generally involve agitation in combination with a moderately high electrode surface area per unit electrode volume for continuous production of metal. The agitation methods have involved rotating electrodes, mechanical stirring, air agitation, turbulence promoters, slurry or fluidised beds<sup>1,2</sup>.

The main objective of this work is to improve the percentage removal of metal ions from dilute solution using concentrator techniques instead of agitation in an

electrochemical reactor. The aim is to increase the concentration of metal ions in the electrolyte in an area close to the cathode surface to effectively create a new cell with a concentrated electrolyte near the electrode.

## 2.2 LEAD

Lead (Pb)<sup>3</sup> is a metal of Group IVA of the periodic table, soft and dense, silvery-white or greyish and a poor electricity conductor. Known in antiquity and believed by the alchemists to be the oldest of the metals. Seven thousand years ago Egyptians used the product for weights, cooking utensils and piping as did the Romans. Lead occurs naturally in the earth's crust at a mean concentration of 12-20 ppm<sup>4</sup>. It is a constituent of more than two hundred sulphide and carbonate minerals and can form both inorganic and organometallic compounds. It has atomic number 82, atomic weight 207.19, melting point 327.5°C, boiling point 1,744°C, density 11.34 g/cm<sup>3</sup> and forms compounds in the oxidation states +2 and +4.

The uses of lead stem from its somewhat unusual properties, notably good ductility, high malleability and excellent corrosion resistance combined with a relatively low melting point. Consequently, lead may be used in a variety of forms, for example, sheet, piping, casting and many different types of coating<sup>5</sup>. In fact, one of the principal applications of metallic lead is in the provision of corrosion protection for base metals, principally iron and steel but also zinc, aluminium and copper and its alloys. Other lead applications include, or have included, acid batteries, radiation protection, soft solders, plumbing, ammunition, gas fittings, paints, pigments, ceramics, glass and some insecticides<sup>6</sup>.

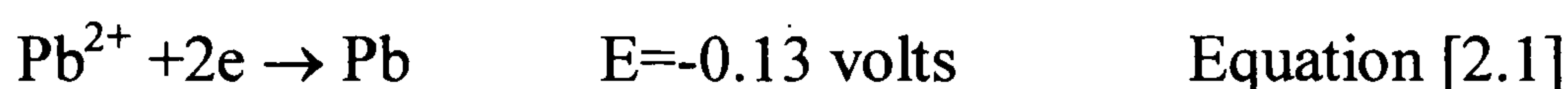
Chemically, lead is well defined and has several well-known salts, but with the exception of lead (II) nitrate and acetate most Pb salts are sparingly soluble (PbF<sub>2</sub>, PbCl<sub>2</sub>) or very insoluble (PbSO<sub>4</sub>, PbCrO<sub>4</sub>, Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, et.) in water. In general, the lead cation (Pb<sup>2+</sup>) is hydrolysed in aqueous solution to form polymerised species with 3, 4 or 6 Pb atoms. The stable and predominant species at the pH where precipitation starts is Pb<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup> and the solids precipitated tend to be derivatives of this in a dehydrated form of the ion<sup>7</sup>. In aqueous solution containing some anions (X<sup>-</sup>), species such as PbX<sup>+</sup> are formed and, on addition of an excess of halogen acid, the stable

species are  $\text{PbX}_3^-$ . The solubility of lead in acetic acid media results from the stability of the triacetatolead (II) ion  $\text{Pb}(\text{CH}_3\text{CO}_2)_3^-$ .

There is an extensive range of organolead compounds, but the most important are  $(\text{CH}_3)_4\text{Pb}$  and  $(\text{C}_2\text{H}_5)_4\text{Pb}$  which have been used since the 1920's as antiknock agents in gasoline. The use of lead in petrol has had a significant impact on atmospheric lead. Up to 75% of lead added to petrol is dispersed through the exhaust as aerosol lead that is inhaled by humans and deposited onto soils and plants<sup>4</sup>.

### 2.2.1 Electrochemistry of Lead and Lead Electrowinning

Lead has a high hydrogen overpotential and, consequently, although it is less noble than hydrogen, it may be electrodeposited from aqueous media at high cathode efficiencies. However, electrodeposition of lead often appears more noble (unreactive) than expected from its standard electrode potential<sup>6</sup>.



This lack of reactivity is partly due to:

- 1- A surface coating of lead oxide  $\text{PbO}_2$  at the anode. Normally, in the electrowinning of lead from several electrolytes, the current density used is low, so it is difficult to achieve evolution of oxygen at the anode surface, resulting in the formation of  $\text{PbO}_2$ .  $\text{PbO}_2$  and Pb can deposit at the same time and in equal amounts on the anode and cathode surfaces respectively. Some attempts have been made to minimise lead dioxide formation by facilitating oxygen evolution at the anode by the addition of oxidizable species such as iron (II), cobalt(II), arsenic or of some acids such as nitrous acid, but none of these methods is satisfactory<sup>10, 9</sup>.
- 2- The high overpotential for the reduction of  $\text{H}^+$  to  $\text{H}_2$  at the lead cathode surface. The production of  $\text{H}_2$  from  $\text{H}^+$  at a lead cathode is kinetically unfavourable and for this reason a much larger potential than the standard lead reduction potential is required for lead deposition<sup>6</sup>.

The presence of ions such as fluoroborate, silicofluoride, sulphamate or pyrophosphate is necessary in the electrodeposition of lead to reduce hydrogen overvoltage at the cathode surface and to produce a satisfactory industrial product that

is smooth and coherent<sup>10</sup>. Lead may also be electrodeposited from an aqueous solution of its salts such as acetate or nitrate, but the resultant electrodeposits have no commercial usefulness other than lead recovery.

Among the heavy metals, lead, mercury and cadmium are said to be among the most dangerous to the environment, and concentrations permitted in effluent are typically lower than  $1 \text{ mg dm}^{-3}$  (1ppm)<sup>11</sup>. Important sources of lead contamination include effluent from pyrometallurgical, hydrometallurgical and lead electrowinning operations. Much research effort has been devoted to lowering lead emissions to meet the consent levels, in particular by using electrolytic processes. The literature on electrolytic lead recovery using a variety of electrode types and cell configurations is extensive. For example, El-Deab et al<sup>12</sup>, studied the electrochemical removal of lead from flowing alkaline electrolytes using packed bed electrodes and concluded that high efficiency can be achieved when working at low electrolyte flow rates, using thick electrodes, or by using electrodes of large specific surface areas. De Leon and Pletcher<sup>13</sup>, studied the removal of lead from different aqueous solutions containing perchlorate, nitrate, tetrafluoroborate, chloride and sulphate using a reticulated vitreous carbon (RVC) cathode. The experimental measurements were made at pH2 to simulate the waste streams resulting from the production of lead-acid batteries. They found that the potential of deposit formation and the extent of Pb(II) removal during electrolysis depended on the anion present, with lead removed more quickly from chloride solution than nitrate, perchlorate, or tetrafluoroborate. Similar studies were performed by Carreno et al<sup>14</sup>, also using RVC and fractured vitreous carbon (FVC) electrodes for removal of lead from nitrate, chloride and sulphate solution. A highly dense lead deposit was obtained from the chloride-containing electrolyte and this was attributed to the increased number of nucleation sites due to chloride co-adsorption at the electrode surface. Deposits formed from the sulfate electrolyte consisted of numerous, isolated and rather small lead clusters, indicating that deposition from sulphate solutions was inhibited by the formation of the passivated salt layer over the lead clusters. Widner et al<sup>15</sup>, reported a reduction in the lead levels from wastewater to  $0.1 \text{ mg dm}^{-3}$  in 20 min on three-dimensional, reticulated vitreous carbon cathodes.

Exposito et al<sup>11</sup> developed a technique based on an electrochemical process for the removal of lead using a three-dimensional carbon-felt cathode and a hydrogen-diffusion anode. They claim that the method can cope with effluent from lead electrowinning processes in fluoroborate baths after the lead has been electrolytically removed to approximately 100 mg dm<sup>-3</sup>. The lead deposit can be removed from carbon-felt electrodes by chemical or electrochemical stripping, yielding a lead-containing solution that can be reused in the electrowinning process. The use of a hydrogen-diffusion electrode (HDE) significantly decreases the cost of the process in comparison with that of a dimensionally stable anode (DSA). Approximately 75% of the hydrogen needed for the HDE anode can be supplied by the hydrogen evolved at the cathode, decreasing the total amount of hydrogen required from external sources.

Ramachandran et al<sup>16</sup> have recovered lead from spent lead acid batteries, by a process involving leaching of the active lead salts from the batteries with fluoroboric acid after desulphurisation followed by electrowinning from the resulting solution. Gopal et al<sup>17</sup> studied the possible lead recovery from waste streams using the membrane-electrode (M-E) process in the presence of Fe<sup>2+</sup> ions and found that the applied cathodic potential is the controlling factor for the rate and selectivity of ion-exchange in the M-E process.

### **2.3 CADMIUM**

Cadmium (Cd)<sup>3</sup> is a metal of Group IIb, or the zinc group, of the Periodic Table silver-white in colour and capable of taking a high polish. Its vapour is deep yellow and monatomic. Chemically, cadmium is very similar to zinc and their geochemical cycles are interrelated as zinc minerals contain cadmium. The metal is not oxidised in dry air but becomes coated with the oxide in moist air and burns on heating to redness. Cadmium has atomic number 48, atomic weight 112.40, melting point 32°C, boiling point 765°C and specific gravity 8.65. A rare element (about 0.2 gram per tonne in the Earth's crust), cadmium occurs in a few minerals and in small quantities in other ores, from which it is produced as a by-product.



World production of cadmium had increased between the 1930s and 1970s from 1000 tonnes to 15,000 tonnes as a result of an increase in demand for zinc and in the 1990's production has been around 21,000 tonnes per year<sup>18</sup>.

Most cadmium produced is electroplated onto steel, iron, copper, brass, and other alloys. Cadmium plated materials are especially resistant to attack by alkali. Some cadmium is used as the anode material in rechargeable storage batteries. Cd-containing alloys have many uses and the applications of cadmium chemicals include use as a stabiliser for plastic. The known toxicity of cadmium has, however, led to pressure for its replacement, for example in plastic food packaging<sup>18</sup>.

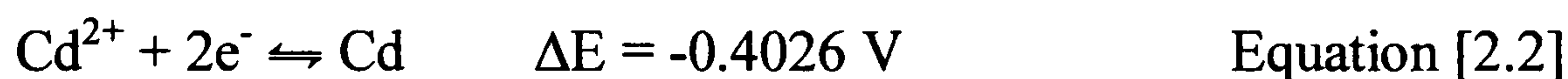
In its compounds cadmium exhibits almost exclusively the +2 oxidation state. A few compounds in the +1 oxidation state have been prepared by dissolving cadmium metal in molten cadmium(II) halides but the resultant diatomic cadmium(I) ion,  $\text{Cd}_2^{2+}$ , is unstable in aqueous solutions and immediately disproportionates to cadmium metal and  $\text{Cd}^{2+}$ .

Cd is a reactive metal and dissolves in non-oxidising acids, but does not dissolve in aqueous alkali;  $\text{Cd}(\text{OH})_2$  is not amphoteric, but cadmium hydroxide dissolves readily in an excess of strong ammonia with the formation of  $[\text{Cd}(\text{NH}_3)_6]^{2+}$  complex ion. Heating the metal in air gives CdO which is a brown powder and provides a convenient starting material for the production of most other cadmium salts. Cadmium halides are soluble in water except cadmium fluoride, which is sparingly soluble. Solutions of cadmium halides have been shown to contain the species  $\text{Cd}^{2+}$ ,  $\text{CdX}^+$ ,  $\text{CdX}_2$ ,  $[\text{CdX}_3]^-$ ,  $[\text{CdX}_4]^{2-}$  and polymeric ion. Cadmium bromide reacts with Grignard reagent and with lithium aryls to form organo-cadmium compounds. A compound of some economic value is cadmium sulfide, CdS, produced by treating cadmium solution with a soluble sulfide. The product CdS is a bright yellow pigment known as cadmium yellow which has been used in high-grade paints because of its colour stability and resistance to sulfur and oxidation. CdS and CdSe mixed in different ratio with ZnS have also been used as red, yellow or orange pigments in a range of products including paints, rubber, enamel glazing and printing inks.

The aqua ion  $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$  is quite acidic, and in dilute aqueous solutions of cadmium salts,  $\text{CdOH}^+$  is formed. Complexes  $[\text{Cd}(\text{NH}_3)_6]^{2+}$  and bridging  $[\text{Cd}_2(\text{CN})_7]^{3-}$  ions together with species containing lower ligand:metal ratios, are formed with ammonia and cyanide respectively.

### 2.3.1 The Electrochemistry of Cadmium and Cadmium Electrowinning

Commercially, the electrodeposition of cadmium can be performed using a cyanide bath, but because of the cyanide toxicity, research has been focused on non-polluting, non-cyanide, simple acidic electrolytes. Successful deposition has been reported from acetate<sup>19</sup>, borate<sup>20</sup>, chloride<sup>21</sup>, sulphate<sup>22</sup> and fluoroborate<sup>23</sup> baths. The cadmium reduction potential is:



In the electrodeposition of cadmium under acidic conditions, the most competitive reaction is hydrogen gas evolution. Additives such as alcohols or thio compounds have been used as selective catalysts and inhibitors of the electrode reactions. These additives generally have two functions, 1)- to complex with Cd (II), which causes a cathodic shift of the reduction potential, and 2)- to act as blocking agents at the cathode surface, to reduce the hydrogen evolution<sup>22</sup>.

The high toxicity of cadmium, and the stringent regulation on cadmium content of wastewater has placed an emphasis on the importance of cadmium recovery from dilute aqueous solutions. A number of different electrochemical methods have been used to remove and recover cadmium from effluent. The attraction of electrodeposition is the ability of this technique to recycle the metal in one step. There are, however, some limitations to the usefulness of this technique, particularly when dealing with low metal ion concentration, mixtures of metal ions and the presence of electrolytes and trace organics which can cause problems of poor efficiency, co-deposition and electrode inhibition<sup>24</sup>.

The main pathway for removing cadmium electrochemically from aqueous solutions at low pH is cathodic reduction. But at high pH > 9.5 and with large enough cathodic potentials, local pH changes can occur at the solution-electrode interface due to water and oxygen reduction. Under these conditions  $\text{Cd}(\text{OH})_2$  is formed and can be

removed from the solution by adsorption on the electrode as a charged colloidal particle<sup>25</sup>.

Several electrode and cell designs have been used for cadmium recovery from aqueous electrolytes. Abda et al<sup>25</sup> used graphite felt electrodes in two types of cell, namely a flow-by type separated by cation exchange membranes and a flow-through type in which no membrane was used. These cells were used to remove cadmium and nickel at high pH, as the metal hydroxide charged colloidal form and at the same time destroy cyanides at the anode surface. The solution used was a model for the waste effluent resulting from Ni/Cd battery recovery processes. They found that the removal of cadmium is much more efficient than that of nickel and that the cadmium concentration could be reduced from 10ppm to less than 10ppb.

Vachon et al<sup>26</sup> described a prototype electrochemical reactor with a carbon-fibre electrode to recover cadmium and destroy cyanide from plating rinsewater. The electrochemical reactor was operated in a closed-loop circuit with a recovery tank installed on the plating line. The cadmium concentration was reduced from 300 to 60 ppm ( $\text{mg dm}^{-3}$ ). Scott and Paton<sup>24</sup> have removed cadmium from process streams in the presence of ferric ( $\text{Fe}^{3+}$ ) using two techniques, a batch cell with a platinum anode and copper cathode and a flow cell, in which the two electrodes were separated by an anion exchange membrane. Tyson<sup>27</sup> described the application of a fluidised bed electrochemical reactor for the recovery of cadmium from a drag-out tank, following a plating bath. The cadmium concentration resulted from drag-out tanks was  $20 \text{ g dm}^{-3}$  and was reduced to the range of  $100\text{-}400 \text{ mg dm}^{-3}$  in the cell.

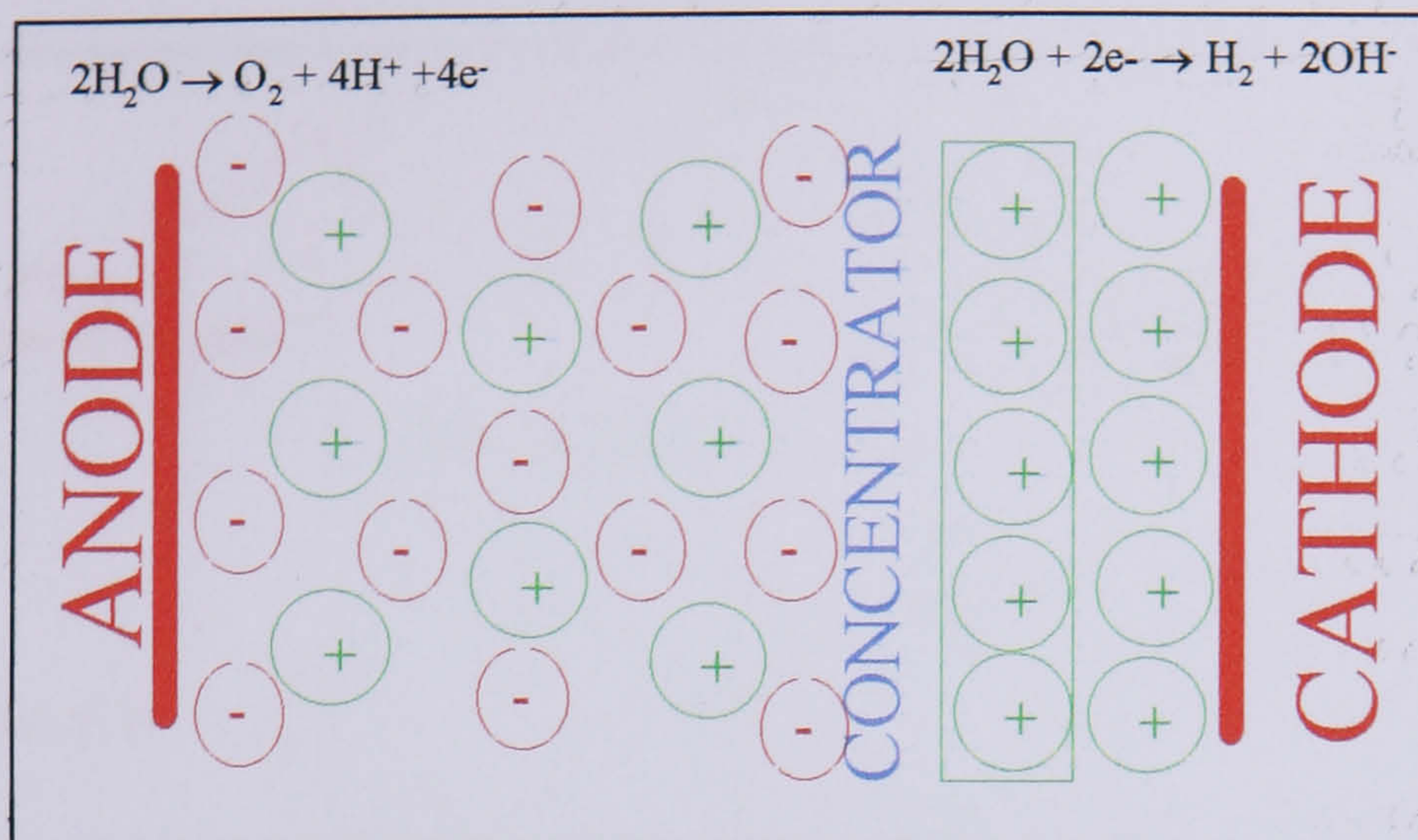
Boyanov, Donaldson and Grimes<sup>28</sup> studied the effect of cathode density, pH, time, type of electrodes, distance between anodes and cathodes and the presence of other ions such as  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  on the removal of Cu and Cd from dilute solution. The solution treated was typical of those found in the hydrometallurgical leach solutions, and the reactor used was a fluidised bed cell. They found that increasing the current density increased the removal rate but not the quality of the deposit and that at high acidity ( $\sim 50 \text{ mg dm}^{-3}$ ), electrolysis of Cd is difficult with about 75% of it remaining in solution. They also found that the presence of Fe along with Cd reduced the effectiveness of Cd recovery while Co and Zn did not have a significant effect.

In this present work, for the first time, the use of an electrochemical cell with concentrator electrodes is applied to the recovery of cadmium and lead from dilute single and mixed ion solutions.

## 2.4 CONCENTRATOR ELECTROCHEMICAL TECHNOLOGY

The Centre for Environmental Research (CER) at Brunel University has developed and patented a concentrator technology for the recovery, removal and recycling of heavy metal ions from dilute industrial effluent streams. The concept of a concentrator technology is to achieve concentration of metal ions in an electrolyte close to the cathode. This effectively creates a new cell with concentrated electrolyte at the cathode and increases the deposition efficiency.

The concentrator material close to the cathode surface collects the metal ions from the bulk of the solution on the active sites and then releases these ions near the cathode surface to improve the ion transfer conditions and ultimately increase the deposition rate. During the electrolytic process reduction of metal ions and water is occurring on the cathode surface along with the oxidation of water and other anions on the anode surface. The oxidation of water on the anode surface releases  $H^+$  ions ( $H_3O^+$ ) and the production of this acid is exploited in the cell to achieve the *in-situ* regeneration of concentrator material. The concept of the concentrator electrode cells used in this work is shown in Figure [2.1]. The concentrator materials used are ion-exchange resins and activated carbon cloth (described later).



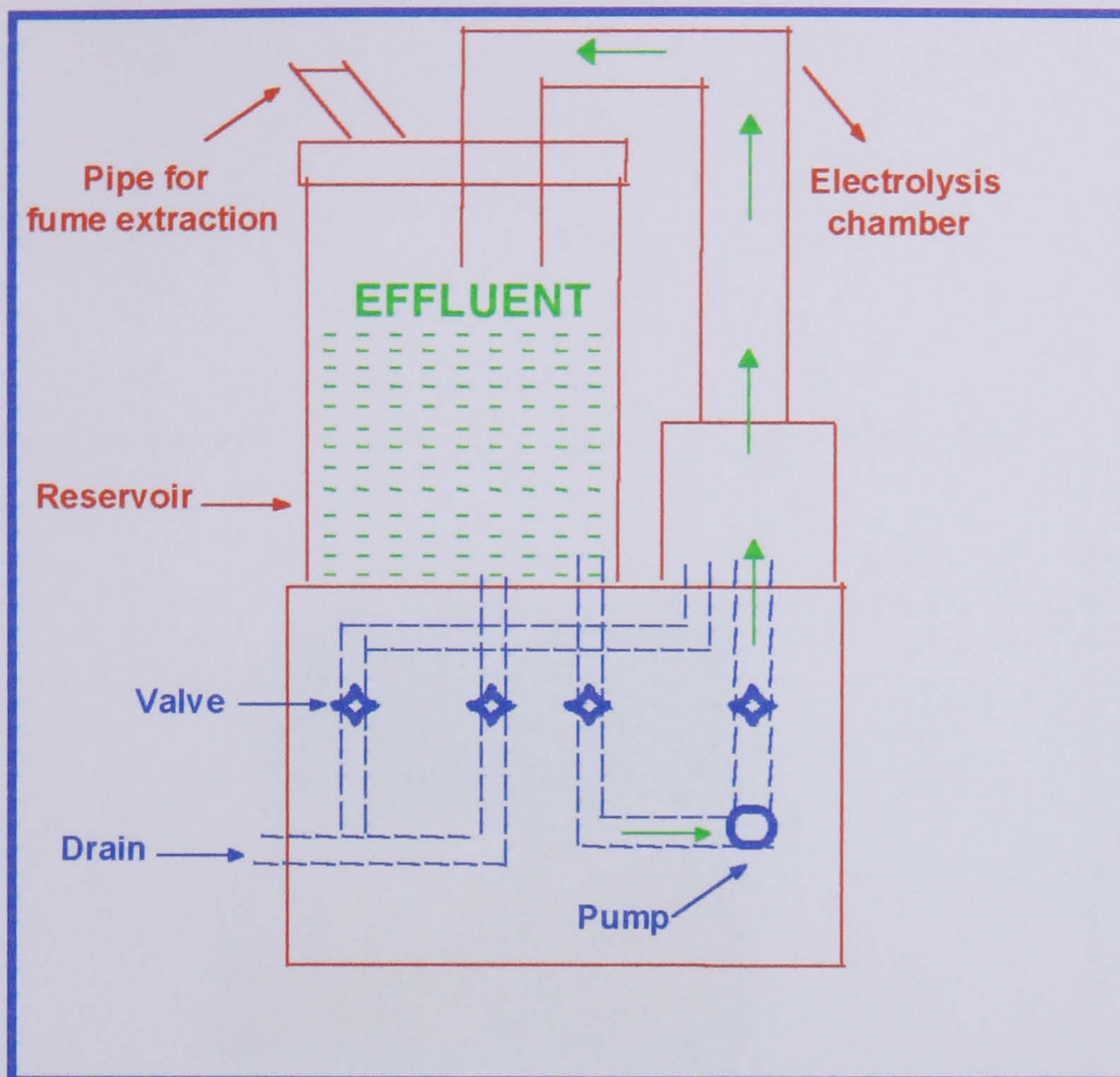
- (1) Initiation  $R-COOH^+ + OH^- \rightarrow R-COO^- + H_2O$  Equation [2.3]
- (2) Absorption  $R-COO^- + M^+ \rightarrow R-COO^-M^+$  Equation [2.4]
- (3) Regeneration  $R-COO^-M^+ + H^+ \rightarrow R-COOH^+ + M^+$  Equation [2.5]

**Figure [2.1]:** The basic concept of a concentrator cell.

## 2.5 EXPERIMENTAL

An electrochemical cell, originally designed as a fluidised bed cell, of 10 dm<sup>3</sup> capacity supplied by BEWT (Water Engineers Ltd.) was used in this work, without the fluidising medium. The electrolyte was circulated with a flow rate of 13.5 l/min. Two platinum coated titanium mesh anodes and a single titanium mesh cathode of the same dimension 16 x 15 cm<sup>2</sup> with surface area of 0.05 m<sup>2</sup> were used for all experiments. The electrodes were placed in the electrolysis chamber in a sequence anode-cathode-anode with an interelectrode gap of 1.5 cm. Experiments were conducted at ambient temperature with an operating current of 1.5A which gives a cathode current density of 30A/m<sup>2</sup>. Figure [2.2] is a schematic diagram of this cell which was used to obtain basic electrodeposition data for comparison with concentrator cell data. The dimensions of the electrolysis chamber and the reservoir were 9x20x35 and 26.5x26.5x30cm respectively.

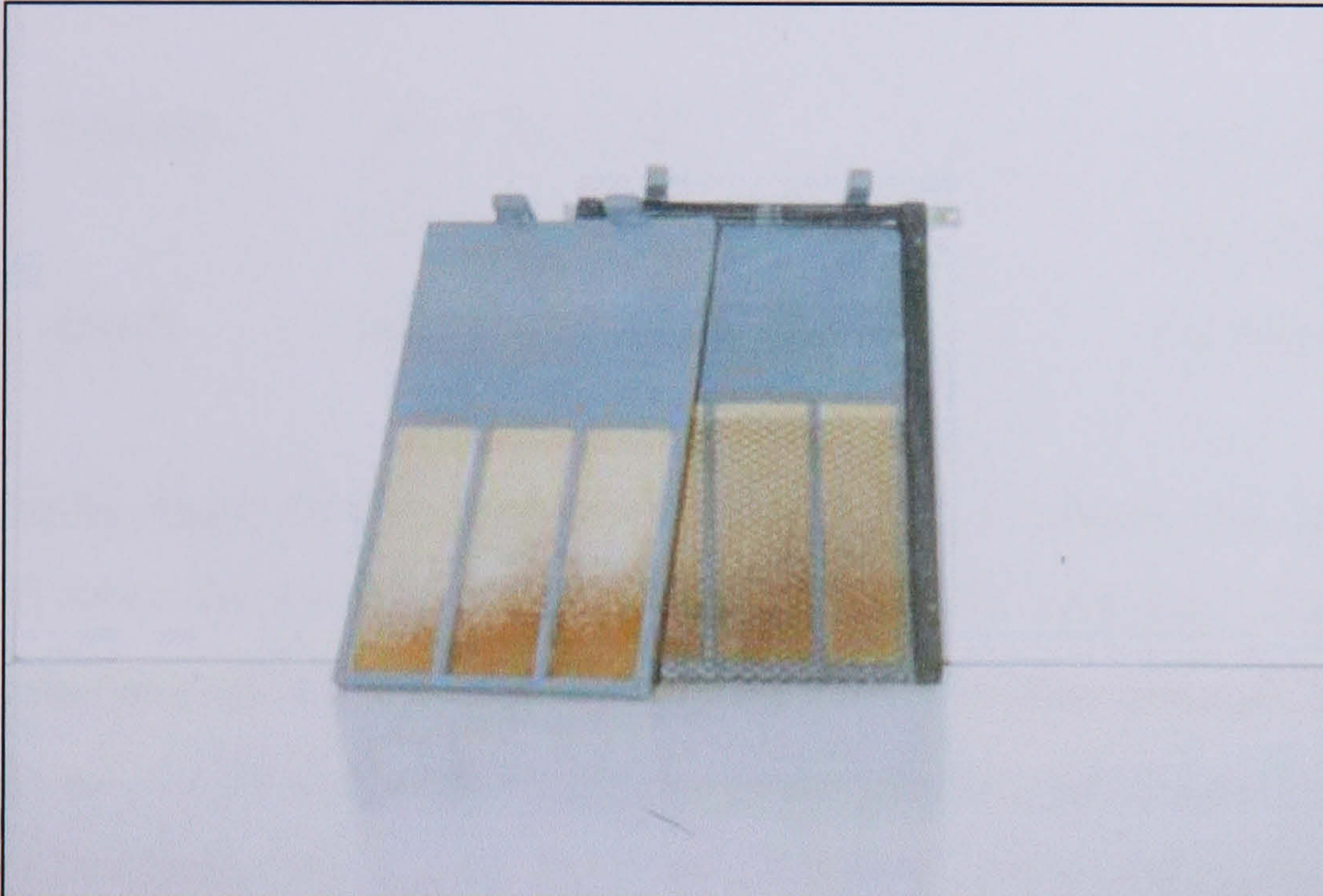
The two types of concentrator cell used in this work were obtained by replacing the single titanium mesh electrode with concentrator cathodes incorporating (a) a cation exchange resin and (b) an activated carbon cloth electrode.



**Figure [2.2]:** Schematic diagram of the fluidised bed cell.

### 2.5.1 The Ion Exchange Resin Concentrator Cathode.

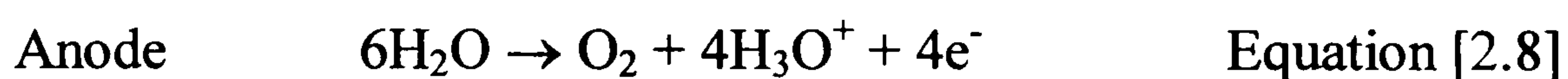
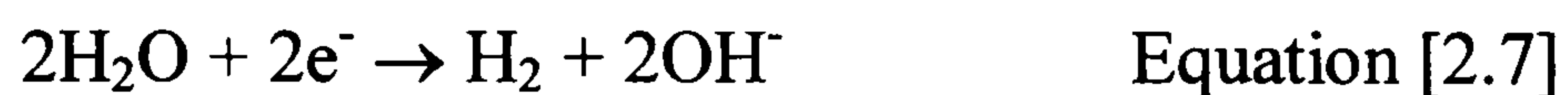
This concentrator cathode consisted of analytical grade Amberlite IR 120(H) ion exchange resin of particle size 0.30-1.18mm packed in two specifically designed plastic mesh containers and placed between the two anodes and the cathode at a distance of 0.3 mm from the cathode. The containers had dimensions of 16.5 x 27.8 cm and 1 cm thickness with 15 x 15 cm transparent mesh walls on both sides, each contained 235 g of resin. The dimensions of the containers were such that they covered the total working area of the titanium mesh cathode. Figure [2.3] shows the two pockets mounted on the titanium mesh cathode.



**Figure [2.3]:** The ion exchange concentrator electrode (IEC), the ion exchange resin packed in two mesh pockets mounted on the titanium mesh cathode.

### 2.5.1.1 In-situ Regeneration of the Ion-exchange Concentrator

Traditionally ion-exchange resins loaded with metal ions are regenerated by passing acid solutions through the resin bed. In the concentrator cell, however, during the electrolytic process, reduction of both metal ions and water is occurring on the cathode surface along with oxidation of water and other anions on the anode surface. These combined processes result in acid ( $\text{H}_3\text{O}^+$ ) production that can be exploited to achieve *in-situ* regeneration of the ion exchange material:



In the initial stages of the reaction there are plenty of metal ions present and these ions will move towards the cathode surface under the influence of the electric field. Before reaching the cathode surface the ions have to pass through the ion-exchange material and will be exchanged with the hydrogen ions and concentrated on the resin until it is saturated. At the same time, the oxidation of water (Equation [2.8]) is taking place with the production of  $\text{H}_3\text{O}^+$  ions. These  $\text{H}_3\text{O}^+$  ions will move towards the cathode surface and replace the absorbed metal ion. The release of these metal ions will increase the metal ion concentration near the cathode surface and increase the deposition efficiency. Figure [2.4] illustrates the basic concept of the deposition processes using ion exchange resin as concentrator.

Ion exchange is the reversible interchange of ions between a solid and liquid phase, in which there is no permanent change in the structure of the solid. A widely used cation exchange resin is that obtained by the copolymerization of styrene (A) (general reaction shown in Scheme [2.1]<sup>29</sup>) and a small proportion of divinylbenzene (B), followed by sulphonation to produce sulfonic acid as a functional group, to give a strongly acidic cation exchange resin. The fixed negative charges on the functional group are balanced by an equivalent number of mobile cations.



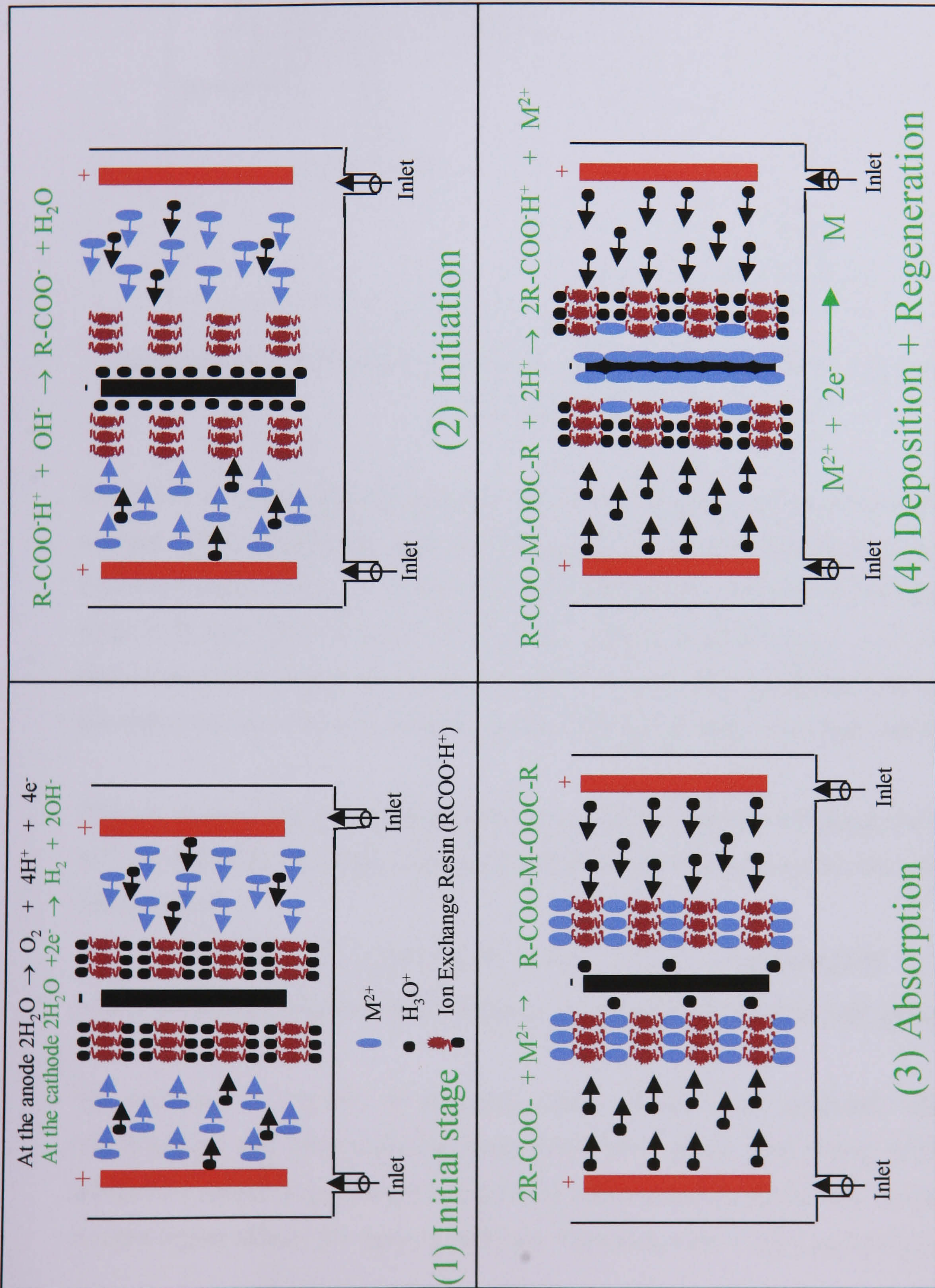
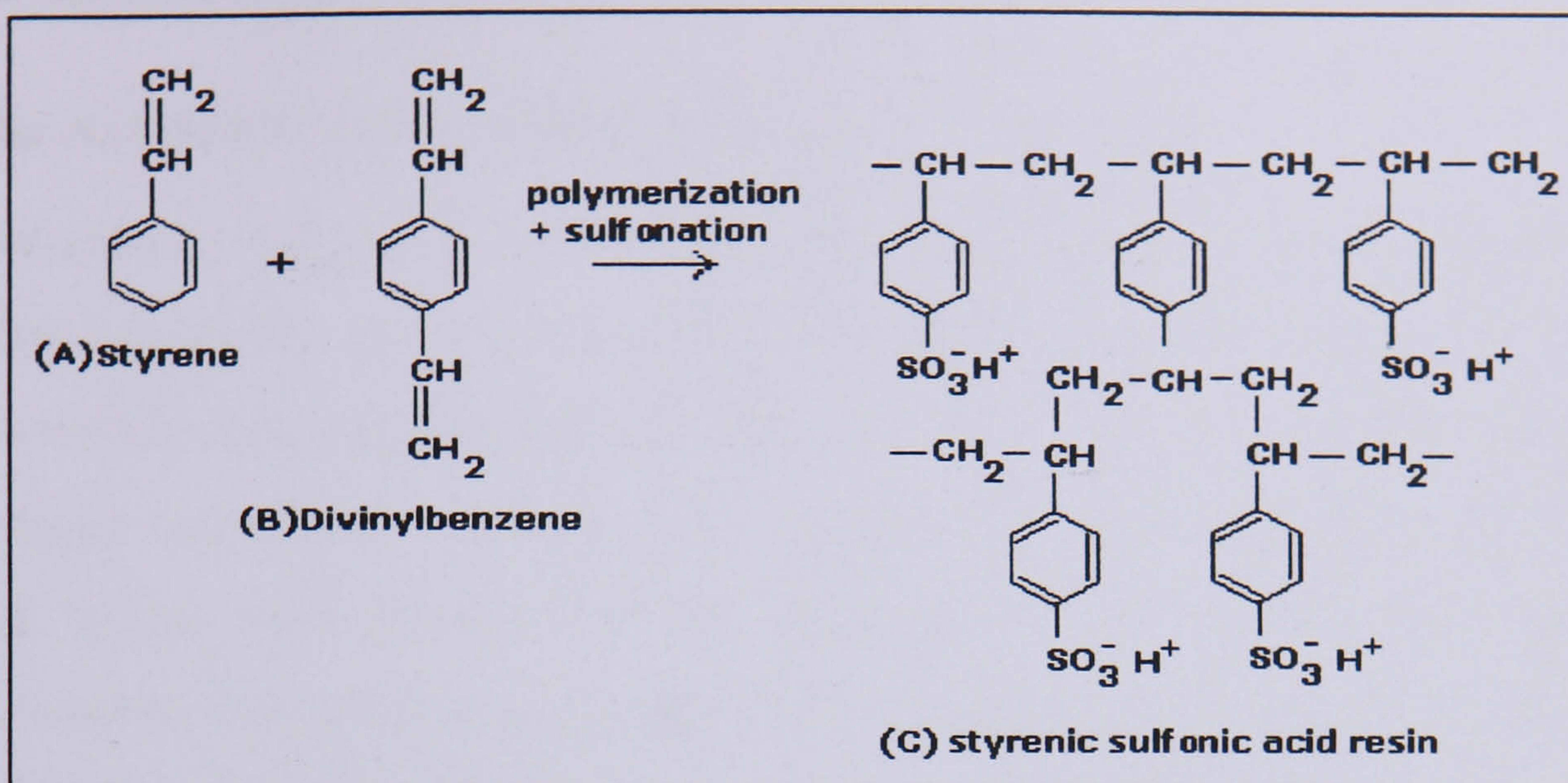


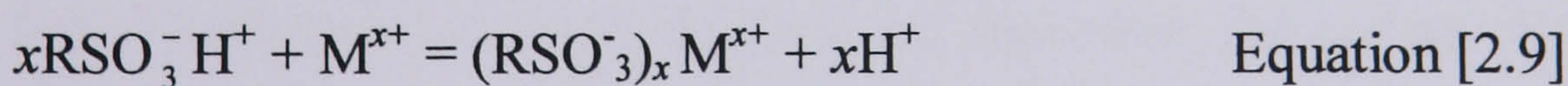
Figure [2.4]: The four different stages (initiation, absorption, deposition and regeneration) in the electrolytic process of metals ions ( $\text{M}^{2+}$ ) using ion exchange concentrator



**Scheme [2.1]:** Addition polymerization synthesis of styrene sulfonic acid cation exchange resins.

In general, ion exchangers are solid high molecular weight polyelectrolytes which can exchange their mobile ions for ions of equal charge from the surrounding medium. Cation exchange resins can be either a strong acid type with sulfonic acid groups or a weak acid type with carboxylic acid groups. Anion exchange resins contain basic amine functional groups attached to the polymer molecule. Strong base exchangers are quaternary amines while weak base resins contain secondary or tertiary amines<sup>30</sup>.

When a cation exchanger is immersed in an aqueous solution containing the cation  $\text{M}^{x+}$ , the following exchange equilibrium is quickly established between the solid and solution phase:



where R represents that part of the exchanger containing one sulfonic acid group.

Ion exchange is capable of removing heavy metals from industrial effluents (electroplating and other finishing operations). With strong acid resins, selectivity favours the uptake of polyvalent cations from dilute solutions. Weak acid resins have an even higher affinity for heavy metal ions. Therefore, even with conventional resins

such as those containing sulfonic or carboxylic groups, it is possible to obtain selective removal of heavy metal ions from effluents.

### **2.5.2 The Activated Carbon Cloth Concentrator Cathode**

Activated carbon cloth (ACC) can be used as an alternative to ion exchange resin in concentrator cathodes. It can be used in two distinct geometric structures, 1) with a gap between the cloth and the titanium mesh electrode similar to that described for the ion exchange concentrator cathode and 2) attached as an integral part of the mesh electrode. In the work described in this thesis the second of these was used. The activated carbon cloth was wrapped around the titanium mesh cathode and the edges were secured to the cathode using edge clamps. Figure [2.5] shows the activated carbon cloth concentrator electrode.

Activated carbon is a non-crystalline solid exhibiting a large internal surface area and pore volume, the characteristics responsible for its adsorptive properties. It has been used in many different liquid and gas phase applications. Activated carbon is an exceptionally versatile adsorbent since the surface charge and pore dimension can be altered to meet the needs of most applications. It can be produced in the form of powders, granules and shaped products according to the specific requirements of any application.

Activated carbon cloth (ACC) has certain advantages over most powdered and granular forms of activated carbon, offering a potentially higher adsorption capacity. In the present work cloth manufactured from viscous rayon is converted into activated carbon cloth, retaining the form of the rayon net. However, the carbon cloth is not as strong as the precursor material<sup>31, 32</sup>. The rayon is carbonised in a furnace by heating it in a stream of N<sub>2</sub> (flow rate, 4000 cm<sup>3</sup> /minute) to 850° C, at a heating rate of 10C°/minute and activated by changing the gas to an oxidising gas, such as CO<sub>2</sub>, at the same flow rate<sup>31, 33</sup>. The effect of activation on carbonised rayon is to produce a vast porous network within the volume of the solid. The carbonisation and activation of the rayon results in the production of highly microporous material (pore width < 2 nm) with small external areas and very little mesoporosity (pore width 2-50 nm)<sup>34</sup>. For certain applications the narrowness of the pores limits the usefulness

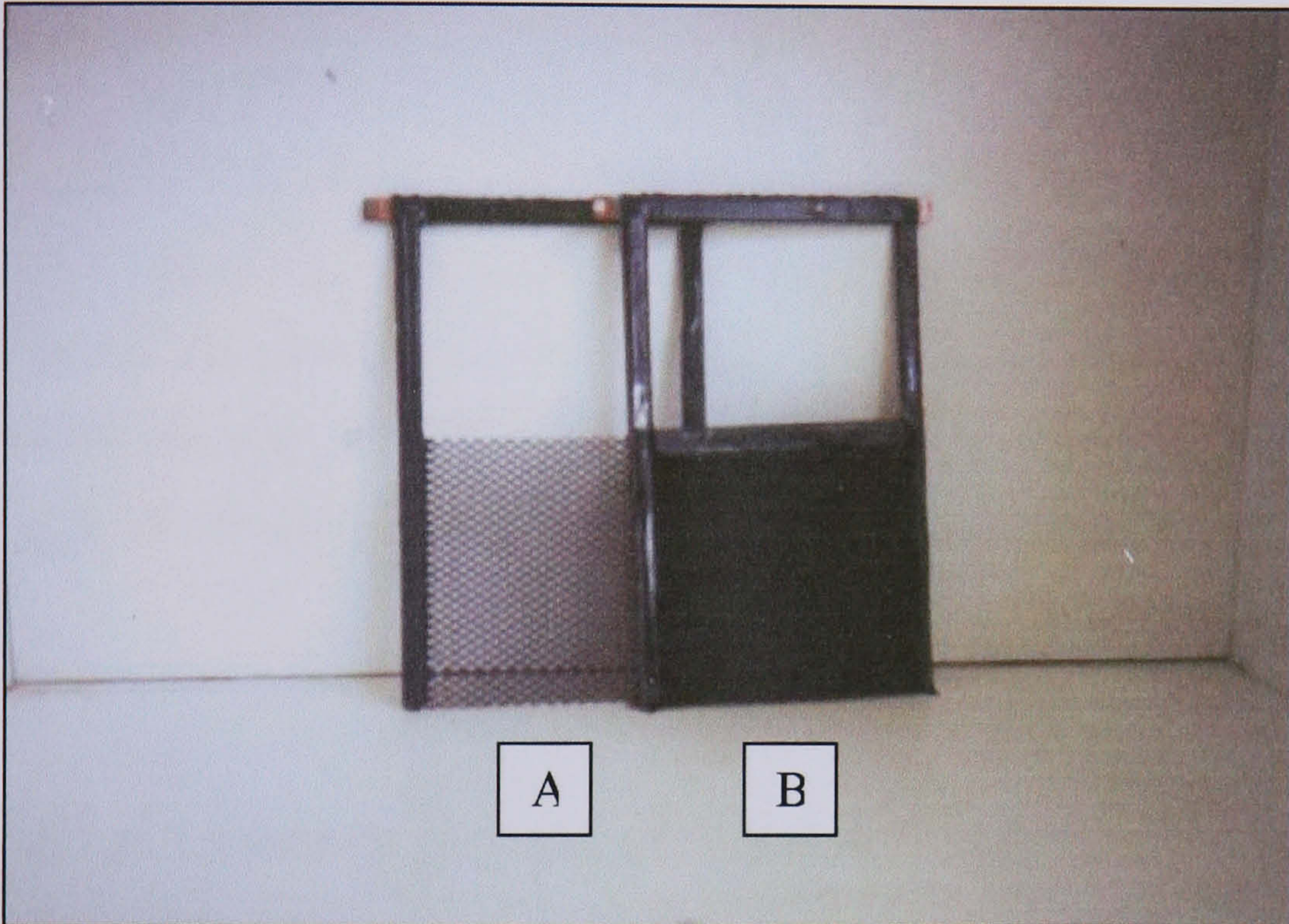


Figure 2.5: Two types of electrodes, A) the titanium mesh cathode (TMC) and B) titanium mesh cathode covered with activated carbon cloth concentrator (ACC)

of the material (such as the removal of large molecules from gaseous and liquid media)<sup>35, 36</sup>. Work has been done on increasing the pore size of ACC, by altering the nature of the activating gas used in the process, by changes in the carbonisation procedure or by pre-treatment of the rayon cloth before carbonisation and activation<sup>37</sup>.

The ACC used in this work was supplied by Charcoal Cloth (International) Limited. The cloth consists of a double 1/1 plain woven stitched fabric, black to grey in colour, consisting wholly of activated charcoal fibres, with approximately 10 threads per centimetre (warp) and 8 threads per centimetre (weft) per side. The typical internal surface area as measured by adsorption methods is in the range 1000-1200 m<sup>2</sup> g<sup>-1</sup>. Appendix 1 gives the full technical specifications of a typical Activated Carbon Cloth. Figures [2.6] and [2.7] are Scanning Electron Microscope (SEM) images of fibre bundles of pure activated carbon cloth (ACC). At the higher magnification, Figure [2.7] shows some adhering dust that is removed when the fibres are placed in solution.

### **2.5.3 Lead and cadmium removal and recovery studies**

To investigate the lead ion removal from different acid media, 50 mg dm<sup>-3</sup> (50ppm) Pb solutions were prepared using reagent grade lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] or lead acetate [Pb(CH<sub>3</sub>COO)<sub>2</sub>.3H<sub>2</sub>O], in different concentrations of nitric or acetic acids respectively. To investigate the cadmium ion removal from different acid media, 50 mg dm<sup>-3</sup> (50ppm) Cd solutions were prepared using reagent grade cadmium sulphate [CdSO<sub>4</sub>.8H<sub>2</sub>O], cadmium nitrate [Cd(NO<sub>3</sub>)<sub>2</sub>], or cadmium acetate [Cd(CH<sub>3</sub>COO)<sub>2</sub>.XH<sub>2</sub>O (formula weight 230.49)] in different concentrations of sulphuric, nitric or acetic acids respectively. To investigate the effect of pH on the percentage of metal removal, the pH was altered using NH<sub>4</sub>OH as a neutralising buffer solution.

Lead and cadmium levels were measured in samples taken every hour during electrolysis experiments by atomic absorption spectroscopy (AAS).

The performance of each cathode type was also studied in successive run experiments using 50mg dm<sup>-3</sup> (50ppm) of metal in solution at the stated pH values. The

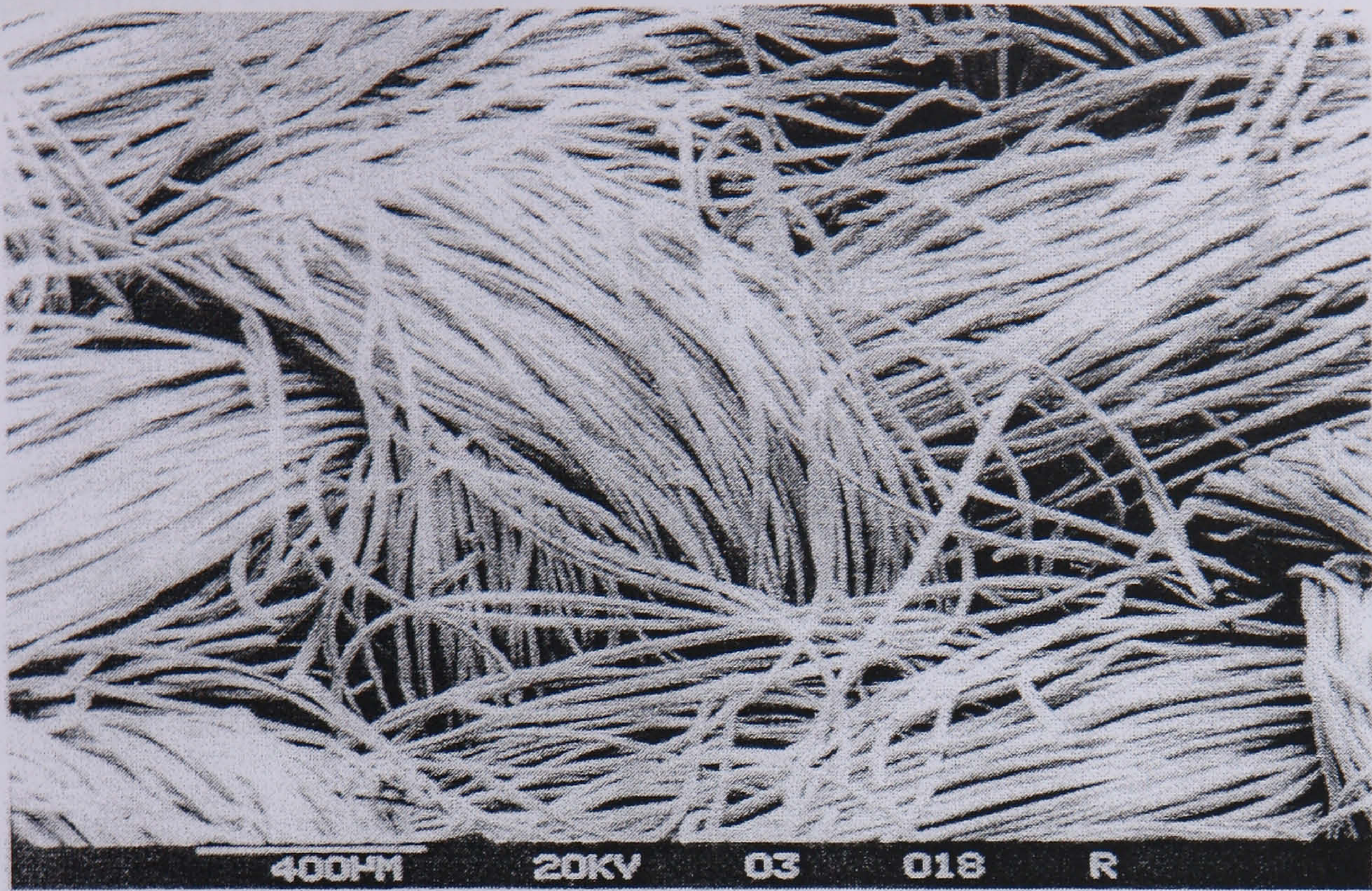


Figure [2.6]: Activated Carbon Cloth (magnification x 50).

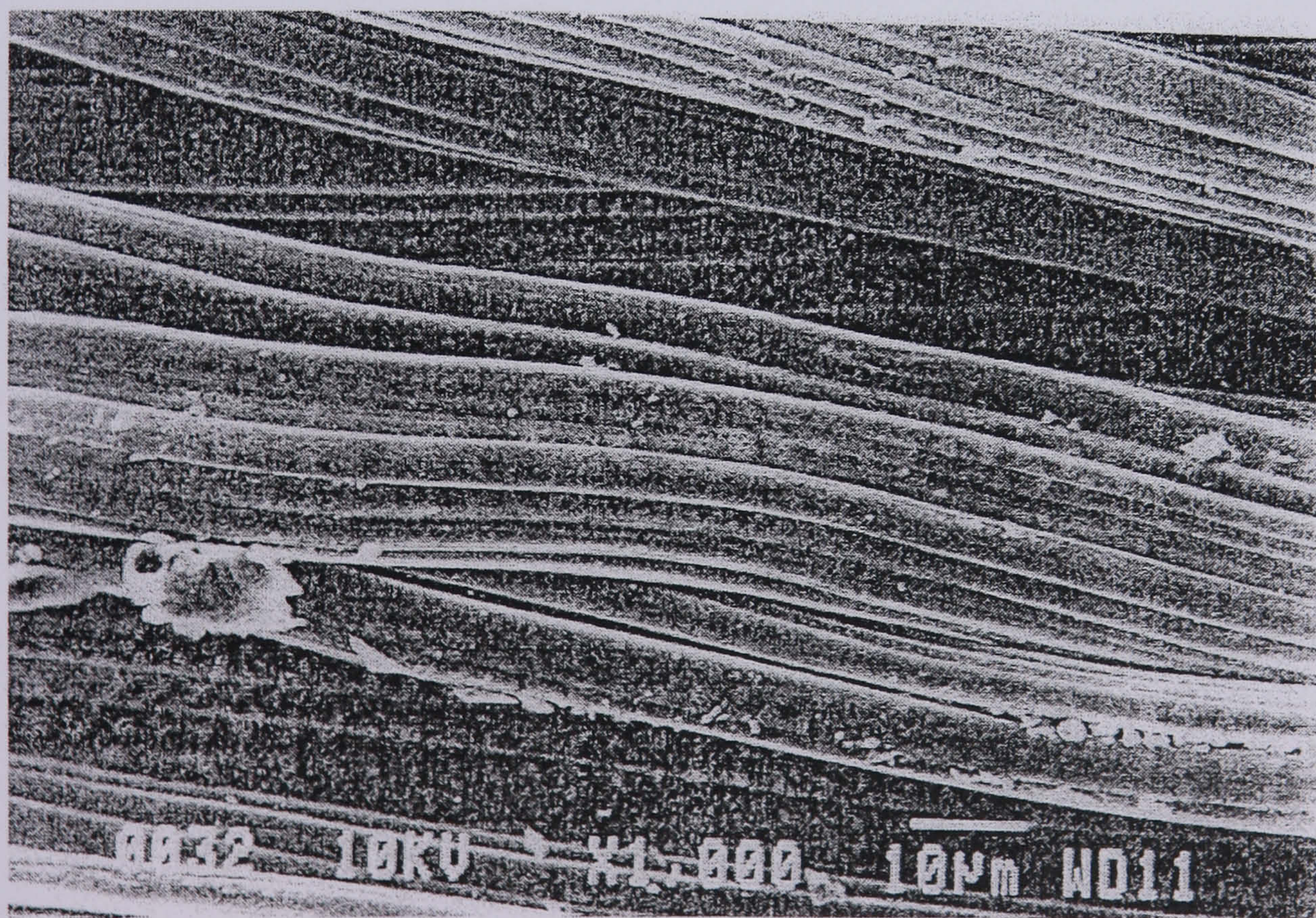


Figure [2.7]: Activated Carbon Cloth (magnification x 1000).

experiments were performed for 6 successive runs by topping up with 100ml solution to bring the metal concentrations back to  $50 \text{ mg dm}^{-3}$  after each run.

The morphology of the deposited metal on different cathodes and on the ACC after 6 successive runs was examined by SEM.

The effectiveness of the electrolysis process was determined and expressed as  $\alpha_M$ , the percentage of total metal removed. The total removal is the amount of metal deposited on the cathode and in the case of lead the amount of the element deposited on both the cathode and the anode.

$$\alpha_M (\%) = \frac{\text{actual metal ions deposition}(g) \times 100}{\text{initial metal ions concentration}(g)} \quad \text{Equation [2.10]}$$

Calculations of the energy consumed were also made for metal removal up to approximately 95% removal (2.5 ppm residual metal). The energy consumption (kWh/kg) of the electrolysis process is a measure of the overall energy consumed to produce 1 kg of metal and is given by the equation:

$$W(\text{kWh/kg}) = \frac{\text{voltage} \times \text{current} \times \text{time}}{\text{weight deposited}} \quad \text{Equation [2.11]}$$

## 2.6 RESULTS

The results reported for lead and cadmium recovery are expressed in graphical and tabulated form in terms of electrode type used:

- (I) TMC is standard titanium mesh cathode.
- (II) ACC is activated carbon cloth concentrator cathode.
- (III) IEC is ion exchange resin concentrator cathode.

## 2.6.1 Lead Recovery

### 2.6.1.1 Lead Recovery from Nitric Acid Media

The percentages of lead recovery from nitric acid solutions of strength 0.01, 0.05, 0.1, 0.5 and 1.0 mol dm<sup>-3</sup> are given in Table [2.1] and in Figure [2.8] while Figure [2.9] shows the energy consumption change for TMC, ACC and IEC cathodes.

The results show that recovery decreases with increasing nitric acid concentration for all these cathodes and reduces to zero when the acid strength is 1.0 mol dm<sup>-3</sup>. The values of the energy consumption up to a recovery value 95% Pb or less are also tabulated and show that there is very little difference between the performances of the ACC concentrator and the TMC cathode (although slightly better lead recovery is achieved using the ACC cathode) but that the IEC concentrator electrode system removes Pb more efficiently and quickly and with lower energy consumption.

Table [2.1]: The percentage removal and the energy consumption values of lead ions in different nitric acid concentrations using TMC, ACC and IEC systems.												
Percentage removal ( $\alpha_{Pb}$ %)												
Time (h) ↓	TMC				ACC				IEC			
Mol dm <sup>-3</sup> →	0.01	0.05	0.1	0.5	0.01	0.05	0.1	0.5	0.01	0.05	0.1	0.5
1	46	28	26	24	50	37	35	32	90	94	26	32
4	87	80	72	61	89	87	80	67	96	97	72	50
6	93	90	84	80	94	94	88	84	96	97	84	54
8	95	94	90	88	96	95	91	92	97	97	90	57
Energy consumption [ $W_{Pb}$ (kWh/kg)]												
1	22	28	26	28	21	22	21	21	20	10	26	21
4	50	39	38	44	49	39	37	41	80	40	38	54
6	72	53	49	51	70	54	50	50	--	--	49	75
8	98	68	61	62	--	72	65	61	--	--	61	114



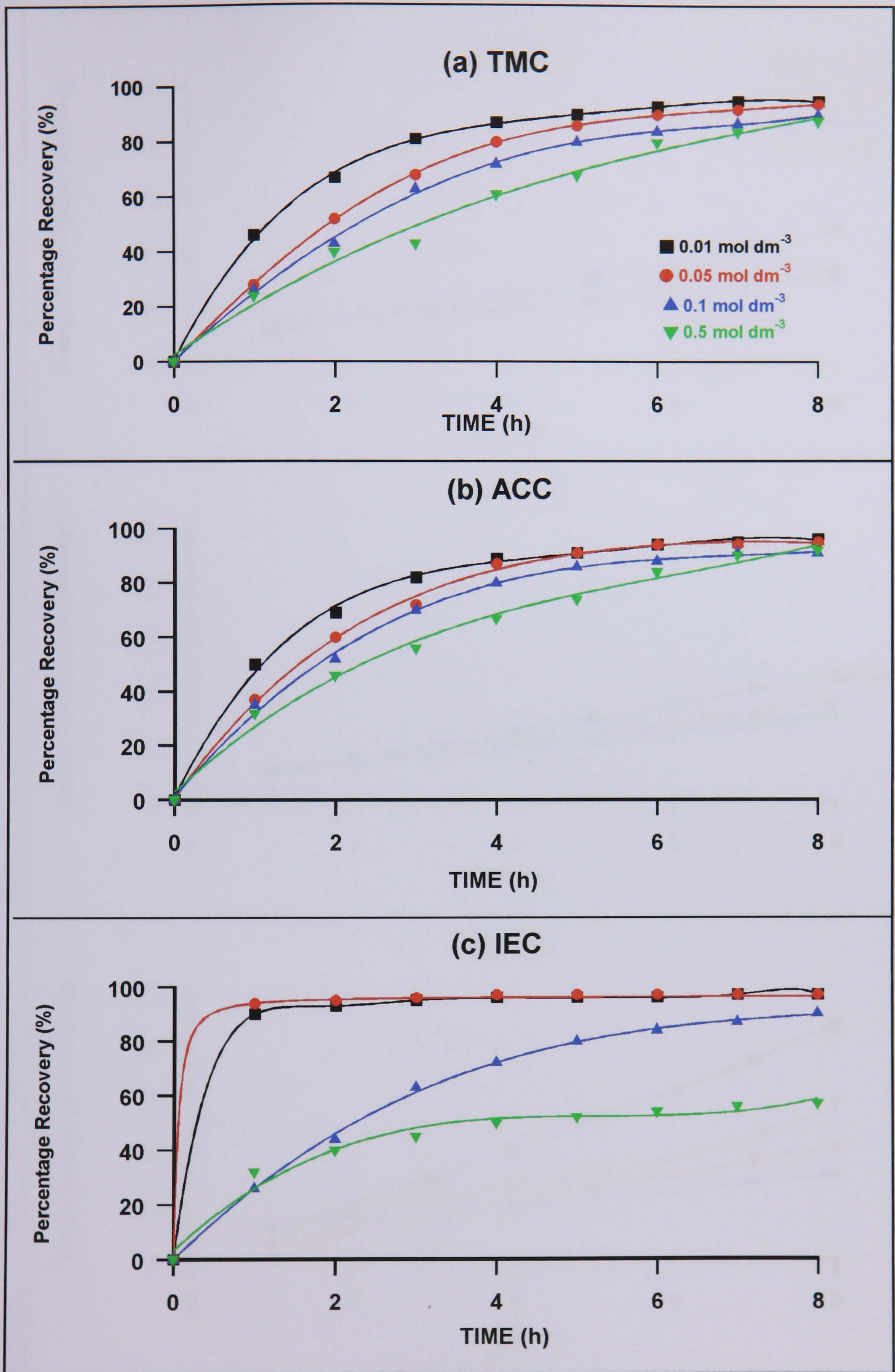


Figure [2.8]: The effect of nitric acid concentration upon the percentage lead recovery using (a) TMC, (b) ACC and (c) IEC.

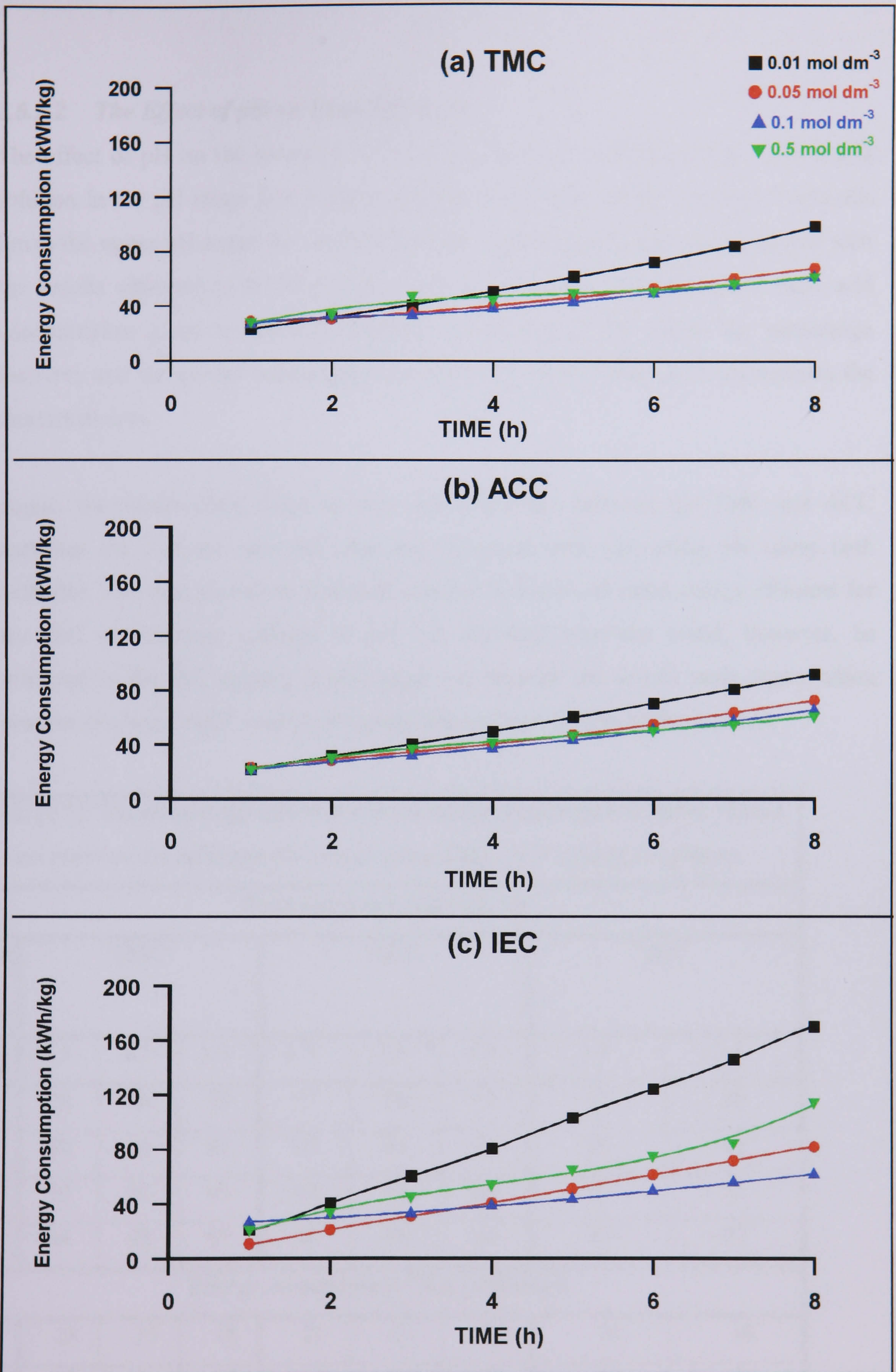


Figure [2.9]: The effect of nitric acid concentration upon the energy consumption of lead recovery using (a) TMC (b) ACC and (c) IEC.

### 2.6.1.2 The Effect of pH on Lead Removal

The effect of pH on the recovery of Pb was studied for a 0.05 mol dm<sup>-3</sup> nitric acid solution in the pH range 2-4. Lead precipitates as a basic nitrate<sup>7</sup> at pH > 5 and this limits the upper pH range for electrodeposition. The removal rate was compared with the results obtained at 0.05mol dm<sup>-3</sup> nitric acid without pH adjustment (this acid concentration gives a pH=1.5). Figures [2.10] and [2.11] show the percentage recovery and the energy consumption respectively, while Table [2.2] summarises the numerical data.

Again, the results show there is very little difference between the TMC and ACC cathodes but that the removal rates are increased with increasing pH using both cathodes. The data also show that lead removal is faster and more energy efficient for the IEC concentrator cathode at pH 1.5. No lead recovery could, however, be achieved in the IEC system at pH range 3-4 because the *in-situ* resin regeneration process produced H<sub>3</sub>O<sup>+</sup> ions very rapidly and reduced the pH of the solution.

Table [2.2]: The percentage removal and the energy consumption values of lead ion removal for different pH values using TMC, ACC and IEC systems.								
Percentage removal ( $\alpha_{Pb}$ %)								
Time (h) ↓	TMC			ACC			IEC	
PH →	1.5	2.5	3.5	1.5	2.5	3.5	1.5	2.5
1	28	45	72	37	54	77	94	80
4	80	90	93	87	91	95	97	95
6	90	96	95	94	96	98	97	95
8	94	98	97	95	98	98	97	97
Energy consumption [ $W_{Pb}$ (kWh/kg)]								
1	28	25	18	22	25	16	10	16
4	39	54	57	39	60	53	40	56
6	53	--	82	54	--	--	--	85
8	68	--	--	72	--	--	--	--

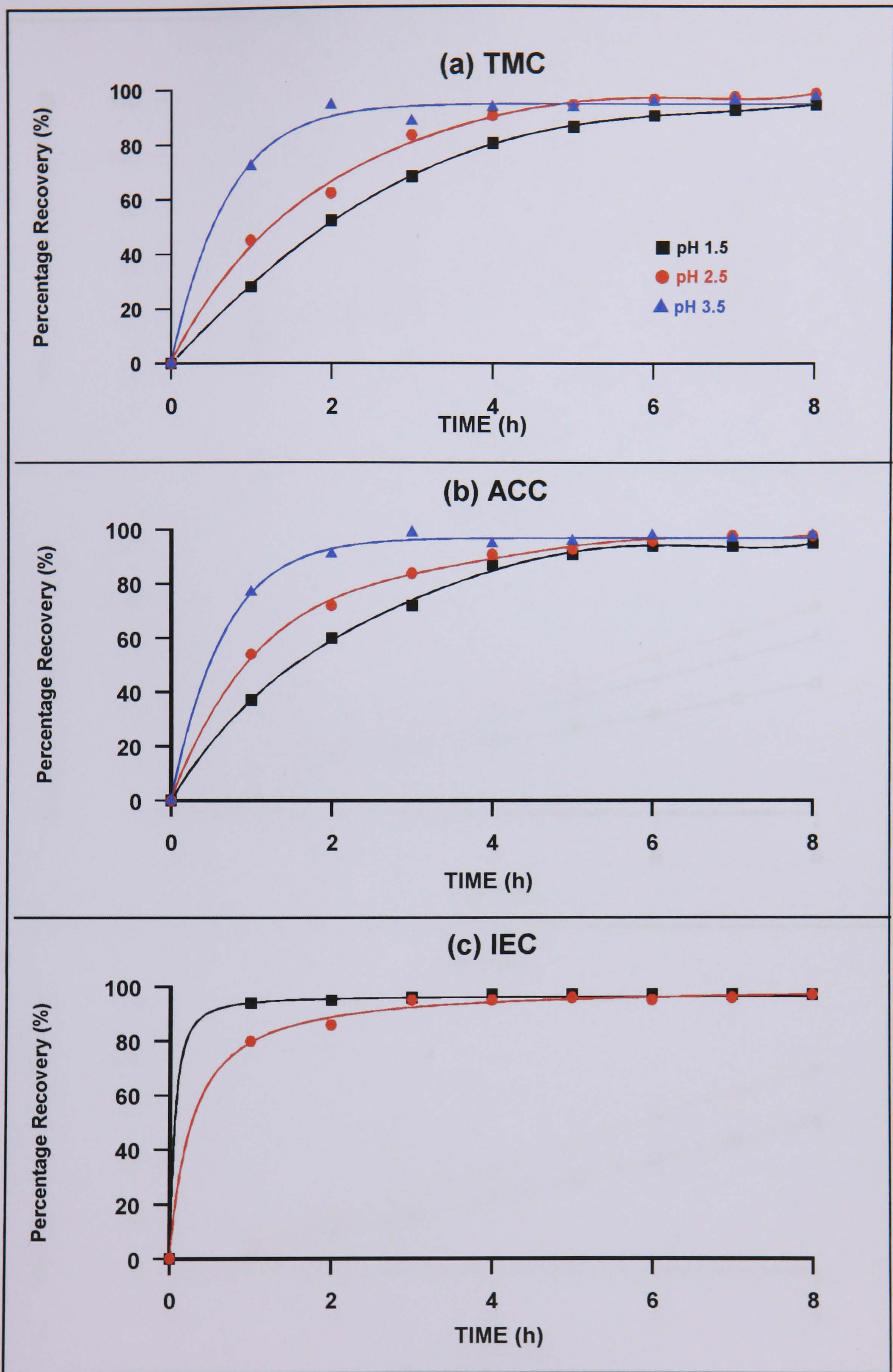


Figure [2.10]: The effect of pH on the percentage lead recovery using (a) TMC, (b) ACC and (c) IEC.

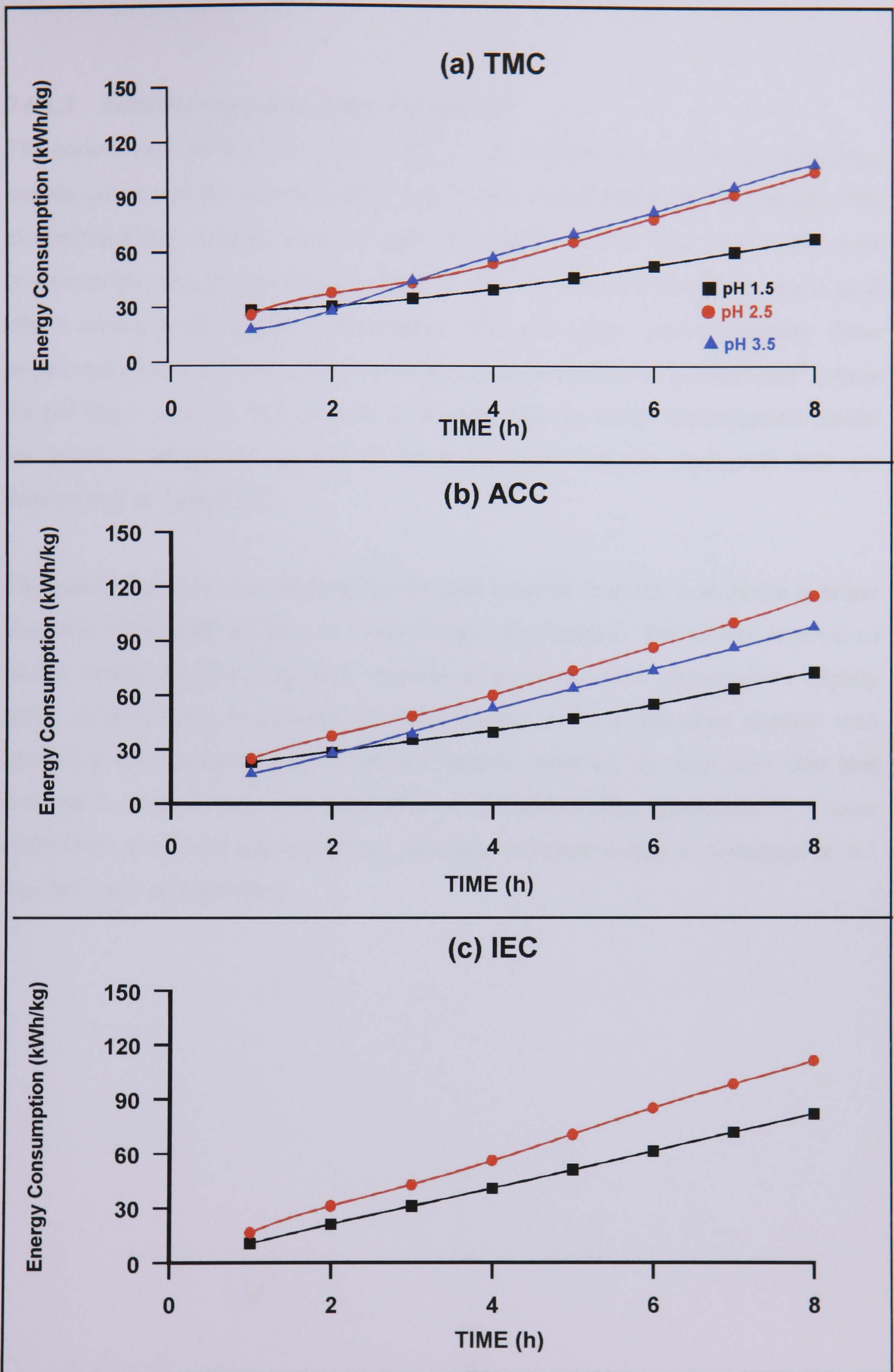


Figure [2.11]: The effect of pH on the energy consumption of lead recovery using (a) TMC, (b) ACC and (c) IEC.

### ***2.6.1.3 Lead Recovery from Acetic Acid Media***

The performance of IEC, ACC, and TMC on the removal process of lead ions from acetate solution ( $0.05 - 1.0 \text{ mol dm}^{-3}$ ) was studied using 50ppm Pb(II) solutions. The electrodeposition of lead, from an aqueous solution at  $0.01 \text{ mol dm}^{-3}$  acetic acid concentration was not possible because of the low conductivity of the acetic acid which increases the energy consumption. The pH range used throughout these experiments was 1-2, except for those with acid concentration of  $0.05 \text{ mol dm}^{-3}$  where the pH range was 2-3. The percentage removal and the energy consumption results are given in Figure [2.12] and [2.13] respectively and the numerical data are summarised in Table [2.3].

The results show that the performance for lead removal in acetic acid media is better than with nitric acid but there is higher energy consumption. The rate removal of lead is similar for TMC and ACC systems although the ACC system gives slightly better performances. In general, the rate removal of lead decreases slightly with increasing acid concentration. In the IEC system, however, the data show that lead removal is much better, with total removal completed after approximately 1 hour electrolysis at all acid concentrations, although minimum energy is consumed at  $0.5 \text{ mol dm}^{-3}$  acid concentration.

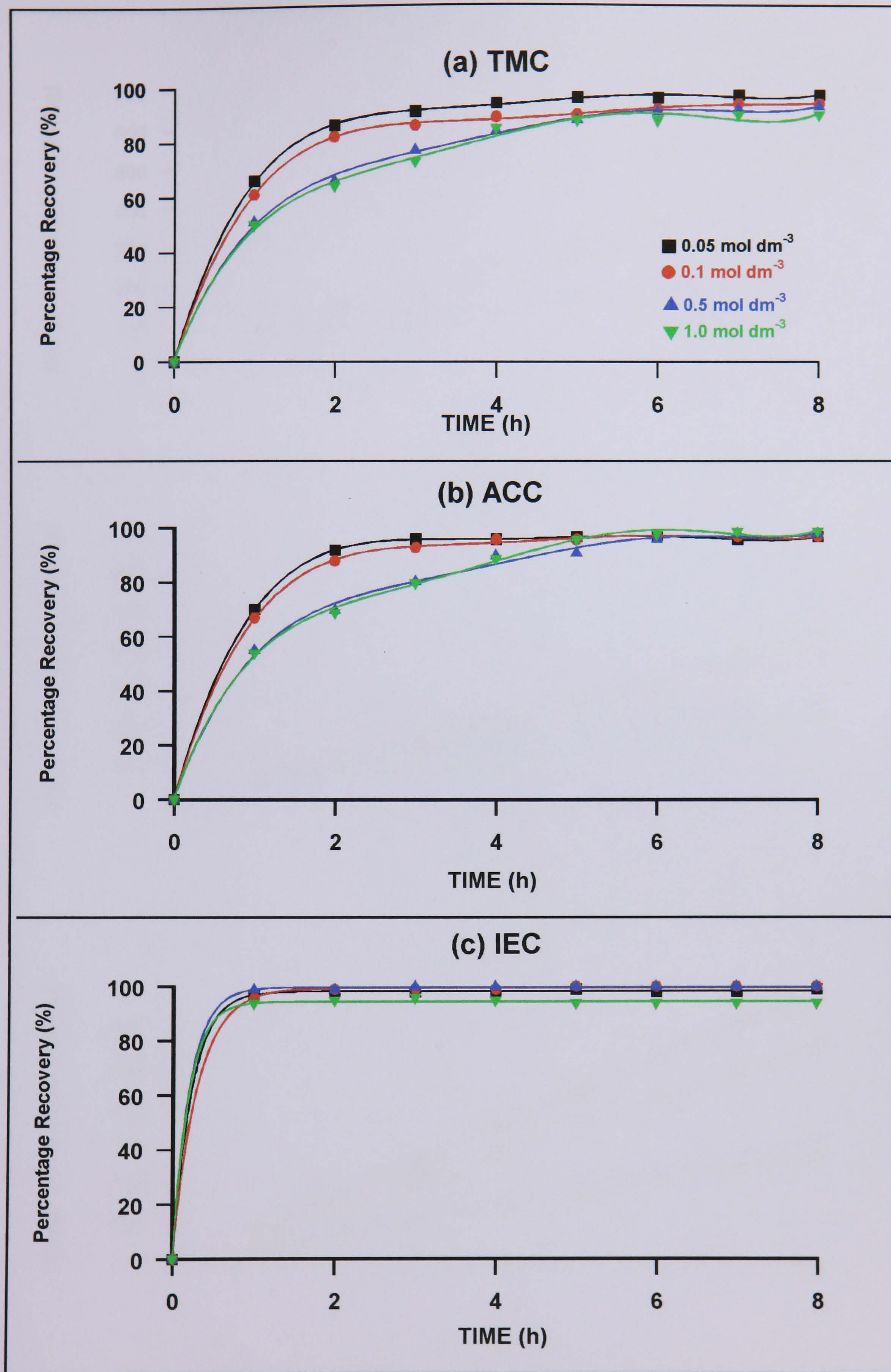


Figure [2.12]: The effect of acetic acid concentration upon the percentage lead recovery using (a) TMC, (b) ACC and (c) IEC.

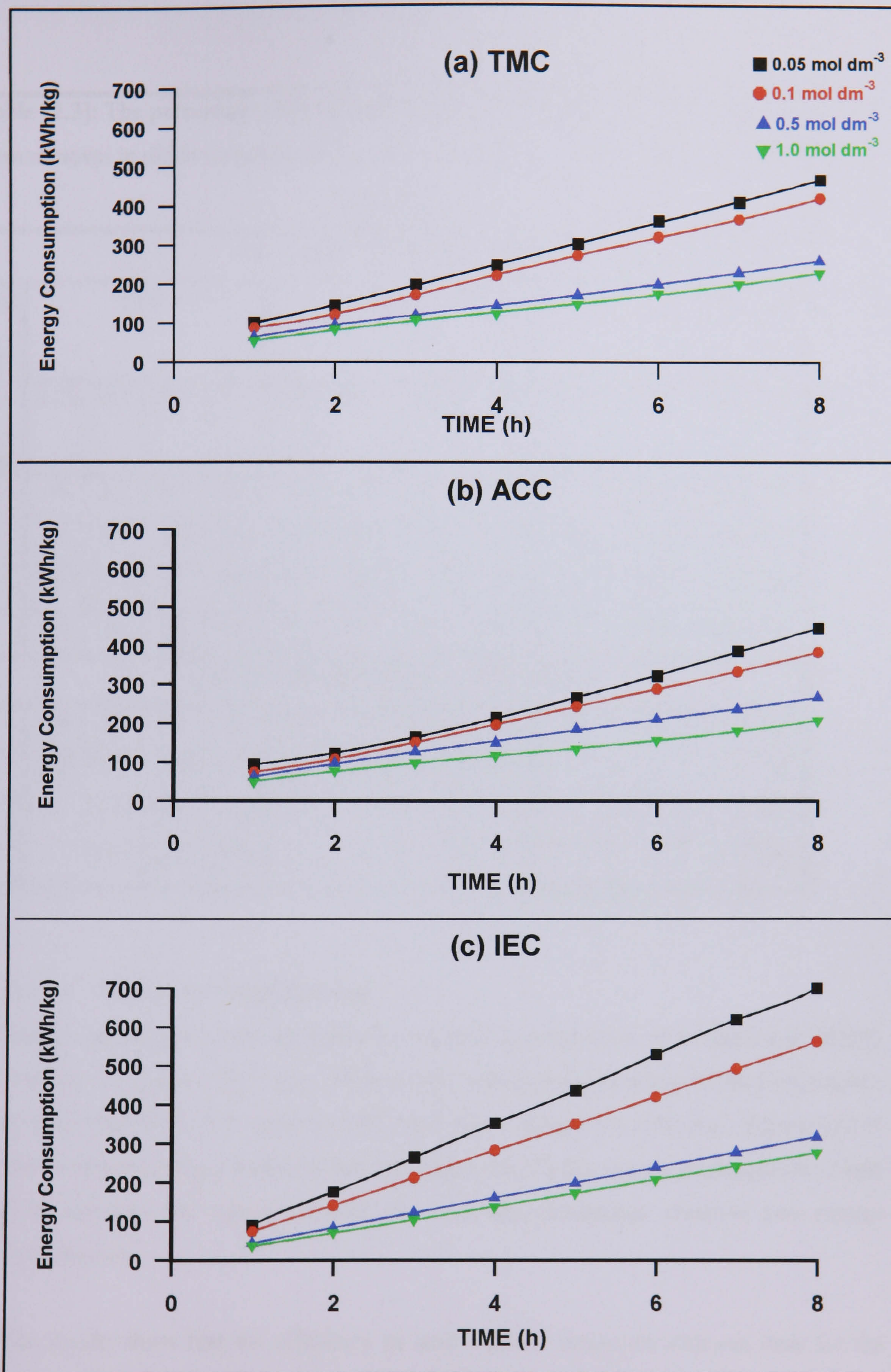


Figure [2.13]: The effect of acetic acid concentration upon the energy consumption of lead recovery using (a) TMC, (b) ACC and (c) IER.



Table [2.3]: The percentage removal and the energy consumption values of lead ion removal in different acetic acid concentrations using TMC, ACC and IEC systems.

Percentage removal ( $\alpha_{Pb}$ %)												
Time (h) ↓	TMC				ACC				IEC			
Mol dm <sup>-3</sup> →	0.05	0.1	0.5	1.0	0.05	0.1	0.5	1.0	0.05	0.1	0.5	1.0
1	66	61	51	50	70	67	55	54	97	96	99	94
4	94	89	84	85	96	96	90	89	98	99	100	95
6	96	92	91	88	97	97	96	98	98	100	100	94
8	97	94	93	90	97	97	98	99	98	100	100	94
Energy consumption [ $W_{Pb}$ (kWh/kg)]												
1	100	88	64	54	94	74	61	49	88	72	43	35
4	248	221	145	123	216	196	150	116	--	--	--	136
6	--	319	199	175	--	--	--	--	--	--	--	206
8	--	419	260	228	--	--	--	--	--	--	--	275

#### 2.6.1.4 Successive Lead Recovery

Further experiments were performed at an acid concentration of  $0.05 \text{ mol dm}^{-3} \text{ HNO}_3$  with the successive use of the different electrode types to investigate the performance of each electrode. The experimental time was 4 hours for each run. Figure [2.14] shows the percentage lead removal and Figure [2.15] the energy consumption. Table [2.4] contains the numerical data for both the percentage removal and energy consumption.

The results show that the efficiency of lead removal decreases with run time for the ACC and TMC cathode systems although the ACC cathode is still slightly more efficient than the TMC cathode. The IEC concentrator system, however, still shows fast and efficient lead removal. Although the removal rate is slightly decreased at the

initial stages with increasing the run time, the removal values become equal and reach the maximum of  $(97 \pm 1)$  after 2 hours electrolysis time. After 6 runs, at the cathode the deposited materials on the titanium mesh surface were collected, washed with distilled water and dried under vacuum. The dried materials, when using ACC and IEC, appear as a metal structure of shiny grey colour in which the surface is oxidised when exposed to air, whereas, using TMC, the deposit is white and crystalline. The deposited lead at the anodes using the three systems, however, shows a white, very thin layer, less in the IEC system that could not be removed from the electrode. This prevented further SEM analysis.

Figures [2.16], [2.17] and [2.18] are scanning electron micrographs and show the morphology of the cathodic deposited material using TMC, ACC and IEC respectively. The deposit obtained using TMC, shows that a crystal shape like a broken sheet with smooth surface and edges which are surrounded with acicular crystals. The deposit obtained using ACC consists of acicular crystals distributed all over the deposit. Finally, the deposit obtained using IEC consists of crystals with rough irregular surface and edges and no evidence for the presence of acicular crystals.

Figures [2.19], [2.20] and [2.21] are scanning electron micrographs and show that the Pb containing crystals electrodeposited on and completely covering the surface of the ACC fibres are dendritic in shape, interspersed with thin plate crystals.

Table [2.4]: The percentage removal and the energy consumption values of lead removal in successive use of the different electrode type TMC, ACC and IEC using 0.05M HNO <sub>3</sub>									
Percentage removal ( $\alpha_{Pb}$ %)									
Time (h) ↓	TMC			ACC			IEC		
	Run 1	Run 3	Run 6	Run 1	Run 3	Run 6	Run 1	Run 3	Run 6
1	34	13	13	37	32	15	93	96	86
4	61	55	46	61	59	40	98	97	96
6	72	66	55	77	68	55	98	97	98
8	83	73	62	95	80	82	98	97	98
Energy consumption [ $W_{Pb}$ (kWh/kg)]									
1	26	70	65	22	25	89	10	9	10
4	29	35	37	27	27	52	--	--	--
6	38	41	46	32	35	45	--	--	--
8	44	49	55	35	40	40	--	--	--

## 2.6.2 Cadmium Recovery

### 2.6.2.1 Cadmium Recovery from Sulphuric Acid Media

The effect of sulphuric acid concentration (0.01 - 1.0 mol dm<sup>-3</sup>) on cadmium deposition was examined using a 50mg dm<sup>-3</sup> Cd solution at a constant current of 1.5A. The results in Figure [2.22] show the percentage removal of Cd and those in Figure [2.23] the energy consumption while Table [2.5] summarises the numerical data for both percentage removal and energy consumption.

The results using the standard TMC and the ACC concentrator cell show that the cadmium is not removed efficiently in sulphuric acid media and that increasing the acid concentration decreases the cadmium removal until the process is stopped completely at acid concentration of 0.1 mol dm<sup>-3</sup>. The results also show that the performance of the ACC concentrator was poorer than that of the normal TMC. Using

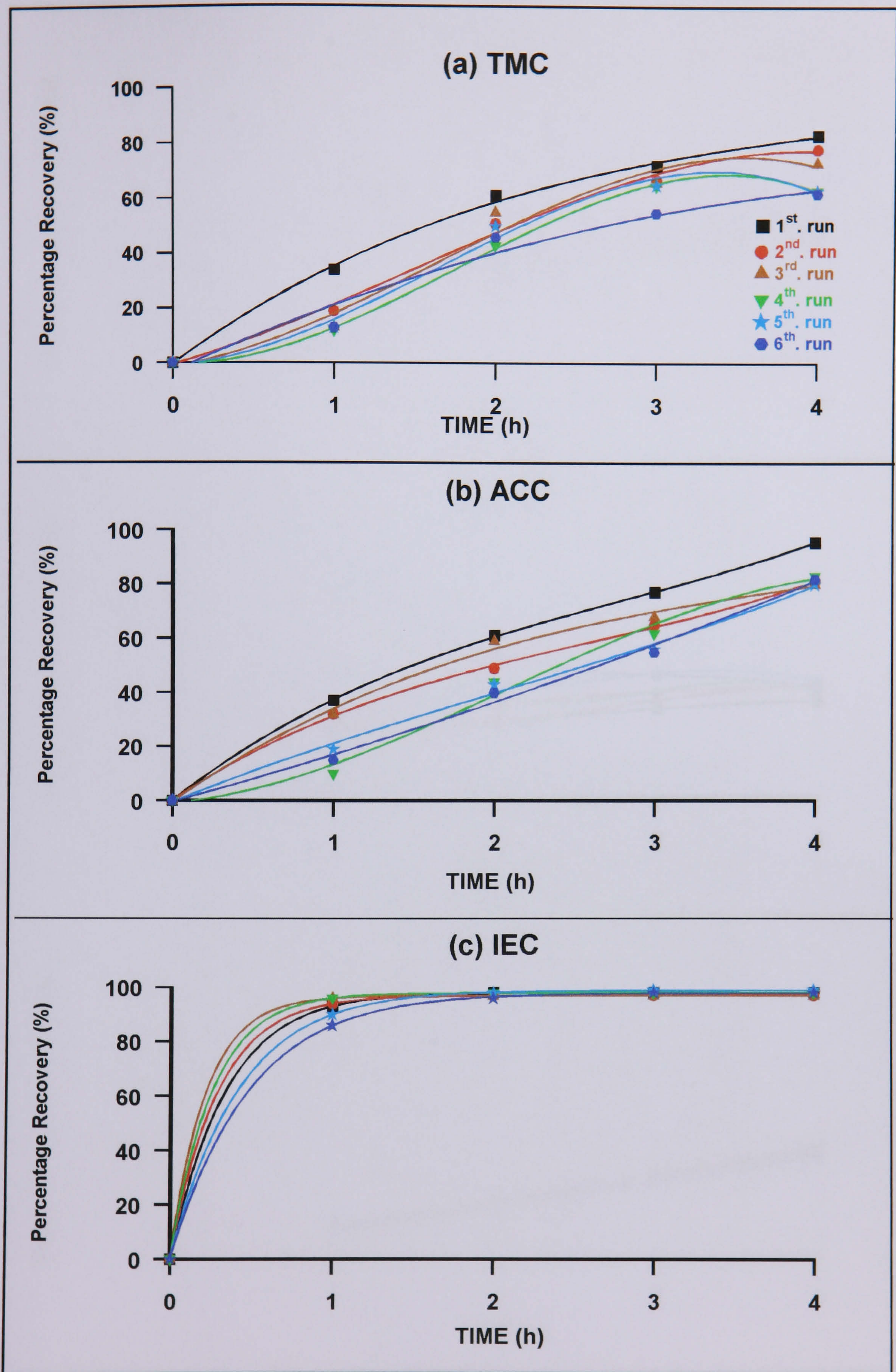


Figure [2.14]: The percentage recovery for successive lead (50ppm) removal from 0.05 M HNO<sub>3</sub> solution using (a) TMC, (b) ACC and (c) IEC.

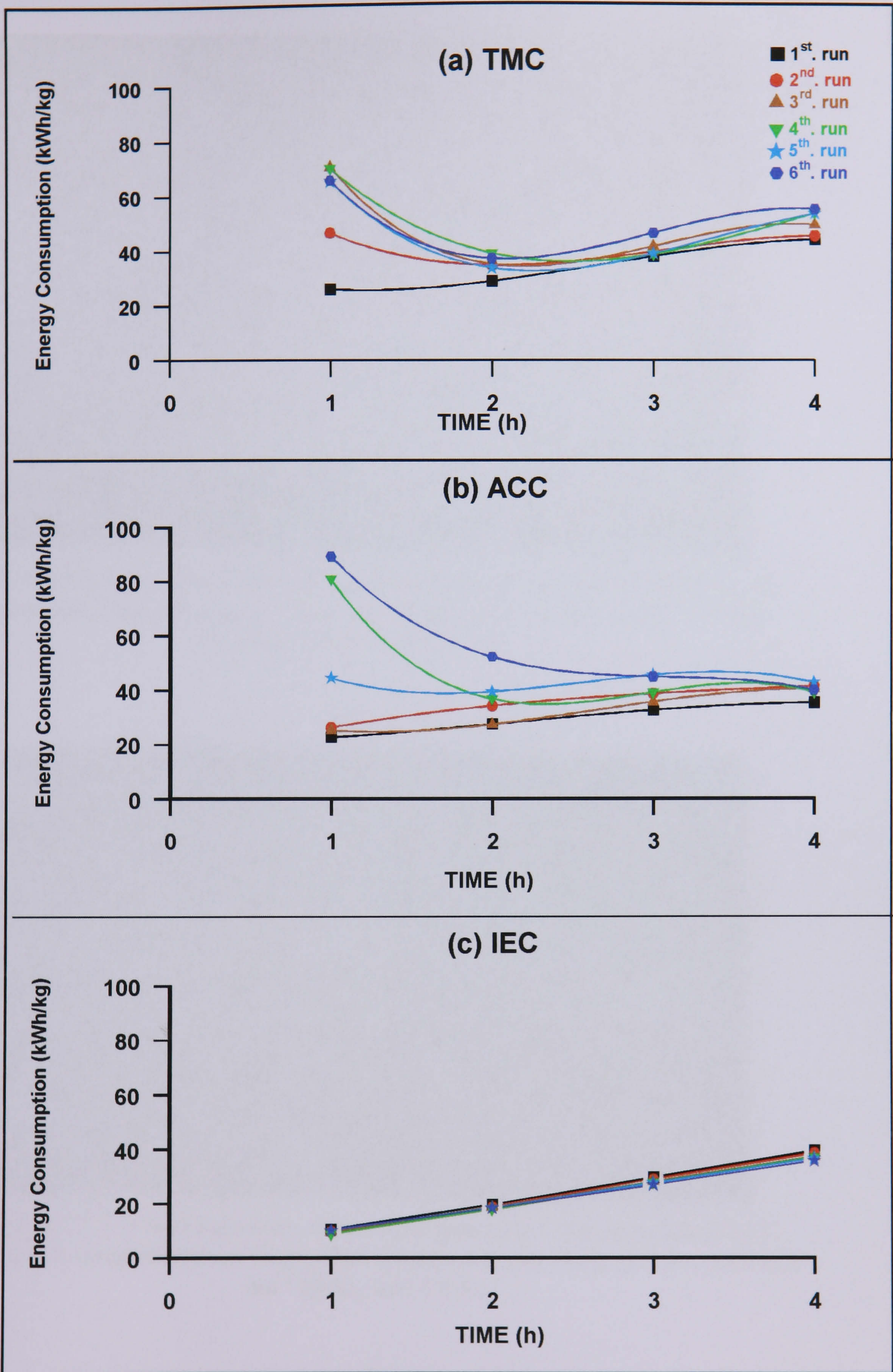


Figure [2.15]: The energy consumption for successive lead (50ppm) removal from 0.05 M HNO<sub>3</sub> solution using (a) TMC, (b) ACC and (c) IEC.

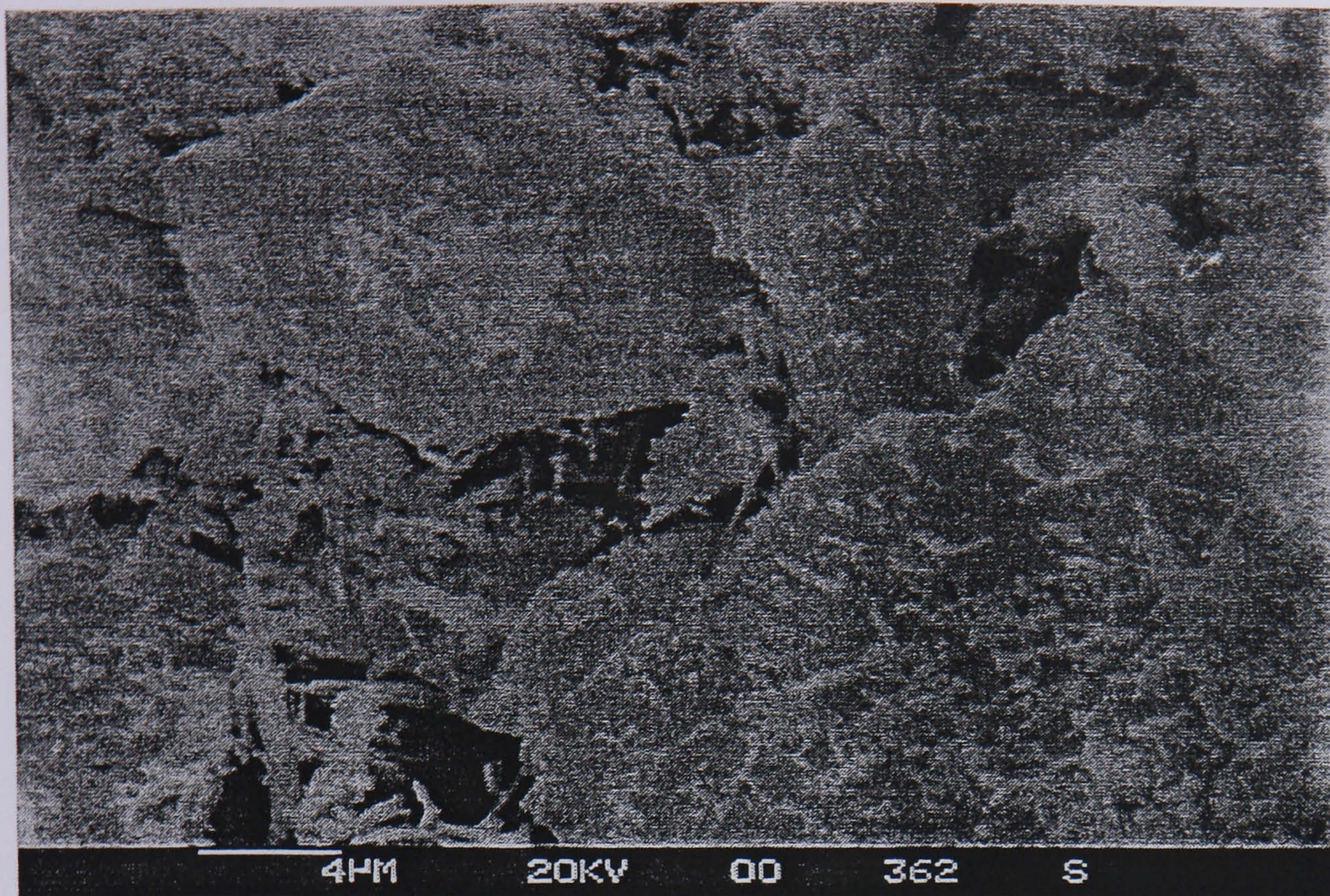


Figure [2.16] The lead deposition on the mesh electrode using control conditions and no concentrator (magnification  $\times 3750$ ), after 6 runs (each run  $50\text{mg dm}^{-3}$  Pb,  $0.05\text{ mol dm}^{-3}$   $\text{HNO}_3$ , and  $1.5\text{ A.}$ )

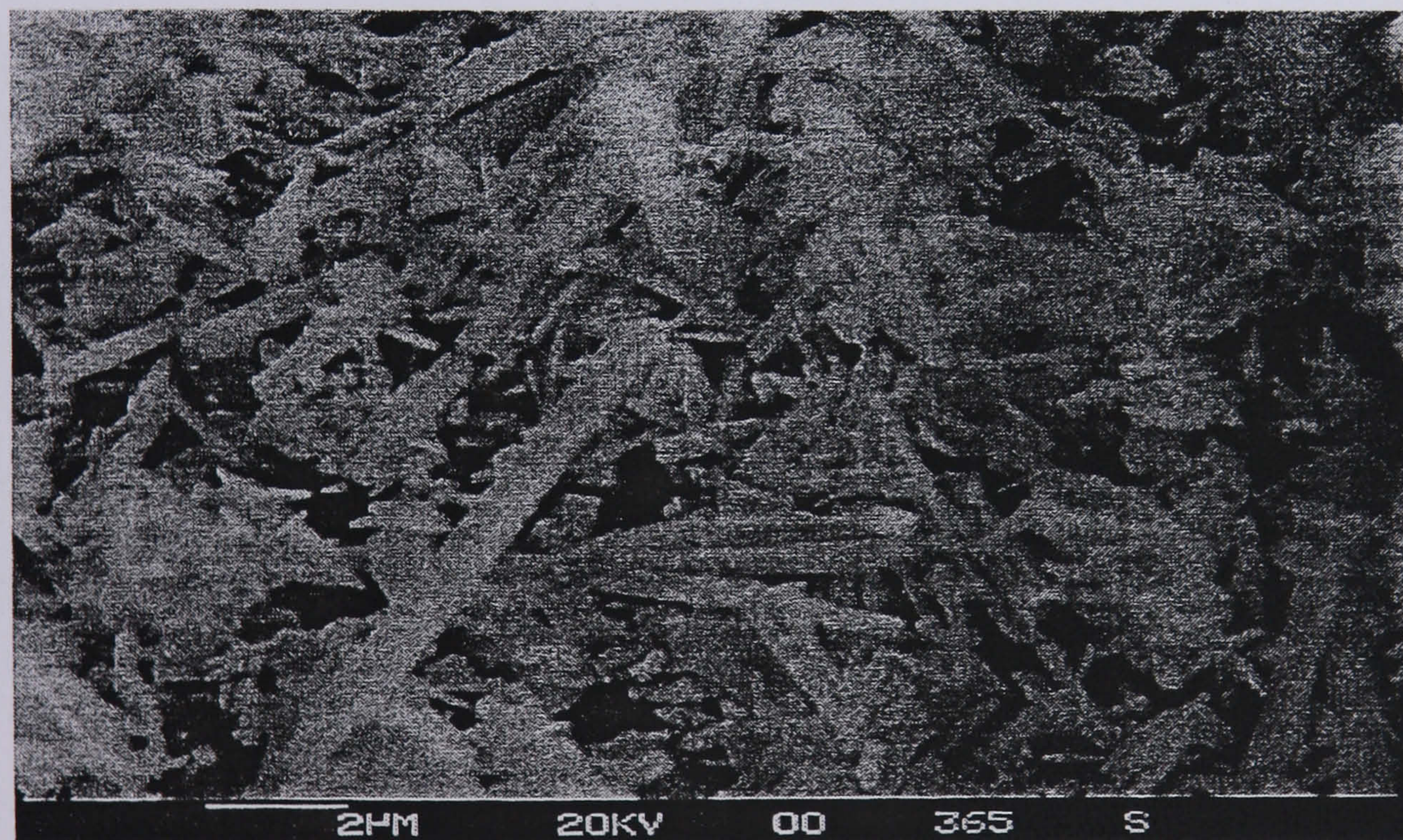


Figure [2.17] The lead deposition on the mesh electrode in the presence of ACC concentrator (magnification  $\times 7500$ ), after 6 runs (each run  $50\text{mg dm}^{-3}$  Pb,  $0.05\text{ mol dm}^{-3}$   $\text{HNO}_3$ , and  $1.5\text{ A.}$ )

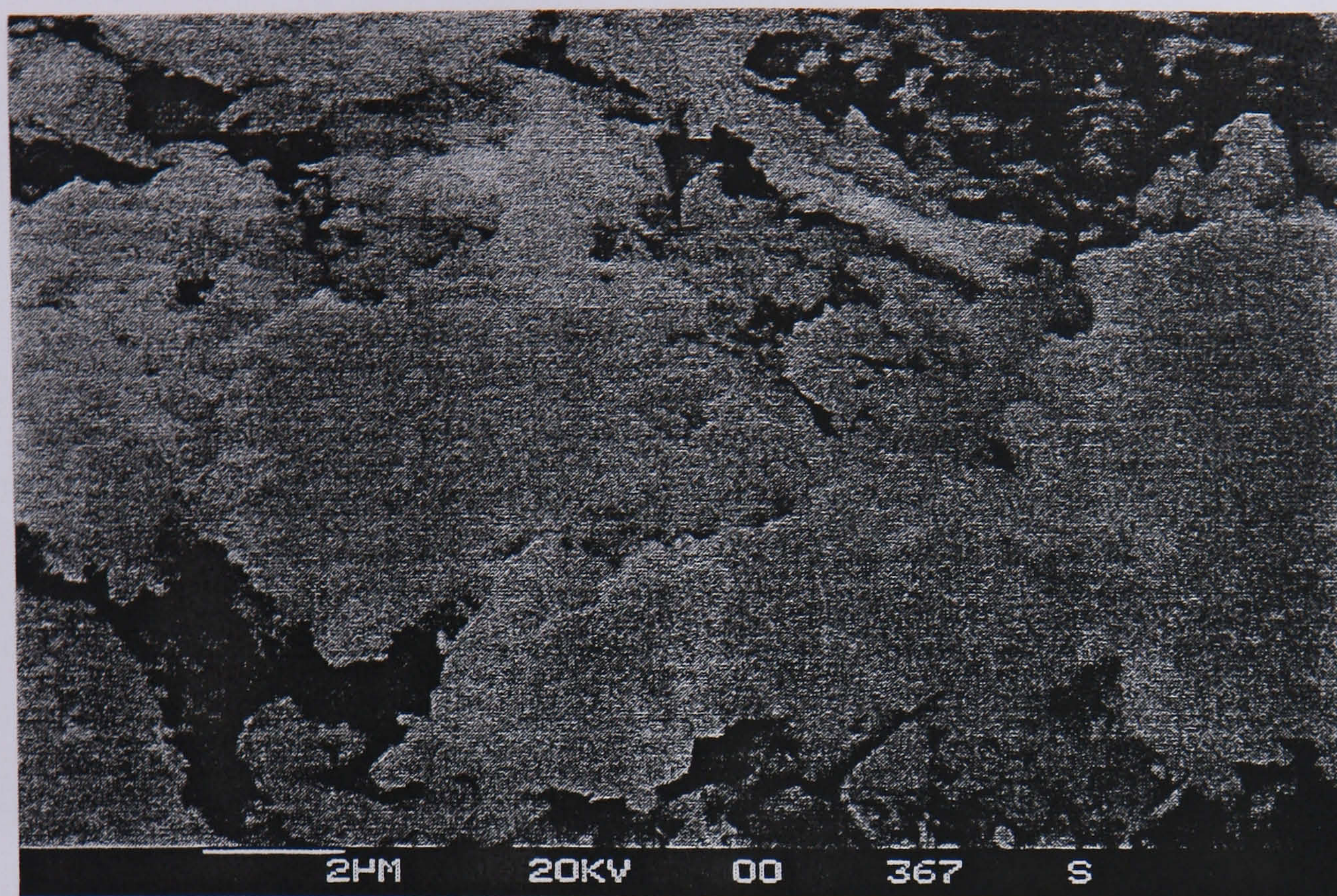


Figure [2.18] The lead deposition on the mesh electrode using IEC concentrator (magnification x 7500), after 6 runs (each run  $50 \text{ mg dm}^{-3}$  Pb,  $0.05 \text{ mol dm}^{-3}$   $\text{HNO}_3$ , and 1.5 A.)

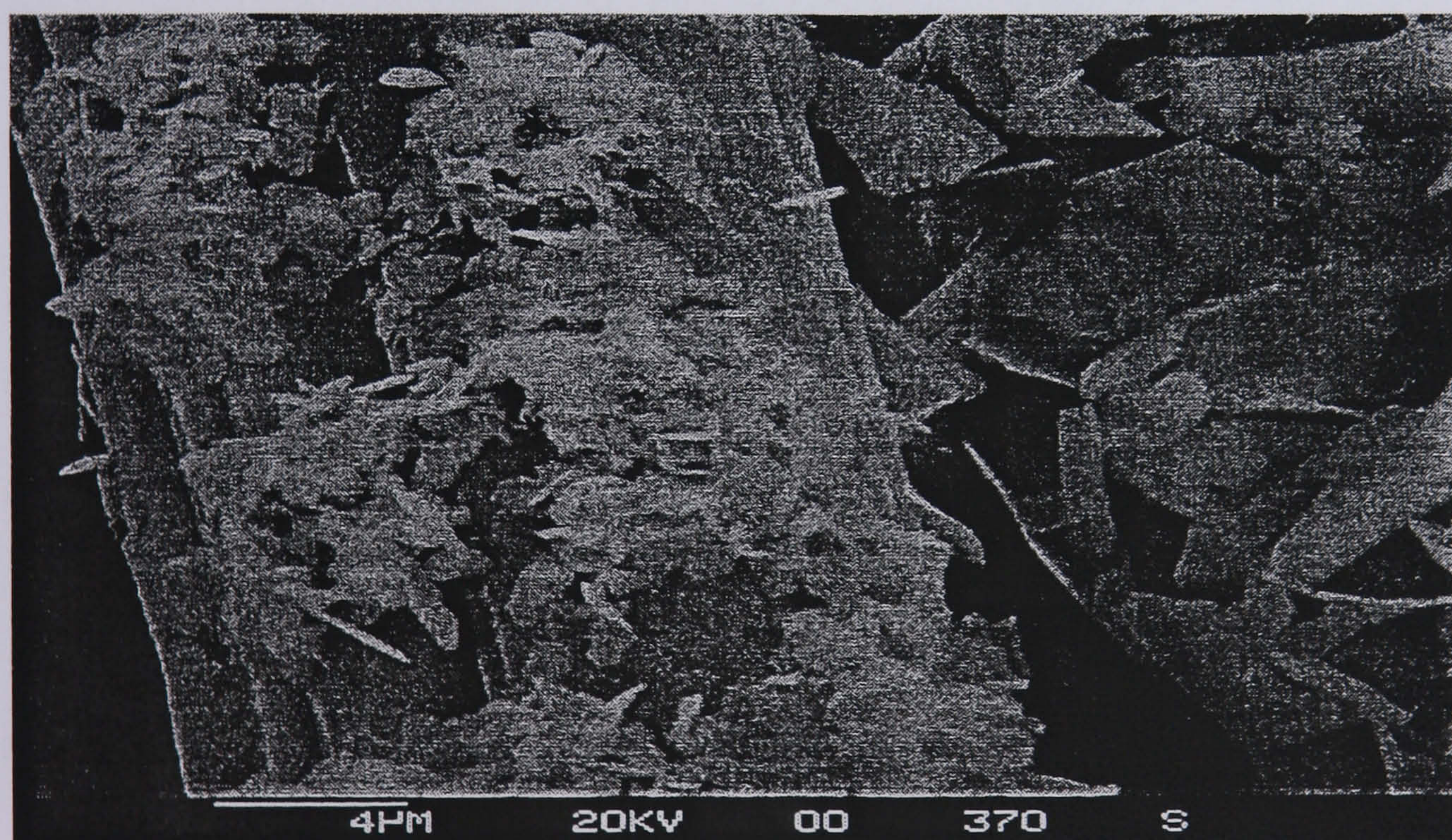


Figure [2.19] ACC (magnification x 3750), after 6 runs (each run  $50 \text{ mg dm}^{-3}$  Pb,  $0.05 \text{ mol dm}^{-3}$   $\text{HNO}_3$ , and 1.5 A.)

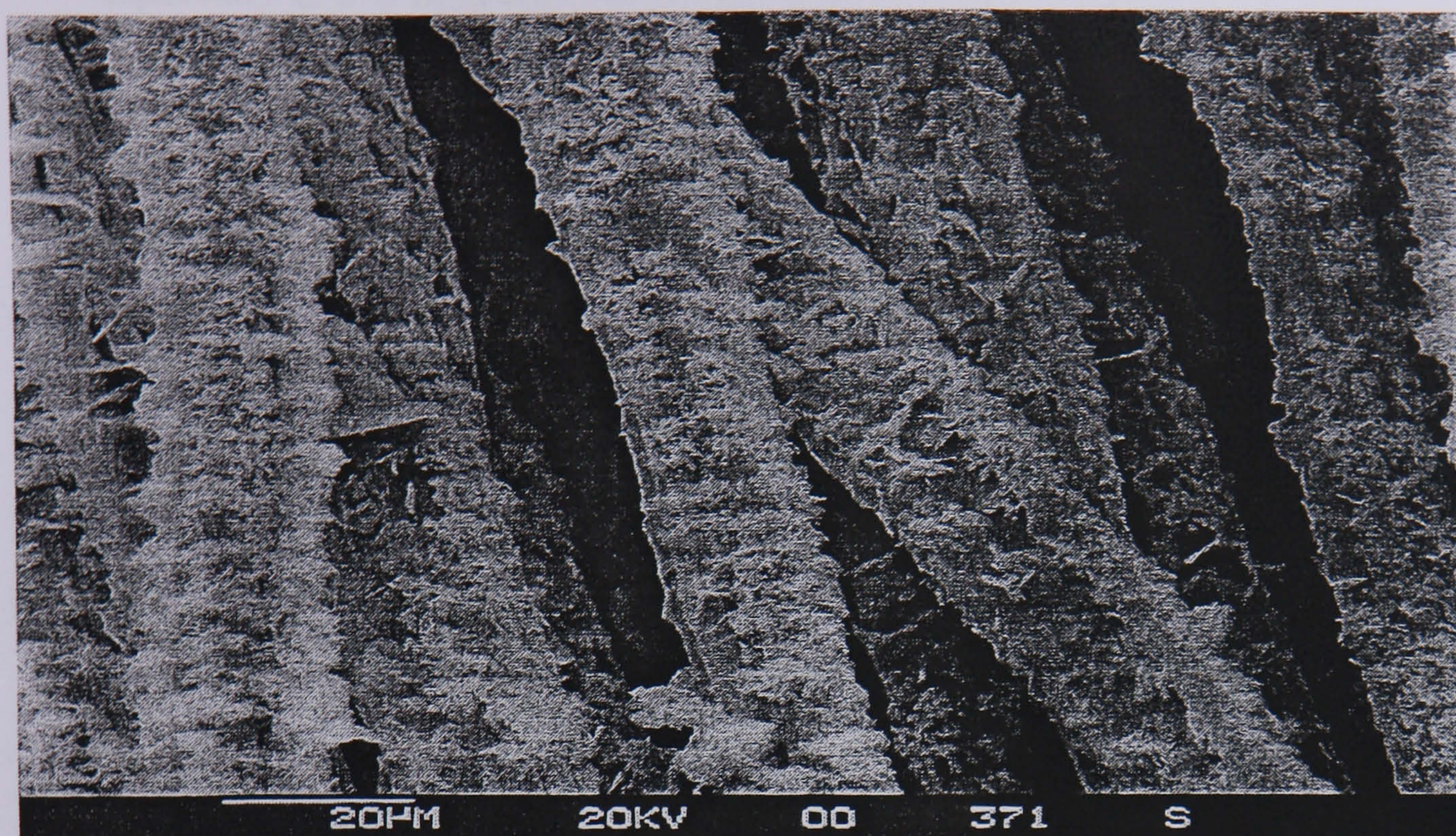


Figure [2.20] ACC (magnification x 750), after 6 runs (each run  $50 \text{ mg dm}^{-3} \text{ Pb}$ ,  $0.05 \text{ mol dm}^{-3} \text{ HNO}_3$ , and 1.5 A.)



Figure [2.21] ACC (magnification x 150, after 6 runs (each run  $50 \text{ mg dm}^{-3} \text{ Pb}$ ,  $0.05 \text{ mol dm}^{-3} \text{ HNO}_3$ , and 1.5 A.)



an ion-exchange concentrator does, however, result in efficient Cd removal, especially at low acid concentrations (0.01 and 0.05 mol dm<sup>-3</sup>).

Table [2.5]: The percentage removal and the energy consumption values of cadmium ion removal in different sulphuric acid concentrations using TMC, ACC and IEC systems.											
Percentage removal ( $\alpha_{Cd}$ %)											
Time (h) ↓	TMC			ACC			IEC				
	Mol dm <sup>-3</sup> →	0.01	0.05	0.1	0.01	0.05	0.1	0.01	0.05	0.1	0.25
1	44	16	0.0	7.5	1.0	0.0	91	92	60	49	7.4
4	84.5	60	0.0	37	6.5	0.0	98	98	76	55	19
6	88	74	0.0	51	7.5	0.0	98	98	78	56	23
8	90.5	84	0.0	65	10	0.0	99	98	79	58	31
Energy consumption [ $W_{Cd}$ (kWh/kg)]											
1	22	49	∞	137	1011	∞	15	8.7	14	17	104
4	46	54	∞	109	609	∞	--	--	45	62	160
6	67	66	∞	120	801	∞	--	--	65	90	200
8	88	78	∞	125	811	∞	--	--	86	118	197

### 2.6.2.2 Cadmium Recovery from Nitric Acid Media

The performance of TMC, ACC and IEC in the removal of cadmium ions from nitric acid media (0.01 - 0.5mol dm<sup>-3</sup>) was examined using 50mg dm<sup>-3</sup> Cd(II) solution, at a constant current of 1.5A. The results show that no cadmium removal is obtained in the TMC and ACC cells at all acid levels. The IEC cell, however, shows a good performance, especially at the lower acid concentrations (0.01 and 0.05mol dm<sup>-3</sup>) and complete cadmium removal can be achieved after 2 hours with the minimum energy consumption value at 0.05mol dm<sup>-3</sup> HNO<sub>3</sub>. The performance decreases with increasing nitric acid concentration, and above 0.5mol dm<sup>-3</sup> there was no cadmium removal. The results in Figure [2.24, a and b] show the percentage removal and the

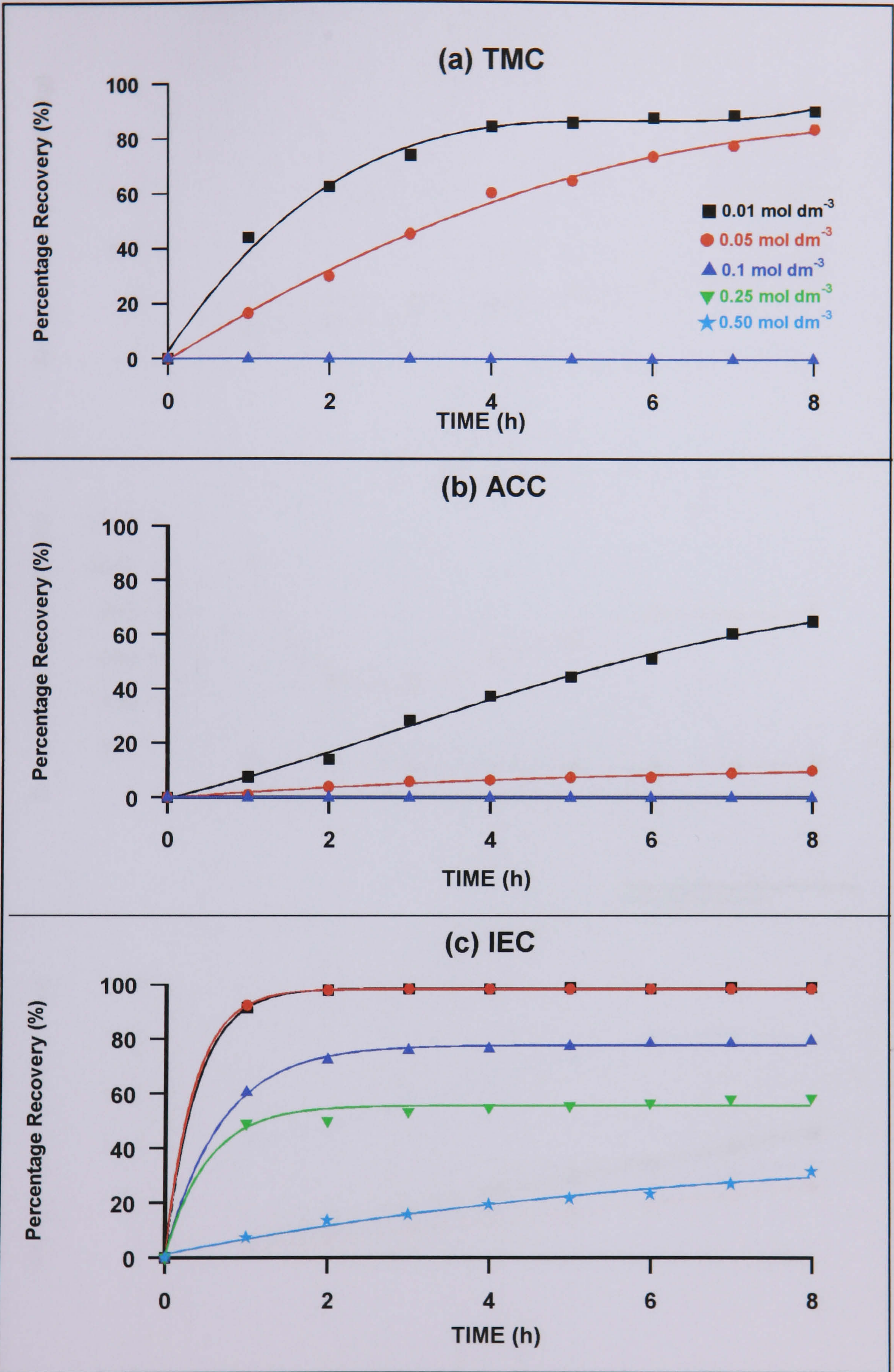


Figure [2.22]: The effect of sulphuric acid concentration on the percentage cadmium recovery using (a) TMC, (b) ACC and (c) IEC.

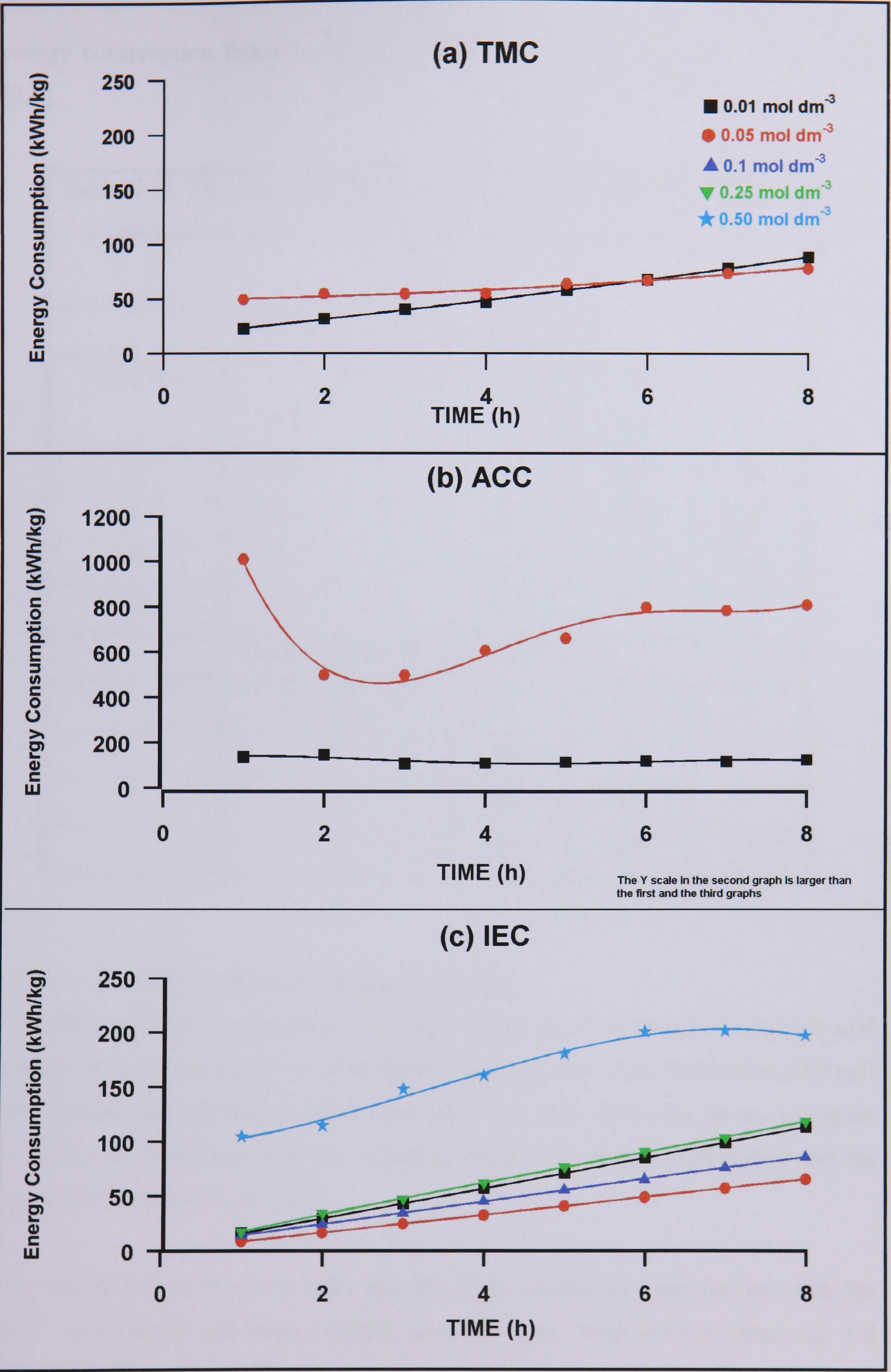


Figure [2.23]: The effect of sulphuric acid concentration upon the energy consumption of cadmium recovery using (a) TMC, (b) ACC and (c) IEC.

energy consumption found in the IEC system and the numerical data are in Table [2.6].

Table [2.6]: The percentage removal and the energy consumption values of cadmium ion recovery in different nitric acid concentrations using IEC system.					
The percentage removal ( $\alpha_{Cd}$ %)					
Time (h)	Nitric acid concentration ( $\text{mol dm}^{-3}$ )				
	0.01	0.05	0.1	0.25	0.5
1	89.0	93.0	79.0	19.0	0.0
4	97.5	98.0	85.0	50.0	0.0
6	97.5	98.0	85.5	53.5	0.0
8	97.5	98.0	86.5	55.6	0.0
Energy consumption [ $W_{Cd}$ (kWh/kg)]					
1	11	8	9	37	$\infty$
4	--	--	36	60	$\infty$
6	--	--	54	84	$\infty$
8	--	--	71	108	$\infty$

### 2.6.2.3 The Effect of pH on Cadmium Recovery

The effect of pH on the recovery of Cd was studied for a  $0.05 \text{ mol dm}^{-3}$  sulphuric acid solution in the pH range 2-5 and the results compared with those obtained at  $0.05 \text{ mol dm}^{-3}$  without pH adjustment which give pH = 1.5. The results are shown in Figure [2.25] for the percentage removal, Figure [2.26] for the energy consumption and the numerical data are in Table [2.7].

The results for the standard TMC and the ACC concentrator are similar (with the ACC concentrator cell being slightly less efficient). With both systems, the Cd removal becomes more efficient at higher pH with maximum removal at pH = 4.5. With the IEC concentrator, however, Cd removal is faster and more energy efficient at pH 1.5, and that, similar to the lead situation, no cadmium recovery can be

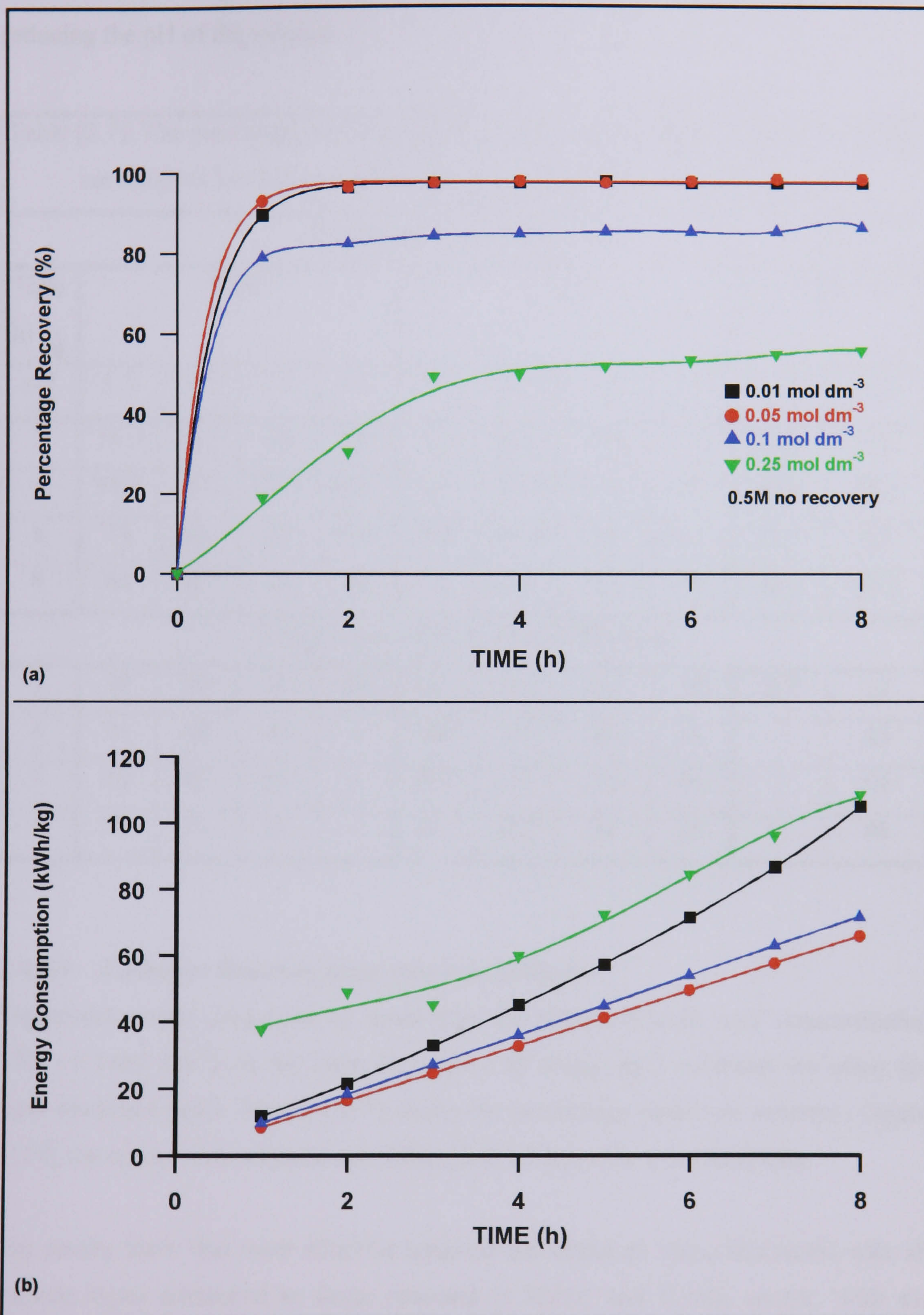


Figure [2.24]: The effect of nitric acid concentration on the (a) Percentage recovery (b) Energy consumption using IEC, in cadmium recovery process.

achieved in pH range 3-4 and above, due to the *in-situ* resin regeneration process reducing the pH of the solution.

Table [2.7]: The percentage removal and the energy consumption values of cadmium ion removal for different pH values using TMC, ACC and IEC systems.											
Percentage removal ( $\alpha_{Cd}$ %)											
Time (h) ↓	TMC				ACC				IEC		
	pH →	1.5	2.5	3.5	4.5	1.5	2.5	3.5	4.5	1.5	2.5
1	16.5	22.5	24	39.5	1.0	6.5	8.0	10	92.5	76	
4	60.5	73	77.5	96.5	6.5	38.5	43.5	49	98.5	88.5	
6	74	85	90	99.5	9.0	54.5	59	65	98.5	89	
8	84	92	94	100	10	65	69	79	98.5	89.5	
Energy consumption [ $W_{Cd}$ (kWh/kg)]											
1	49	40	40	24	1011	138	111	90	8.7	12	
4	54	48	49	--	609	92	80	72	--	43	
6	66	62	63	--	801	97	86	80	--	64	
8	78	75	82	--	811	107	98	88	--	86	

#### 2.6.2.4 Cadmium Recovery from Acetic Acid Media

Experiments were performed to investigate the effect of acetic acid (concentration 0.05 - 0.1 mol dm<sup>-3</sup>) on the removal process of 50 mg dm<sup>-3</sup> cadmium ion using the three electrode types. Figure [2.27] shows the percentage cadmium recovery, Figure [2.28] the energy consumption and Table [2.8] contains the numerical data.

The results show that more effective removal was obtained using this media with all cathode types compared to those obtained in HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> media. With the standard TMC, the removal of cadmium ion increases with increasing acetic acid concentration and complete Cd removal at all acid concentrations is achieved after 8 hours. The performance of the ACC concentrator cell, on the other hand, decreases with increasing acetic acid concentration. Again the IEC concentrator cell is shown to

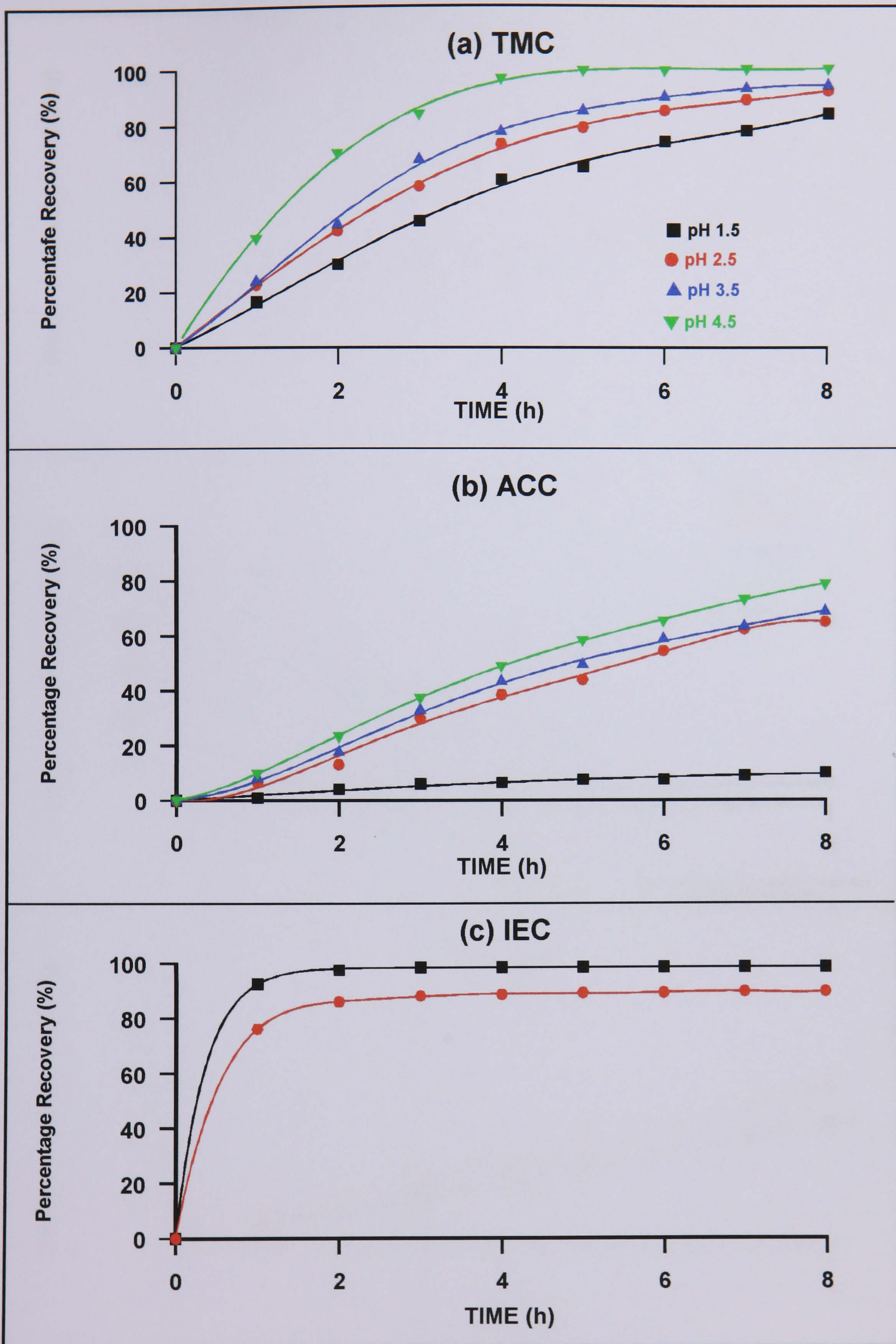


Figure [2.25]: The effect of pH on the percentage cadmium recovery using (a) TMC, (b) ACC and (c) IEC.

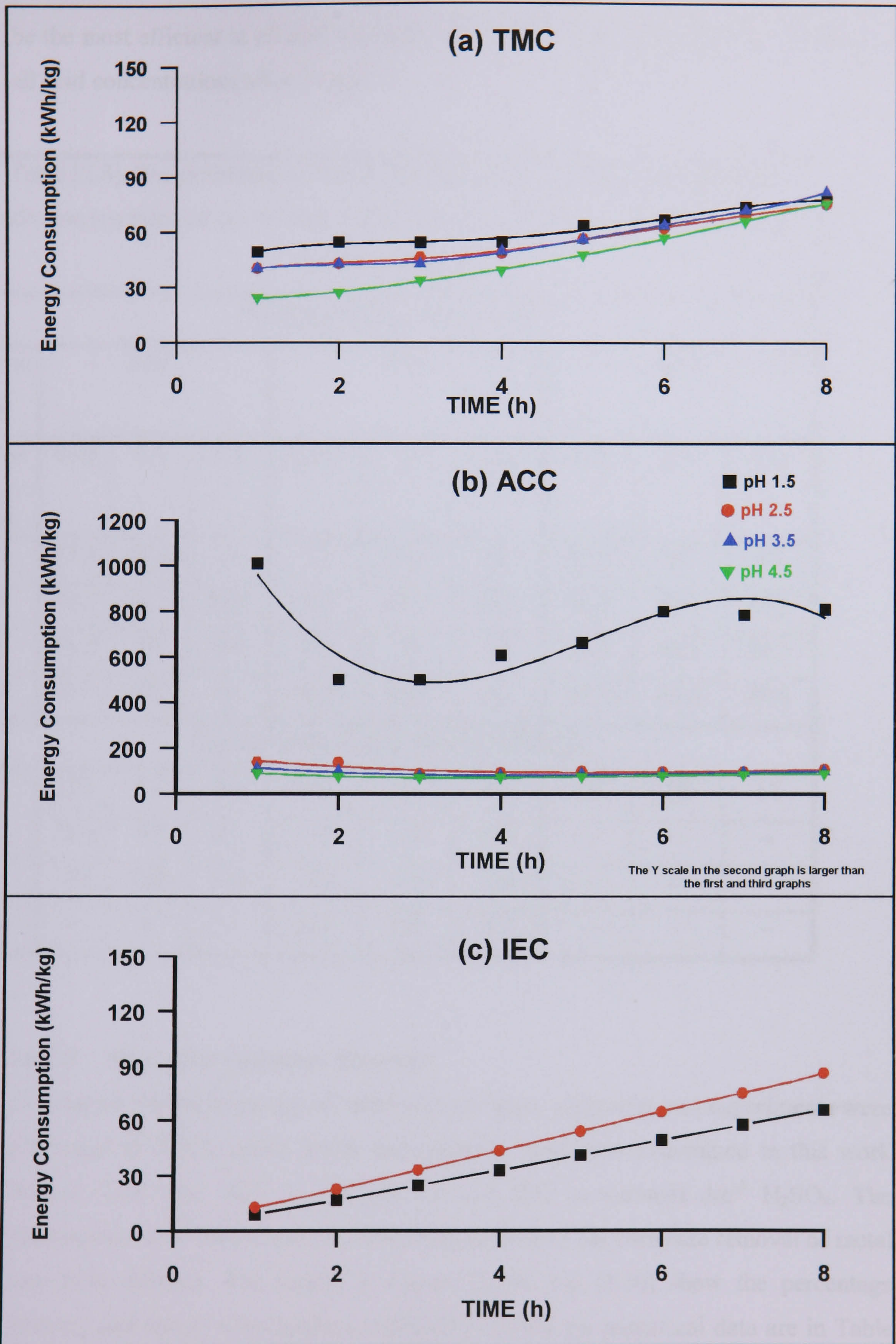


Figure [2.26]: The effect of pH on the energy consumption of cadmium recovery using (a) TMC, (b) ACC and (c) IEC.



be the most efficient at all acid concentrations with complete Cd removal obtained at all acid concentrations after 2 hours.

Table [2.8]: The percentage removal and the energy consumption values of cadmium ion removal in different acetic acid concentrations using TMC, ACC and IEC systems.									
Percentage removal ( $\alpha_{Cd}$ %)									
Time (h) ↓	TMC			ACC			IEC		
Mol dm <sup>-3</sup> →	0.05	0.5	1.0	0.05	0.5	1.0	0.05	0.5	1.0
1	17.5	30.5	36	23	20.5	18	95.5	92	87
4	71.5	81	86.5	50.5	44.5	39.5	99.5	99.5	99.5
6	91.5	94	94	63	59	55	99.5	99.5	99.5
8	97	98	99	69.5	68.5	64	99.5	99.5	99.5
Energy consumption [ $W_{Cd}$ (kWh/kg)]									
1	130	67	53	93	84	80	45	25	19
4	124	96	81	154	151	154	--	--	--
6	145	120	112	185	173	170	--	--	--
8	--	--	--	227	199	191	--	--	--

#### 2.6.2.5 Successive Cadmium Recovery

To examine the performance of each electrode type, successive run experiments were performed in H<sub>2</sub>SO<sub>4</sub> media under the optimum conditions determined in this work namely, TMC and ACC in the pH 4.5 and IEC in 0.05mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. The experimental time was 8 hours for each run, to achieve the complete removal of metal ions from solution. The results in Figure [2.29] and [2.30] show the percentage recovery and energy consumption respectively while the numerical data are in Table [2.9].

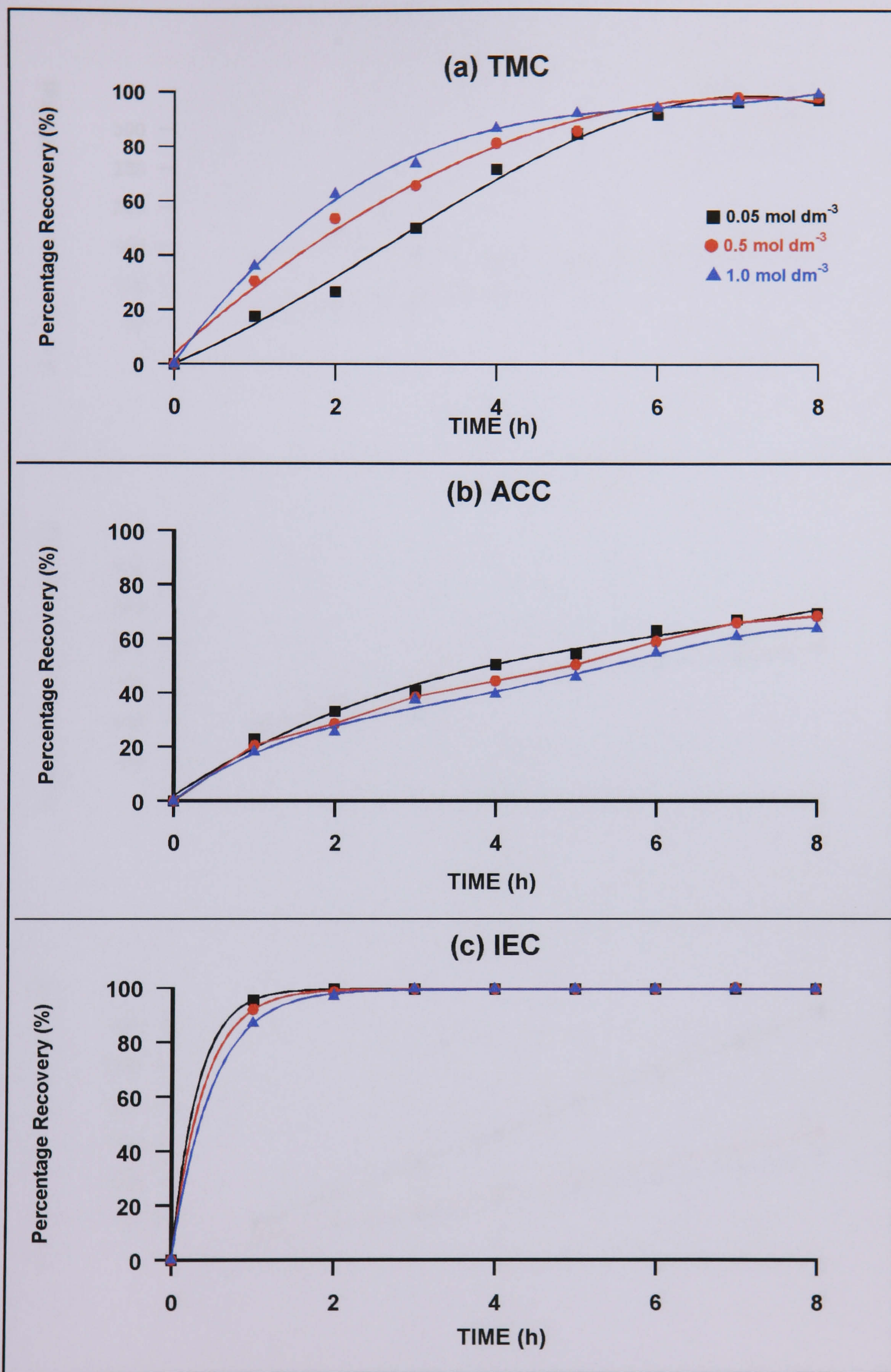


Figure [2.27]: The effect of acetic acid concentration on the percentage cadmium recovery using (a) TMC, (b) ACC and (c) IEC.

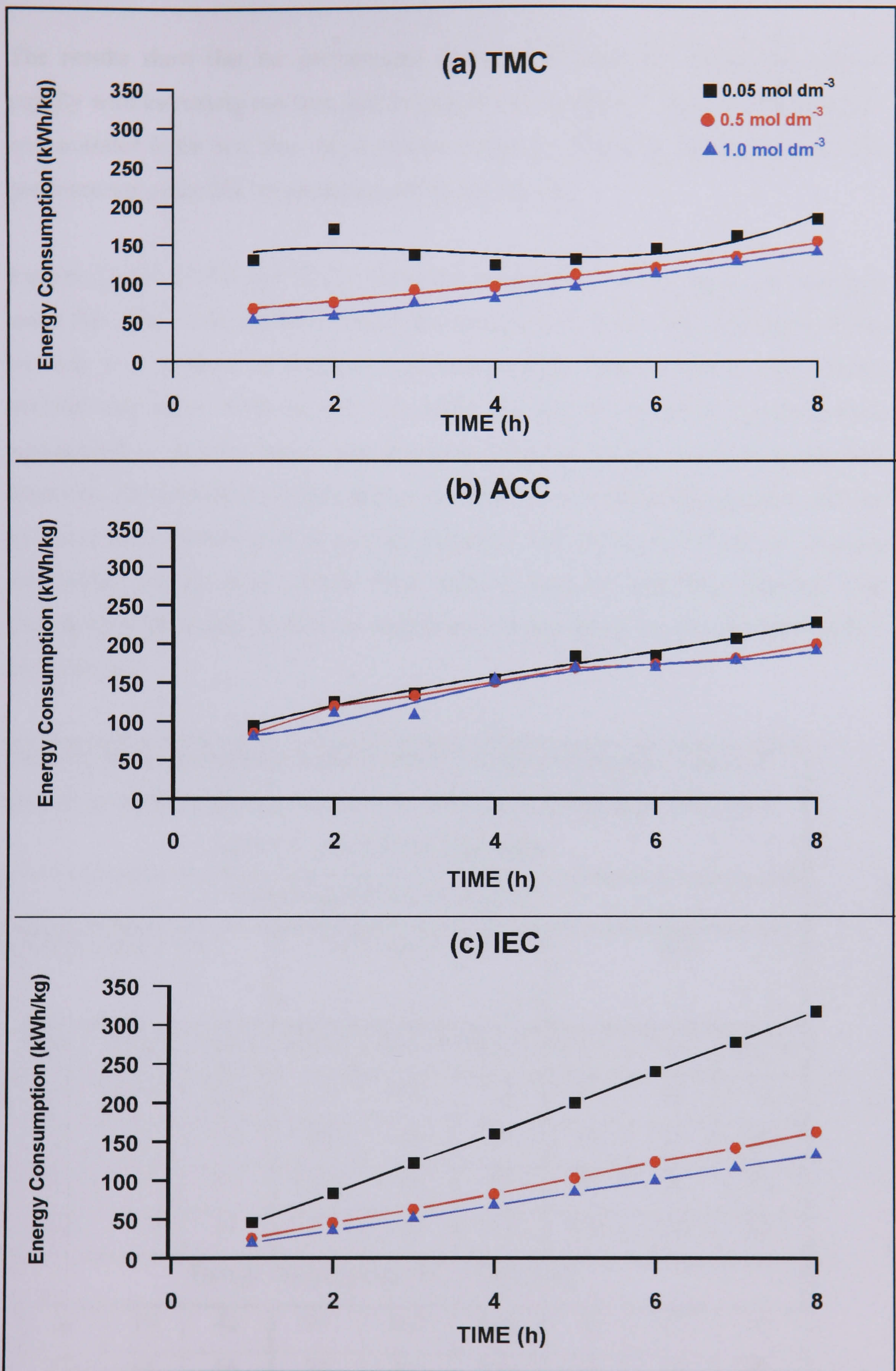


Figure [2.28]: The effect of acetic acid concentration on the energy consumption of cadmium recovery using (a) TMC, (b) ACC and (c) IEC.

The results show that the performance of the TMC and ACC electrodes reduces rapidly with increasing run time and in general the percentage removal with the ACC concentrator is far less than those observed with the standard TMC electrode. The performance of the IEC concentrator cell is much better.

Figures [2.31], [2.32] and [2.33] show the morphology of the deposited cadmium using the TMC, ACC and IEC electrodes respectively. With TMC, the shape of the crystals is a mixture of dendritic and non-dendritic broken sheets with smooth surfaces and edges. With the ACC electrode, the deposit appears as a broken sheet surrounded by powder which may originate from the bigger sheet. With the IEC electrode, the deposited crystals appear as different sized dendritic particles with no evidence of the broken sheet or powder. Figures [2.34], [2.35], [2.36] and [2.37] show the surface of activated carbon cloth after 6 runs for cadmium removal. The photographs show that there is no significant Cd deposition on the activated carbon cloth surface.

Table [2.9]: The percentage removal and the energy consumption values of cadmium removal in successive use of the different electrode type TMC, ACC and IEC in 0.05M H <sub>2</sub> SO <sub>4</sub> media									
Percentage removal ( $\alpha_{Cd}$ %)									
Time (h) ↓	TMC at pH = 4.5			ACC at pH = 4.5			IEC		
	Run 1	Run 3	Run 6	Run 1	Run 3	Run 6	Run 1	Run 3	Run 6
1	39	27.5	23.6	10	9.2	8.2	84	84	77
4	96	79	71	49	43	30	94	93	86
6	99.5	96	82	65.5	66	52	98	98	92
8	100	100	92	79	78	73.6	100	100	96
Energy consumption [ $W_{Cd}$ (kWh/kg)]									
1	24	39	42	90	109	120	10	10	11
4	39	53	56	72	93	130	39	38	41
6	--	--	73	80	91	112	--	--	58
8	--	--	87	88	103	105	--	--	--

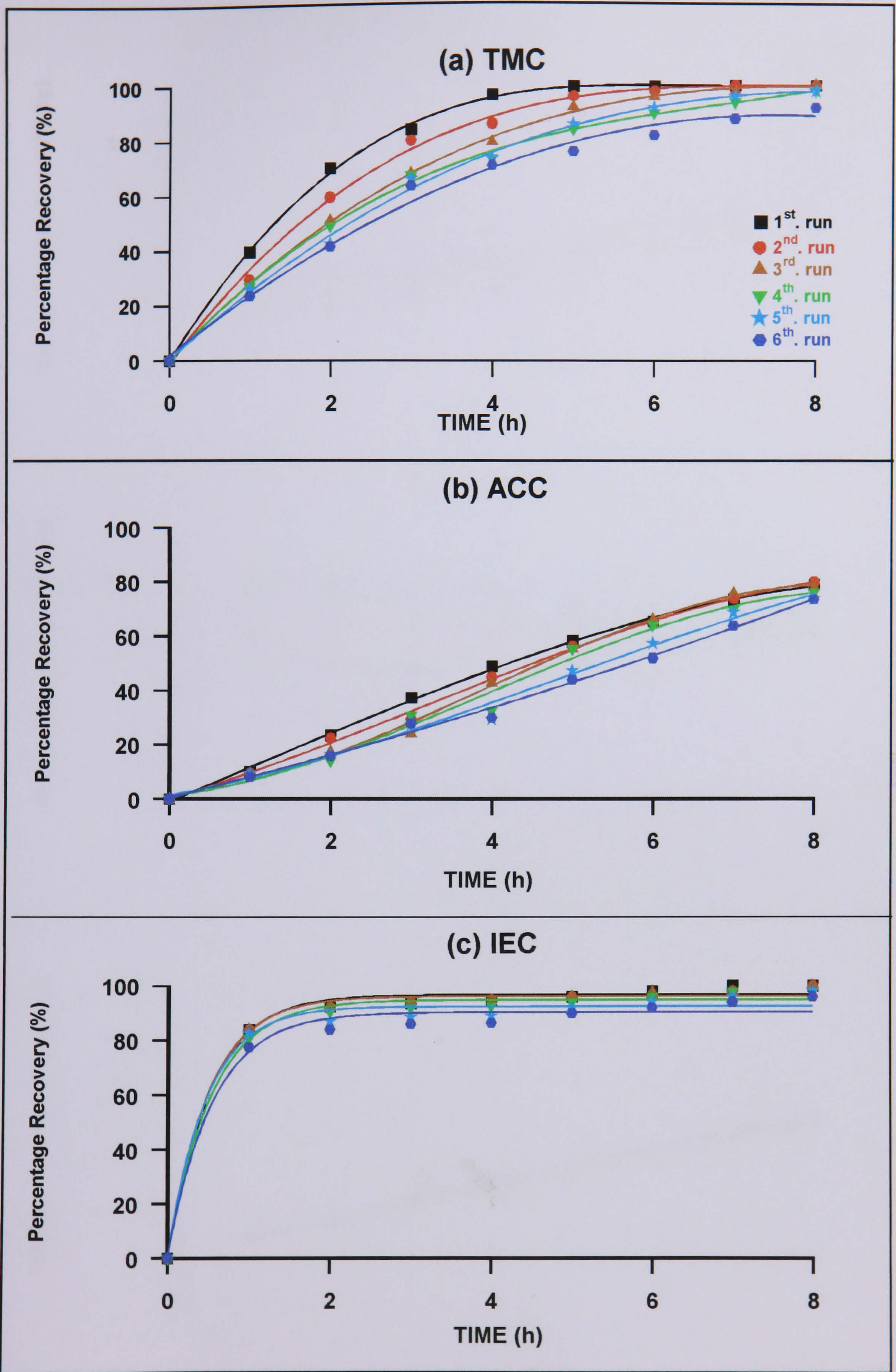


Figure [2.29]: The percentage recovery for successive cadmium (50ppm) recovery from 0.05 M HNO<sub>3</sub> solution using (a) TMC, (b) ACC and (c) IEC.

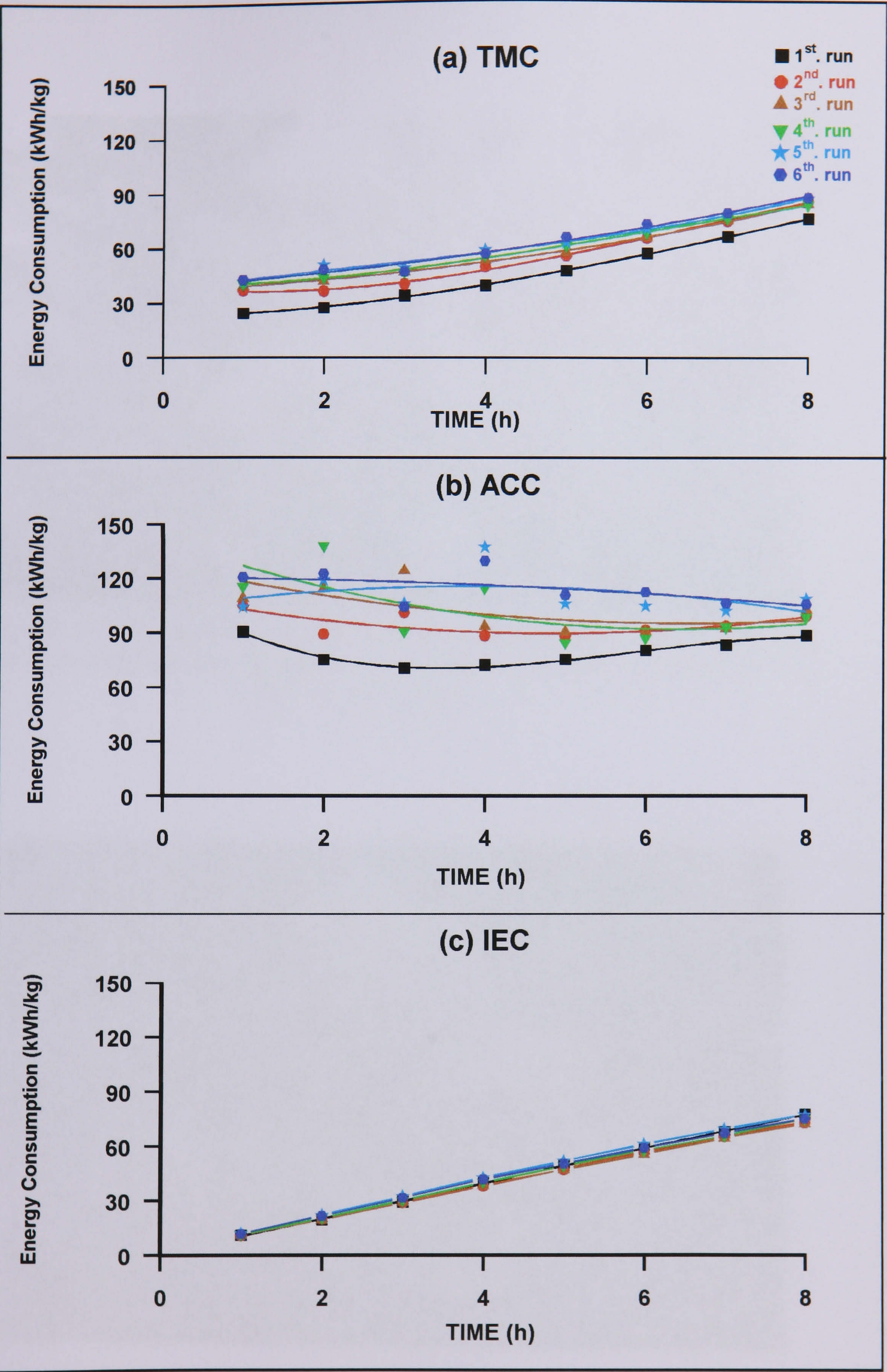


Figure [2.30]: The Energy consumption for successive cadmium (50ppm) recovery from 0.05 M HNO<sub>3</sub> solution using (a) TMC, (b) ACC and (c) IEC.

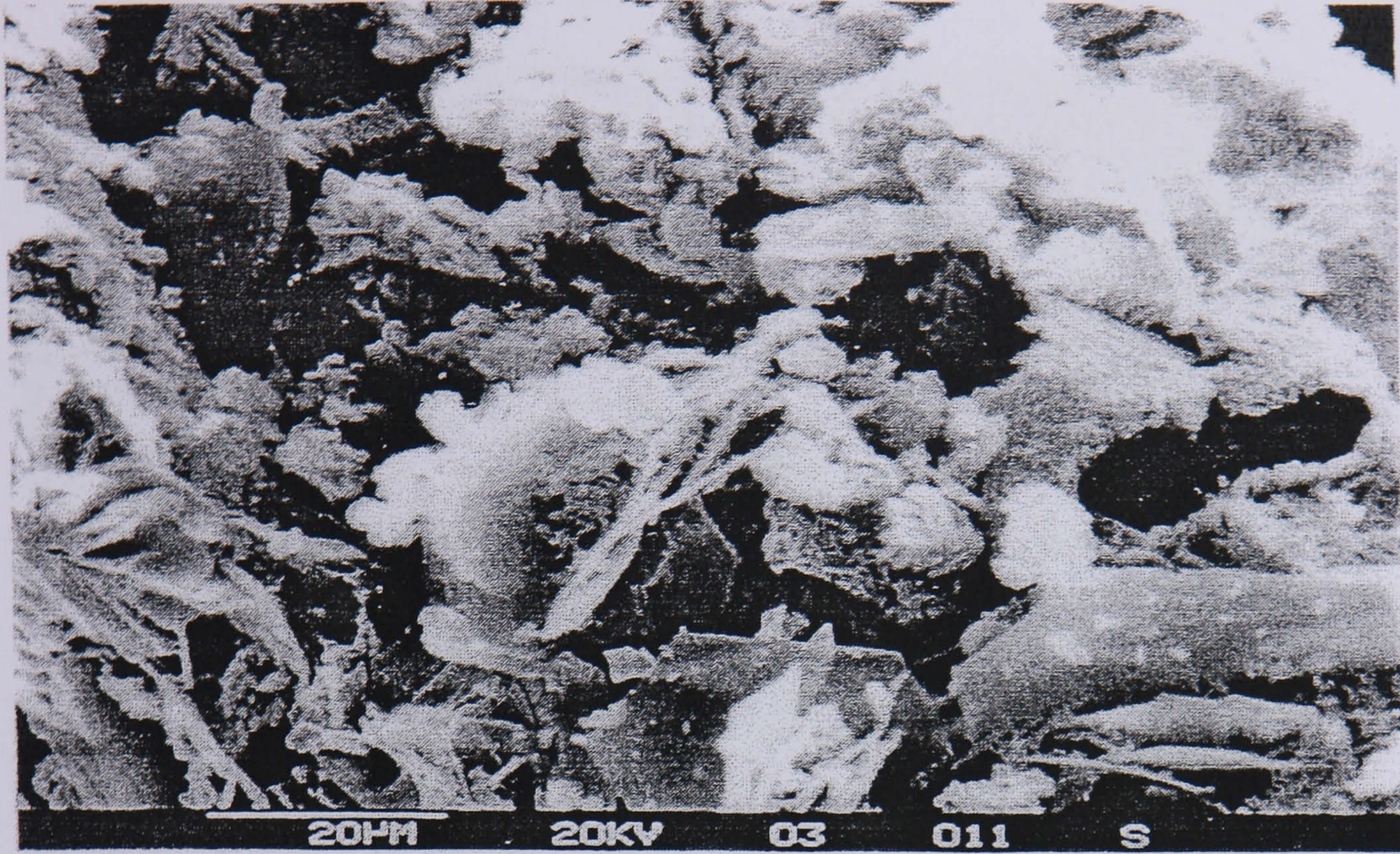


Figure [2.31]: The cadmium deposition on the mesh electrode in control conditions with no concentrator (magnification x 1000), after 6 runs (each run  $50 \text{ mg dm}^{-3} \text{ Cd}$ , pH 3-4, and current 1.5 A.)

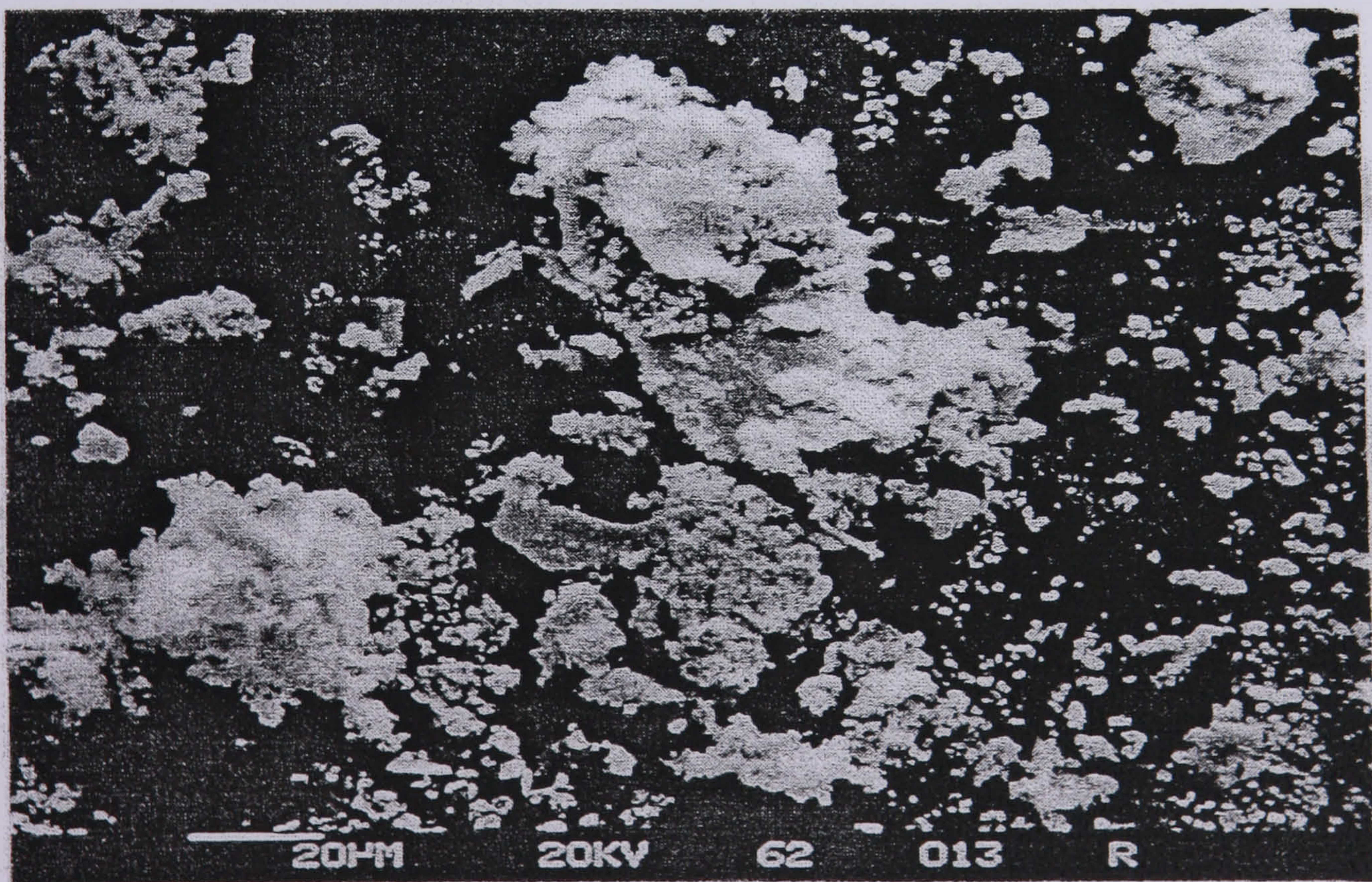


Figure [2.32]: The cadmium deposition on the mesh cathode using ACC concentrator (magnification x 500), after 6 runs (each run  $50 \text{ mg dm}^{-3} \text{ Cd}$ , pH 3-4, and current 1.5A).

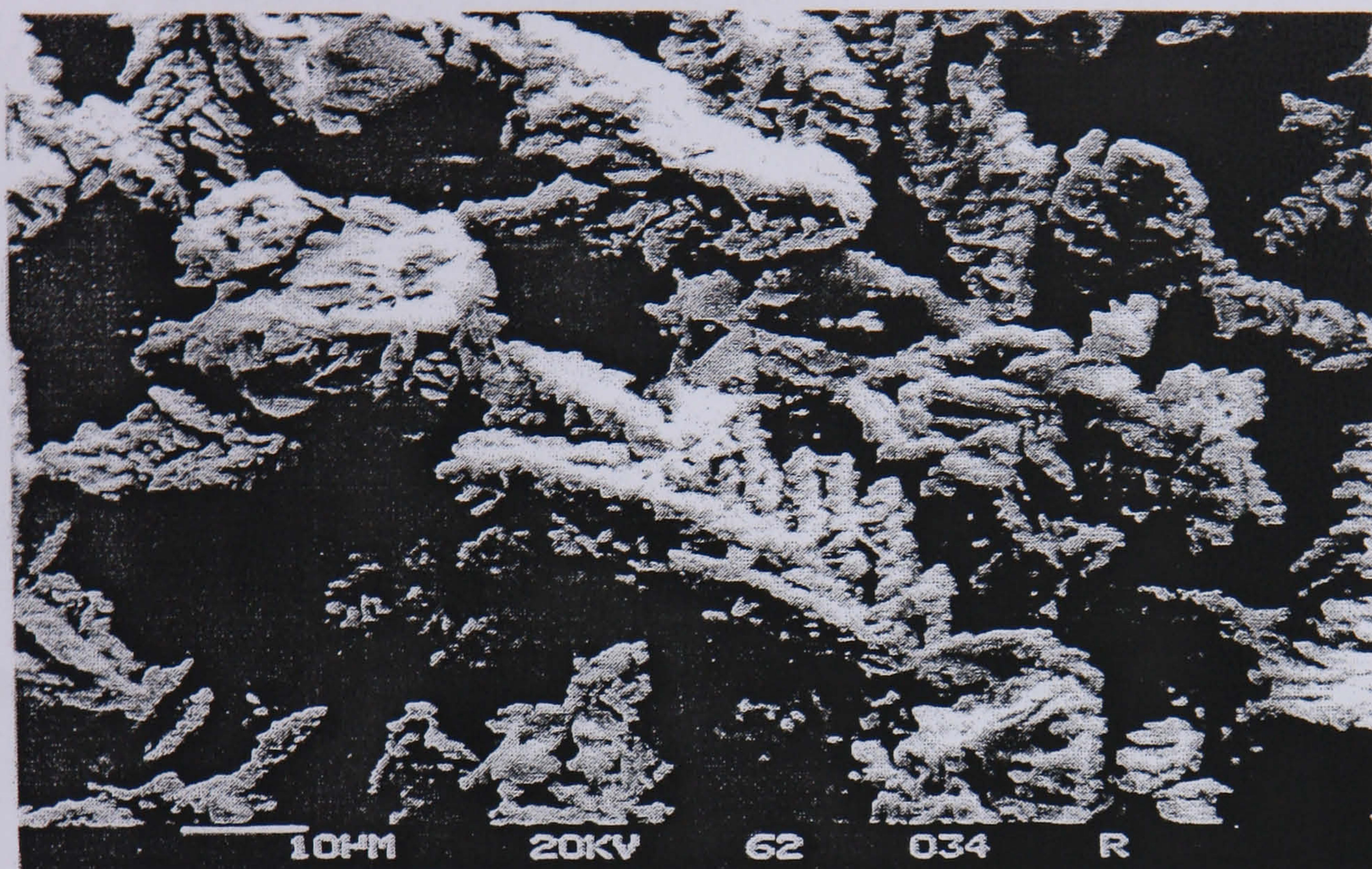


Figure [2.33]: The cadmium deposition on the mesh cathode using IEC concentrator (magnification x 1000), after 6 runs (each run  $50 \text{ mg dm}^{-3} \text{ Cd}$ ,  $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  and current 1.5 A.)



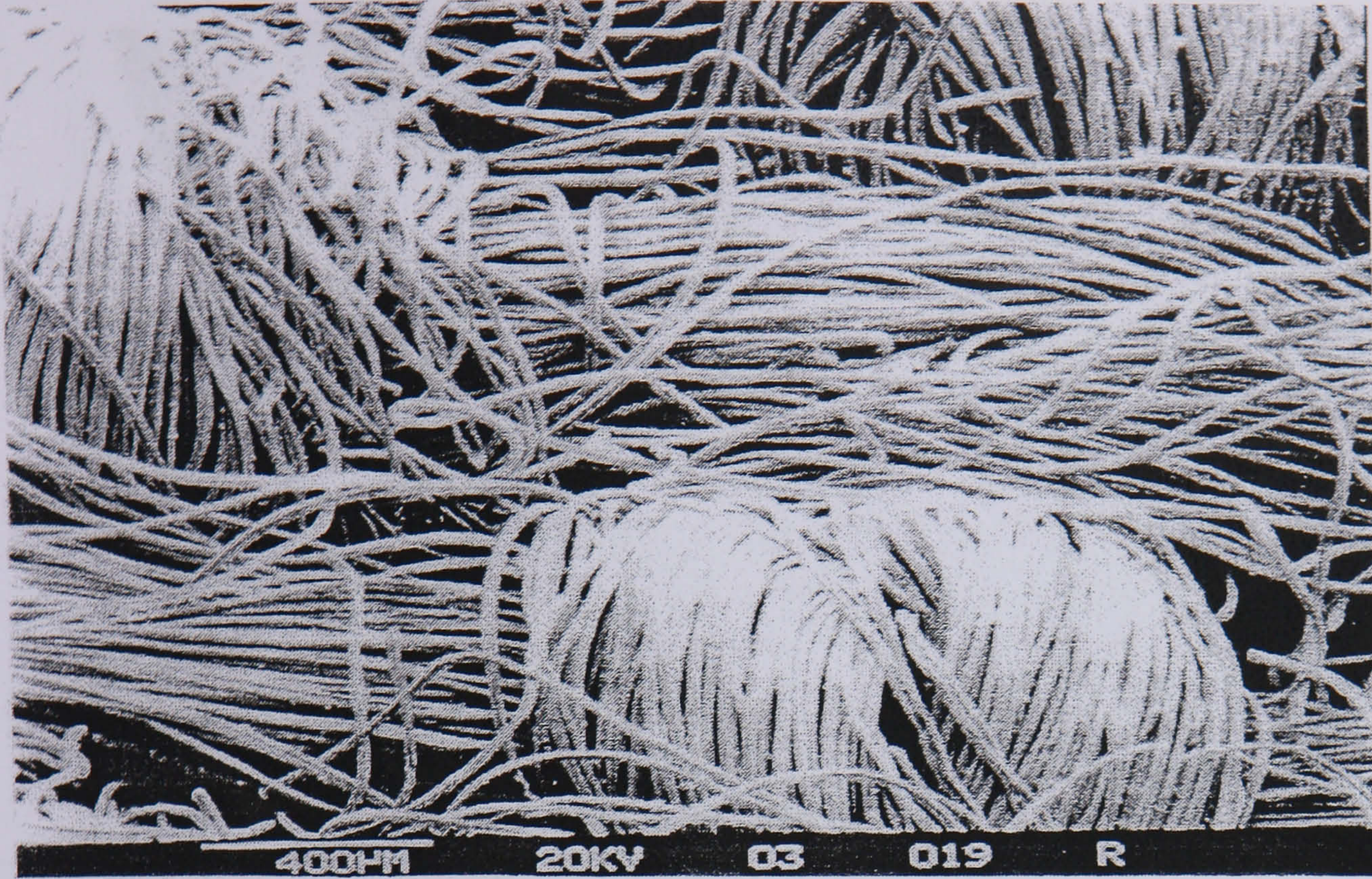


Figure [2.34]:ACC (magnification x 50), after 6 runs (each run  $50 \text{ mg dm}^{-3}$  Cd, pH 3-4, and current 1.5 A.)

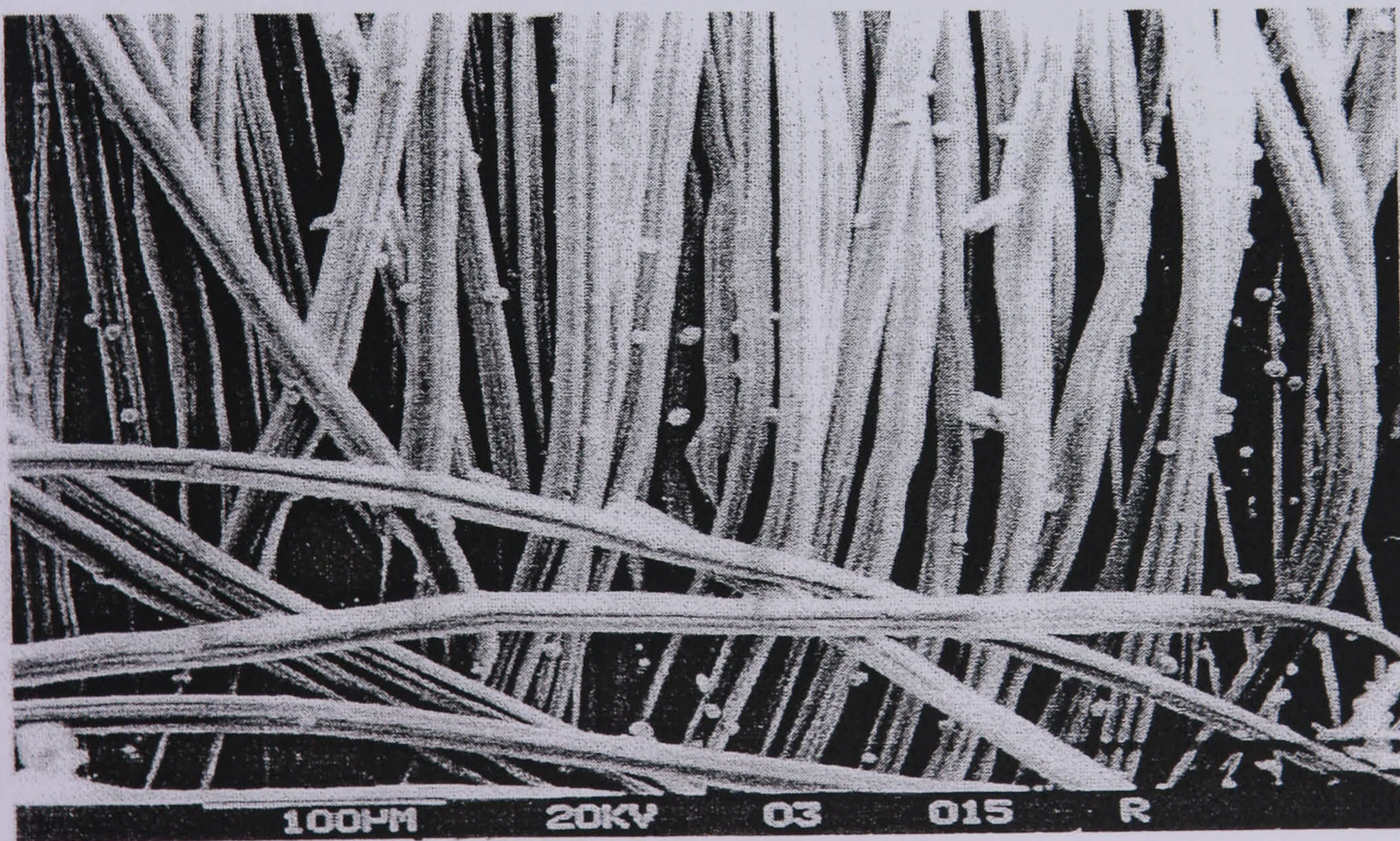


Figure [2.35]: ACC (magnification x 200), after 6 runs (each run  $50 \text{ mg dm}^{-3}$  Cd, pH 3-4, and current 1.5 A.)

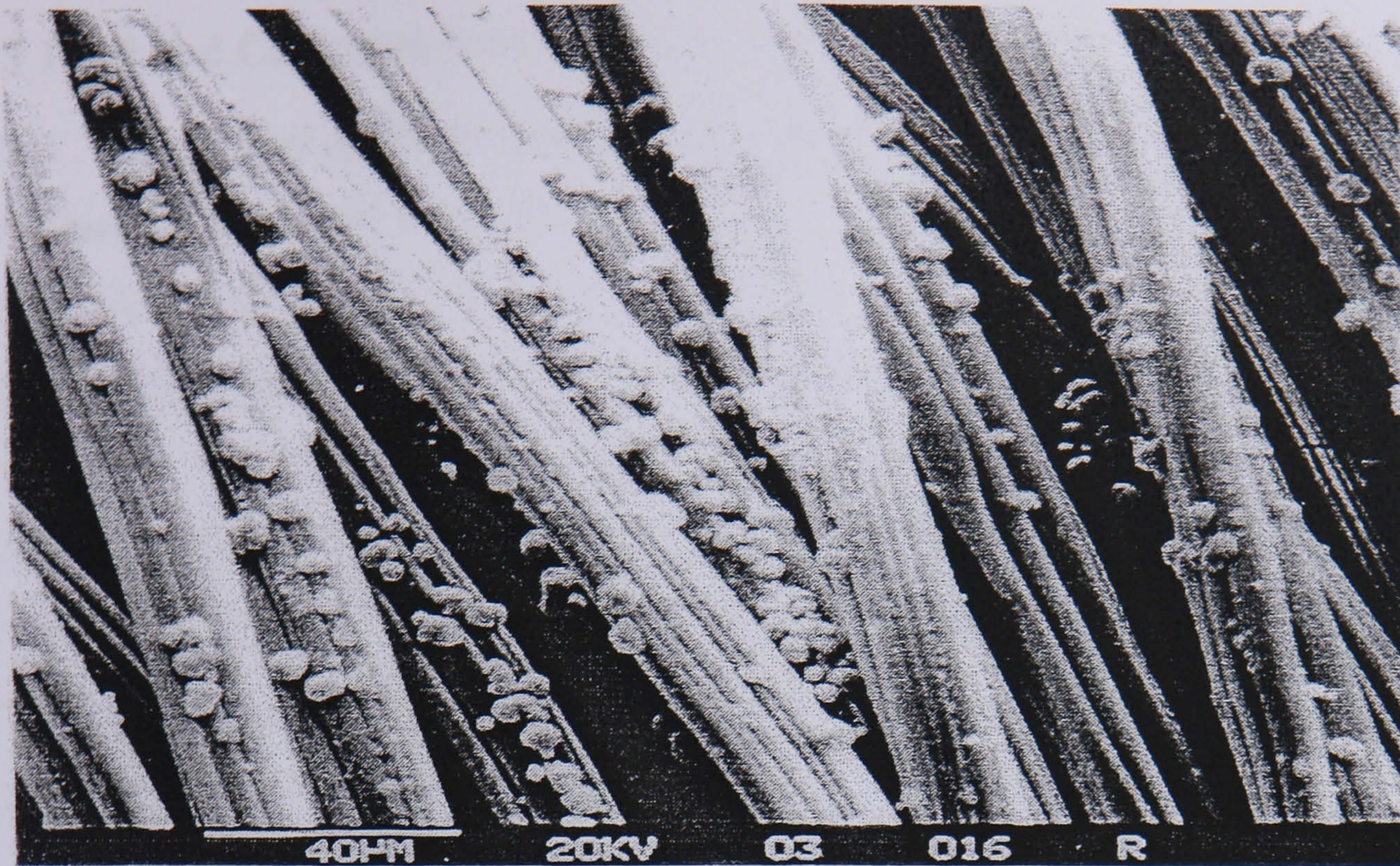


Figure [2.36]: ACC (magnification x 500), after 6 runs (each run  $50 \text{ mg dm}^{-3}$  Cd, pH 3-4, and current 1.5 A.)

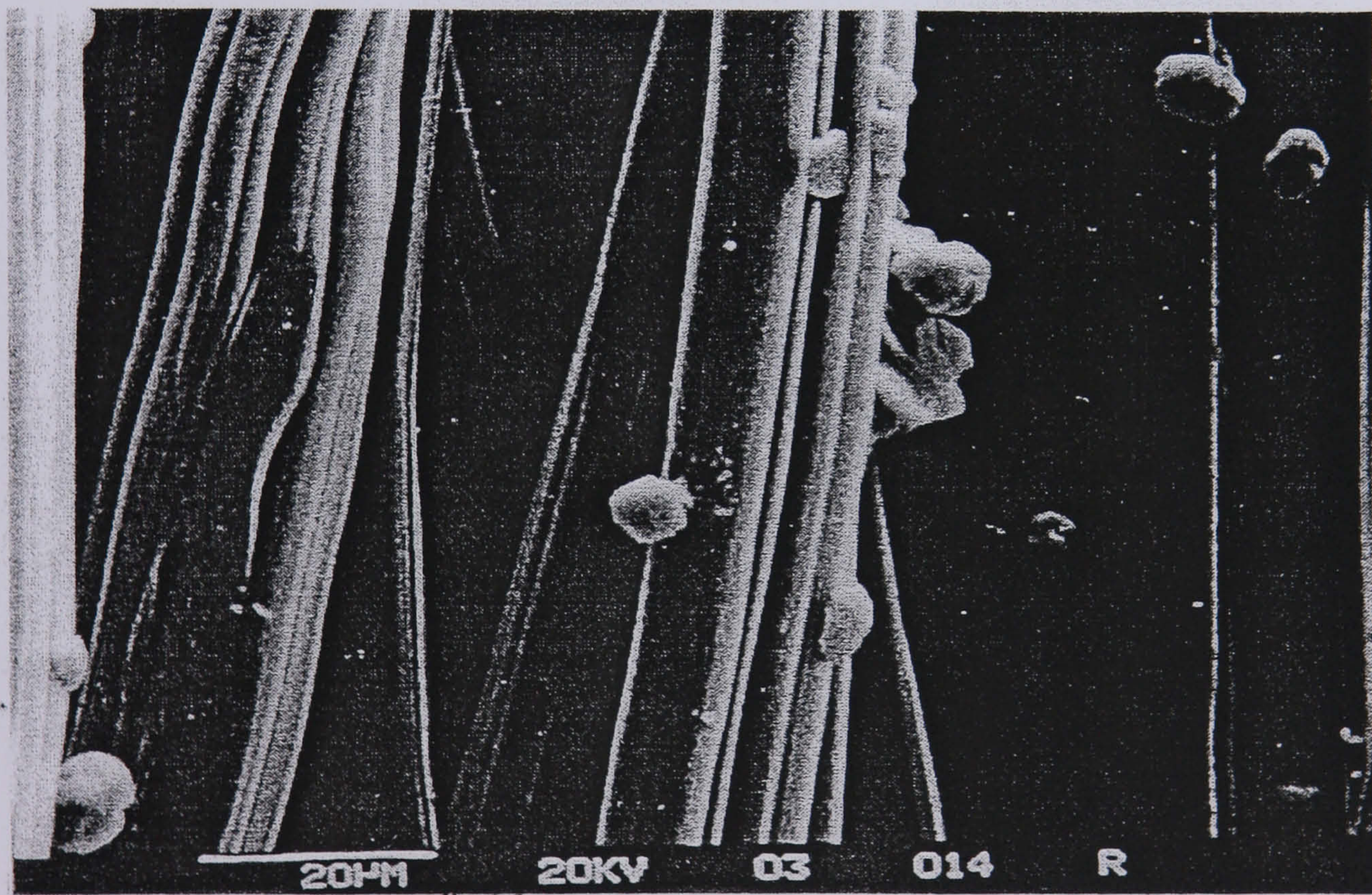


Figure [2.37]: ACC (magnification x 1000), after 6 runs (each run  $50 \text{ mg dm}^{-3}$  Cd, pH 3-4, and current 1.5 A.)

## 2.6.3 Lead and Cadmium Recovery in a Combined System

### 2.6.3.1 The Effect of Nitric Acid Concentration on the Recovery of Cd and Pb

The effect of nitric acid concentration (0.01 to 0.5 mol dm<sup>-3</sup>) was examined using a solution containing 50mg dm<sup>-3</sup> of both Pb and Cd at 1.5A. The percentage lead removal using three electrode systems and cadmium percentage removal using only IEC system are presented in Figure [2.38]. Tables [2.10] and [2.11] show a comparison of the numerical data on lead removal in the presence and absence of cadmium ions using the TMC and ACC cells respectively. Table [2.12] shows the data on lead and cadmium removal in the presence and absence of each other using the IEC system.

The results show that using standard TMC and ACC concentrators, no cadmium removal was observed at all acid concentrations, but in general the presence of Cd improves the percentage removal of Pb especially at acid concentrations of 0.1 and less, whereas, increasing the acid concentration further to 0.5mol dm<sup>-3</sup> decreases the lead removal values to the levels found in the absence of cadmium ions.

Table [2.10]: The percentage Pb removal using the TMC system in the presence and absence of Cd ions in different nitric acid concentrations.

Time (h)	0.01 M HNO <sub>3</sub>		0.05 M HNO <sub>3</sub>		0.1 M HNO <sub>3</sub>		0.5 M HNO <sub>3</sub>	
	Absence of Cd	Presence of Cd	Absence of Cd	Presence of Cd	Absence of Cd	Presence of Cd	Absence of Cd	Presence of Cd
1	46	68	28	78	26	69	24	35
4	87	96	80	96	72	96	61	66
6	93	98	90	95	84	94	80	74
8	95	97	94	96	90	96	88	83

Table [2.11]: The percentage Pb removal using the ACC system in the presence and absence of Cd ions in different nitric acid concentrations.

Time (h)	0.01 M HNO <sub>3</sub>		0.05 M HNO <sub>3</sub>		0.1 M HNO <sub>3</sub>		0.5 M HNO <sub>3</sub>	
	Absence of Cd	Presence of Cd	Absence of Cd	Presence of Cd	Absence of Cd	Presence of Cd	Absence of Cd	Presence of Cd
1	50	72	37	80.0	35	73.0	32	31
4	89	92	87	96.0	80	96.0	67	68
6	94	95	94	96.0	88	96.0	84	86
8	96	95	95	97.0	91	97.0	92	93

The IEC concentrator cell gives the best performance but there is no selectivity in the removal of the metals. Increasing the acid concentration to 0.1 mol dm<sup>-3</sup> decreases the removal until the process is stopped completely at 0.5 mol dm<sup>-3</sup> for Cd and 1.0 mol dm<sup>-3</sup> for Pb. The results also show that the presence of cadmium enhances lead removal, whereas the presence of lead decreases cadmium removal.

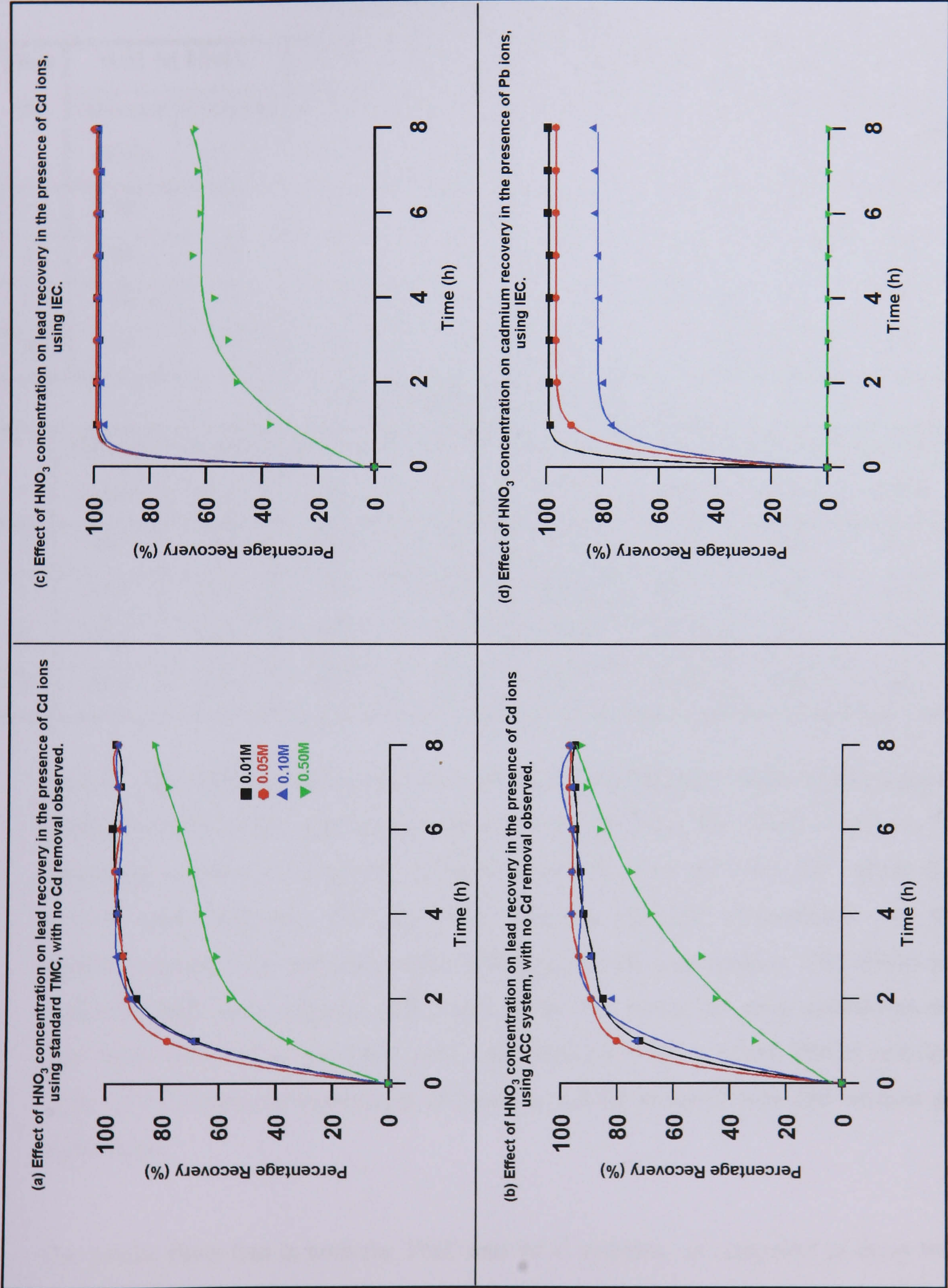


Figure [2.38]: The percentage recovery of lead and cadmium ions from combined solution, the effect of changing the HNO<sub>3</sub> concentration

Table [2.12]: The percentage Pb and Cd removal using the IEC system in the presence and absence of the other ion in different nitric acid concentrations.								
The percentage Pb removal								
Time (h)	0.01 M HNO <sub>3</sub>		0.05 M HNO <sub>3</sub>		0.1 M HNO <sub>3</sub>		0.5 M HNO <sub>3</sub>	
	Absence of Cd	Presence of Cd	Absence of Cd	Presence of Cd	Absence of Cd	Presence of Cd	Absence of Cd	Presence of Cd
1	90	99	94	98	26	96	32	37
4	96	99	97	99	72	98	50	57
6	96	98	97	99	84	98	54	62
8	97	99	97	100	90	98	57	64
The percentage Cd removal								
	Absence of Pb	Presence of Pb	Absence of Pb	Presence of Pb	Absence of Pb	Presence of Pb	Absence of Pb	Presence of Pb
1	89.5	98	93.0	91	79.0	76.5	0.0	0.0
4	97.5	99.5	98.0	96.5	85.0	81.0	0.0	0.0
6	97.5	99.5	98.0	96.5	85.0	82.5	0.0	0.0
8	97.5	99.5	98.5	96.5	86.5	83.0	0.0	0.0

### 2.6.3.2 The Effect of pH on the Recovery of Cd and Pb from Nitric Acid Solution

Duplicate experiments were performed at pH 3.5 to study the effect of pH on the percentage removal of 50mg dm<sup>-3</sup> of both Cd and Pb from 0.05 mol dm<sup>-3</sup> nitric acid solution using only the TMC and ACC systems. The IEC concentrator was not studied because of the pH adjustment effects of *in-situ* regeneration. The results are compared with those obtained with single metal ions under the same conditions and with those obtained at the same acid concentration with a mixed Pb/Cd solution. Table [2.13] shows the percentage of both Pb and Cd removal with and without pH adjustment.

The results show that in both the TMC and ACC systems, as compared to those with no pH adjustment, increasing the pH to 3.5 increased Cd but not Pb removal, although the results obtained from mixed metal ion solutions show improvements.

Table [2.13]: The effect of pH on the mixed Cd and Pb ions removal using TMC and ACC concentrator.

TMC						
Time (h)	No pH adjustment		pH 3.5 from single metal ions		pH 3.5 from mixed metal ions	
	Cd	Pb	Cd	Pb	Cd	Pb
1	0.0	78.0	24.0	72.0	26.0	76.0
4	0.0	96.0	77.5	93.0	82.0	94.0
6	0.0	95.0	90.0	95.0	94.0	94.0
8	0.0	96.0	94.0	97.0	98.0	97.0
ACC						
1	0.0	80.0	8.0	77.0	12.0	82.5
4	0.0	96.0	43.5	95.0	51.0	97.0
6	0.0	96.0	59.0	98.0	72.5	99.0
8	0.0	97.0	69.0	98.0	89.0	99.0

## 2.7 CONCLUSION

The purpose of the work described in this chapter is to test the applicability of concentrator cathode cells to the removal of metals from solution using lead and cadmium as examples. The basic concept of the concentrator cell is to concentrate ions from solution on a concentrator medium as they move towards an electrode under the driving force of an electric potential. When the concentrator becomes saturated metals are released into a small volume of electrolyte close to the electrode improving the efficiency of cathodic reduction and anodic oxidation processes. In this work the efficiency of a concentrator cell containing an ion-exchange material close to but not in contact with the cathode is compared with a concentrator cell in which activated carbon cloth is attached to a metal cathode. Removal of both lead and cadmium is found to be much more efficient using the ion-exchange concentrator system. No real advantage of the activated carbon cloth concentrator electrode over a standard cathode was found for lead and cadmium removal. A particular advantage of the ion-exchange concentrator cell is that the ion-exchange material is regenerated *in-situ* by the electrode reaction producing  $H_3O^+$  within the cell.

The effect of pH, electrolyte acid, successive use and of mixing lead and cadmium has been studied and the conditions for Pb and Cd removal using the control and the concentrator cell systems TMC, ACC and IEC was optimised.



## 2.8 REFERENCES

- [1] R.W.Houghton and A.T.Kuhn, *Journal of Applied Electrochemistry*, 1974, **4**, 173-190.
- [2] C. L. Lopez-Cacicedo, *Transactions of The Institute of Metal Finishing*, 1975, **53**, 74-77.
- [3] F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, "Advanced Inorganic Chemistry", 6<sup>th</sup> edition, A Willey-Interscience Publishers. 1999.
- [4] P. O. Neill, "Environmental Chemistry", Chapman & Hall, London, 1995.
- [5] Department of Health and Social Security, "Lead and Health", Report of a DHSS Working Party on Lead in the Environment, HMSO, London, 1980.
- [6] A. T. Kuhn, "The Electrochemistry of Lead", Academic Press INC. London, 1979.
- [7] S. M. Grimes, S. R. Johnston and I. Abrahams, *J. Chem. Soc. Dalton Trans.* 1995, 2081-2086.
- [8] P. Ramachandran, K. V. Venkateswaran and R.Srinivasan., *Journal of Applied Electrochemistry*, 1985, **15**, 937-945.
- [9] E. R. Cole, A. Y. Lee, and D. L. Paulson, *Journal of Metals*, 1983, **August**, 42 - 46.
- [10] M. Gircis and E. Ghali, *Journal of Applied Electrochemistry*, 1987, **17**, 1234 - 1245.
- [11] E. Exposito, A. Saez, E. Herrero and A. Aldaz, *Water Environment Research*, 1998, **70**(3), 306-315.
- [12] M. S. El-Deab, M. M. Saleh, B. E. El-Anadouli and B. G. Ateya, *Journal of the Electrochemical Society*, 1999, **146** (1), 208-213.
- [13] C. Ponce De Leon and D. Pletcher, *Electrochimica Acta*, 1996, **41**, 533.
- [14] G. Carreno, E. Sosa, I. Gonzalez, C. Ponce-de-leon, N. Batina and M. T. Oropeza, *Electrochimica Acta*, 1999, **44**, 2633-2643.
- [15] R. C. Widner, M. F. B. Sousa and R. Bertazzoli, *Journal of Applied*

- Electrochemistry*, 1998, **28**, 201-207.
- [16] P. Ramachandran, V. Nandakumar and K. V. Venkateswaram, *Trans. Indian Inst. Met.* October 1998, **51** (5), 389-391.
- [17] V. Gopal, G. C. April and V. N. Schrodt, *Separation and Purification Technology*, (1998), **14**, 85-93.
- [18] E. A. Laws, "Aquatic Pollution" (an Introductory Text), 2<sup>nd</sup> edition, Interscience Publication, 1993.
- [19] A. Elhalim, S. Elwahaab, S. Elrehim and E. Elmeguid, *Journal of Applied Electrochemistry*, 1987, **17** (1), 49-56.
- [20] S. Srivastava, R. Kashyap and S. Srivastava, *Acta Chimica Hungarica-Models in Chemistry*, 1984, **117** (1), 3-9.
- [21] A. M. Abd El-Halim, A. O. Baghlaf and M. I. Sobahi, *Surface Technology*, 1984, **22**, 129-142.
- [22] T. C. Franklin and T. S. N. Sankara Narayanan, *Journal of Electrochemical Society*, 1996, **143** (9), 2759-2764.
- [23] D. Eyre, D. R. Gabe and D. R. Eastham, *Plating and Surface Finishing*, 1985, **April**, 74-80.
- [24] K. Scott and E. M. Paton, *Electrochimica Acta*, 1993, **38** (15), 2191-2197.
- [25] M. Abda and Y. Oren, *Water Research*, 1993, **27** (10), 1535-1544.
- [26] D. T. Vachon, W. Bissett, B. A. Calver and G. C. Dickson, *Plating and Surface Finishing*, 1986, **April**, 68-73.
- [27] A. G. Tyson, *Plating and Surface Finishing*, 1984, **December**, 44-47.
- [28] B. S. Boyanov, J. D. Donaldson and S. M. Grimes, *Journal of Technology and Biotechnology*, 1988, **41**, 317-328.
- [29] C. E. Harland, "Ion Exchange Theory and Practice", 2<sup>nd</sup> Edition, Royal Society of Chemistry, 1994. Call QD561. G75 1994.
- [30] F. Helfferich, "Ion Exchange", Mc Graw-Hill Book Company, 1962.
- [31] A. Bailey and F. A. P Maggs, *Br. Pat. 1310101*, (1971).
- [32] P. N. Brown, G. G. Jayson, B. Mile and M.C. Wilkinson, *Carbon*, 1989, **27**, 171-176.
- [33] A. Bailey, F.A.P. Maggs and J.H. Williams, *Br. Pat. 1310011*,

(1971).

[34] J. J. Freeman, F.G.R. Gimblett, R.A. Roberts and K.S.W. Sing, *Carbon*, 1987, **25**(4), 559-563.

[35] J. F. Alder, P.R. Fielden and S.J. Smith, *Carbon*, 1988, **26**(5), 701-711.

[36] A. Capon, B.R. Alves, M.E. Smith and M.P. White, *Carbon*, 1982, **20**(2), 137.

[37] J. J. Freeman and F.G.R. Gimblett, *Carbon*, 1987, **25**(4), 565-568.

## CHAPTER THREE

### APPLYING THE ELECTROCHEMICAL TECHNIQUE FOR THE REMOVAL AND NOVEL SEPARATION PROCESSES OF LEAD, TIN, AND INDIUM IN MIXED ION SOLUTIONS.

3.1	INTRODUCTION .....	94
3.2	INDIUM.....	96
3.2.1	<i>Chemistry of Indium</i> .....	96
3.2.2	<i>Distribution and Industrial Usage of Indium</i> .....	96
3.2.3	<i>Electrochemistry of Indium</i> .....	97
3.3	TIN.....	99
3.3.1	<i>Chemistry and Properties of Tin</i> .....	100
3.3.2	<i>Electrochemistry of Tin</i> .....	101
3.4	EXPERIMENTAL.....	103
3.4.1	<i>The Effect of Different Acid Strength and Types</i> .....	104
3.4.2	<i>Effect of Potassium Thiocyanate Additive</i> .....	104
3.5	RESULTS AND DISCUSSION.....	104
3.5.1	<i>Lead Electrodeposition</i> .....	104
3.5.1.1	<b>Lead Electrodeposition Using Nitric Acid Media</b> .....	105
3.5.1.2	<b>Lead Electrodeposition Using Perchloric Acid Media</b> .....	107
3.5.1.3	<b>Lead Electrodeposition Using Acetic Acid Media</b> .....	107
3.5.2	<i>Tin Electrodeposition</i> .....	111
3.5.2.1	<b>Tin Electrodeposition Using Nitric Acid Media</b> .....	111
3.5.2.2	<b>Tin Electrodeposition Using Perchloric Acid Media</b> .....	114
3.5.2.3	<b>Tin Electrodeposition Using Acetic Acid Media</b> .....	114
3.5.3	<i>Indium Electrodeposition</i> .....	118
3.5.3.1	<b>Indium Electrodeposition Using Nitric Acid Media</b> .....	118
3.5.3.2	<b>Indium Electrodeposition Using Perchloric Acid Media</b> .....	120
3.5.3.3	<b>Indium Electrodeposition Using Acetic Acid Media</b> .....	120
3.5.4	<i>Recovery and Separation of Pb, Sn and In</i> .....	120
3.5.4.1	<b>Recovery and Separation of Pb, Sn and In from Nitric Acid Media</b> .....	120
3.5.4.2	<b>Recovery and Separation of Pb, Sn and In from Perchloric Acid Media</b> .....	124
3.5.4.3	<b>Recovery and Separation of Pb, Sn and In from Acetic Acid Media</b> .....	125
3.5.4.4	<b>Removal of Pb-Sn-In Mixture Using Nitric Acid Media in the Presence of Potassium Thiocyanate</b> .....	125
3.5.5	<i>Separation of Pb-Sn-In Using Nitric Acid Media with the Addition of Complexing Agent Potassium Thiocyanate</i> .....	126
3.6	CONCLUSION.....	128
3.7	REFERENCES .....	129

### 3.1 INTRODUCTION

The importance of electrodeposition in the removal and recycling of metal ions is demonstrated in many reports<sup>1</sup>. Often, however, the solution to be treated will contain more than one metal ion, for example those produced in the dissolution of spent Pb/Sn/In solder, wire scrap, and in mining and hydrometallurgical leach solutions. In these examples there is a requirement to reclaim the individual metals separately to achieve efficient economic recovery. It is, therefore, unattractive to adopt precipitation to recover the metals from solution and methods such as electrodeposition have attractions if selective deposition of the individual metals has to be achieved. There have been several studies of electrodeposition from mixed metal ion solutions, e.g. Cu/Ni, Zn/Cu<sup>2</sup>, and Pb/Cu<sup>3</sup>. In many cases, especially those involving Cu, the difference in standard electrode potential ensures that selective electrodeposition is effective. A selective electrodeposition process can be performed by stabilising the cathode voltage at the metal potential, which allows the selected metal at the selected potential to deposit on the cathode surface. The selectivity, however, can be disturbed if impurities or complexing agents are present.

The main objective of the work described in this chapter is to study the electrochemical removal and the possible separation of lead, tin and indium from dilute model solutions at different acidic concentrations.

From standard potentials of Sn, Pb and In (-0.1364, -0.1263 and -0.338V respectively), it can be predicted that selective separation of Sn/In and Pb/In should be possible but that Pb/Sn, which have similar electrode potentials, is not favoured.

Lead can be separated from tin or from indium by chemical precipitation as sulphate or possibly as chloride. It has been separated from indium by adding zinc chloride followed by water leaching and cementation of lead with zinc dust and deposition of indium on a zinc cathode<sup>4</sup>. Indium has very similar chemical properties in solution to tin<sup>5</sup>, but chemical separation can be achieved by<sup>6</sup>:

- 1- Addition of excess NaOH which precipitates indium but not tin.

- 2- Addition of diammonium phosphate in ammoniacal solution which precipitates indium and leaves tin in the solution.
- 3- Eliminating tin as a volatile bromide by evaporation from a mixture of hydrobromic acid and either perchloric or sulphuric acid.
- 4- In cold 10% sulphuric or hydrochloric acid solution, cupferron will precipitate tin, which can be extracted later into chloroform leaving indium in the aqueous acid layer.

The recovery of indium from lead or tin in hydrometallurgical leach solution has been described<sup>7</sup>, but there are few references to treatment of solutions containing all three metals. The work performed by Barakat<sup>8</sup>, described the recovery of the three metals from alloy wire scrap by acid/alkali leaching. The purities obtained were 99.0, 99.7 and 99.8% for lead, tin and indium respectively. The scrap material was leached with hot HCl-HNO<sub>3</sub> solution and the lead was separated as lead chloride and cementation with indium powder. Tin was precipitated with NaOH as hydrated tin oxide in the pH range 2.0-2.8 and the remaining indium was recovered either via a phosphate precipitate followed by conversion to the oxide by treatment with NaOH. or cementation with zinc powder.

The only effective method described for Pb/Sn/In recovery and separation is for concentrated leach solutions. The purpose of the present research, however, is to apply electrochemical methods to study the possible separation and recovery of lead, tin and indium from dilute solution in nitric or perchloric acids as noncomplexing acids and acetic acid as a complexing media. The use of hydrochloric, sulphuric or phosphoric acids is not suitable because the formation of low solubility compounds would hinder the electrolysis process. The separation of lead, indium and tin from nitrate solutions was also studied in the presence of potassium thiocyanate (KSCN) as a complexing agent.

The chemical and electrochemical properties of lead were described in chapter 2.

Those of indium and tin are described in this chapter.

## **3.2 INDIUM**

### **3.2.1 Chemistry of Indium**

Indium<sup>9</sup>, atomic number 49, is a main group IIIA element of the periodic table. Indium is a metal with melting point 156.6°C, boiling point 2075°C and silvery-white lustre. Indium is softer than lead, can be scratched with a fingernail and undergoes almost limitless deformation. Like tin, the pure metal emits a high-pitched "cry" when bent. Natural indium is a mixture of two isotopes: indium-113 (4.28 percent) and indium-115 (95.72 percent). In aqueous systems only In(III) compounds are stable, but solid state compounds in the (+1) oxidation state are known (halides). Indium metal is unaffected by air at ambient temperatures, but at red heat it burns with a blue-violet flame to form the yellow oxide  $\text{In}_2\text{O}_3$ . The metal dissolves in mineral acids but is not attacked by alkalis or boiling water. Concentrated oxidising acids, cold acetic acid and oxalic acid dissolve indium. When heated in the presence of the halogens or sulfur, direct combination takes place. Indium (III) salts are precipitated as  $\text{In}(\text{OH})_3$  at pH~3.4. With the main Group V elements, indium forms compounds (indium phosphide, arsenide, antimonide) that have semiconductor properties.

### **3.2.2 Distribution and Industrial Usage of Indium<sup>16</sup>**

Indium is about as rare as silver. The Earth's crust contains on the average about 0.05 part per million indium by weight. The element does not occur uncombined nor in independent minerals but as a trace in many minerals, particularly those of zinc and lead, from which it is obtained as a by-product.

Indium has the unusual property when molten of clinging to or wetting clean glass and other surfaces, which makes it valuable for producing hermetic seals between glass, metals, quartz, ceramics and marble. The alloys of indium are highly resistant to corrosion and thus find application in jewellery and dental work. Indium has an

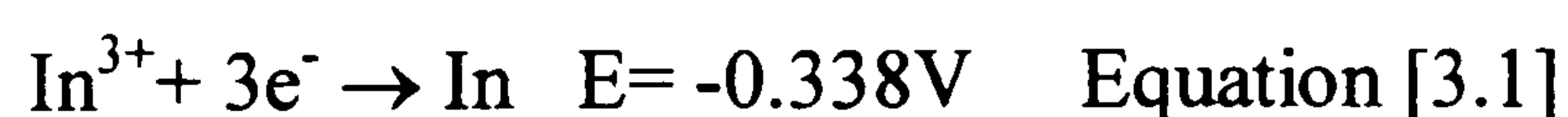
application in low melting alloys and is used in coating aircraft engine bearings because it improves corrosion resistance and enables the surface to retain a more adherent oil film. Indium is an ingredient in some low-melting alloys with Bi, Cd, Pb and Sn (melting point 50-100°C) which are used in sprinkler heads, fire-door links, fusible plugs and meltable safety devices. The metal is extensively employed in the manufacture of semiconductor devices and for soldering various parts of germanium transistors and rectifiers. Indium antimonide, arsenide, and phosphide, are used in infrared detector and semiconductor applications. Indium is used as an alloying element with other metals to harden and strengthen them and to increase corrosion and wear resistance. Other uses are to reduce the melting point, or to suppress the volatility of other alloying metals in high-vacuum work. Indium-silver alloys are used in brazing as a substitute for toxic cadmium. Electroplated indium metal (from a sulfamate bath) is used for electrical connectors. Indium is also used to measure the thermal neutron flux of nuclear reactors and to monitor neutrons for the protection of personnel and equipment. Further commercial uses of indium metal are in optical communication in sealer cells.

Some studies have indicated that indium can be potentially toxic to animals, but the exact nature of the toxicity and the threshold toxic levels have yet to be established<sup>10</sup>,<sup>11</sup>. On the other hand, increasing usage of indium in industry makes it likely that it will become an increasing part of industrial waste discharge, contributing to environmental pollution.

### 3.2.3 Electrochemistry of Indium

Indium may be electroplated successfully onto nearly all metal and alloy cathodes; it belongs to a group of triply charged metal ions whose electrochemical properties are strongly influenced by the composition and concentration of the electrolyte solution<sup>12</sup>. The most favoured electrolyte for the electrodeposition of indium is a sulphate solution<sup>5</sup>.

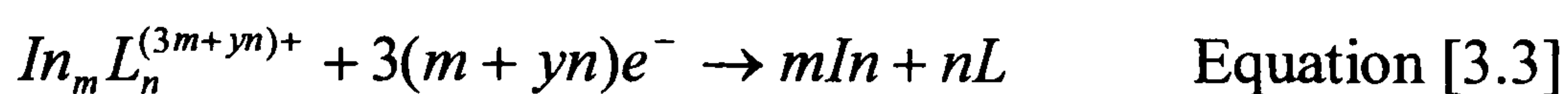
The standard indium reduction potential is:



Two parallel reduction processes have been found: indium is reduced either by direct discharge of the  $\text{In}(\text{H}_2\text{O})_6^{3+}$  ion, or by discharge of the partially hydrolysed indium



ions  $\text{In}(\text{H}_2\text{O})_5\text{OH}^{2+}$ . The rate constant for the process involving  $\text{In}(\text{H}_2\text{O})_5\text{OH}^{2+}$  is about  $10^5$  times faster than that of  $\text{In}(\text{H}_2\text{O})_6^{3+}$ . In other words, hydrolysis of the hexaquo-complex influences the course of the reduction. For example at high perchloric acid concentrations where indium exists only as the  $\text{In}(\text{H}_2\text{O})_6^{3+}$  ion, the deposition of the metal is difficult<sup>5, 13</sup>. On the other hand, the pH of an In(III) solution must be controlled during electrolysis to prevent the formation of the colloidal species  $\text{In}(\text{OH})_3$ <sup>(12, 14)</sup>. The electrolysis of indium ions in the presence of complexing agents proceeds via the corresponding complex species, as follows:



where (m) is the number of moles of indium ion; (n) the number of moles of ligand; and (y) the charge of the complexing agent. Adsorption of the complexing agent at the cathode surface prevents metal oxidation and gives a smooth film of the deposited metal<sup>15</sup>.

The recovery and refining of indium from zinc ores after roasting and leaching has been described using an electrochemical method. The In is deposited on aluminium plates immersed in the solution containing 3 g/l HCl and indium metal of 99.99 percent purity can be obtained by electrorefining using the metal deposited on the aluminium as an anode<sup>7</sup>. The electrochemical refining method involves the use of indium sulphate solutions containing sodium chloride and glue at pH 2 to 2.5<sup>(16)</sup>.

The preconcentration of indium by electrodeposition from different complexes has been studied under different conditions of pH, temperature, metal-ion ratio, current density, time, electrode types and complexing agents<sup>15</sup>. The quantity and quality of indium deposited was found to depend on the type of bath used. The baths can be arranged in the following order of efficiency according to the potential complexing species present:

Alizarin yellow > Oxalic acid > Thiourea > 1,10-Phenanthroline > Dimethyl

formamide > Thiosemicarbazide > Phenylhydrazine > Dimethylsulphoxide > 1-(Pyridyl-2-azo)-naphthol > 2-(5-Sulphophenylazo-1,8-dihydroxynaphthalene-3,6-disulphonic acid, trisodium salt > Tetrahydroxy-*p*-benzoquinone > 2,2'-Dipyridyl > Adipic acid > Methyl red > Acetylacetoacetate > Diphenylsulphoxide > Pyridine > NaI > NaBr = methyl violet > Succinic acid > Pyrogallol > NaCl > Tartaric acid > Gallic acid > Alizarin > Thiocyanate.

### 3.3 TIN

The element tin<sup>17</sup> has played a major role in the development of human civilization, and was discovered around 3500 BC. Smelting tin with copper produces bronze which was invented in the early civilized centuries, and heralded the advent of the Bronze Age. Nowadays, tin finds industrial application both as a metal and its chemical compounds. Metallurgical uses account for 65% of the volume of tin produced with the major applications being in tinsplate, solder alloys, tin and alloy coatings, pewter, bronzes, and fusible alloys. Because pure tin is relatively weak, it is not used for structural purposes unless alloyed with other metals. Numerous alloys of tin are used, including soft solder-type metal, pewter, bronze, bell metal, and low-temperature casting alloys. Tin-lead solders are widely used in the electrical and plumbing industries. Such alloys are also utilized as solder brass and copper automobile radiators.

In its chemical reactions, tin can form bonds directly with carbon to give organometallic compounds. These properties have given rise to many important uses for tin chemicals, e.g. as biocide agents, pharmaceutical products and stabilizing additives for PVC. Of all the metals, tin has the greatest number of organometallic compounds in commercial use, with global production on the order of 40,000 metric tons per year<sup>18</sup>.

A considerable amount of work has been done on the environmental impact and treatment of organotin compounds<sup>19-21</sup>, but little has focused on inorganic tin

compounds, even though significant quantities of inorganic tin appear in the waste streams from mining<sup>22</sup>, and tin electroplating and anodizing baths<sup>23</sup>. It is also possible that inorganic tin, like mercury, could be biologically methylated, which provided an impetus to the investigation of their biological chemistry, and the necessity for care in the use of tin compounds.

### 3.3.1 Chemistry and Properties of Tin

The influence of tin (Sn) on alloy properties is so marked, that it is sometimes called “diabolus metallorum”, the devil of metals, because its presence made other metals hard and brittle. Tin has an atomic number of 50, atomic weight of 118.69, melting point 231.97°C, boiling point 2,270°C, density, 7.28 (white), 5.75 (grey), oxidation states 2 and 4. Tin has two crystalline modifications  $\beta$ -tin or white tin and  $\alpha$ -tin or grey tin.  $\alpha$ -tin is thermodynamically stable below 13.2°C. These two modifications have different structures, which accounts for many of the differences in their properties.  $\beta$ -tin is typically a metallic conductor, whereas,  $\alpha$ -tin which has the diamond structure exhibits high resistivity and is a semiconductor.

The bonding in tin compounds is related to the outer electronic configuration of  $5s^2 5p^2$ , which permits the formation of both tin (IV) and tin (II) compounds. In tin (II), only the outer p-electrons are being lost or used in bond formation, whereas, with tin (IV), bonding involves the loss or use of all the valence shell electrons<sup>24</sup>.

At ambient temperature tin is inert to oxygen, nitrogen, hydrogen, water and ammonia. Surface oxidation, however, does occur at elevated temperatures (200°C with air and 700°C with water vapour), in which a film of oxide forms over the surface. The formation of this surface oxide film prevents corrosion under most conditions.

Tin (II) oxide, SnO, is amphoteric, dissolves in aqueous solution of acids to form tin (II) salts, and alkalis to form tin (II) hydroxide. Tin (II) oxide is the usual starting

material for the preparation of tin salts and electroplating solution.

The predominant species present in acid solutions containing tin(II) and complexing anions are the pyramidal triligandstannate(II) ions,  $[\text{SnX}_3]^-$  e.g. with  $\text{X}=\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{CH}_3\text{CO}_2^-$  and  $\text{NCS}^-$ , this is expected because of the filling of the empty p-orbital in a normal tin (II) compound ( $\text{SnX}_2$ ). When insufficient  $\text{X}^-$  is present to complex all of the tin as  $(\text{SnX}_3)^-$ , the evidence has been found for  $(\text{SnX})^+$ ,  $\text{SnX}_2$  and  $\text{Sn}_2\text{X}_5^-$  in addition to the predominant  $(\text{SnX}_3)^-$  ions in the solution. There is very little evidence for the formation of complexes with co-ordination greater than three<sup>25</sup>.

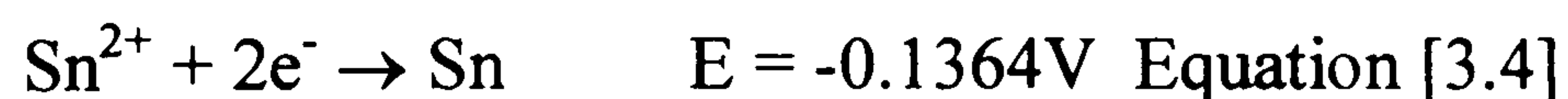
Tin(IV) compounds of significance include tin(IV) chloride,  $\text{SnCl}_4$ , formed by attacking tin metal with chlorine, widely used as a stabiliser for perfumes and as a starting material for other tin salts; and tin (IV) oxide,  $\text{SnO}_2$ , a useful catalyst in certain industrial processes and a polishing powder for steel. Tin (IV) oxide, is also amphoteric but is more acidic than basic.

The metal reacts slowly with dilute acid to give a tin (II) salt, but in concentrated nitric acid gives a hydrated tin (IV) oxide (metstannic acid). Tin (II) compounds readily oxidise to tin (IV) compounds, and consequently are often used as reducing agents<sup>26</sup>.

### 3.3.2 Electrochemistry of Tin

The electrodeposition of tin can be performed in alkaline ( $\text{Sn}^{4+}$ ) or acidic ( $\text{Sn}^{2+}$ ) conditions<sup>27</sup>. The most commonly used solutions for the electrodeposition of tin are solutions of tin(II) sulphate<sup>28, 29</sup>, tin(II) chloride<sup>30</sup>, tin(II) fluoroborate<sup>31</sup> and sodium and potassium stannates(IV)<sup>32</sup>.

The standard tin reduction potential is:



The electrodeposition of tin is a process that has been used for tin coating<sup>28, 29, 32, 33</sup>,

electrowinning<sup>34</sup> and recovery<sup>27</sup>. At the start of the electrodeposition of tin using acidic conditions, the predominant species is  $\text{SnX}_3^-$  in equilibrium with other species including  $\text{Sn}_{aq}^{2+}$ . Electrodeposition depletes the  $\text{Sn}_{aq}^{2+}$  species and a shift in the equilibrium occurs to compensate for the depleted species.



At high acid concentrations, the predominant species is  $[\text{SnX}_3]^-$  and reductions at the cathode surface are achieved and because of the high acidity, any deposited metal redissolves and returns to the solution.

Some other factors also influence tin electrodeposition. Firstly, while the electrolysis is proceeding, the pH of the solution decreases because of the production of  $\text{H}^+$  ions at the anode. Secondly, tin is more electronegative than hydrogen and the hydrogen overvoltage on tin is high ( $10^{-8} \text{ A m}^{-2}$ )<sup>(23)</sup>. This overvoltage slightly inhibits hydrogen evolution and means that, by the time tin is deposited, the pH decrease is also inhibited so that the major interfering cathodic reaction occurring during the electrodeposition of tin is the evolution of hydrogen. The rate of hydrogen evolution increases with decreasing pH<sup>35</sup>.

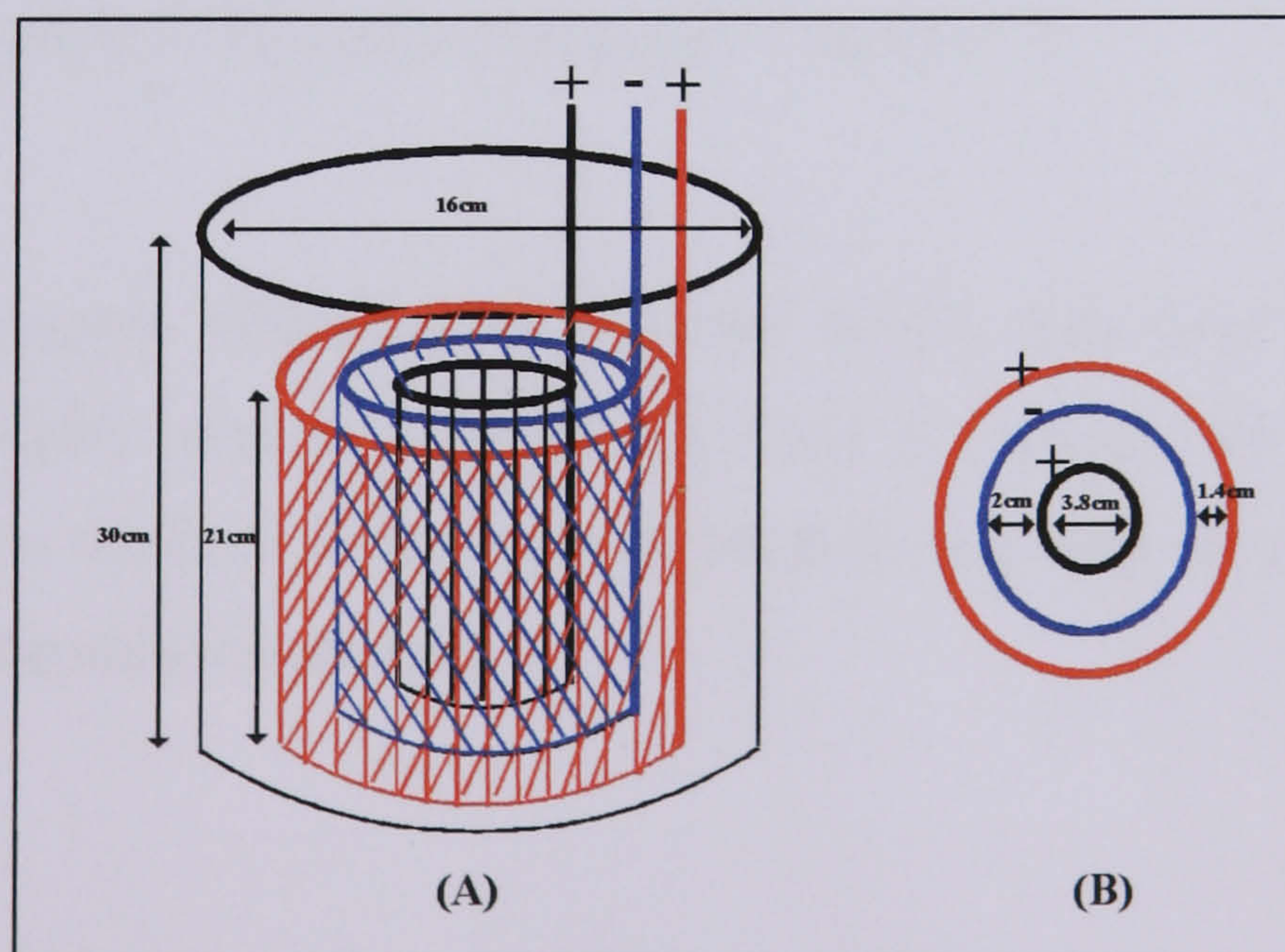
Some researchers have reported that tin can be deposited from tin (II) solution in the presence of a complexing agent. Petrenko et al<sup>36</sup> and Orio et al<sup>37</sup> reported that the metal can be deposited in the presence of indole and thiourea respectively. Fouada et al<sup>34</sup> studied the deposition of tin from tinstone ore by an electrolytic method in the presence of different complexing agents at different current densities and tin concentrations. The deposition efficiency was found to depend on the type of the complexing agent present and to decrease in the order: pyrogallol (90.0) > ethyl alcohol (81.5) > thiocyanate = sulphate = fluoride (78.5) > citrate (75.0) > oxalate (72.5) > pyridine (70.0), where the numbers in brackets, reflect the current efficiency.

It has been suggested that thiocyanate complexes enhance the cathodic deposition of tin giving a current efficiency of 78.5%, whereas, for indium (Section 3.2.3)

thiocyanate is the poorest complexing agent. This information is utilised in the present work to enhance the separation process of tin from indium in the Pb-Sn-In mixture.

### 3.4 EXPERIMENTAL

A cylindrical Pyrex beaker of 3 litres capacity with an outer diameter of 16 cm and height 30 cm was used as a static electrochemical cell. The cell contained two cylindrical titanium mesh anodes (diameters 3.8 and 10.6 cm) coated with iridium oxide, on either side of a cylindrical mild steel mesh cathode of diameter 7.8 cm. The two anodes and the one cathode have the same height of 21 cm and gaps of 2 and 1.4cm respectively between the electrodes, to give the electrode sequence anode-cathode-anode. Figure [3.1] is a schematic diagram of the electrochemical cell used. The cathode surface area is  $0.109 \text{ m}^2$ . Lead, tin and indium solutions were prepared from reagent grade lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , tin chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and indium chloride  $\text{InCl}_3$ . All experiments were performed at a constant cathodic current density of  $13.7 \text{ A m}^{-2}$  (1.5 A) and an ambient temperature. During the reaction, electrolyte samples were collected every hour for 8 hours for analysis of residual metal ions by atomic adsorption. In some experiments the electrolysis time was extended to 24 hours.



**Figure [3.1]:** (A) the schematic diagram of the electrochemical cell and (B) cross section of the electrodes.

To determine the conditions under which the metal (Pb, Sn and In) ions can be separated the following experiments were performed.

### **3.4.1 The Effect of Different Acid Strength and Types**

The effects of various acids *viz.* nitric, perchloric and acetic in different concentrations (0.01, 0.05, 0.1, 0.5 and 1.0 mol dm<sup>-3</sup>) were studied for the removal of 50ppm (50mg dm<sup>-3</sup>) of each of the metals alone and in the presence of 50ppm of one or both of the other metal ions. Using acetic acid media, because of the low conductivity at the low acid concentration (0.01 mol dm<sup>-3</sup>), the experiments were only performed using the acid concentration range of (0.05, 0.1, 0.5 and 1.0 mol dm<sup>-3</sup>). In some experiments this acid range was extended to 2, 3, 4 and 5 mol dm<sup>-3</sup>.

### **3.4.2 Effect of Potassium Thiocyanate Additive**

To examine the effect of thiocyanate as an additive on the electrodepositions of tin, indium and the Pb-In-Sn mixture from nitric acid media, reagent grade potassium thiocyanate (KSCN) was added. The experiments were performed in two different sets *viz* : a)- changing the nitric acid concentration (0.05- 0.5 mol dm<sup>-3</sup>), at a constant KSCN concentration (0.05 mol dm<sup>-3</sup>). b)- changing the KSCN concentration (0.02-0.1 mol dm<sup>-3</sup>), at a constant HNO<sub>3</sub> concentration (0.1 mol dm<sup>-3</sup>).

In general, the current efficiency was found to be very low and the energy consumption relatively high (Appendix 2). This is because of the competitive hydrogen evolution reaction at the cathode surface and the use of low metal ion concentrations in the solution studied.

## **3.5 RESULTS AND DISCUSSION**

### **3.5.1 Lead Electrodeposition**

The results in Table [3.1] summarise the percentage lead deposition and the effect of

the presence of indium and indium together with tin in HNO<sub>3</sub>, HClO<sub>4</sub> and CH<sub>3</sub>COOH at the different acid concentrations. The percentage depositions equal to and above 95% are presented in bold.

### ***3.5.1.1 Lead Electrodeposition Using Nitric Acid Media***

Experiments were performed to study the effects of HNO<sub>3</sub> concentration on the percentage lead removal. The results (Figure [3.2, a]) show that increasing the HNO<sub>3</sub> concentration decreases the percentage of lead removal especially in the initial stages. However, the percentage removal increased with time to reach 95% and above after 8 hours electrolysis with all acid concentrations except with 1.0 mol dm<sup>-3</sup> HNO<sub>3</sub> when only 13% removal is achieved. A similar result was obtained using the standard electrochemical cell described in the previous chapter.

In the presence of 50ppm indium, results [Figure [3.2, b] show that the percentage of lead removal at the initial stages using low acid concentration (0.01 mol dm<sup>-3</sup> HNO<sub>3</sub>) is lower than in the absence of indium. Increasing the acid concentration, in the presence of indium, to 0.05 mol dm<sup>-3</sup> and above slightly increased lead deposition in the initial stages, whereas, at an acid concentration of 1.0 mol dm<sup>-3</sup>, significantly increased lead deposition

In the presence of 50ppm of indium and of tin in a combined lead-indium-tin solution using different HNO<sub>3</sub> concentrations, [Figure [3.2, c] the rate of lead removal, especially at the initial stages, is different from that from a solution containing only lead. For example, using a HNO<sub>3</sub> concentration of 0.05 and 0.1 mol dm<sup>-3</sup>, the presence of indium and tin ions increases the lead deposition in the initial stages, whereas, at the lower HNO<sub>3</sub> concentration of 0.01 mol dm<sup>-3</sup> or at higher the concentration of 0.5 mol dm<sup>-3</sup>, the presence of both indium and tin decreases lead deposition. Increasing the HNO<sub>3</sub> concentration to 1.0 mol dm<sup>-3</sup> results in no lead deposition from the Pb-In-Sn solution.



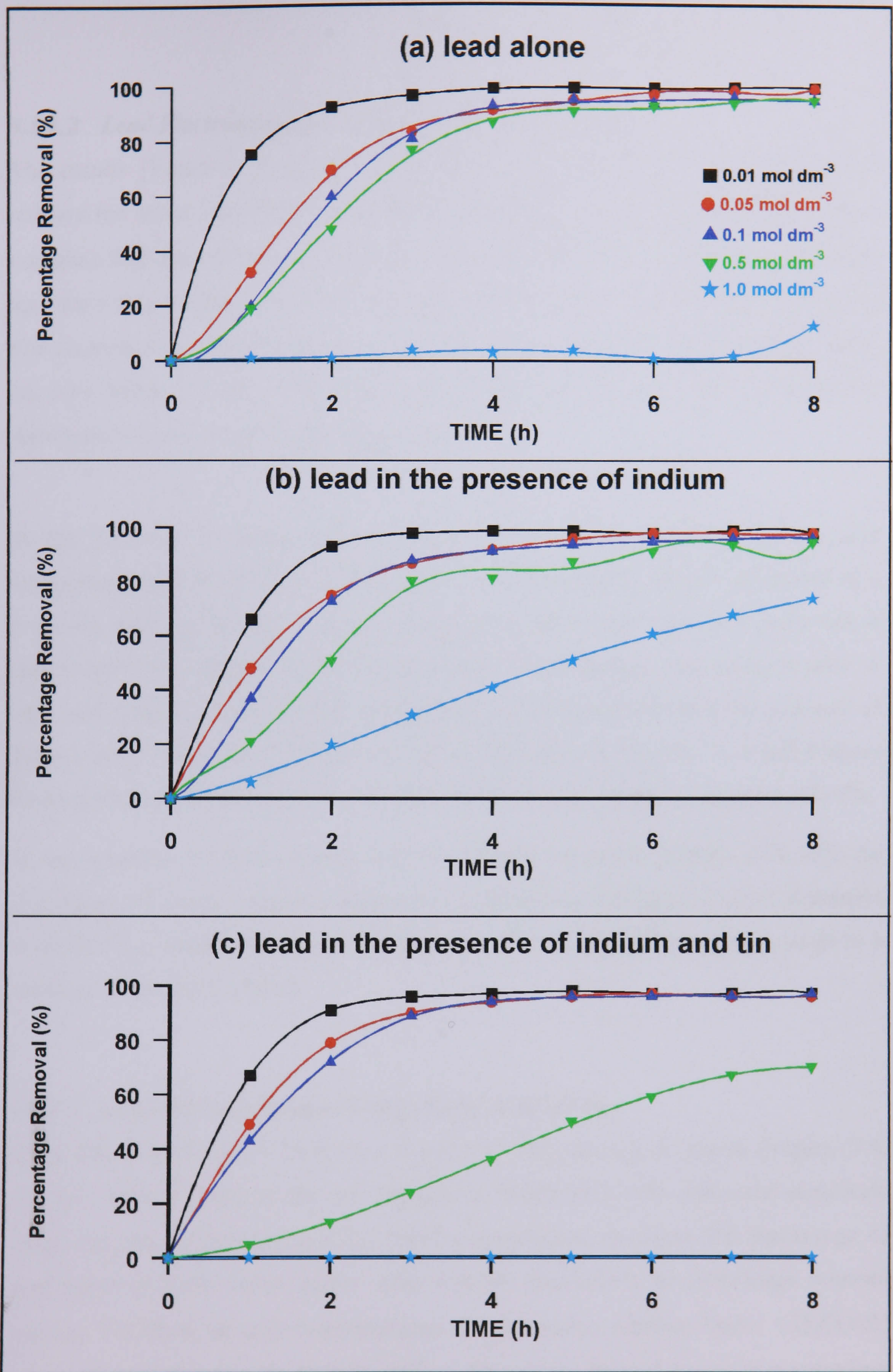


Figure [3.2]: The effect of nitric acid concentration on the percentage of lead removal from solution containing (a) lead alone, (b) lead and indium and (c) lead, indium and tin.

### **3.5.1.2 Lead Electrodeposition Using Perchloric Acid Media**

The results [Figure (3.3, a)] show that increasing the  $\text{HClO}_4$  concentration also reduces the initial rate of lead removal but that after electrolysis for 8 hours, almost complete lead removal of  $(97\pm 2\%)$  is achieved at all  $\text{HClO}_4$  concentrations. The data also show that perchloric acid is a more efficient electrolyte medium than nitric acid. For example at a concentration of  $1.0\text{mol dm}^{-3}$  using  $\text{HNO}_3$  the lead removal values are poor being 1.0 and 13.0% after 1 and 8 hours respectively, while with  $\text{HClO}_4$  these values are 21.6 and 97.8% respectively.

In the presence of 50ppm indium [Figure (3.3, b)] at the lower  $\text{HClO}_4$  acid concentrations ( $0.01$  to  $0.1\text{mol dm}^{-3}$ ), lead removal decreases slightly compared to a lead only solution, whereas, at higher acid concentrations lead removal is improved in the presence of indium in the initial stages. Significantly, this improvement is observed using  $1\text{mol dm}^{-3}$   $\text{HClO}_4$ . The percentages of lead removal in the presence of indium using  $1.0\text{mol dm}^{-3}$   $\text{HClO}_4$  were 57.0, 90.0 and 93.0% after 1, 4 and 8 hours respectively, compared with 21.0, 82.2 and 97.8% in the solution containing only Pb.

In the presence of both indium and tin (50ppm of each) [Figure (3.3, c)], the percentage of lead deposition, compared to a solution containing only lead, decreases at all  $\text{HClO}_4$  concentrations and increasing the  $\text{HClO}_4$  concentration again leads to a decrease in the lead removal.

### **3.5.1.3 Lead Electrodeposition Using Acetic Acid Media**

In the  $\text{CH}_3\text{COOH}$  range of  $0.05$  to  $1.0\text{mol dm}^{-3}$  the electrolysis results [Figure (3.4, a)] show that, in general, the lead removal is better than with nitric and perchloric acids, but that increasing the  $\text{CH}_3\text{COOH}$  concentration decreases the percentage of lead removed at the initial stages. After 6 hours electrolysis the percentage removal reaches  $97\pm 2\%$  at all acid concentrations. To determine whether higher  $\text{CH}_3\text{COOH}$  concentrations decrease the lead deposition, data were obtained at acid concentrations of  $2.0$ ,  $3.0$ ,  $4.0$  and  $5.0\text{mol dm}^{-3}$ . The results, however, show that the deposition process is still good even at high  $\text{CH}_3\text{COOH}$  concentrations.

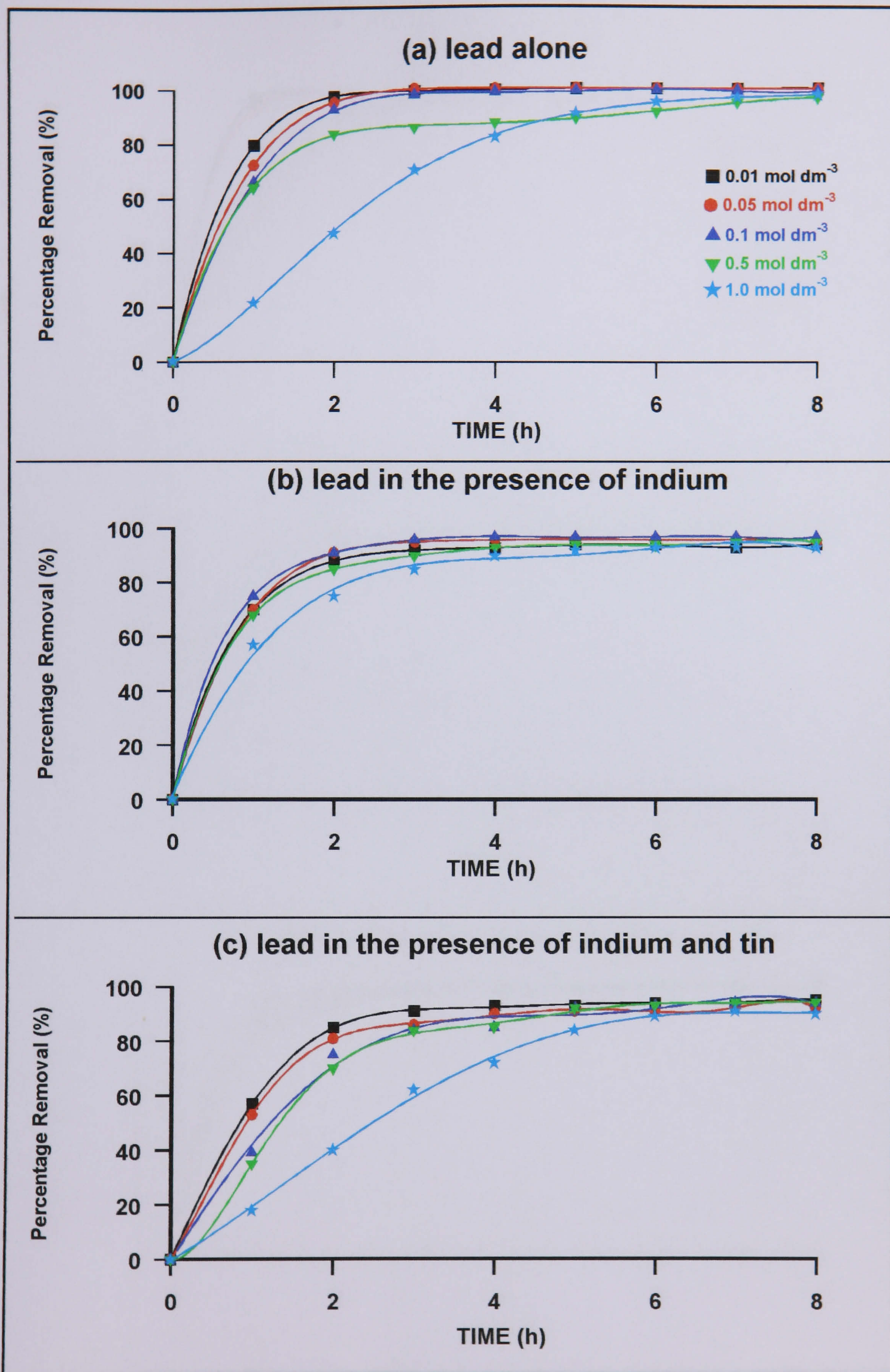


Figure [3.3]: The effect of perchloric acid concentration on the percentage of lead removal from solution containing (a) lead alone, (b) lead and indium and (c) lead, indium and tin.

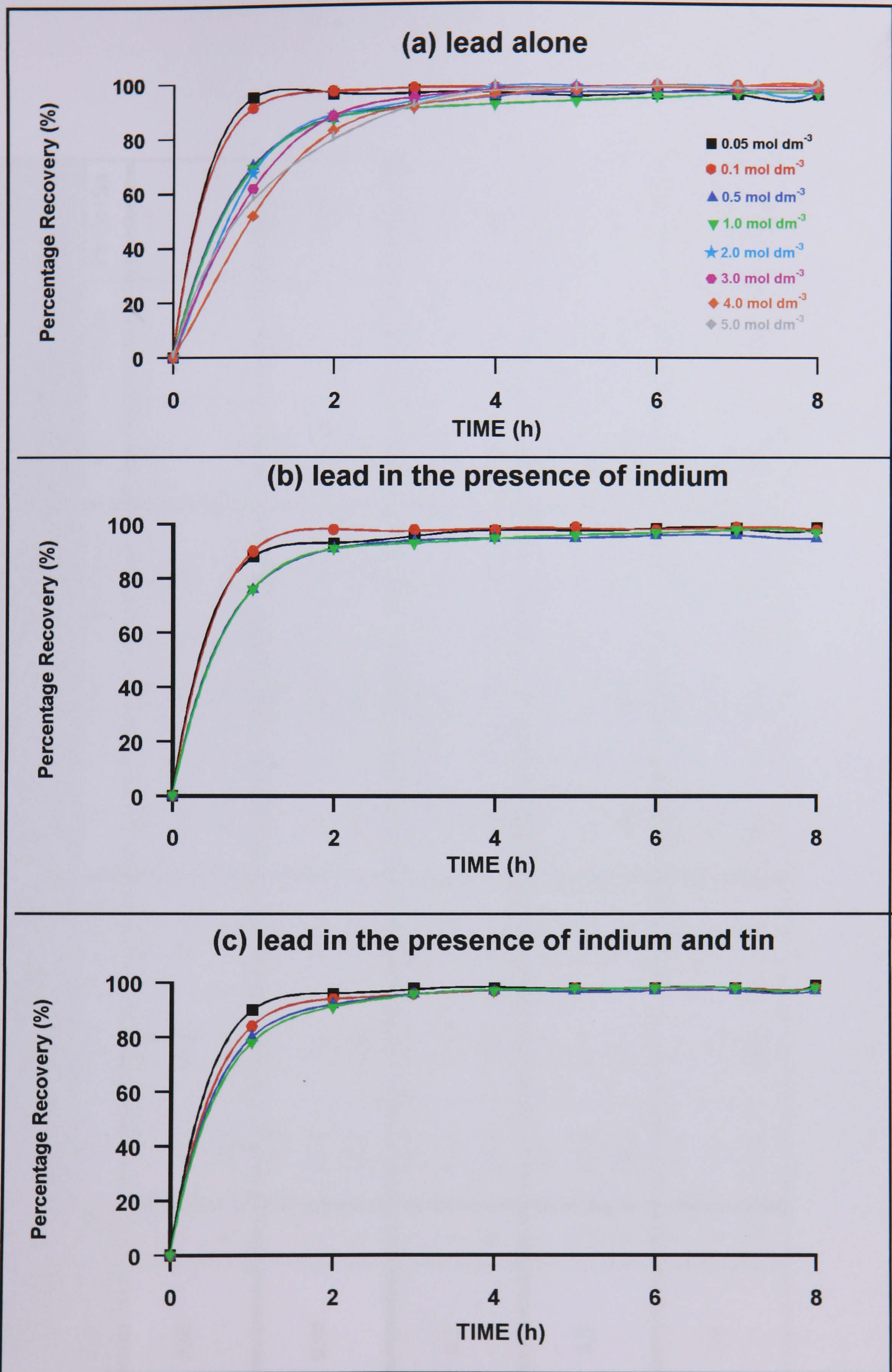


Figure [3.4]: The effect of acetic acid concentration on the percentage of lead removal from solution containing (a) lead alone, (b) lead and indium and (c) lead, indium and tin.

Table [3.1]: The effect of indium and indium together with tin on the deposition of lead in HNO<sub>3</sub>, HClO<sub>4</sub> and CH<sub>3</sub>COOH at different concentrations.

Acid concentration mol dm <sup>-3</sup>	Time (h)	Lead deposition (%)								
		HNO <sub>3</sub>			HClO <sub>4</sub>			CH <sub>3</sub> COOH		
		Pb	Pb+In	Pb+In+Sn	Pb	Pb+In	Pb+In+Sn	Pb	Pb+In	Pb+In+Sn
0.01	1	75.1	66.0	67.0	79.5	70.0	57.0	--	--	--
	4	99.1	99.0	97.0	99.4	93.0	93.0	--	--	--
	8	99.5	98.0	97.0	99.9	94.0	95.0	--	--	--
0.05	1	32.2	48.0	49.0	72.3	70.0	53.0	95.0	88.0	90.0
	4	91.5	92.0	94.0	99.7	96.0	90.0	95.0	97.6	98.0
	8	99.2	98.0	96.0	99.8	95.0	92.0	96.0	98.8	99.0
0.1	1	20.0	37.0	43.0	66.0	75.0	39.0	91.0	90.0	84.0
	4	93.0	91.6	94.0	98.5	97.0	85.0	98.0	98.0	97.0
	8	95.0	96.0	97.0	99.1	97.0	94.0	99.0	98.0	98.0
0.5	1	19.0	21.0	5.0	64.0	68.0	35.0	70.0	76.0	80.0
	4	97.0	81.6	36.0	87.3	93.0	85.0	95.0	95.0	97.0
	8	95.0	94.7	70.0	96.6	95.0	94.0	97.0	95.0	97.0
1.0	1	1.0	6.0	0.0	21.6	57.0	18.0	69.0	76.0	78.0
	4	3.0	41.0	0.0	82.2	90.0	72.0	92.0	95.0	97.0
	8	13.0	74.0	0.0	97.8	93.0	90.0	96.0	97.0	98.0

In the presence of indium or both indium and tin (50ppm for each) the results [Figure (3.4, b and c)] show that, only at the low acid concentration of  $0.05 \text{ mol dm}^{-3}$  there is a decrease in the percentage lead removal in the initial stages compared to the solution containing only lead. But the data do show that lead is eventually recovered completely in the presence of both indium and tin.

### **3.5.2 Tin Electrodeposition.**

The results in Table [3.2] summarise the tin percentage deposition and the effect of the presence of indium and indium together with lead in  $\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{CH}_3\text{COOH}$  at different acid concentration. Percentage deposition values above 95% are shown in bold.

#### ***3.5.2.1 Tin Electrodeposition Using Nitric Acid Media***

The results [Figure (3.5, a)] show that the electrolysis of tin using different  $\text{HNO}_3$  concentrations generally gives a poor deposition. The best deposition is obtained at low acid concentration of  $0.01 \text{ mol dm}^{-3}$  but even here the removal of tin does not exceed 65% after 8 hours. At acid concentrations of  $0.1 \text{ mol dm}^{-3}$  and above tin does not deposit.

The presence of indium ions in the solution containing tin at different  $\text{HNO}_3$  concentrations does not have a significant effect on the tin deposition [Figure (3.5, b)]. But the presence of both lead and indium (50ppm for each) results [Figure (3.5, c)] in a significant improvement in the percentage of tin removal compared to the results obtained from the solution containing only tin or indium and tin. However, the tin is still not completely removed after 8 hours and also there is still no deposition at acid concentrations of 0.5 and more.

##### **3.5.2.1.1 Tin deposition from nitric acid solution in the presence of complexing agent potassium thiocyanate**

The results in Table [3.1] show that changing the  $\text{HNO}_3$  concentration ( $0.05$ -  $0.5 \text{ mol dm}^{-3}$ ), at a constant  $\text{KSCN}$  concentration ( $0.05 \text{ mol dm}^{-3}$ ), the presence of  $\text{KSCN}$  leads

to a significant improvement in the tin deposition compared to the results obtained from the solution in the absence of a complexing agent. However, even in the presence of complexing agent, increasing the  $\text{HNO}_3$  concentration still results in a decrease in the percentage tin removal and increasing the KSCN concentration (0.02-0.1  $\text{mol dm}^{-3}$ ) at a constant  $\text{HNO}_3$  concentration of 0.1  $\text{mol dm}^{-3}$  results in a decrease in the percentage of tin deposition [Table 3.4].

Table [3.3]: The effect of adding 0.05  $\text{mol dm}^{-3}$  KSCN on the removal of 50ppm tin from varied  $\text{HNO}_3$  concentration.

Time (hours)	0.05 $\text{mol dm}^{-3}$ $\text{HNO}_3$		0.1 $\text{mol dm}^{-3}$ $\text{HNO}_3$		0.5 $\text{mol dm}^{-3}$ $\text{HNO}_3$	
	Control	KSCN	Control	KSCN	Control	KSCN
2	0.0	41.0	0.0	17.0	0.0	0.0
4	3.4	75.6	0.0	27.4	0.0	0.0
6	10.0	89.6	0.0	45.4	0.0	0.0
8	25.4	94.4	0.0	58.2	0.0	0.0

Table [3.4]: The percentage removal of 50ppm tin using constant  $\text{HNO}_3$  concentration of 0.1  $\text{mol dm}^{-3}$ , at varied KSCN concentration.

Time (hours)	Control	KSCN ( $\text{mol dm}^{-3}$ )		
		0.02	0.05	0.1
2	0.0	27.4	17.0	8.2
4	0.0	63.6	27.4	19.4
6	0.0	91.0	45.4	27.2
8	0.0	97.6	58.2	37.0

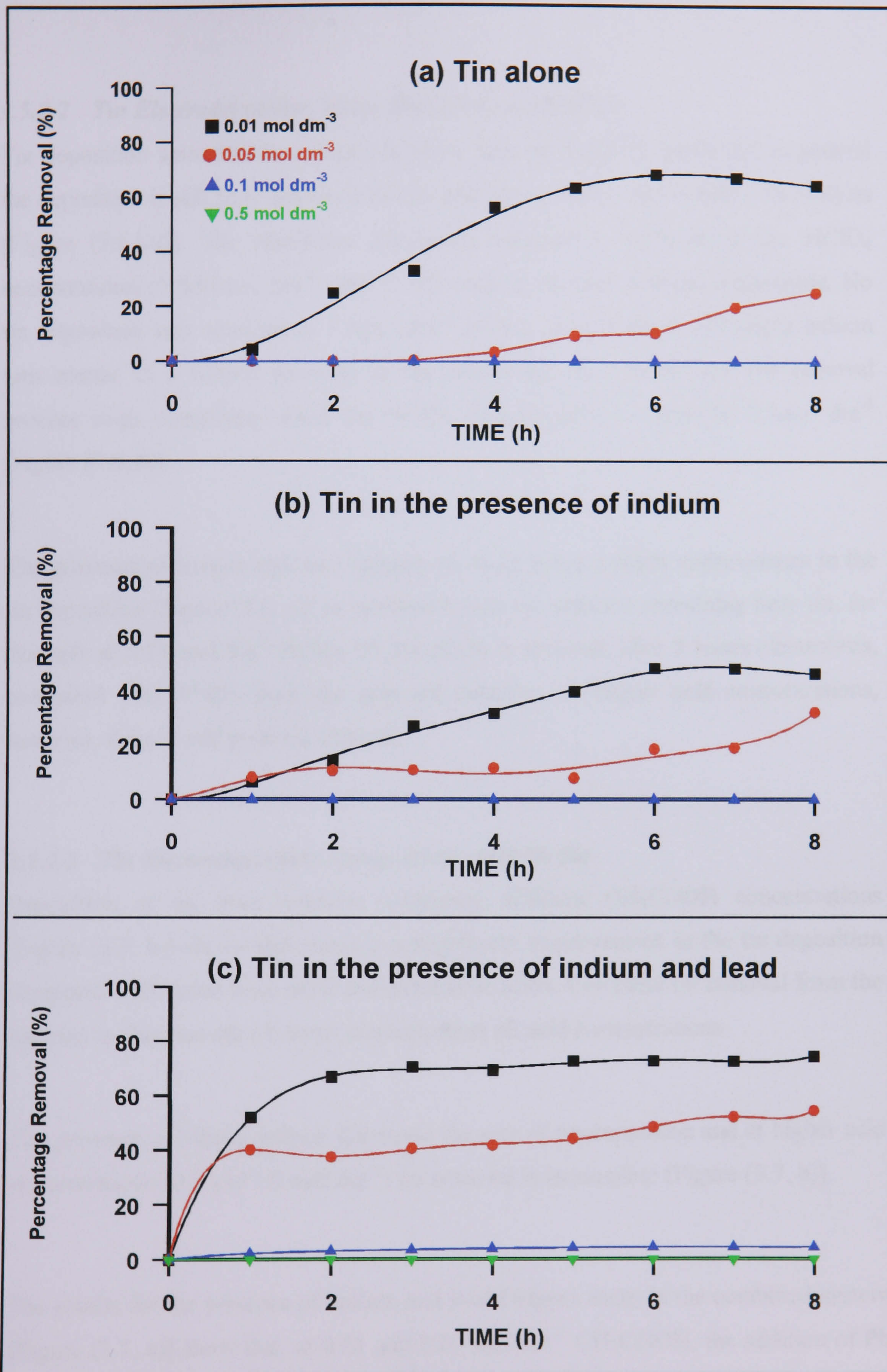


Figure [3.5]: The effect of nitric acid concentration on the percentage of tin removal from solution containing (a) tin alone, (b) tin and indium and (c) tin, indium and lead.



### ***3.5.2.2 Tin Electrodeposition Using Perchloric Acid Media***

Tin deposition from  $\text{HClO}_4$  solution is better than from  $\text{HNO}_3$  media but in general the deposition is still poor and tin is not completely removed after 8 hours electrolysis [Figure (3.6, a)]. The maximum percentage removal is achieved at the  $\text{HClO}_4$  concentration of  $0.01 \text{ mol dm}^{-3}$  with 77.8% deposition after 8 hours electrolysis. No tin deposition was obtained at  $1.0 \text{ mol dm}^{-3}$   $\text{HClO}_4$ . The addition of 50ppm indium ions results in a further decrease in the percentage tin removal and the removal process stops completely when the  $\text{HClO}_4$  concentration is raised to  $0.1 \text{ mol dm}^{-3}$  [Figure (3.6, b)].

The presence of indium and lead (50ppm of each) gives a slight improvement in the tin deposition [Figure (3.6, c)] as compared with the solution containing only tin, for example at  $0.01 \text{ mol dm}^{-3}$   $\text{HClO}_4$  95.8% of tin is removed after 8 hours electrolysis, compared with 77.8% from the only tin solution. At higher acid concentrations, however, there is still poor tin removal.

### ***3.5.2.3 Tin Electrodeposition Using Acetic Acid Media***

Deposition of tin from solution containing different  $\text{CH}_3\text{COOH}$  concentrations [Figure (3.7, b)] shows that there is a significant improvement in the tin deposition compared with those from nitric and perchloric acids. Complete tin removal from the solution is obtained after 6 hours electrolysis at all acid concentrations.

The presence of 50ppm indium decreases the rate of tin deposition and at higher acid concentrations ( $0.5$  and  $1.0 \text{ mol dm}^{-3}$ ) tin removal is incomplete [Figure (3.7, b)].

The results for the presence of indium and lead (50ppm each) in the combined system [Figure (3.7, c)] show that, at  $0.01$  and  $0.05 \text{ mol dm}^{-3}$   $\text{CH}_3\text{COOH}$ , the addition of Pb and In increases the percentage of tin removal slightly compared to the values obtained from the solution containing only tin. At higher acid concentrations of  $0.5$  and  $0.1 \text{ mol dm}^{-3}$  a decrease in the tin removal occurs in the final stages.

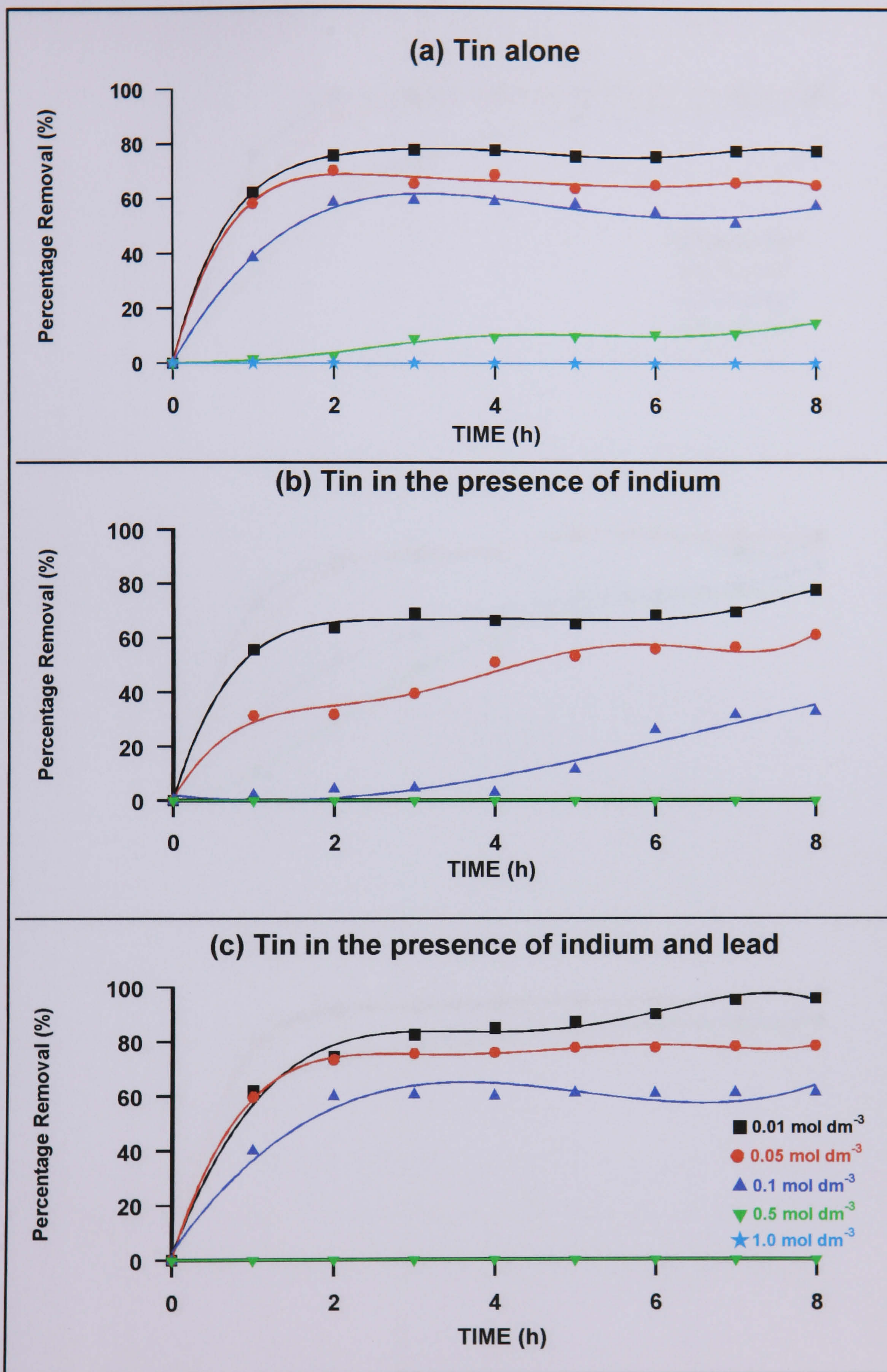


Figure [3.6]: The effect of perchloric acid concentration on the percentage of tin removal from solution containing (a) tin alone, (b) tin and indium and (c) tin, indium and lead.

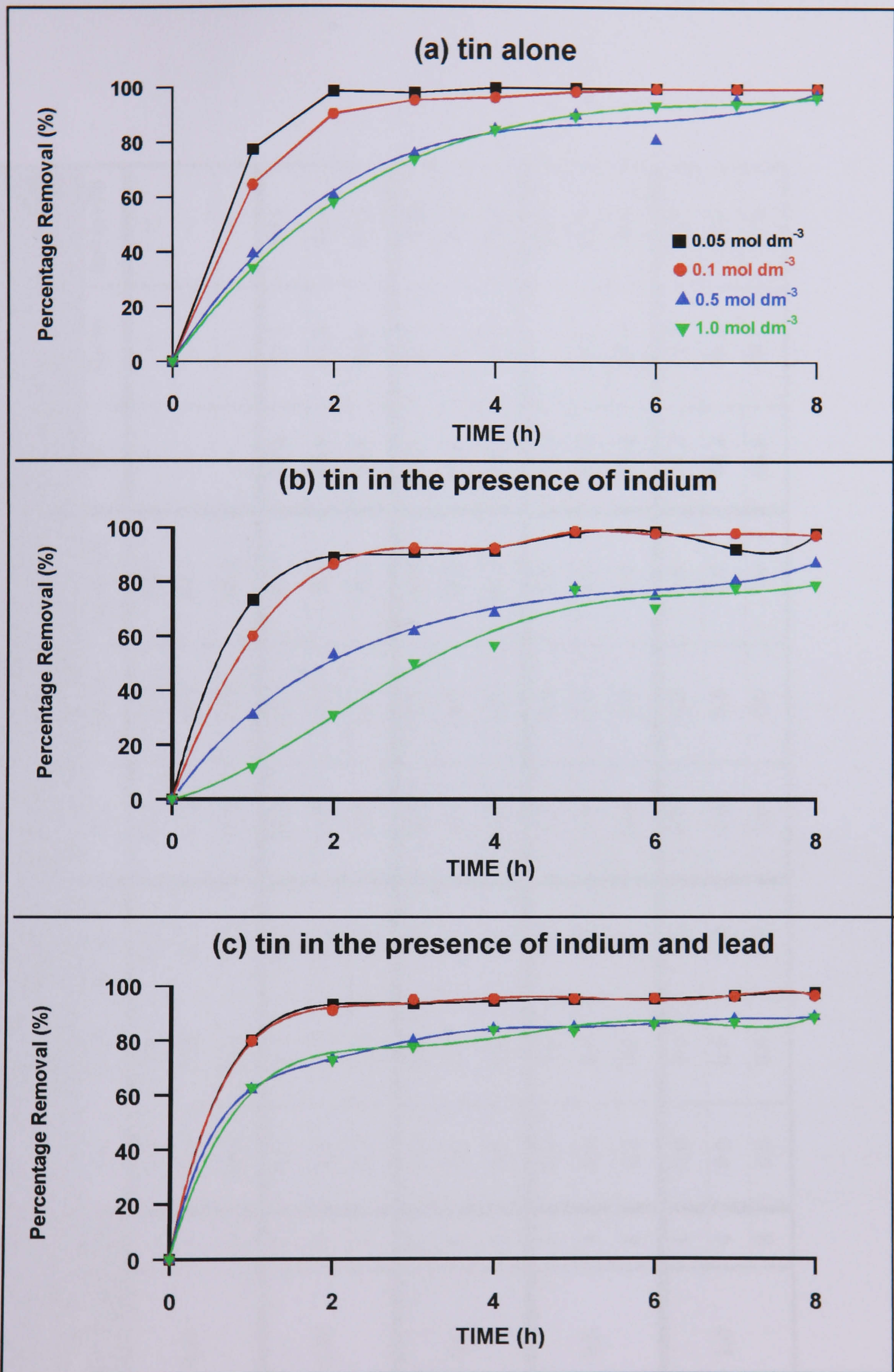


Figure [3.7]: The effect of acetic acid concentration on the percentage of tin removal from solution containing (a) tin alone, (b) tin and indium and (c) tin, indium and lead.

Table [3.2]: The effect of indium and indium together with lead on the deposition of tin in HNO<sub>3</sub>, HClO<sub>4</sub> and CH<sub>3</sub>COOH at different concentrations.

Acid concentration mol dm <sup>-3</sup>	Time (h)	Tin deposition (%)								
		HNO <sub>3</sub>			HClO <sub>4</sub>			CH <sub>3</sub> COOH		
		Sn	Sn+In	Sn+In+Pb	Sn	Sn+In	Sn+In+Pb	Sn	Sn+In	Sn+In+Pb
0.01	1	4.0	6.4	52.0	62.2	55.5	62.0	--	--	--
	4	56.0	31.8	69.3	77.8	66.4	84.9	--	--	--
	8	64.6	46.4	74.2	77.8	77.8	95.8	--	--	--
0.05	1	0.0	8.2	40.2	58.2	31.3	59.5	77.4	73.3	80.2
	4	3.4	11.8	41.8	68.8	51.1	76.0	99.9	91.8	94.4
	8	25.4	32.2	54.4	65.3	61.3	78.4	99.9	98.0	97.3
0.1	1	0.0	0.0	2.2	38.6	2.1	40.0	64.6	60.1	79.8
	4	0.0	0.0	4.0	59.1	3.0	60.0	96.6	92.7	95.3
	8	0.0	0.0	4.4	57.8	32.7	61.3	99.9	97.3	96.4
0.5	1	0.0	0.0	0.0	1.5	0.0	0.0	39.4	31.1	62.2
	4	0.0	0.0	0.0	9.6	0.0	0.0	85.2	68.9	84.4
	8	0.0	0.0	0.0	14.8	0.0	0.0	97.4	87.3	88.8
1.0	1	0.0	0.0	0.0	0.0	0.0	0.0	34.2	11.7	62.9
	4	0.0	0.0	0.0	0.0	0.0	0.0	84.8	56.9	84.0
	8	0.0	0.0	0.0	0.0	0.0	0.0	96.8	79.1	88.4

### 3.5.3 Indium Electrodeposition

The results in Table [3.5] summarise the percentage deposition of indium and the effects of the presence of tin, lead, and tin and lead together in HNO<sub>3</sub>, HClO<sub>4</sub> and CH<sub>3</sub>COOH at the different acid concentrations. The percentage depositions above 95% are shown in bold.

#### 3.5.3.1 Indium Electrodeposition Using Nitric Acid Media

In HNO<sub>3</sub> media indium deposition [Figure (3.8, a)] is poor. Increasing the acid concentration to 0.1 mol dm<sup>-3</sup> suppresses indium deposition, and the best removal is obtained when the acid concentration is 0.01 mol dm<sup>-3</sup> although the percentage indium removal in this acid concentration does not exceed 42% after 8 hours electrolysis. In the presence of tin, lead or both lead and tin ions (50ppm of each) the results [Figure (3.8, b, c and d)] show that the indium deposition is significantly increased compared to the solution containing only indium. Indium removal in the presence of tin is increased in 0.01 and 0.05 mol dm<sup>-3</sup> HNO<sub>3</sub> and gives complete removal after 8 hours electrolysis.

##### 3.5.3.1.1 Indium deposition from nitric acid solution in the presence of complexing agent potassium thiocyanate

The addition of 0.05 mol dm<sup>-3</sup> KSCN to the solution containing 0.1 mol dm<sup>-3</sup> HNO<sub>3</sub> and 50ppm In does not improve indium deposition over 8 hours electrolysis. Extending the experimental time to 24 hours results in 71% of the indium being deposited at the anode surface as a light brown powder. Analysis of this powder using X-ray fluorescence shows the presence of indium contaminated with iron. The presence of iron could have originated from the dissolution of the stainless steel cathode which is not recommended in such conditions and prevents further analysis of indium material which is probably indium oxide.

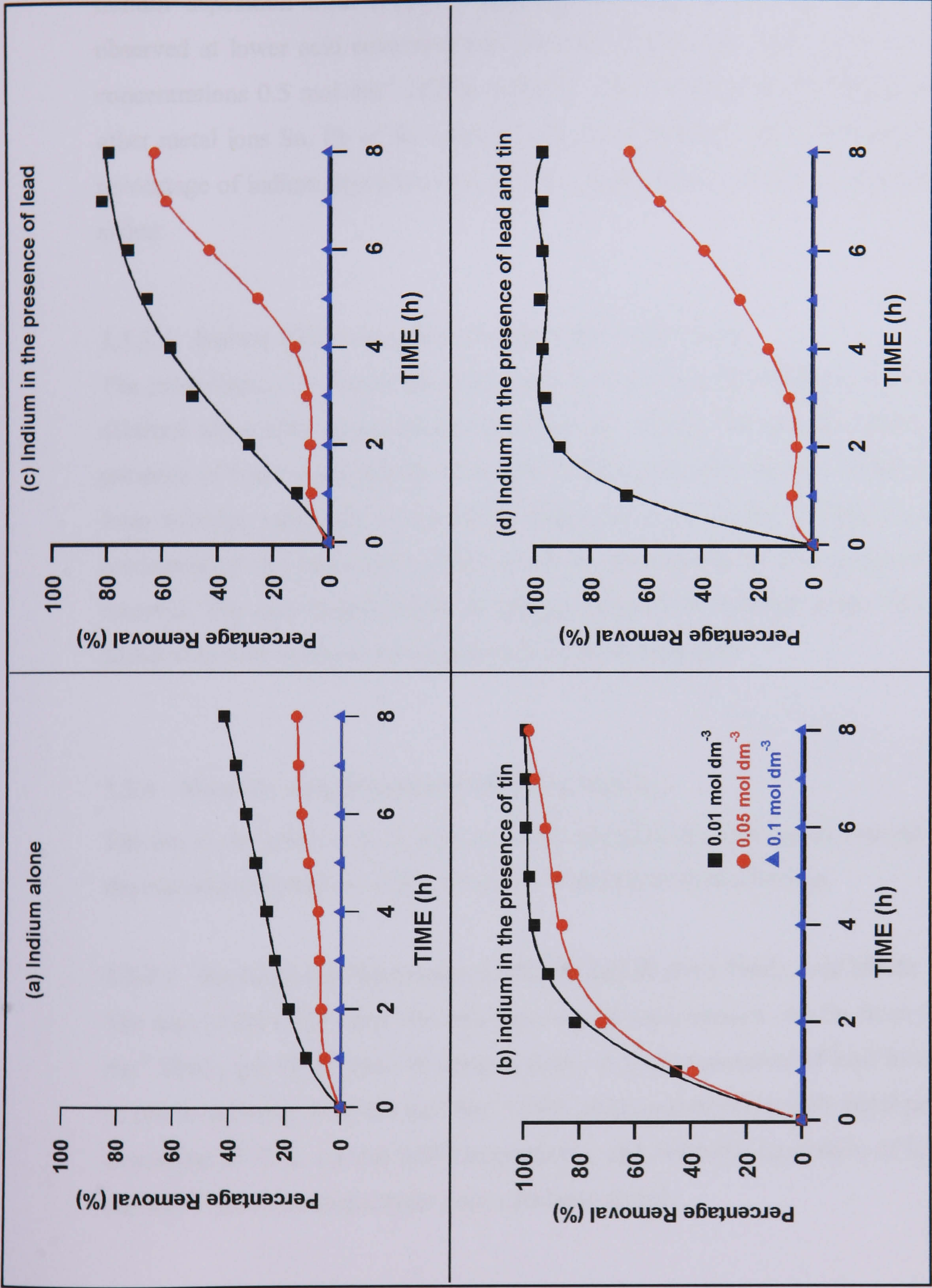


Figure [3.8]: The effect of nitric acid concentration on the percentage of indium removal from solution containing (a) indium alone, (b) indium and tin, (c) indium and lead, and (d) indium, lead and tin.

### ***3.5.3.2 Indium Electrodeposition Using Perchloric Acid Media***

Indium deposition from  $\text{HClO}_4$  [Figure (3.9)] is poor but better performance is observed at lower acid concentrations with no indium deposition occurring at acid concentrations  $0.5 \text{ mol dm}^{-3} \text{ HClO}_4$  or more. The results show that the presence of other metal ions Sn, Pb or Sn together with Pb (50ppm of each) does improve the percentage of indium deposition but that this improvement was best when only Sn is added.

### ***3.5.3.3 Indium Electrodeposition Using Acetic Acid Media***

The percentage of indium removal from  $\text{CH}_3\text{COOH}$  is good compared to the results obtained using nitric or perchloric acids [Figure (3.10)]. The data also show that the presence of other metal ions Sn, Pb or Sn together with Pb improve indium removal from solution, especially in the initial stages except when Pb is added at the acid concentration of  $1.0 \text{ mol dm}^{-3}$  which results in decreases in the percentage of indium removal. The best improvement in indium removal is obtained when Pb ions are added at an acid concentration between  $0.05$  and  $0.5 \text{ mol dm}^{-3}$ .

## **3.5.4 Recovery and Separation of Pb, Sn and In**

The use of the above data to determine the condition for total metal removal and for the maximum separation of Pb, Sn and In is discussed in this section.

### ***3.5.4.1 Recovery and Separation of Pb, Sn and In from Nitric Acid Media***

The data [Table 3.6] show that the recovery of lead, indium and tin from  $0.01 \text{ mol dm}^{-3} \text{ HNO}_3$  are 97, 97 and 74% respectively. A good separation of lead from Sn and In can be achieved from  $0.1 \text{ mol dm}^{-3} \text{ HNO}_3$  acid concentration with metal percentage deposition of 97.0, 4.4 and 0.0% respectively, and complete separation of lead in  $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$  by electrolysis over a 24 hour period.

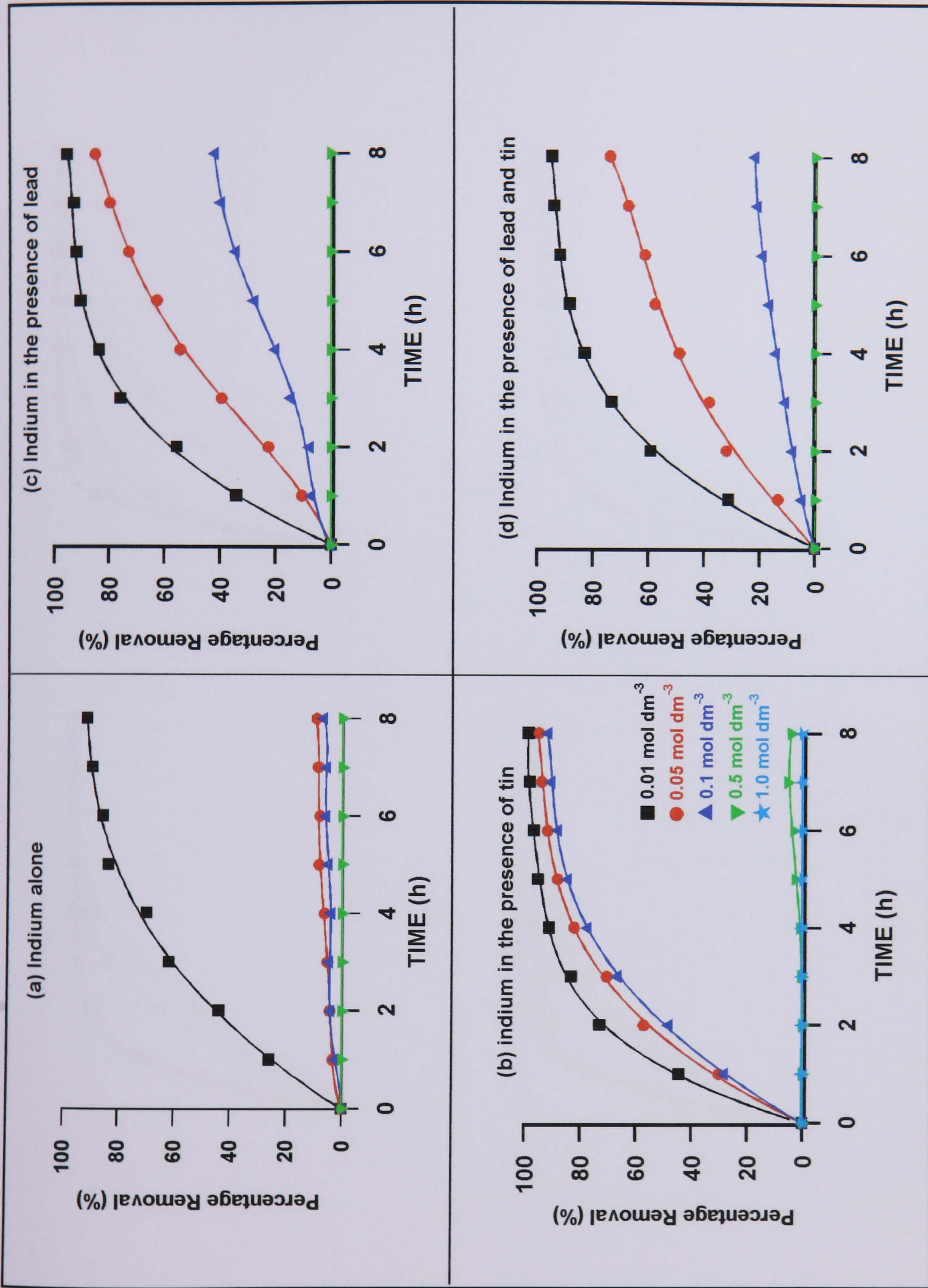


Figure [3.9]: The effect of perchloric acid concentration on the percentage of indium removal from solution containing (a) indium alone, (b) indium and tin, (c) indium and lead, and (d) indium, lead and tin.



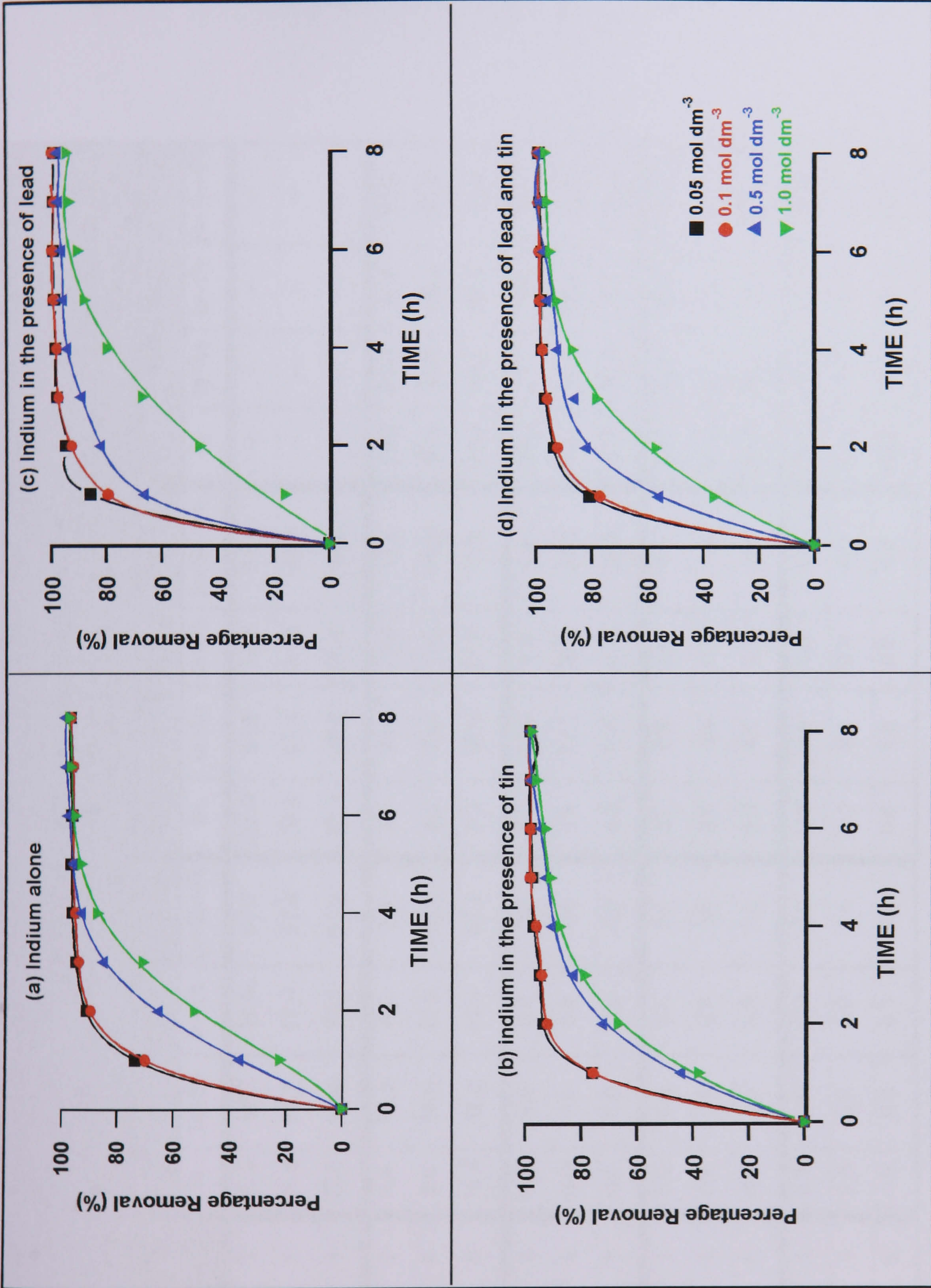


Figure [3.10]: The effect of acetic acid concentration on the percentage of indium removal from solution containing (a) indium alone, (b) indium and tin, (c) indium and lead, and (d) indium, lead and tin.

Table [3.5]: The effect of tin, lead and tin together with lead on the deposition of indium in HNO<sub>3</sub>, HClO<sub>4</sub> and CH<sub>3</sub>COOH at different concentrations.

Acid concentration on mol dm <sup>-3</sup>	Time (h)	Indium deposition (%)											
		HNO <sub>3</sub>				HClO <sub>4</sub>				CH <sub>3</sub> COOH			
		In	In+Sn	In+Pb	In+Sn+Pb	In	In+Sn	In+Pb	In+Sn+Pb	In	In+Sn	In+Pb	In+Sn+Pb
0.01	1	12.2	45.2	11.4	67.0	26.0	44.6	34.2	31.4	--	--	--	--
	4	26.6	96.2	57.0	97.0	70.0	91.4	83.8	83.0	--	--	--	--
	8	42.0	99.4	79.4	97.0	92.0	98.8	95.6	94.8	--	--	--	--
0.05	1	5.4	39.0	6.0	7.4	3.0	30.0	10.4	13.2	73.6	76.0	85.8	80.8
	4	8.0	86.0	11.8	16.2	6.2	82.0	54.2	48.8	96.4	97.0	98.6	97.8
	8	15.8	98.0	62.6	65.8	9.2	95.0	85.0	73.8	97.4	98.2	99.2	98.8
0.1	1	0.0	0.0	0.0	0.0	2.2	28.0	6.8	4.6	70.0	75.6	79.3	77.0
	4	0.0	0.0	0.0	0.0	3.8	77.2	20.0	14.0	95.4	96.0	98.2	97.6
	8	0.0	0.0	0.0	0.0	6.6	91.6	41.8	21.8	97.2	98.0	99.6	99.0
0.5	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	36.2	44.0	66.0	55.6
	4	0.0	0.0	0.0	0.0	0.0	0.6	0.0	0.0	92.8	90.0	94.0	92.2
	8	0.0	0.0	0.0	0.0	0.0	4.0	0.0	0.0	99.0	98.0	97.6	98.4
1.0	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	22.2	38.0	15.8	36.2
	4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	87.4	87.6	79.8	87.0
	8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	98.0	97.6	94.6	96.8

Table [3.6]: Effect of HNO<sub>3</sub> concentration on the percentage recovery of lead, tin and indium from mixed solution after 8 hours of reaction time.

HNO <sub>3</sub> concentration mol dm <sup>-3</sup>	Metal recovery			Separation factor Pb:Sn:In
	Pb (%)	Sn (%)	In (%)	
0.01	97.0	74.0	97.0	1.3:1:1.3
0.05	97.0	54.4	65.8	1.7:1:1.2
0.1	97.0	4.4	0.0	22.0:1:0.0
0.5	70.0	0.0	0.0	∞:0.0:0.0
1.0	0.0	0.0	0.0	-----

#### 3.5.4.2 Recovery and Separation of Pb, Sn and In from Perchloric Acid Media

The effects of HClO<sub>4</sub> concentration on the percentage recovery and separation of lead, tin and indium after 8 hours are shown in Table [3.7] and are similar to those of nitric acid. Maximum separation of lead from In and Sn is achieved when the acid concentration is 0.5 mol dm<sup>-3</sup> where is 94% Pb is recovered leaving tin and indium in the solution.

Table [3.7]: The percentage of Pb, Sn and In removal after 8 hours electrolysis, using HClO<sub>4</sub> media.

HClO <sub>4</sub> concentration mol dm <sup>-3</sup>	Metal recovery			Separation factor Pb:Sn:In
	Pb (%)	Sn (%)	In (%)	
0.01	95	95.7	94.8	1.0:1.0:1.0
0.05	92	78.4	73.8	1.2:1.06:1
0.1	94	61.3	21.8	4.3:2.8:1
0.5	94	0.0	0.0	∞:0.0:0.0
1.0	90	0.0	0.0	∞:0.0:0.0

### 3.5.4.3 Recovery and Separation of Pb, Sn and In from Acetic Acid Media

The effects of varying the CH<sub>3</sub>COOH concentration on the recovery and separation of lead, tin and indium after 8 hours are shown in Table [3.8]. Almost total removal by co-deposition occurs for all three metals at CH<sub>3</sub>COOH concentrations of 0.05 and 0.1 mol dm<sup>-3</sup>. There are no conditions under which effective separation of Pb, Sn and In can be achieved in CH<sub>3</sub>COOH media.

Table [3.8]: The percentage of Pb, Sn and In removal after 8 hours electrolysis, using CH <sub>3</sub> COOH media.				
CH <sub>3</sub> COOH concentration mol dm <sup>-3</sup>	Metal recovery			Separation factor Pb:Sn:In
	Pb (%)	Sn (%)	In (%)	
0.05	99	97.3	98.8	1.0:1.0:1.0
0.1	98	96.4	99	1.0:1.0:1.0
0.5	98	88.8	98.4	1.1:1.0:1.1
1.0	98	88.4	96.8	1.1:1.0:1.1
5.0	98.3	36.8	52.7	2.6:1.0:1.4

### 3.5.4.4 Removal of Pb-Sn-In Mixture Using Nitric Acid Media in the Presence of Potassium Thiocyanate

Changing the HNO<sub>3</sub> concentration (0.05-0.5 mol dm<sup>-3</sup>) at a constant KSCN concentration (0.05 mol dm<sup>-3</sup>), the results [Table 3.9] show that, the presence of KSCN in 0.05 and 0.1 mol dm<sup>-3</sup> HNO<sub>3</sub> solution improves tin removal but not indium and lead. Increasing the HNO<sub>3</sub> concentration to 0.5 mol dm<sup>-3</sup> shows no tin and indium deposition with a decrease in lead deposition compared to the results obtained from the solution in the absence of KSCN.

The data in Table [3.10] show that increasing the KSCN concentration decreases the tin removal but had no significant effect on the lead and indium removal.

Table [3.9]: The percentage of Pb, Sn and In removal after 8 hours electrolysis, from different HNO<sub>3</sub> concentration in the presence or absence of KSCN.

Metal	0.05mol dm <sup>-3</sup> HNO <sub>3</sub>		0.1 mol dm <sup>-3</sup> HNO <sub>3</sub>		0.5 mol dm <sup>-3</sup> HNO <sub>3</sub>	
	Control	KSCN	Control	KSCN	Control	KSCN
Pb%	96.0	92.0	97.0	79.0	70.0	34.0
Sn%	54.4	94.0	4.4	56.4	0.0	0.0
In%	65.8	26.4	0.0	0.0	0.0	0.0

Table [3.10]: The percentage of Pb, Sn and In removal after 8 hours electrolysis, using constant HNO<sub>3</sub> concentration of 0.1mol dm<sup>-3</sup> and varying KSCN.

Metal	Control	KSCN 0.02mol dm <sup>-3</sup>	KSCN 0.05 mol dm <sup>-3</sup>	KSCN 0.1 mol dm <sup>-3</sup>
Pb (%)	97.0	78.0	79.0	81.0
Sn (%)	4.4	93.2	56.4	49.2
In (%)	0.0	0.0	0.0	0.0

### 3.5.5 Separation of Pb-Sn-In Using Nitric Acid Media with the Addition of Complexing Agent Potassium Thiocyanate

Almost total removal of tin, lead and indium from solution can be achieved in nitric, perchloric and acetic acid media under appropriate conditions, but their separation required careful control of the conditions.

The difference between the lead, tin and indium deposition processes in nitric acid solution in the presence of potassium thiocyanate can be exploited. The choice of nitric acid over perchloric acid was due to two reasons, 1) higher recovery of lead at lower nitric acid concentration (0.1mol dm<sup>-3</sup>) compared to perchloric acid (0.5mol dm<sup>-3</sup>) and 2) to avoid the evolution of poisonous chlorine gas during the process. The following scheme is recommended:

Stage 1. Lead is first removed from Pb-Sn-In solutions by electrodeposition from a  $0.1 \text{ mol dm}^{-3} \text{ HNO}_3$ , in the absence of KSCN over 8 hours to give lead of about 95% purity containing about 5% tin. The lead-coated cathode is then removed and replaced with a clean one.

Stage 2. The tin in solution is then removed by electrodeposition over an 8 hour period following the addition of  $0.02 \text{ mol dm}^{-3} \text{ KSCN}$ . The residual tin concentration in the solution after this stage is only 2ppm, with no indium removed from the solution. High purity tin is obtained on the cathode, which is then removed and replaced with a clean one.

Stage 3. The indium remaining in the solution is removed by electrodeposition on the anode over 16 hours after topping up the solution with KSCN to give a total concentration of  $0.1 \text{ mol dm}^{-3}$ . The indium concentration left in the solution at the end of the experiment was 1ppm.

### 3.6 CONCLUSION

The work in this chapter shows that the removal and separation of combined metal solutions of Pb-Sn-In can be achieved using an electrochemical cell. Separation depends on the acidity and the presence of complexing agents.

All three metals are co-deposited from an acetic acid medium, which is surprising in view of the differences in the strengths of the complexes that they form with acetate ions. The complex stability constants of the acetate ion with lead, tin and indium are 2.19, 3.63 and 3.50 respectively<sup>38</sup>.

### 3.7 REFERENCES

- [1] K. Scott, *Electrochemical Processes for Clean Technology*, The Royal Society of Chemistry, 1995, UK.
- [2] C. M. S. Raats, H. F. Boon and G. Van der Heiden, *Chemistry and Industry*, 1978, July, 465.
- [3] A. M. Polcaro and S. Palmas, *Electrochemical Engineering and the Environment*, Icheme Symposium Series no. 127, (1992) 85.
- [4] E. Browning, *Toxicity of industrial metals*, 2<sup>nd</sup> Edition, Butterworths, 1969.
- [5] R. Piercy and N. A. Hampson, *Journal of Applied Electrochemistry*, 1975, **5**, 1-15.
- [6] R. S. Young, *Separation Procedures in Inorganic Analysis: A Practical Handbook*, Griffin, London, 1980.
- [7] P. Halsall, *Transactions of the Institution of Mining and Metallurgy section C-Mineral Processing and Extractive Metallurgy*, 1988, **97**, pp.C93-C99.
- [8] M. A. Barakat, *Hydrometallurgy*, 1998, **49** (1-2), 63-73.
- [9] F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, 6<sup>th</sup> Edition, A Willey-Interscience Publishers. 1999.
- [10] S. A. Abbasi, *Analytical Letters*, 1988, **21** (9), 1705-1721.
- [11] F. W. Oehme, "Toxicity of Heavy Metals in the Environment", Marcel Dekker, New York and Basel, 1986.
- [12] M. Zelic, M. Mlakar and M. Branica, *Analytica Chimica Acta*, 1994, **289**, 299-306.
- [13] K. Sykut, G. Dalmata, B. Nowlck and J. Saba, *Anal. Chem.*, 1982, **54**, 600-602.
- [14] A. M. Bond, *Journal of Electrochemical Society*, 1972, **119**, 1503.
- [15] I. Kenawy, M. Hafez and S. Abd El Wanees, *Bull Soc Chim Fr*, 1991, **128**, 677-683.
- [16] I. C. Smith, B. L. Carson and F. Hoffmeister, *Trace metals in the environment*, Volume 5, Indium: An Appraisal of Environmental Exposure, Ann Arbor Science, 1978.



- [17] P. J. Smith, *Chemistry of Tin*, Blackie Academic & Professional, Second edition, 1998.
- [18] S. E. Manahan. *Environmental Chemistry*, 6<sup>th</sup> Edition. 1994.
- [19] T. M. Foreman, N. N. Sauer, B. F. Smith and T. W. Robinson, *Abstract of Papers of the American Chemical Society*, 1993, **206** (August), 8.
- [20] T. Sonada, H. Nanafune and S. Mizumoto, *Plating and Surface Finishing*, 1992, **79**(7), 57.
- [21] A. Aragou, M. G. Figueroa, R. E. Gana and J. H. Zagal, *Journal of Applied Electrochemistry*, 1991, **22**(6), 558.
- [22] P. J. Somerfield, J. M. Gree and R. M. Warwick, *Marine Pollution Bulletin*, 1994, **28**(6), 363-369.
- [23] O. E. Abdel-Salam, 1<sup>st</sup> International Chemical Conference on Silicon and Tin, 23- 26<sup>th</sup> October 1989, Kuala Lumpur, Oxford University Press, 1992.
- [24] J. D. Donaldson and S. M. Grimes, *Chemistry of Tin*, edited by P. G. Smith, Blackie Academic & Professional, Second edition, 1998.
- [25] J. D. Donaldson, *Progress in Inorganic Chemistry*, 1967, **8**, 287.
- [26] P. J. Smith, D. V. Sanghani, K. D. Bos and J. D. Donaldson, *Chemistry and Industry*, 1984, **5 March**, 167-172.
- [27] T. Stefanowicz, T. Golik, S. N. Zagozda and M. Osinska, *Resources, Conservation and Recycling*, 1991, **6**, 61-69.
- [28] G. S. Tzeng, *Plating and Surface Finishing*, 1995, **82**(11), 67-71.
- [29] G. S. Tzeng, S. H. Lin, Y. Y. Wang and C. C. Wan, *Journal of Applied Electrochemistry*, 1996, **26**(4), 419-423.
- [30] T. Tamura and S. Yasuda, *Metal Finishing*, 1984, **82**, 17-23.
- [31] J. P. Langan, *Plating and Surface Finishing*, 1983, **January**, 21-23.
- [32] J. Sadwowska-Maazur and M. E. Warwick, *Plating and Surface Finishing*, 1985, **May**, 120-125.
- [33] M. Carano, *Plating and Surface Finishing*, 1999, **86**(11), 66-67.
- [34] A. S. Fouda, L. H. Madkour and M. E. Khalifa, *Bulletin De La Societe Chimique De France*, 1986, N° **4**, 504-506.

- [35] I. A. Ammar, S. Darwish, M. W. Khalil and S. El-Taher, *Materials Chemistry and Physics*, 1989, **21**, 1-47.
- [36] A. T. Petrenko, E. G. Kharitonov and T. B. Kudryashova, *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki*, 1973.
- [37] A. P. Orio, L. R. Lery and M. Gulla, *Chem. Abstr.*, 1982, **96**, 23617C.
- [38] D.D Perrin, *Stability Constants of Metal-ion Complexes, Part B, Organic Ligands*, IUPAC Chemical Data Series-No. 22, Pergamon Press, 1979.

## CHAPTER FOUR

### PROCESS OPTIMISATION FOR THE SEPARATION OF NICKEL FROM COBALT USING ELECTRODIALYSIS SYSTEMS IN THE PRESENCE OF EDTA AS A COMPLEXING AGENT.

4.1	INTRODUCTION .....	133
4.2	COBALT .....	135
4.2.1	<i>Cobalt Toxicology</i> <sup>15</sup> .....	136
4.3	NICKEL.....	137
4.3.1	<i>Nickel Toxicology</i> .....	138
4.4	ETHYLENEDIAMINETETRA-ACETIC ACID.....	138
4.4.1	<i>Stability Constant of EDTA Complexes</i> .....	140
4.5	ELECTRODIALYSIS.....	142
4.5.1	<i>Electrodialysis Cation Membranes:</i> .....	144
4.5.2	<i>Electrodialysis Anion Membrane:</i> .....	145
4.6	EXPERIMENTAL.....	146
4.6.1	<i>Electrodialysis Using a Two-Compartment Cell</i> .....	147
4.6.2	<i>Electrodialysis Using a Three-Compartment Cell</i> .....	147
4.6.3	<i>The Application of Electrodialysis Using Different Complexing Agents</i> .....	148
4.6.4	<i>Application of Electrolysis to Different Metal Mixtures</i> .....	148
4.7	RESULTS AND DISCUSSION.....	149
4.7.1	<i>The Study of a Two-Compartment Cell</i> .....	149
4.7.1.1	The Effect of EDTA.....	150
4.7.1.1.1	The Effect of Changing the Concentration of EDTA .....	153
4.7.1.1.2	The Effect of Changing the Solution pH in the Presence of EDTA.....	155
4.7.1.1.3	The Effect of Changing the Cobalt-Nickel Ratio.....	157
4.7.1.1	<i>The Study of a Three-Compartment Cell</i> .....	161
4.7.1.1.1	The Effect of EDTA on Cobalt-Nickel Electrodialysis .....	162
4.7.1.1.1	The Effect of Changing the Current.....	168
4.7.1.1.2	The Effect of Changing the Concentration of H <sub>2</sub> SO <sub>4</sub> in the Middle Chamber.....	170
4.7.1.1.3	The Effect of Changing the Cobalt-Nickel Ratio.....	172
4.7.1.1	<i>The Application of Electrodialysis of a Cobalt-Nickel Mixture Using Different Complexing Agents</i> .....	180
4.7.1.1	<i>The Effect of Other Metal Impurities</i> .....	182
4.7.1.2	<i>The Application of Electrodialysis to Different Metal Mixtures</i> .....	183
4.7.1.2.1	Electrodialysis of Co-Cu Mixture in the Presence of EDTA: .....	183
4.7.1.2.2	Electrodialysis of Co-Zn Mixture in the Presence of EDTA: .....	184
4.7.1.2.3	Electrodialysis of Co-Fe Mixture in the Presence of EDTA: .....	187
4.7.1.1.1	Electrodialysis of Co-Pd Mixture in the Presence of EDTA: .....	189
4.2	SUMMARY .....	191
4.3	REFERENCES.....	192

## 4.1 INTRODUCTION

A major part of any recovery process for cobalt is concerned with its separation from other elements. Because of the similarities in the chemical behaviour of cobalt and nickel the separation of these two elements from one another is often the most difficult purification stage. The methods in use are generally more efficient in removing cobalt from nickel rather than nickel from cobalt. Most are based on differences in the solubility or the kinetic or thermodynamic stability of their chemical compounds. The main methods of separation<sup>1</sup> exploit the small differences in the behaviour of the hydroxides, oxides, carbonates, amine complexes and ammonium salts, sulphides, chlorides, carbonyls and sulphites of the metals and also the differences in the rates of cementation of the dissolved metal ions when reduced with hydrogen or other metals such as zinc.

The physico-chemical methods that have been used for mixed Co-Ni ions separation include ion exchange<sup>2</sup>, solvent extraction<sup>3</sup>, liquid membrane technology<sup>4</sup> and electro dialysis in the presence of complexing agents<sup>5</sup>.

Exploiting the difference in the solubility constants of cobalt and nickel ions with chelating agents such as ethylenediaminetetraacetic acid (EDTA) has been used for the separation of cobalt from nickel. EDTA can form negatively charged chelates with both cobalt and nickel. The stability constant of the Ni-EDTA<sup>2-</sup> ( $10^{-18.6}$ ) complex is greater than the Co-EDTA<sup>2-</sup> ( $10^{-16.2}$ ) complex. The difference in the stability constants makes the use of EDTA as a material to complex Ni and separate Co-Ni. The methods which use EDTA as a complexing agent are liquid membrane technology<sup>4</sup>, ion exchange resins<sup>6-7</sup> and electro dialysis<sup>5</sup>.

In the liquid membrane technique EDTA has been used as a masking reagent for Ni ions. Good separation is obtained, but pH adjustment is required and the presence of other metal ions such as Cu<sup>2+</sup> or Ca<sup>2+</sup> can affect the separation<sup>4</sup>.

Ion exchange resins have been used either as cation resins in which the eluent is combined with EDTA and NH<sub>3</sub> to complex and elute Ni preferentially<sup>6</sup>, or as anion exchange resins to extract Ni-EDTA complexes leaving the hydrated Co in the

solution<sup>7</sup>.

Co-Ni separation by electrodialysis has been achieved using ion exchange membranes in the presence of EDTA, but the method has not been optimised for the removal of nickel from cobalt solution<sup>5</sup>. The work described in this chapter is concerned with the optimisation studies to separate nickel impurities from cobalt model solutions and the method developed was extended to study the possible separation of cobalt from other metals ions such as copper (II), zinc (II), iron (II or III) and palladium.

Electrodialysis in the presence of a complexing agent seems to be an attractive method not only for Co-Ni separation but also for other metal ion mixtures. Kubal et al<sup>8</sup> have described the separation of calcium and cadmium ions by electrodialysis in the presence of EDTA. Rozhkova et al<sup>9</sup> have studied the effect of pH and current density on the separation of cations with different charges, such as sodium and calcium, using electrodialysis as a technique with EDTA as a complexing agent. Karlin et al<sup>10</sup> have performed similar studies using different membranes. Cherif et al<sup>11</sup> have reported on the separation of  $\text{Ag}^+$  from  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions using a monovalent cation specific membrane.

The basic principle of electrodialysis separation in the presence of EDTA is that, preliminary complexation can enhance the selectivity of electrodialysis towards similarly charged ions. The simplest model system for studies on the separation of ions with complexation is provided by mixed solutions of cobalt and nickel sulphate containing ethylenediaminetetraacetic acid ions ( $\text{EDTA}^{4-}$ ) as the complexing agent present in stoichiometric proportions to the amount of nickel. When such a system is subjected to electrodialysis, the nickel ion complexes are extracted through an anion-exchange membrane and the cobalt ions pass through a cation-exchange membrane. This study is concerned with the effect of pH, current density the relative amounts of EDTA and  $\text{Ni}^{2+}$  on the separation of  $\text{Ni}^{2+}$  from  $\text{Co}^{2+}$  ions by electrodialysis, using Nafion (cation-exchange) and ADP (anion-exchange) membranes from Solvay.

## 4.2 COBALT

Cobalt (Co)<sup>1, 12</sup>, is a transition metal with atomic number 27, atomic mass 58.99, outer

electronic configuration  $3d^7 4s^2$ , melting point  $1,495^\circ\text{C}$  and density 8.9 ( $20^\circ\text{C}$ ). In general, the chemical properties of cobalt are intermediate between those of iron and nickel. Polished cobalt is silver-white with a faint bluish tinge. The main oxidation states of cobalt are the (II+) and (III+) states. The nature of the ligand bonded to cobalt has a dramatic effect on the stabilities of these oxidation states. There is no simple aqueous chemistry of cobalt (III) but there is an extensive range of complexes. For cobalt (II) the reverse is true; simple salts and aquo-complexes are stable in aqueous solution but the addition of other ligands makes for more facile conversion into the +3 state. Cobalt forms two well-defined binary compounds with oxygen: cobalt(II) oxide,  $\text{CoO}$ , and tricobalt tetraoxide  $\text{Co}_3\text{O}_4$ . The latter contains cobalt in both valences and comprises up to 40 percent of the commercial cobalt oxide used in the manufacture of ceramics, glass, and enamel and in the preparation of catalysts and cobalt metal powder.

The element cobalt constitutes about 0.001 per cent of the earth's crust and is the thirtieth most abundant element<sup>13</sup>. Although it is frequently considered to be a rare metal, it is only slightly less abundant than zinc and lead. Cobalt is widely distributed, being present in many rocks and soils. It is usually recovered as a co-product or by-product of copper, nickel and silver production.

The cobalt minerals exploited commercially are sulfides, arsenides and oxidized compounds. The arsenical cobalt minerals are usually found associated with nickel, silver, and gold, while the sulfides and oxidized minerals occur most frequently with copper.

The separation of cobalt-bearing minerals from the gangue contained in the ore and from other desirable minerals which do not contain cobalt is accomplished mostly by hand sorting, gravity concentration, flotation, and magnetic separation. In extracting cobalt from concentrates, and in some instances directly from ore, pyrometallurgical, hydrometallurgical, and electrometallurgical processes all have their application. Pyrometallurgical treatments are used with both oxidized and nonoxidized minerals for reduction to metal or cobalt-bearing alloy. Hydrometallurgical processes are likewise applied to both oxidized and nonoxidized minerals for leaching, precipitation and

separation, and for reduction to metal. Electrometallurgical methods are used in electrorecovery, or electrowinning, of cobalt metal and in the electrorefining of metal produced by pyrometallurgical or hydrometallurgical processes.

In the past, the main application of cobalt was in the ceramic and glass industry. Nowadays, technological demands have caused a rapid growth in the use of cobalt alloy. Advantages of cobalt alloys are high melting point, strength and resistance to oxidation. Most of the cobalt consumption is in the production of steel and alloys, especially in so-called superalloys used in jet engines. The use of cobalt in applications such as magnet steels, battery, catalysts, driers, and hard surfacing of machinery parts is also important.

A marginal use of refined cobalt is in fertilisers, since a low cobalt concentration in soil may cause cobalt deficiency in sheep and cattle. Cobalt is also used in human medicine in the treatment of certain iron-resistant anaemia<sup>14</sup>

#### **4.2.1 Cobalt Toxicology<sup>15</sup>**

Cobalt is an essential trace element for mammalian nutrition. The genetic toxicology of cobalt indicates that the element may interfere with DNA-repair processes. The testicular toxicity of cobalt has been related to the general hypoxia that occurs after exposure to the metal. The actions of cobalt on the male reproductive tract are dose- and time-dependent. Cobalt causes a decrease in sperm production along with diminished motility. Cobalt has a higher affinity than iron for serum transferrin, but the affinities of these metals for gonadal transferrin is not known.

Prolonged exposure to the powder may produce allergic sensitisation and chronic bronchitis. Occupational cobalt poisoning is caused primarily by inhalation of dust containing cobalt particles and by skin contact with cobalt salts. Skin irritation is considered in two different types, one appears as erythema, which is normally found on the hands shortly after contact with cobalt especially during warm weather; the other appears as eczema. These symptoms, however, do not appear until after many years of contact with cobalt compounds<sup>12</sup>.

### 4.3 NICKEL

Nickel (Ni)<sup>16-17</sup> is one of the transition metals of group VIII in the Periodic Table. Silvery-white, tough, harder than iron, atomic number 28, atomic weight 58.69, melting point 1,453°C and density 8.902 (25°C). Nickel is one of the more abundant elements in the universe but forms only about 0.016 per cent of the earth's crust, making it twenty-second<sup>18</sup> in order of abundance of the elements present.

Nickel shows a range of oxidation states -1, 0, +1, +2, +3 and +4, but its chemistry is predominantly divalent and ionic in simple compounds. Nickel forms a large number of complexes in its II+ oxidation state, encompassing coordination numbers 4, 5, and 6. These complexes are mainly square planar or octahedral in configuration. Nickel dissolves readily in dilute acids, giving hydrated  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ions. Nickel is unaffected by aqueous alkalis and is therefore used to make apparatus for manufacturing NaOH. Nickel does not tarnish or react with air or water at normal temperatures and is often electroplated onto other metals to provide a protective coating.

Nickel resembles iron in strength and toughness but is more like copper in resistance to oxidation and corrosion, a combination accounting for many of its applications. More than half the nickel produced is used in alloys with iron (particularly in stainless steels), and most of the rest is used in corrosion-resistant alloys with copper (including Monel) and in heat-resistant alloys with chromium. Nickel is also used in electrically resistive, magnetic, and many other alloys. Finely divided nickel is employed to catalyse the hydrogenation of unsaturated organic compounds (e.g., fats and oils).

Nickel(II) compounds have a variety of industrial applications. For example, nickel chloride, nitrate, sulphate and sulfamate are used in nickel electroplating baths and in the preparation of catalysts, ground-coat enamels, and mordants (fixatives) for dyeing and textile printing. Nickel oxide, NiO, and nickel peroxide, Ni<sub>2</sub>O<sub>3</sub>, are used in fuel cells and storage batteries, respectively. Nickel ferrites are utilised as magnetic cores for various types of electrical equipment such as antennae and transformers.



Among other important commercial compounds are tetracarbonylnickel,  $\text{Ni}(\text{CO})_4$  which is used primarily as a carrier of carbon monoxide in the synthesis of acrylates (compounds utilised in the manufacture of plastics) from acetylene and alcohols<sup>19</sup>.

#### **4.3.1 Nickel Toxicology**

Nickel compounds are usually toxic and carcinogenic and are the most prevalent and potent causes of contact dermatitis. The carbonyl is acutely very poisonous and volatile (b.pt  $43^\circ\text{C}$ ), and breathing the vapour leads to pulmonary oedema (fluid accumulation), pneumonia, and respiratory failure. It was originally suspected of being the prime cause of nasal and pulmonary cancer among smelter workers, now recognised to stem primarily from inhalation of finely divided  $\text{Ni}_3\text{S}_2$ ,  $\text{NiO}$  and  $\text{Ni}$  itself. In general, insoluble or weakly soluble nickel compounds have greater toxicity than soluble particles, which are cleared more rapidly from the lung<sup>15</sup>.

Among inorganic compounds, nickel compounds are the most prevalent and potent causes of contact dermatitis. Mere contact with nickel plate or coins can cause a rash in sensitive individuals, and there is evidence that even elevated levels of  $\text{Ni}$  in food may cause sensitisation<sup>20</sup>.

#### **4.4 ETHYLENEDIAMINETETRA-ACETIC ACID**

Professor G. Schwarzenbach at the end of World War II<sup>21</sup>, found that the aminopolycarboxylic acids are excellent complexing agents, the most important being 1,2-diaminoethanetetra-acetic acid (ethylenediaminetetra-acetic acid EDTA) Figure [4.1].

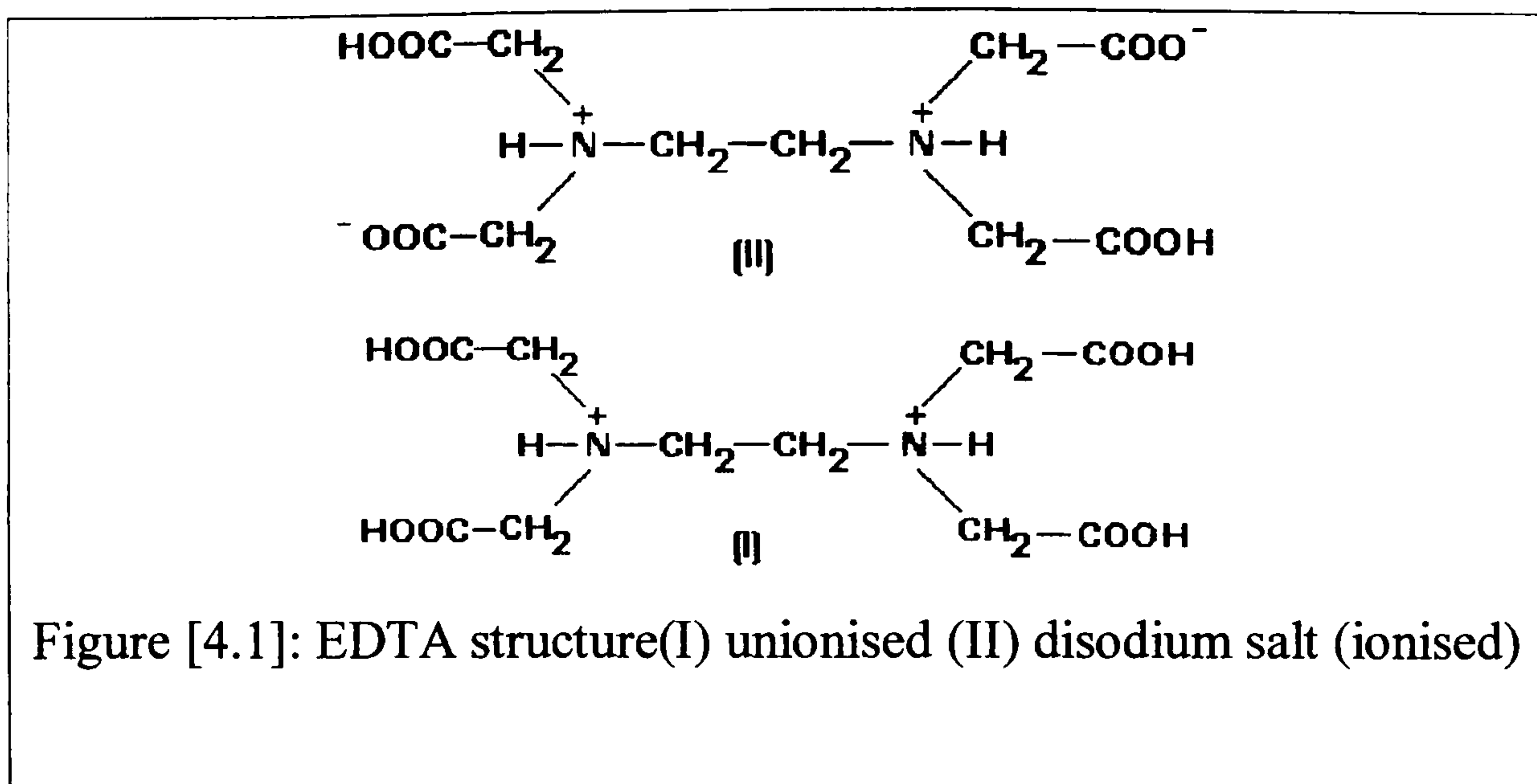
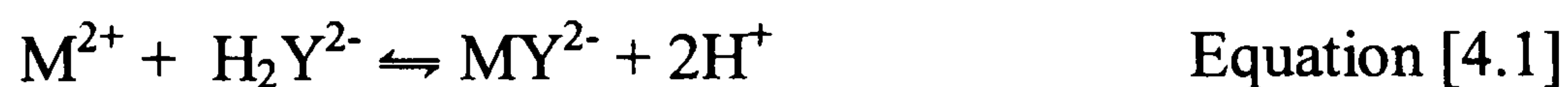


Figure [4.1]: EDTA structure(I) unionised (II) disodium salt (ionised)

EDTA, a man-made amino acid chelating agent, was first produced by I.G. Farbenindustrie in the mid-1930s<sup>22</sup>. Commercially known as Complexone or Sequestrene because of its ability to reduce the concentration of simple metal ions in solution by forming stable complexes. Its elemental formula is  $C_{10}H_{16}O_8N_2$ ; its molecular weight is 292.1. EDTA has found applications in water-softening, volumetric analysis, masking agents in medical treatment (to complex the poisoning metal ions such as lead, mercury and cadmium in the body) and in many industrial situations such as the preservation of organic substances, like vegetable oils and rubber, when it combines with traces of transition metal ions that would catalyse oxidation of the organic substances<sup>17</sup>.

EDTA is assigned the formula  $H_4Y$  [Figure 4.1, (I)]; the disodium salt is  $Na_2H_2Y$  and supplies the complex forming ion  $H_2Y^{2-}$  [Figure 4.1, (II)] in aqueous solution. The ligand is normally hexadentate and reacts with all metals in a 1:1 ratio. Thus divalent metal ions ( $M^{2+}$ ) for example react with the disodium salt as follows<sup>21-22</sup>:



The structure of the metal (M)- EDTA complex is given in Figure [4.2]<sup>17</sup>.

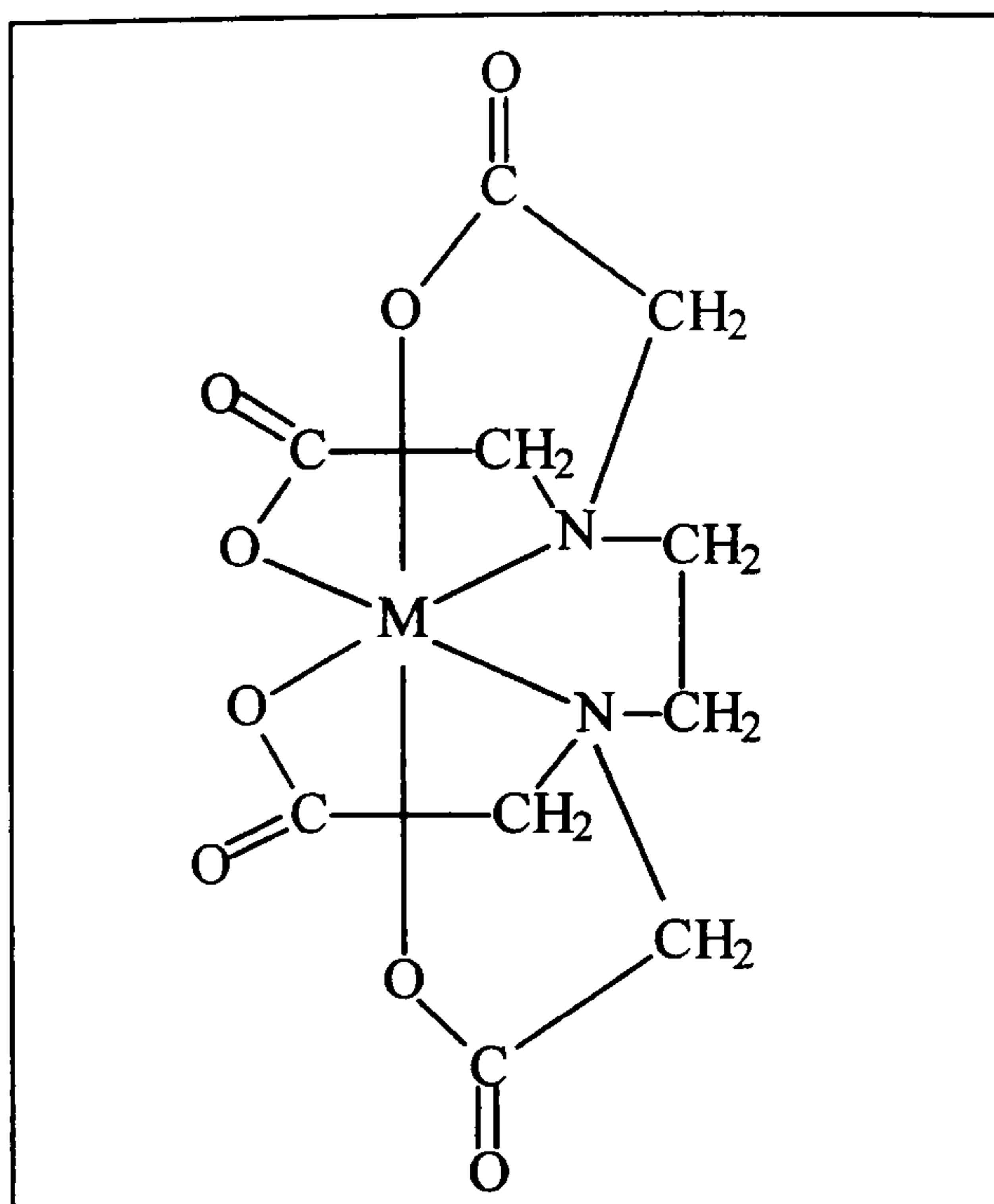


Figure [4.2]: Metal complex of the metal EDTA

#### 4.4.1 Stability Constant of EDTA Complexes

Most EDTA metal complexes are very soluble in water, and few are only sparingly soluble<sup>21</sup>. In aqueous solution the stability of the complex is characterised by the stability constant [or formation constant (K)]:



$$K = \frac{[(MY)^{(n-4)+}]}{[M^{n+}] [Y^{4-}]} \quad \text{Equation [4.3]}$$

Some values of the stability constants (expressed as log K) of metal-EDTA complexes are given in Table [4.1]<sup>23</sup>.

In equation [4.3] only the fully ionised form of EDTA, i.e. the ion  $Y^{4-}$ , has been taken into account, but at low pH, the species  $HY^{3-}$ ,  $H_2Y^{2-}$ ,  $H_3Y^-$  and even undissociated  $H_4Y$  may also be present. Hence, for each metal ion, there exists an optimum pH which will give rise to a maximum value for the apparent stability constant with EDTA. The dissociation of a metal-EDTA complex is governed by the pH of the solution; lowering the pH will decrease the stability of the complex. Table [4.2]<sup>23</sup> indicates the minimum pH values for the existence of EDTA complexes of some selected metals.

Mg <sup>2+</sup>	8.7	Zn <sup>2+</sup>	16.7	Lu <sup>3+</sup>	20.0
Ca <sup>2+</sup>	10.7	Cd <sup>2+</sup>	16.6	Sc <sup>3+</sup>	23.1
Sr <sup>2+</sup>	8.6	Hg <sup>2+</sup>	21.9	Ga <sup>3+</sup>	20.5
Ba <sup>2+</sup>	7.8	Pb <sup>2+</sup>	18.0	In <sup>3+</sup>	24.9
Mn <sup>2+</sup>	13.8	Al <sup>3+</sup>	16.3	Th <sup>4+</sup>	23.2
Fe <sup>2+</sup>	14.3	Fe <sup>3+</sup>	25.1	Ag <sup>+</sup>	7.3
Co <sup>2+</sup>	16.3	Y <sup>3+</sup>	18.2	Li <sup>+</sup>	2.8
Co <sup>3+</sup>	36.0	Cr <sup>3+</sup>	24.0	Na <sup>+</sup>	1.7
Ni <sup>2+</sup>	18.6	Ce <sup>3+</sup>	15.9		
Cu <sup>2+</sup>	18.8	La <sup>3+</sup>	15.7		

Minimum pH at which complexes exist	Selected metals
1-3	Zr <sup>4+</sup> ; Hf <sup>4+</sup> ; Th <sup>4+</sup> ; Bi <sup>3+</sup> ; Fe <sup>3+</sup>
4-6	Pb <sup>2+</sup> ; Cu <sup>2+</sup> ; Zn <sup>2+</sup> ; Co <sup>2+</sup> ; Ni <sup>2+</sup> ; Mn <sup>2+</sup> ; Fe <sup>2+</sup> ; Al <sup>3+</sup> ; Cd <sup>2+</sup> ; Sn <sup>2+</sup>
8-10	Ca <sup>2+</sup> ; Sr <sup>2+</sup> ; Ba <sup>2+</sup> ; Mg <sup>2+</sup>

If other complexing agents (such as NH<sub>3</sub>) are also present in the solution, then in equation [4.3] the value [M<sup>n+</sup>] may be reduced by complex formation with the alternative ligand.

From the above discussion it can be seen that the stability constant of EDTA-metal complexes depends on the pH and the presence of other competing complexing agents. The apparent stability constant of the metal-EDTA complex is, therefore, given by<sup>23</sup>:

$$\log K_{HZ} = \log K - \log \alpha - \log \beta \quad \text{Equation [4.4]}$$

where:

K = The stability constant.

- $\alpha =$  The ratio of the total uncombined EDTA (in all forms) to the form  $Y^{4-}$
- $\beta =$  The ratio of the sum of the concentrations of all forms of the metal ion not complexed with EDTA to the concentration of the simple (hydrated) ion.

Trivalent metal ions are usually more firmly chelated than divalent metals and thus the complexes of the trivalent transition metals are stable even in strongly acid solution. The remarkable stability of the cobalt (III) complex is shown in Table [4.1]. This complex in fact does not decompose even in concentrated hydrochloric acid<sup>21</sup>.

#### 4.5 ELECTRODIALYSIS

Electrodialysis is the combined process of dialysis and electrolysis using semipermeable membranes to confine the solution under treatment. In this method a direct electric current is used to transport ions through sheets of ion-selective membranes, which are either anionic (permeable to anions and impermeable to cations), or cationic (permeable to cations but impermeable to anions)<sup>24</sup>. These membranes are effectively impermeable to the hydraulic transport of water and other solvents. In practical applications the membranes are arranged alternately between anodes and cathodes.

The application of a direct electric current causes anions to move towards the anode, passing through the anion-exchange membrane. The cations behave in a similar manner, but move in the opposite direction towards the cathode crossing the cation-exchange membrane. In time, one compartment will become ion enriched and the other will become ion depleted, forming the concentrate and dilute compartments known as a cell pair. In an electrodialysis cell more than 300 cell pairs can be employed to separate ions by fractionation<sup>24</sup>.

The first Patent in electrodialysis was issued in 1889 to Maigrot and Sabates for a three-cell apparatus to purify sugar syrup with the aid of an electric current<sup>25</sup>. Nowadays, the main applications of electrodialysis are for the concentration of electrolyte solutions, or for diluting, or de-ionising solutions. The latter application has over the years been the dominant technique for the desalination of brackish water. Electrodialysis is also used extensively for desalination and concentrating seawater

for salt and water production. In principle, the technique has many potential applications for the removal or recovery of ionic species. Applications, which have been commercially adopted, are in the food and dairy industries, pharmaceutical industries and chemical industry<sup>26</sup>. Generally the process of electrodialysis is used to perform several operations including<sup>24</sup>:

- The separation of salts, acids, and bases from aqueous solution.
- The separation of ionic compounds from neutral molecules.
- The separation of monovalent ions from multivalent ions.
- The introduction of ionic moieties to generate new species.

Electrodialysis competes with other separation processes, such as reverse osmosis, ion exchange, dialysis and liquid membrane technology in many applications and can offer several significant advantages such as:

- High selectivity for charged components.
- Lower energy and investment costs.
- Continuous operation
- High product recovery rate.
- Minimal change of feed water constituents due to chemical or thermal degradation.
- No requirement for chemical regeneration or significant feed water pre-treatment.
- Proven membrane life.

In electrodialysis two effects are of particular importance. The first is the electro-osmotic transport of water through the membranes, which tends to dilute the dialyzate. The second is the tendency of any membrane placed in the solution between electrodes to assume a charged condition on the two faces of the membrane such that the surface nearest the anode becomes negatively charged, and that nearest the cathode becomes positively charged. This results in an accumulation of hydroxyl ions (alkaline reaction) at the anode face, and an acid reaction at the cathode face. This phenomena is known as polarisation. In general, an increase in polarisation causes a decrease in the efficiency of the separation process as the flow of the more permeable species decreases. The magnitude and direction of the effect is dependent on the acidity of the solution, the nature of the membrane, and the composition of the

electrolyte. The effect of polarisation is to increase the cell voltage and also to instigate transport of other species, typically  $\text{H}_3\text{O}^+$  ions, in cation-exchange membranes and  $\text{OH}^-$  ions in anion-exchange membranes, which lead to changes in the pH of the electrolyte solutions, because of the difference in mobilities of the anions and cations involved.

The membranes used must be resistant to fouling or poisoning. Fouling can be caused by any material which settles on the membrane surface and de-activates the ion diffusion capability. The de-activation may be from organic macromolecules present in the water or precipitated colloids or calcium salts on the membrane surface. Procedures, which are adopted to minimise the effect of fouling, include pre-treatment of the feed, acidification of the concentrate compartment and polarity reversal.

#### **4.5.1 Electrodialysis Cation Membranes:**

The chemical structure of a typical cationic exchange membrane consists of a network of polymerised carbon chains with sulphonic acid groups attached to the network. When the structure is immersed in aqueous solution, it swells due to the hydrophilic affinity of the sulphonic acid groups. The water creates channels across the membrane through which the ions can diffuse and the quantity of water present controls the maximum size of ion which can be transported. The sulphonic acid group dissociates to give negatively charged fixed ions bound to the hydrocarbon matrix, and mobile hydrogen ions. The hydrogen ions are free to exchange with other cations diffusing into the membrane, or to migrate under the influence of an applied electric field.

In an electrodialysis system both positive and negative ions take part in the transport of the electrical charge. In practice it is found that the transport number of the hydrogen in the membrane exceeds the value in free solution. This means that it is the electrostatic repulsion force between the fixed negative ions of the membrane and the negatively charged ions in the solution that causes the selective permeability. Consequently the negatively charged ions are prevented from entering the membrane in appreciable numbers, and therefore cannot take part in the transport of current in the membrane to the same extent as they can in free solution<sup>27</sup>.

The cation membrane used in the present work is a Nafion perfluorinated cationic membrane. This membrane is ion-selective or permselective - terms that describe membranes which show selective permeability to ions of a particular charge, in this case to cations. The membrane is formed by the copolymerisation of a vinyl ether with tetrafluoroethylene (TFE) to form a melt-fabricable precursor polymer. After fabrication into the desired shape, the sulphonyl fluoride group is hydrolysed to the ionic sulphonate form (Figure [4.3]). The hydrophobic fluorocarbon component and the hydrophilic ionic groups are incompatible, and therefore a degree of phase separation occurs leading to the formation of interconnected hydrated ionic clusters. Solid Nafion is created by evaporating the solvent at 100-120°C, which fuses together the dispersed fluorocarbon phase leaving an insoluble film<sup>28</sup>.

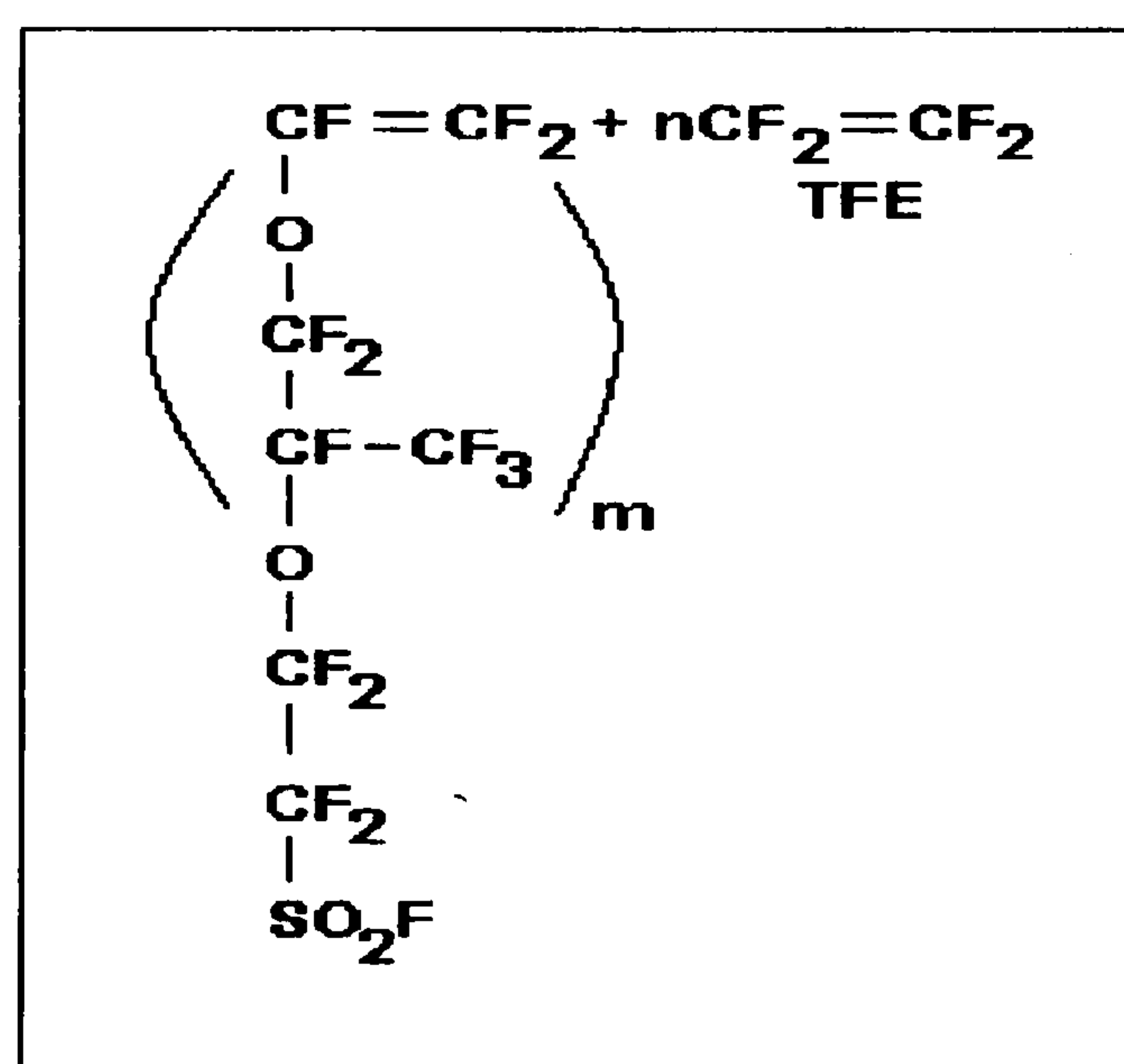


Figure [4.3]: The structure of Nafion Co-polymers

#### 4.5.2 Electrodialysis Anion Membrane:

The anion exchange membrane used in this work was ADP anion membrane from Solvay. This membrane has extremely low electrical resistance, which minimises the amount of power needed in electrodialysis. The ADP membrane is manufactured by a two step radiochemical grafting technique. A fluorinated film is irradiated under an electron beam (Beta irradiation), to create reactive radicals inside the film. These sites are used as anchor to graft a polymer with the ion exchange sites. The irradiated film



is then used for the radiochemical grafting. During this step the film is put in contact with a monomer which diffuses into the film and polymerises. Polymerisation starts on the reactive radicals which are anchoring the small grafted polymer chains on the main fluorinated trunk polymer. The grafted polymer and the film polymer create an interpenetrating network linked by the anchoring points. The grafted film is then functionalised in order to obtain ion exchange sites. In the case of the ADP membrane these sites are trimethylamine type groups, with cross-linking to improve its properties<sup>29</sup>.

#### 4.6 EXPERIMENTAL

Two types of electro dialysis cell were used in this study *viz.* a two-compartment and a three-compartment cell. The electrodes used in both cells were titanium mesh anodes coated with mixed metal oxide and stainless steel mesh cathodes. The cathodes and anodes have an identical surface area of 0.024 m<sup>2</sup>. Cobalt and nickel solutions were prepared from reagent grade cobalt (II) sulphate (CoSO<sub>4</sub> 7H<sub>2</sub>O) and reagent grade nickel (II) sulphate (NiSO<sub>4</sub> 6H<sub>2</sub>O). EDTA was used either as the free acid or as the disodium salt. A current of 0.2 A, which gives a cathodic current density of 8.3 Am<sup>-2</sup>, was applied unless otherwise stated and the voltage was kept at a maximum. The purification of cobalt resulting from the separation of nickel was calculated from the Co:Ni ratio in the catholyte chamber and the purification of nickel was calculated from the Ni:Co ratio in the anolyte chamber. Experiments were performed in replicate and are reproducible.

The ratio Co:Ni or Ni:Co is calculated from the percentage of each metal transferred to the catholyte or to the anolyte chamber respectively divided by the initial metal ratio in the feed compartment. These ratios are  $\frac{C_{Co^{++}} / C_{Ni^{++}}}{C_{Co^{++}}^0 / C_{Ni^{++}}^0}$  for the Co<sup>++</sup>:Ni<sup>++</sup> ratio in

the catholyte chamber and  $\frac{C_{NiY^{2-}} / C_{CoY^{2-}}}{C_{Ni^{++}}^0 / C_{Co^{++}}^0}$  for Ni:Co ratio in the anolyte chamber

Where:

- $C_{NiY^{2-}}$  and  $C_{CoY^{2-}}$  are the concentration of complex ions transferred through the anion membrane, mg dm<sup>-3</sup>.

- $C_{Co}$  and  $C_{Ni}$  are the concentration of ions in the catholyte chamber,  $\text{mg dm}^{-3}$ .
- $C_{Co}^o$  and  $C_{Ni}^o$  are the concentration of ions in the initial solution under separation,  $\text{mg dm}^{-3}$ .

#### 4.6.1 Electrodialysis Using a Two-Compartment Cell

This cell (Figure [4.4, a]) consists of two 400ml compartments, an anolyte chamber and a catholyte chamber, separated by a Nafion cation exchange membrane (C) of dimension 5 x5cm, with a gap of 1.5 cm between each electrode and the membrane. The initial anolyte solutions were mixtures of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions in  $0.01\text{mol dm}^{-3}$  sulphuric acid containing EDTA while the initial catholyte solution was  $0.01\text{mol dm}^{-3}$  sulphuric acid. Small quantities of  $\text{H}_2\text{SO}_4$  were added to the catholyte chamber when required during the electrolysis process to prevent the formation of metal hydroxide precipitates, with the rise in the pH. The following factors affecting the separation were studied:

- 1- The concentration effect of EDTA as free acid and disodium salt.
- 2- The effect of pH.
- 3- The effect of initial Co:Ni ratio.

#### 4.6.2 Electrodialysis Using a Three-Compartment Cell

This cell (Figure [4.4, b]) consists of two  $400\text{ cm}^3$  compartments, namely, a catholyte chamber and an anolyte chamber separated by a  $100\text{ cm}^3$  feed compartment between Nafion cation (C) and ADP Solvay anion exchange (A) membranes in the sequence anode: anion exchange membrane: feed compartment: cation exchange membrane: cathode. The cation exchange and the anion exchange membrane have the same square dimension of 5 x5cm.  $0.01\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$  was the initial electrolyte in the anolyte and catholyte chambers and the initial feed solution consisted of nickel and cobalt ions in  $0.01\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$  in the presence of the complexing agent EDTA as the di-sodium salt. The feed compartment was fed by circulating the Co-Ni solution through the feed compartment from a  $400\text{ cm}^3$  reservoir using a peristaltic pump at a flow rate of 200 ml/min. Small quantities of  $\text{H}_2\text{SO}_4$  were added to the catholyte chamber when required during the electrolysis process to prevent the formation of cobalt hydroxide precipitates. The effects of the following variables on the separation of nickel from cobalt were studied; EDTA concentration, current, initial Co:Ni ratio and  $\text{H}_2\text{SO}_4$  concentration.

The transfer and fate of EDTA in the electro dialysis process was also followed in the three-compartment cell by HPLC using a 12.5cm x 4.5mm o.d. separation column packed with a polystyrene divinylbenzene copolymer (PLRP-S5). EDTA was eluted from the column in a 25:75 acetonitrile : water system containing  $3\text{g dm}^{-3}$  tetrabutyl ammonium bromide at pH 6.0 and analysed by monitoring the UV absorbance at 300nm wavelength.

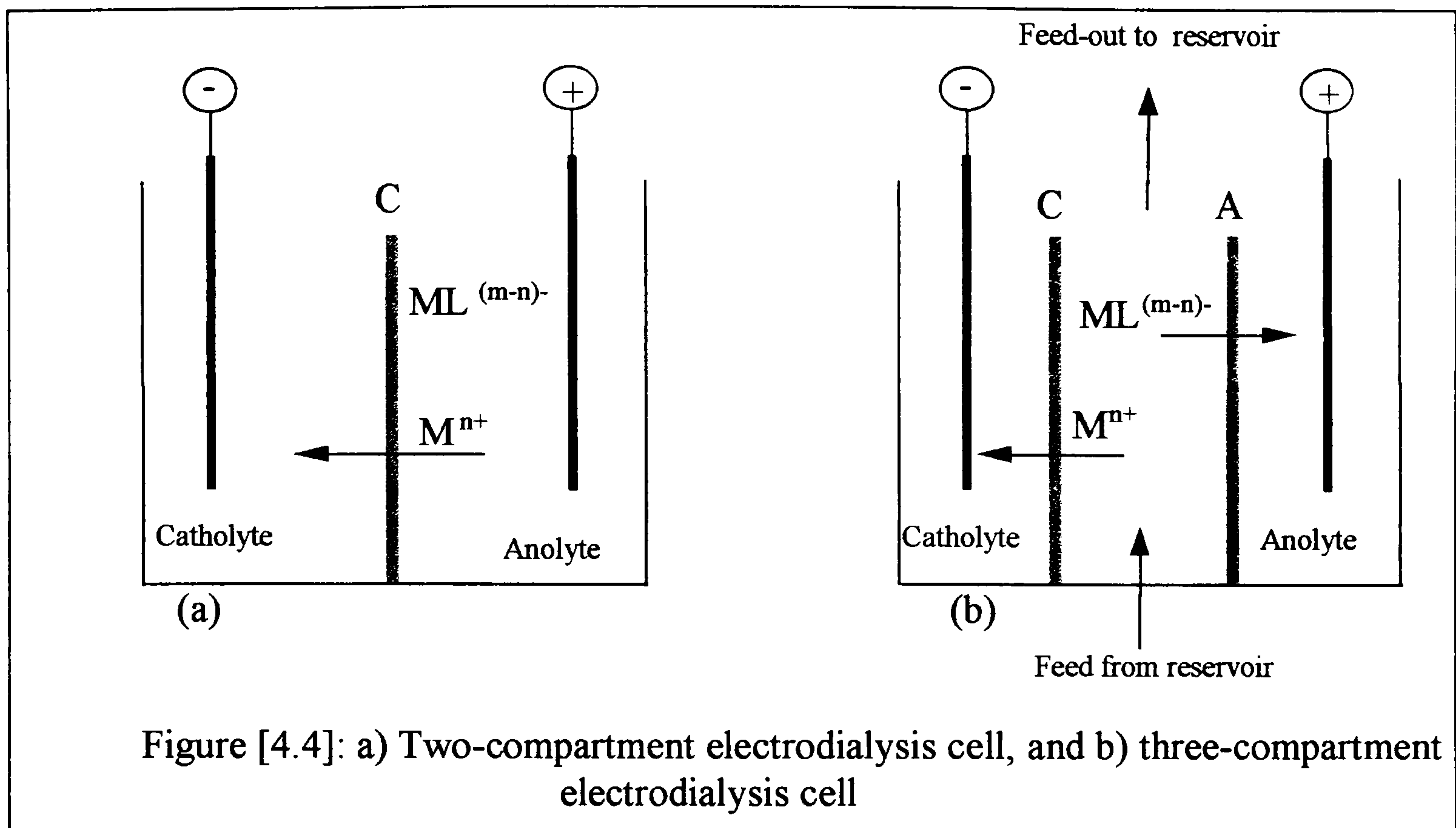
#### **4.6.3 The Application of Electrodialysis Using Different Complexing Agents**

The studies of the electro dialysis process with different complexing agents were performed using the three-compartment cell under the same experimental conditions. The feed solution contained an equal Co and Ni ion concentrations ( $500\text{mg dm}^{-3}$ ) with the following reagents:

- 1- Citric acid of  $0.01\text{ mol dm}^{-3}$  concentration in  $0.01\text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  and the metal reagent grades of metal sulphate.
- 2- Salicylaldoxime: the experiments were performed in two different sets
  - a)- Changing the concentration of salicylaldoxime using  $0.01$  and  $0.025\text{mol dm}^{-3}$  in  $0.01\text{mol dm}^{-3}$   $\text{H}_2\text{SO}_4$ .
  - b)- Changing the pH to 3 and 4 by addition of  $\text{NH}_4\text{OH}$ .
- 3- Acetic acid of  $1\text{mol dm}^{-3}$  concentration with reagent grade of metal acetates.
- 4- Hydrochloric acid of strong ( $8\text{mol dm}^{-3}$ ) concentration with the reagent grades of metal chlorides.

#### **4.6.4 Application of Electrolysis to Different Metal Mixtures**

To investigate the electro dialysis process for different metal mixtures, experiments were performed with the metal mixtures of Co:Cu, Co:Zn, Co:Fe(II), Co:Fe(III) and Co:Pd. These were performed using the following reagent grade chemicals as source materials; cobalt sulphate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ) copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), zinc sulphate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), iron(III) sulphate [ $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ], iron(II) sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), palladium chloride ( $\text{PdCl}_2$ ), and cobalt chloride ( $\text{CoCl}_2$ ).



## 4.7 RESULTS AND DISCUSSION

### 4.7.1 The Study of a Two-Compartment Cell

A two-compartment cell was used to determine whether nickel separation from cobalt could be achieved using a cation exchange membrane in the presence of EDTA. The results showed that very little separation could be achieved using a single cation exchange membrane. Although the Ni-EDTA complex is formed preferentially and should not be transferred through the cation exchange membrane, the fact that the EDTA is destroyed at the anode surface, means that uncomplexed  $\text{Ni}^{2+}$  is released and this permits the transfer of free hydrated  $\text{Ni}^{2+}$  ions along with  $\text{Co}^{2+}$  to the catholyte chamber.

The results do, however, demonstrate that the complexing agent does have a slight selectivity for cobalt ions over nickel in the transport across a single cation exchange membrane.

#### **4.7.1.1 The Effect of EDTA**

##### **(I) Electrodialysis without EDTA (control)**

The first experiment was performed to investigate the transport of Co-Ni ions in the electro dialysis cell without any EDTA addition. The anolyte solution consisted of cobalt and nickel both of concentration  $500\text{mg dm}^{-3}$  in  $0.01\text{mol dm}^{-3}$   $\text{H}_2\text{SO}_4$ .

Electrodialysis of a Co-Ni solution shows no selectivity in the metal ions crossing the membrane. The metal ions were removed from the anolyte chamber at the same rate. Figure [4.5, a] shows that the percentage of both metal ions maintained in the anolyte chamber is approximately equal with time. The metal ions removed from the anolyte chamber after 4 hours were 40% and 41.2% for Co and Ni respectively. This increased after 8 hours to a value of 55.8% for cobalt and 57.4% for nickel. The ratio Co:Ni in the catholyte chamber was showing a constant value of 0.9:1 during 8 hours electrolysis.

##### **(II) Electrodialysis in the presence of free EDTA**

This experiment was performed to examine the effect of  $0.01\text{mol dm}^{-3}$  EDTA addition on the electro dialysis process of a Co-Ni mixture. The metal ion concentrations were the same as in the control experiment ( $500\text{mg dm}^{-3}$  for both Co and Ni).

The addition of EDTA was found to have an effect on the selectivity for cobalt over nickel ions penetrating across the membrane. The nickel ions removed from the anolyte solution were less than cobalt ions. Figure [4.5, b] shows the different levels of the metal ions maintained in the anolyte chamber with time. The percentage removal values after 4 hours were 34.6% and 15.4% for cobalt and nickel respectively. This increased after 8 hours to 59.6% and 29% for cobalt and nickel respectively. The ratios Co:Ni in the catholyte chamber were 2.5:1 and 1.8:1 after 4 and 8 hours respectively.

##### **(III) Electrodialysis in the presence of EDTA disodium salt**

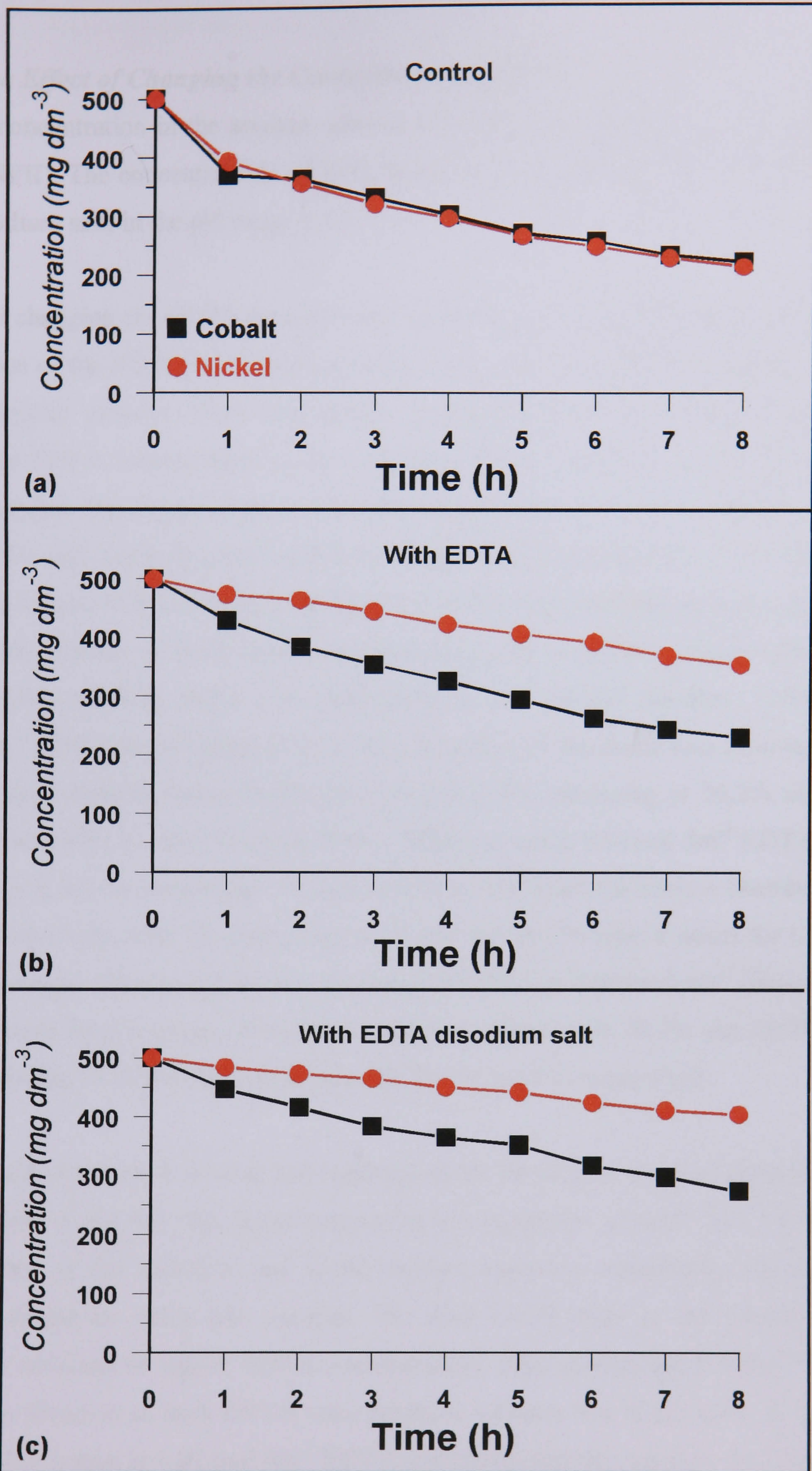
The experiment described in section [4.7.1.1.2] was repeated using EDTA disodium salt instead of free-EDTA.

Similar results were obtained, but the rate of metal ion removal was different. Figure [4.5, c] shows the difference in metal ion levels maintained in the anolyte chamber with time. The percentage of metals removed after 4h were 27% and 10% for cobalt and nickel respectively. These values increase to 45.2% and 19.2% after 8h for Co and Ni respectively. The ratios Co:Ni in the catholyte chamber were 2.7:1 and 2.3:1 after 4 and 8 hours respectively.

*(IV) Discussion of EDTA effect*

The addition of EDTA demonstrates the importance of the complexing agent on the selectivity during the electrodialysis process. The results obtained show that with the addition of EDTA there is a slight selectivity of cobalt ions over nickel penetrating across the cation exchange membrane. Since the Ni-EDTA complex is stronger than the Co-EDTA complex the presence of  $\text{Co}^{2+}$  ions in the anolyte chamber will be favoured over  $\text{Ni}^{2+}$  which are more likely to complex as  $\text{Ni-EDTA}^{2-}$ . This will result in the favoured transfer of  $\text{Co}^{2+}$  through the membrane to the catholyte chamber. The difference in selectivity of Co transfer in the absence and presence of EDTA (as  $\text{H}_4\text{Y}$  and  $\text{Na}_2\text{H}_2\text{Y}$ ) is shown in Table [4.3].

Table [4.3]: The effect of EDTA addition on the metal levels in the catholyte chamber in electrodialysis processes of Co-Ni mixture using two-compartment cell									
Time (h)	Control without EDTA addition			EDTA as acid complexing agent			EDTA as di-sodium salt complexing agent		
	mg dm <sup>-3</sup>		Co:Ni	mg dm <sup>-3</sup>		Co:Ni	mg dm <sup>-3</sup>		Co:Ni
	Co	Ni		Co	Ni		Co	Ni	
4	200	205	0.9:1	173	77	2.5:1	135	50	2.7:1
8	279	287	0.9:1	269	145	1.8:1	226	96	2.3:1



**Figure [4.5]: The effect of EDTA on the levels of metal ions maintained in the anolyte chamber in the electro dialysis of Co-Ni using a two-compartment cell**

#### ***4.1.1.1 The Effect of Changing the Concentration of EDTA***

The EDTA concentration in the anolyte solution was varied for  $500\text{mg dm}^{-3}$  of both Co(II) and Ni(II). The concentrations of EDTA used were 0.005, 0.01, and  $0.025\text{mol dm}^{-3}$  as di-sodium salt, in the pH range 1.5-2.

The effect of changing the EDTA concentration in the anolyte chamber demonstrates the importance of the EDTA complexation in the separation of nickel from cobalt in the electrodialysis process. From the results (Table [4.4]), it can be seen that increasing the EDTA concentration gives a slight increase in the Co:Ni ratio in the catholyte chamber. The values of the Co:Ni ratio after 4h were 1.7:1, 2.7:1 and 6.3:1 for 0.005, 0.01, and  $0.025\text{mol dm}^{-3}$  of EDTA. These ratios became 1.5:1, 2.3:1 and 5.9:1 after 8h respectively. Increasing the EDTA concentration, however, resulted in a decrease in the amount of both metal ions penetrating the membrane. Figure [4.6] shows the levels of both metal ions maintained in the anolyte chamber. Using  $0.025\text{mol dm}^{-3}$  EDTA, from Figure [4.6, c] the percentage of the metal ions removed from the anolyte chamber, were 15.2% and 2.4% after 4h, increasing to 26.2% and 4.4% after 8 hours for Co and Ni, respectively. Whereas, using  $0.01\text{mol dm}^{-3}$  EDTA, from Figure [4.6, b]) the percentage of metal ions removed from the anolyte chamber was 27.0% and 10.0% after 4h, increasing to 45.2% and 19.2% after 8 hours for Co and Ni, respectively. Decreasing the concentration of EDTA to  $0.005\text{mol dm}^{-3}$  (Figure [4.6, a] increased the percentage of metal ion removal. These were 34.4% and 20.0% after 4h, increasing to 52.8% and 36.0% after 8h for Co and Ni, respectively.

From the results obtained, it is clear that variation of the metal ions removed from the anolyte chamber is not the only factor controlling the separation process. The Co:Ni and Ni:Co ratio in the catholyte and in the anolyte chamber respectively, are the factors that should be taken into account. The best Co:Ni ratio in the catholyte chamber was obtained at higher EDTA concentration. This means that a better Co purification is obtained at high EDTA concentration, whereas the Ni:Co ratio in the anolyte chamber is best at  $0.01\text{mol dm}^{-3}$  EDTA (stoichiometrically equal to the initial nickel concentration). The EDTA concentration of  $0.01\text{mol dm}^{-3}$ , giving a Ni:EDTA molar ratio of 0.85:1, was chosen for use in the later experiments.



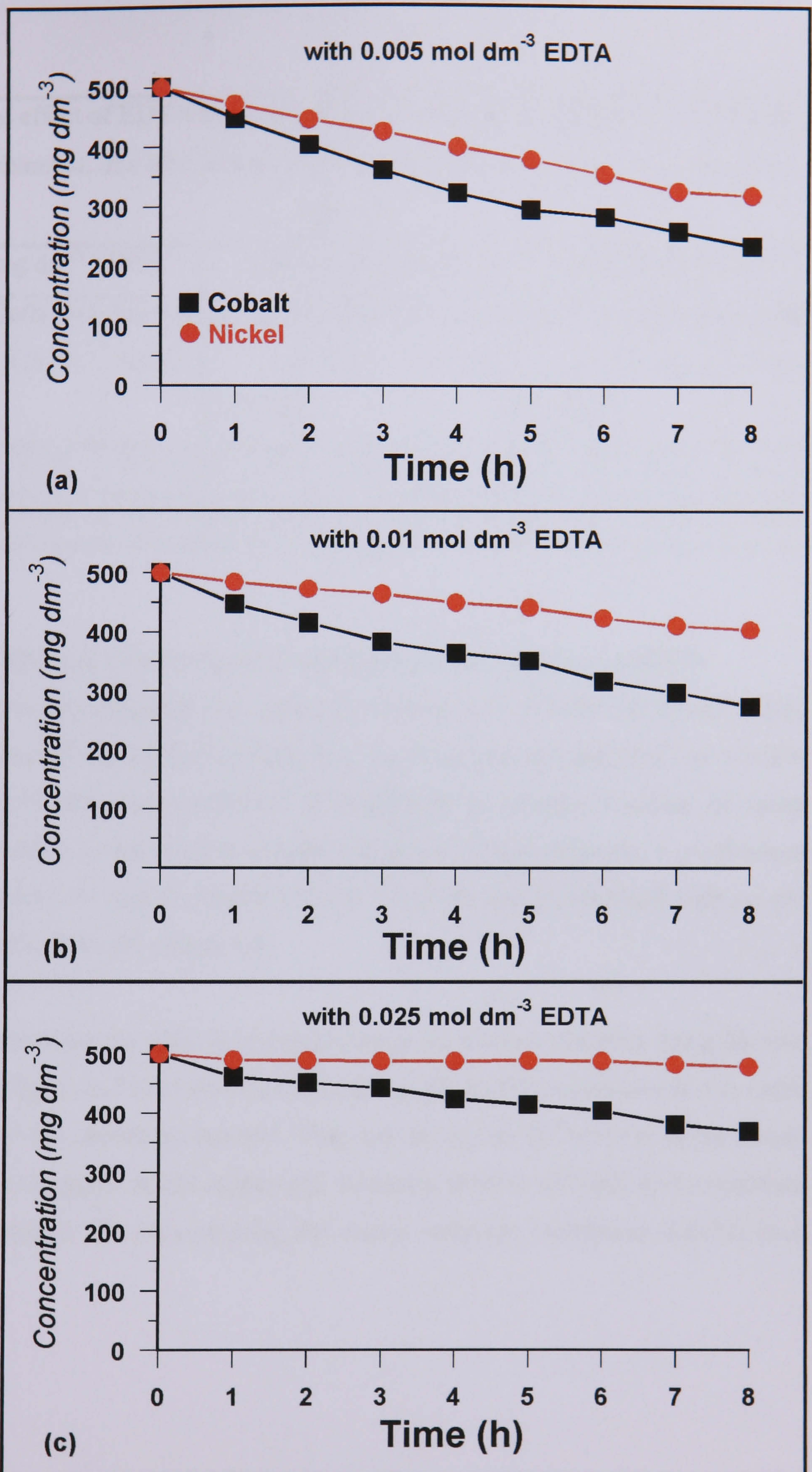


Figure [4.6]: The effect of changing the EDTA concentration on the levels of the metal ions in the anolyte chamber in the electro dialysis of Co-Ni using a two-compartment cell.

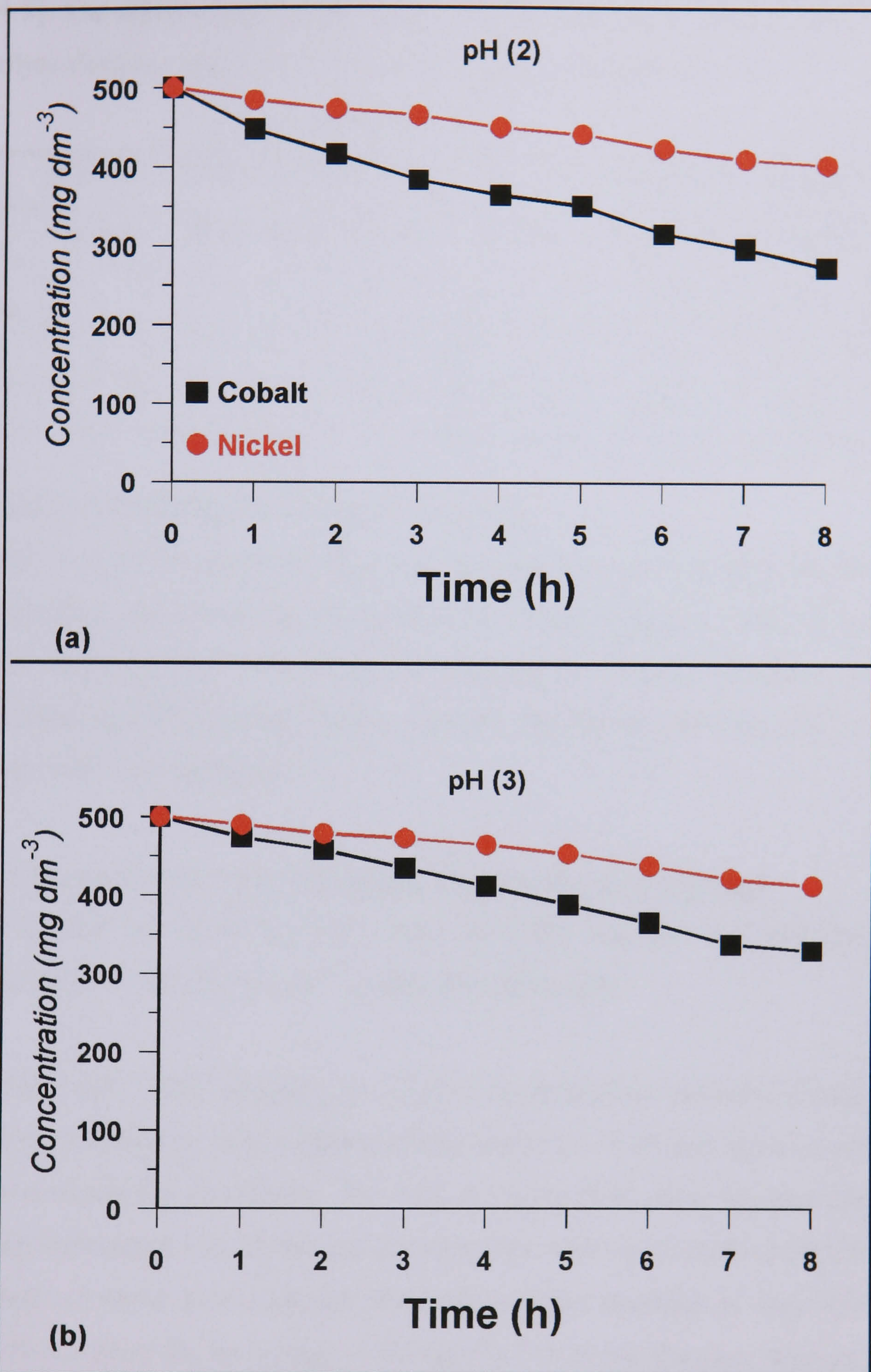
Table [4.4]: The effect of EDTA concentration on the Co and Ni level and Co:Ni ratio in the catholyte chamber, and Ni:Co ratio in the anolyte chamber using two-compartment cell.

Time (h)	0.005 mg dm <sup>-3</sup> EDTA				0.01 mg dm <sup>-3</sup> EDTA				0.025mg dm <sup>-3</sup> EDTA			
	mg dm <sup>-3</sup>		Catholyte Co:Ni	Anolyte Ni:Co	mg dm <sup>-3</sup>		Catholyte Co:Ni	Anolyte Ni:Co	Mg dm <sup>-3</sup>		Catholyte Co:Ni	Anolyte Ni:Co
	Co	Ni			Co	Ni			Co	Ni		
4	127	100	1.7:1	1.2:1	135	50	2.7:1	1.2:1	76	12	6.3:1	1.1:1
8	264	180	1.5:1	1.3:1	226	96	2.3:1	1.4:1	131	22	5.9:1	1.2:1

#### 4.1.1.2 The Effect of Changing the Solution pH in the Presence of EDTA

The pH in the anolyte chamber was varied for 500mg dm<sup>-3</sup> of both Co(II) and Ni(II), using an EDTA concentration of 0.01mol dm<sup>-3</sup> as di-sodium salt and NaCl as a buffer solution. The pH adjustment above 3 was difficult to achieve because of metal hydroxide formation in the anolyte chamber. Because of this difficulty a comparison was made between the results obtained at pH 3 and the results obtained with no pH adjustment which gives pH values 1.8.

A comparison between the amount of metal ions in the anolyte chamber using the two different pHs (Figure [4.7]), shows that increase in pH lead to a decrease in the metal transportation to the catholyte chamber. This may be due to the increase in the metal-EDTA complex strength. At the higher pH, however, there is still selectivity resulting in greater amounts of Co ions crossing the cation exchange membrane than Ni ions, Table [4.5].



**Figure [4.7]:** The effect of pH on the levels of the metal ions maintained in the anolyte chamber in the electro dialysis of Co-Ni mixture using a two-compartment cell.

Table [4.5]: The effect of pH on the Co and Ni levels and Co:Ni ratio in the catholyte chamber and Ni:Co ratio in the anolyte chamber using two-compartment cell								
Time (h)	pH (2) + 0.01mol dm <sup>-3</sup> EDTA				pH (3) + 0.01mol dm <sup>-3</sup> EDTA			
	mg dm <sup>-3</sup>		Catholyte	Anolyte	mg dm <sup>-3</sup>		Catholyte	Anolyte
	Co	Ni	Co:Ni	Ni:Co	Co	Ni	Co:Ni	Ni:Co
4	135	50	2.7:1	1.2:1	87.5	35	2.5:1	1.1:1
8	226	96	2.3:1	1.4:1	170	87	1.9:1	1.2:1

#### 4.1.1.3 The Effect of Changing the Cobalt-Nickel Ratio

The ratio of cobalt to nickel in the electrolyte was changed in order to investigate the possibility of separating small amounts of nickel from cobalt solution. These metal ratio changes were studied in two different sets of experiments. The first changing the metal ratio while keeping EDTA concentration constant and the second changing the metal ratio and the EDTA concentration.

##### (I) Changing the metal ratio while keeping EDTA concentration constant.

The metal ratios studied (as Co:Ni mg dm<sup>-3</sup>) were 500:500, 500:300, and 500:100. The EDTA concentration was 0.01mol dm<sup>-3</sup> as the di-sodium salt.

Changing the metal ratio while keeping the EDTA concentration constant (Table [4.6]) shows that decreasing the concentration of the nickel ion decreases the amount of the cobalt ions crossing the membrane. The data in Figure [4.8] show the changes in the levels of the both metal ions in the anolyte chamber with time. At the 500:100 ratio the percentage of metal ions removed from the anolyte chamber is very low (43mg dm<sup>-3</sup> = 8.3% Co after 4h, increasing to 98 mg dm<sup>-3</sup> = 19.6% Co after 8 hours, with no nickel removal). For the 500:300 the percentage removal of cobalt ions from the anolyte chamber after 4h is 16.4%, with no nickel removal. This is increased to 30% Co and 5.3% Ni after 8 hours. The excess EDTA present over the stoichiometric amount required for Ni complexation results in the formation of greater amounts of Co-EDTA<sup>2-</sup> and therefore leads to a decrease in the amount of Co<sup>2+</sup> transfer to the catholyte chamber. The Co:Ni ratio in the catholyte chamber seemed to be very high,

due to the low transportation of both metal ions toward the catholyte chamber, leading to a low Ni:Co ratio in the anolyte chamber.

Table [4.6]: The effect of initial Co:Ni ratio in the anolyte chamber while keeping the EDTA constant at  $0.01 \text{ mol dm}^{-3}$  on the Co and Ni levels and Co:Ni ratio in the catholyte chamber and Ni:Co ratio in the anolyte chamber after 4 and 8 hours electrolysis using two-compartment cell.

Time (h)	Co:Ni = 500:300				Co:Ni = 500:100			
	mg dm <sup>-3</sup>		Catholyte	Anolyte	mg dm <sup>-3</sup>		Catholyte	Anolyte
	Co	Ni	Co:Ni	Ni:Co	Co	Ni	Co:Ni	Ni:Co
4	82	0	∞	1.2:1	43	0	∞	1.1:1
8	150	16	5.6:1	1.3:1	98	0	∞	1.2:1

(II) Changing the metal ratio and the EDTA concentration

The metal ratios studied as (Co:Ni mg dm<sup>-3</sup>) were 500:300, 500:100, and 500:50 with EDTA concentration 0.006, 0.002, and 0.001 mol dm<sup>-3</sup> respectively. These EDTA concentrations were calculated, so that the Ni:EDTA mol dm<sup>-3</sup> ratio remained constant at 0.85:1.

The results in Table [4.7] show a slight improvement in the Co:Ni and Ni:Co ratio in the catholyte and in the anolyte chamber respectively, which means improvement in the separation with the lowest initial nickel concentration.

Results in Figure [4.9] show the concentration change of both cobalt and nickel ions in the anolyte chamber with time. The percentage removal of cobalt ions increases slightly with decreasing initial nickel ratio. For example, after 4 hours the percentage of cobalt removal is 31.8, 37.6 and 42.2% with the initial metal ion ratios of 500:300, 500:100, and 500:50 respectively, increasing after 8 hours to 51.6, 57.4 and 63.8% respectively. Whereas, the percentage nickel removal from the anolyte chamber decreases slightly with increasing initial nickel ratio, being 9.6, 10 and 10% after 4 hours increasing to 20, 24 and 32% after 8 hours with the initial Co:Ni ratio of 500:300, 500:100 and 500:50 respectively.

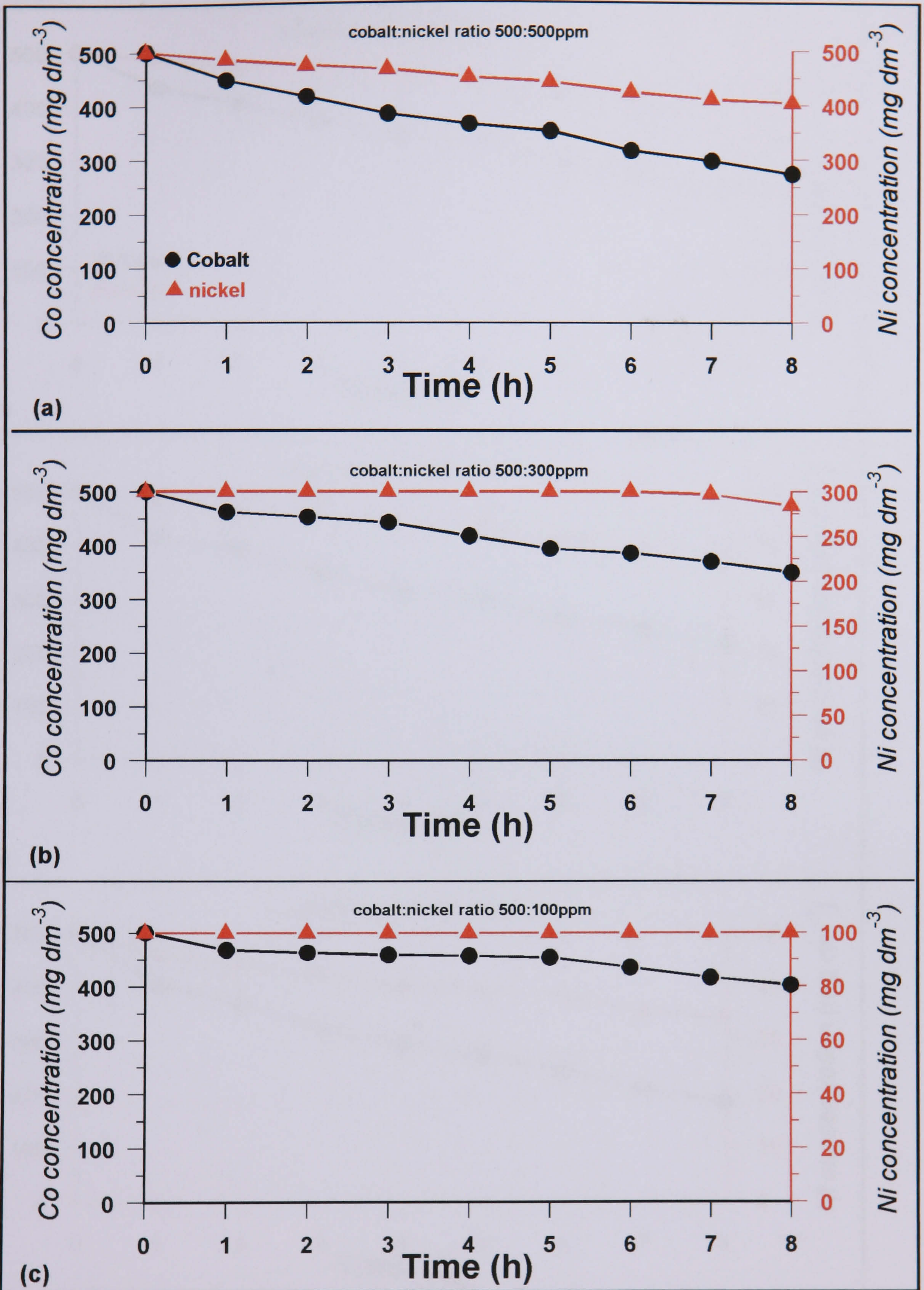


Figure [4.8]: Cobalt and nickel in the anolyte chamber in the electro dialysis process using a two-compartment cell changing Co/Ni ratio with EDTA concentration constant.

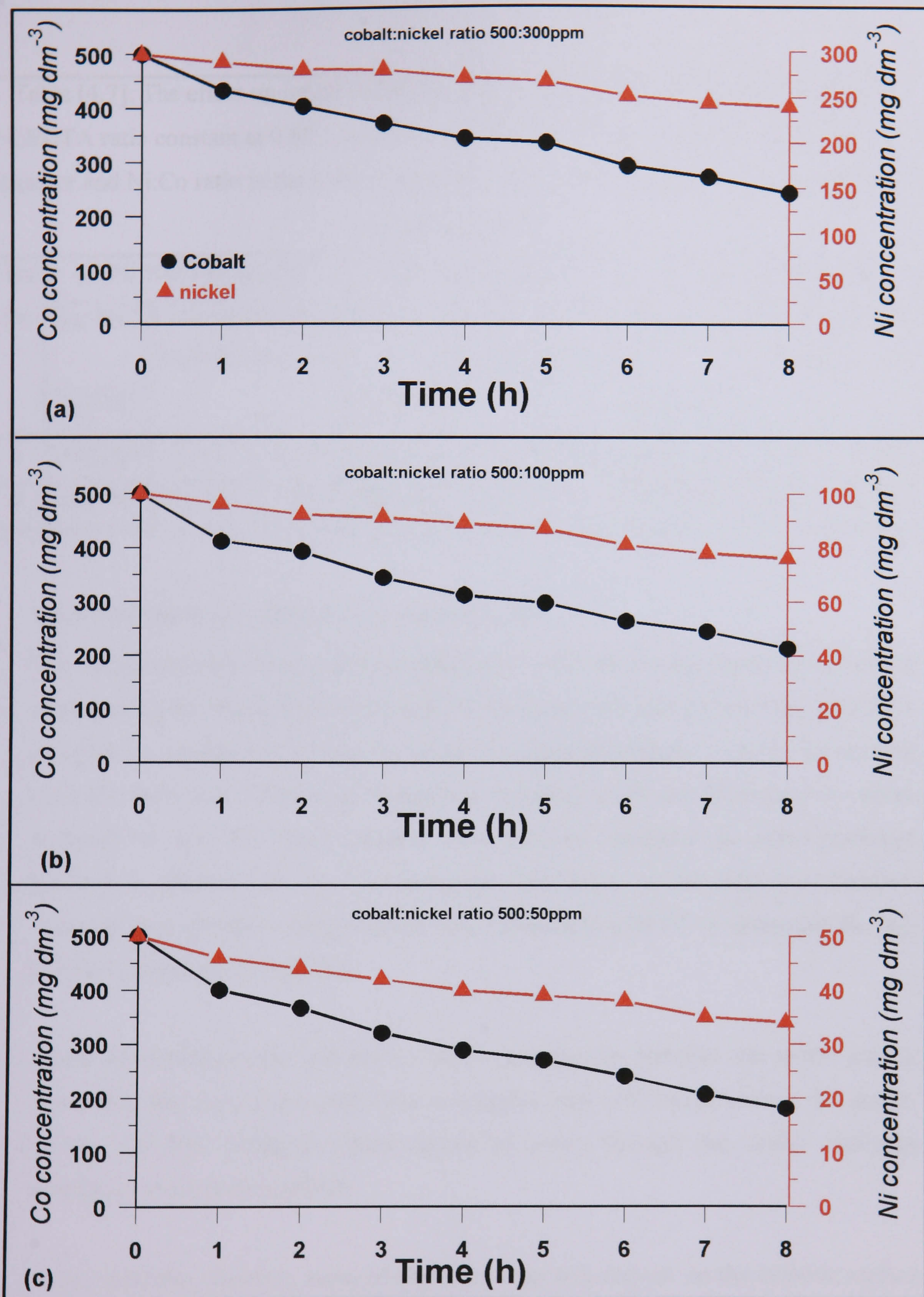


Figure [4.9]: The effect of changing the Co/Ni ratio while keeping Ni:EDTA mol dm<sup>-3</sup> ratio constant (0.85:1) on the levels of the metal ions in the anolyte chamber using a two-compartment cell.

Table [4.7]: The effect on initial Co:Ni ratio in the anolyte chamber while keeping the Ni:EDTA ratio constant at 0.85:1 on the Co and Ni levels and Co:Ni ratio in the catholyte chamber and Ni:Co ratio in the anolyte chamber after 4 and 8 hours electrolysis using two-compartment cell.

Time (h)	Co:Ni 500:300 mg dm <sup>-3</sup>			Co:Ni 500:100 mg dm <sup>-3</sup>			Co:Ni 500:50 mg dm <sup>-3</sup>					
	mg dm <sup>-3</sup>		Catholyte Co:Ni%	Anolyte Ni:Co%	Mg dm <sup>-3</sup>		Catholyte Co:Ni%	Anolyte Ni:Co%	mg dm <sup>-3</sup>		Catholyte Co:Ni%	Anolyte Ni:Co%
	Co	Ni			Co	Ni			Co	Ni		
4	159	28.8	3.3:1	1.3:1	188	10	3.7:1	1.4:1	211	5	4.2:1	1.4:1
8	258	60	2.5:1	1.6:1	287	24	2.4:1	1.7:1	319	16	3.9:1	1.8:1

#### 4.1.1 The Study of a Three-Compartment Cell

The results obtained from a three-compartment cell show a much improved separation compared to the two-compartment cell. In the three-compartment cell the Ni-EDTA complex is transferred through the anion exchange membrane towards the anolyte chamber. EDTA in the anolyte chamber is degraded at the anode surface to release hydrated Ni ions, but these hydrated cations cannot penetrate the anion exchange medium to return to the feed compartment and thence to the catholyte chamber. Aliquots from all three-compartments were examined by HPLC to determine the fate and the concentration of EDTA.

When the stoichiometric quantity of EDTA required to complex the nickel ions is used, only the nickel ions will form a complex that will move toward the anode, leaving the free hydrated cobalt cations to move through the cation exchange membrane towards the cathode.

In the catholyte chamber, some of the metal ions will deposit on the cathode surface as metal. This electrodeposition process is pH-dependent for cobalt and nickel. Since, within the electro dialysis process, some of the metal ions remain adsorbed on the ion exchange membranes the metal concentration in the catholyte chamber does not reflect the actual amount of metal ion transferred from the feed chamber. Experiments



were, therefore, performed over 24 hours to ensure a high amount of metal ion transfer to both anolyte and catholyte chambers. The total metal ions transferred to the catholyte chamber after 24 hour electrolysis were equal to [initial metal concentration in the middle chamber - the total metal transfer to the anolyte chamber - the remaining metal in the middle chamber].

The metal-EDTA complexes are pH-dependent. Altering the pH in the middle chamber using  $\text{NH}_4\text{OH}$  can complex the free metal ions ( $\text{M}^{2+}$ ) and form a mixed metal ion complexes solution with metal-EDTA complex. On the other hand, altering the pH using  $\text{NaOH}$  can enhance the formation of the metal hydroxide on the membrane surface, which causes membrane failure by stopping the cation from penetrating the membrane. For these reasons pH adjustment was achieved only by altering the  $\text{H}_2\text{SO}_4$  concentration.

In order to optimise the separation conditions, the following factors affecting the separation were studied in detail:

- 1)- The effect of EDTA on the separation of Ni from Co ions
  - A- The effect of presence of EDTA.
  - B- The effect of changing the concentration of EDTA.
- 2)- The effect of changing the current.
- 3)- The effect of pH by changing the concentration of  $\text{H}_2\text{SO}_4$  in the middle chamber.
- 4)- The effect of changing the cobalt / nickel ratio.
- 5)- The application of electrodialysis to different metal mixtures.

#### ***4.1.1.1 The Effect of EDTA on Cobalt-Nickel Electrodialysis***

##### ***(1) The effect of presence of EDTA***

Two comparative experiments were performed to examine the effect of EDTA ( $0.01\text{mol dm}^{-3}$ ) on the electrodialysis of a Co-Ni mixture, using a three-compartment system. The first was a control experiment, where the feed solution contained Co and Ni in  $0.01\text{mol dm}^{-3}$   $\text{H}_2\text{SO}_4$ . In the second experiment the conditions were the same as in the first with the addition of  $0.01\text{mol dm}^{-3}$  EDTA.

The results (Figure [4.10]), show that in the control experiment there was no

separation of nickel from cobalt, but that the addition of EDTA results in a significant selectivity for Co transfer to the catholyte chamber and of Ni to the anolyte chamber. In the control experiment no metals transferred to the anolyte chamber over a 24 hour experiment, (Figure [4.10, c]) and the amounts of cobalt and nickel ions transferred to the catholyte chamber were approximately equal, (Figure 4.10, b)). The ratio Co:Ni did not exceed the value 1:1 throughout the experiment.

With the addition of EDTA the concentration of metal ion transferred to the anolyte chamber increased with time, and was significantly higher for nickel than cobalt, (Figure [4.10, c]). The difference in the metal ratio crossing the anion exchange membrane to reach the anolyte chamber gives a Ni:Co ratio of 5.8:1 after 24h (487 mg dm<sup>-3</sup> for nickel and 84 mg dm<sup>-3</sup> for cobalt). The metal concentration in the catholyte chamber also increased with time, but with significantly greater amounts of cobalt than of nickel (Figure [4.10, b]). The concentration of cobalt reached 416 mg dm<sup>-3</sup> and nickel 13 mg dm<sup>-3</sup> after 24 hours to give a Co:Ni ratio of 32:1. Table [4.8] summarises the results obtained.

Table [4.8]: The effect of EDTA addition on the electrolysis processes of Co-Ni mixture using three-compartment cell								
Time Hours	Control in absence of EDTA							
	Cobalt concentration (mg dm <sup>-3</sup> )			Nickel concentration (mg dm <sup>-3</sup> )			Purification	
	Catholyte	Feed	Anolyte	Catholyte	Feed	Anolyte	Catholyte Co:Ni	Anolyte Ni:Co
0	0	500	0	0	500	0	-----	-----
4	131	195	0	139	197	0	0.9:1	0:0
8	340	6	0	360	2	0	0.9:1	0:0
24	499	1	0	499	1	0	1:1	0:0
With the addition of EDTA (0.01 mol dm <sup>-3</sup> )								
0	0	500	0	0	500	0	-----	-----
4	121	290	16	8	340	91	15.1:1	5.7:1
8	305	50	51.5	12	131	265	25:1	5.3:1
24	416	0	84	13	0	487	32:1	5.8:1

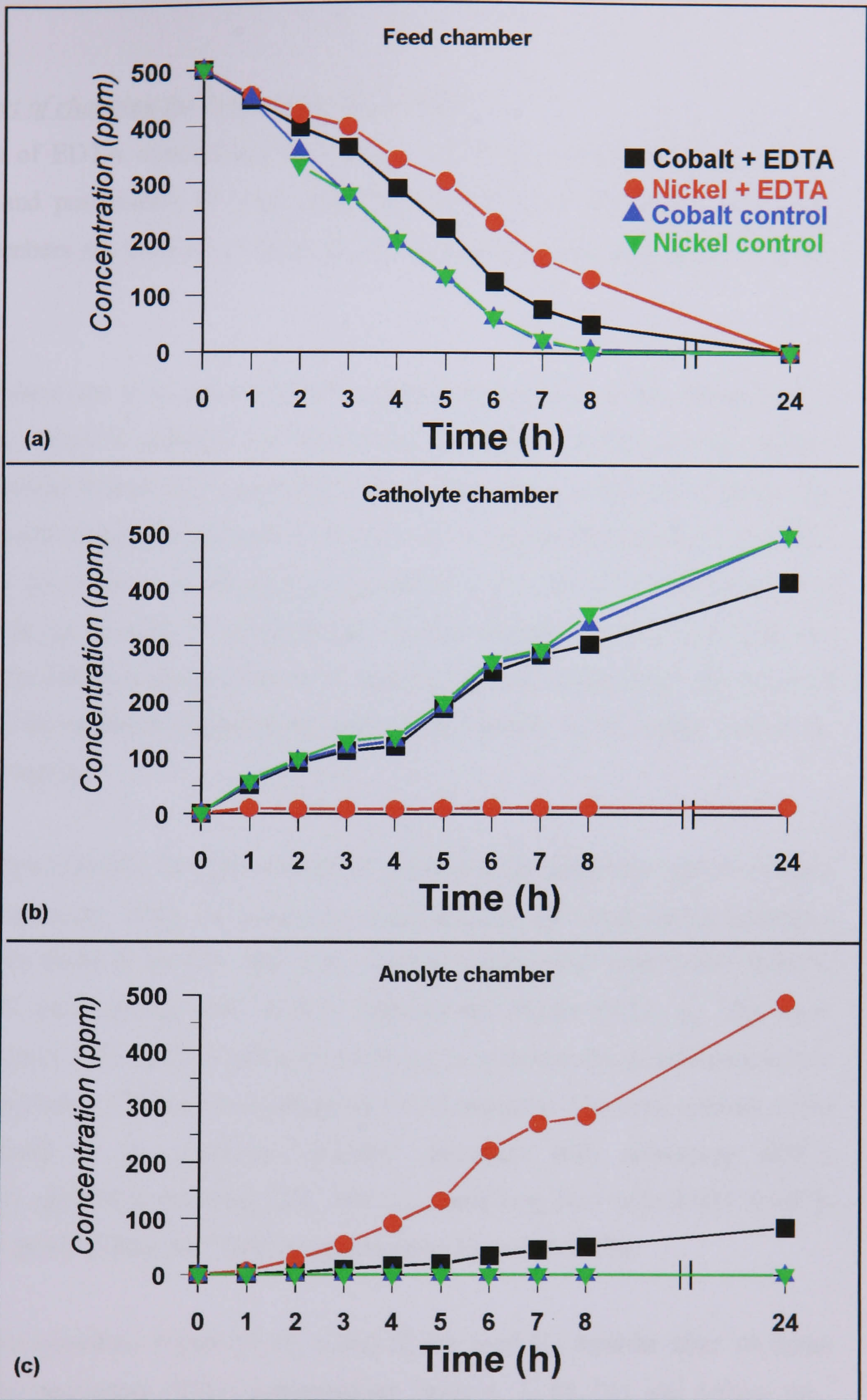


Figure [4.10]: The effect of the presence of EDTA on the metal levels with time in the electrodesialysis of Co-Ni using a three-compartment cell.

### (II) The effect of changing the concentration of EDTA

The effects of EDTA concentrations ( $0.005 - 0.0125 \text{ mol dm}^{-3}$ ) with time on the separation and purification of both cobalt and nickel in the catholyte and in the anolyte chambers are shown in Figure [4.11] with the 24 hour data given in Table [4.9].

The results show that an increase in EDTA concentration enhances the purification of cobalt in the catholyte chamber but reduces the separation efficiency in the anolyte chamber, because it leads to a significant increase in cobalt transportation toward the anolyte chamber along with the nickel. At low EDTA concentrations ( $0.0075 \text{ mol dm}^{-3}$  and less) the cobalt purity in the catholyte chamber is low due to the co-transport of some Ni ions but transfer of cobalt to the anolyte chamber is also very low. An increase in the EDTA concentration ( $0.01 \text{ mol dm}^{-3}$  or above) increases the purity of the cobalt in the catholyte chamber but leads to an increase in the cobalt transfer to the anolyte chamber.

In the catholyte chamber, the total amount of cobalt transfer decreases with increasing EDTA concentration. After 24 hours the concentrations of cobalt in the catholyte chamber were found to be 492, 489, 416, 285 and  $130 \text{ mg dm}^{-3}$  with 0.005, 0.0075, 0.01, 0.0125 and  $0.015 \text{ mg dm}^{-3}$  EDTA respectively, Figure [4.11, c]. The most important aspect of the present study is, however, to consider the purification of Co ions in the presence of lower concentrations of Ni impurity. The total amount of Ni ions transferred to the catholyte chamber decreases with increasing EDTA concentration, after 24 hours being 254, 109, 13, 7 and  $8 \text{ mg dm}^{-3}$  with 0.005, 0.0075, 0.01, 0.0125 and  $0.015 \text{ mg dm}^{-3}$  EDTA respectively, Figure [4.11, b].

In the anolyte chamber, Figure [4.11, e and f], the total Co transfer after 24 hours increases with increasing EDTA concentration being 4, 5, 84, 211 and  $362 \text{ mg dm}^{-3}$  with 0.005, 0.0075, 0.01, 0.0125 and  $0.015 \text{ mg dm}^{-3}$  EDTA respectively. Increasing EDTA concentrations also increases the total amount of Ni transfer towards the anolyte chamber being 244, 376, 487, 489 and  $486 \text{ mg dm}^{-3}$  with 0.005, 0.0075, 0.01, 0.0125 and  $0.015 \text{ mg dm}^{-3}$  EDTA respectively after 24 hours.

The measured values of Co:Ni ratios in the catholyte chamber increase to a maximum value of 41:1 with an EDTA concentration of 0.0125M. This indicates a good purification of Co from Ni at high EDTA levels. On the other hand the Ni:Co ratio in the anolyte chamber shows a maximum value of 63:1 at an EDTA concentration of 0.0075M indicating a good separation of Ni from Co at low EDTA levels.

The results show that the EDTA concentration which gives greater nickel purity in the anolyte chamber, results in a less pure cobalt in the catholyte chamber, and vice versa. The use of EDTA at a concentration of  $0.01 \text{ mg dm}^{-3}$  (which gives a Ni: EDTA ratio of  $0.85:1 \text{ mol dm}^{-3}$ ), however, gives a good degree of nickel separation from cobalt and good purification of cobalt in the catholyte chamber.

Table [4.9]: The effect of changing the EDTA concentration on the total purification and transportation for both Co and Ni after 24 hours electrolysis, using a three-compartment cell, current 0.2A, acid 0.01M H<sub>2</sub>SO<sub>4</sub> and Co=Ni  $500 \text{ mg dm}^{-3}$ .

EDTA mole $\text{dm}^{-3}$	Ratio of Ni to EDTA	Catholyte chamber			Anolyte chamber		
		mg $\text{dm}^{-3}$		Ratio of Co to Ni	mg $\text{dm}^{-3}$		ratio of Ni to Co
		Co	Ni		Co	Ni	
0.0050	1.5:1	492	254	2:1	4	244	61:1
0.0075	1.13:1	489	109	5.4:1	5	379	63.1
0.0100	0.85:1	416	13	32:1	84	487	5.8:1
0.0125	0.68:1	285	7	41:1	211	489	2.3:1
0.0150	0.56:1	130	8	16:1	362	486	1.3:1

### (III) HPLC study

The studies on the transport and fate of EDTA in the electro dialysis show that initially EDTA gives a peak with a retention time of 6 minutes. The peak height varies with EDTA concentration. The results in Figure [4.12] show that there is a decrease in the EDTA concentration in the feed chamber over time with the greatest decrease occurring during the first 2 hours of the reaction. The concentration continues to decrease gradually over the next 22 hours and after 24 hours of electrolysis time the minimum concentration of  $0.0005 \text{ mol dm}^{-3}$  is reached.

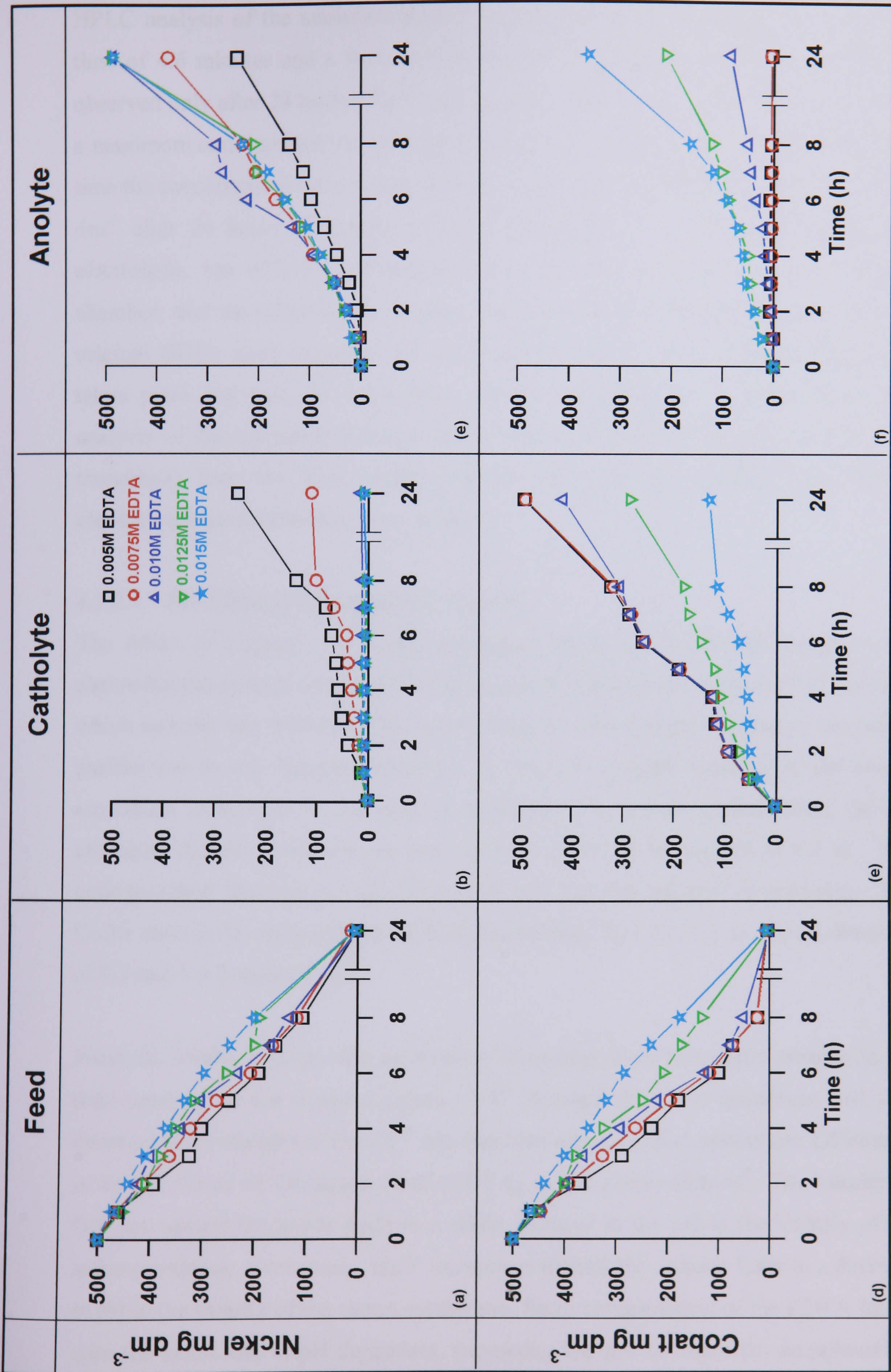


Figure [4.11]: Effect of EDTA concentration on the separation of nickel-cobalt mixture using a three-compartment electroanalysis cell

HPLC analysis of the anolyte chamber solution shows a major peak at a retention time of 4.6 minutes and a broad second peak with a retention time of 7.6 minutes observed only after 24 hours. The major peak observed in the anolyte chamber shows a maximum concentration of  $0.001 \text{ mg dm}^{-3}$  after 5 hours reaction time, but after this time the concentration starts to decrease to show a value of approximately  $0.0002 \text{ mol dm}^{-3}$  after 24 hours electrolysis. From these results, it is clear that during the electrolysis, the EDTA is transferred from the middle chamber to the anolyte chamber. And the difference in retention time between the major anolyte peak and the original EDTA peak suggests that degradation of EDTA at the anode surface has taken place and that the degradation product has the lower retention time. The analysis of the catholyte solutions shows that no significant amount of EDTA is transferred from the feed compartment to the catholyte chamber. The HPLC chromatograms are showing in appendix 2.

#### ***4.1.1.1 The Effect of Changing the Current***

The effect of current (0.2-1.0A) on mass transfer of cobalt and nickel in the electro dialysis process was studied. The results in Table [4.10] show the 24 hour data which indicate that increasing the current leads to only a slight increase in the cobalt purification in the catholyte chamber, but also to a small decrease in the cobalt separation efficiency in the anolyte chamber. The cobalt concentration, in the catholyte chamber, was  $416 \text{ mg dm}^{-3}$  after 24 hours at the current of 0.2 A. The corresponding values at 0.5 and 1.0 A were 413 and  $406 \text{ mg dm}^{-3}$  respectively. The Co:Ni ratio in the catholyte chamber increased from 32:1 to 37:1 at current densities of 0.2 and 1.0 A respectively.

From the results, it seems that an increase in current leads to a slight increase in the total transport of the complex anions  $\text{CoY}^{2-}$  through the anion membrane and to a decrease in the transfer of the  $\text{Co}^{2+}$  free ions through the cation membrane. Of interest is the behaviour of the ligand itself (EDTA) in the electro dialysis<sup>9</sup>. The transfer of  $\text{OH}^-$  ion toward the anode leads to a slight increase in the pH in the vicinity of the anion membrane. Conversely,  $\text{H}_3\text{O}^+$  movement toward the cathode leads to a decrease in pH in the vicinity of the cation membrane. Since complexation of the EDTA ligand with the metal ions is pH dependent, increasing the pH increases the complexation. Increasing the current will lead to an increase of the complexation for the metal ions

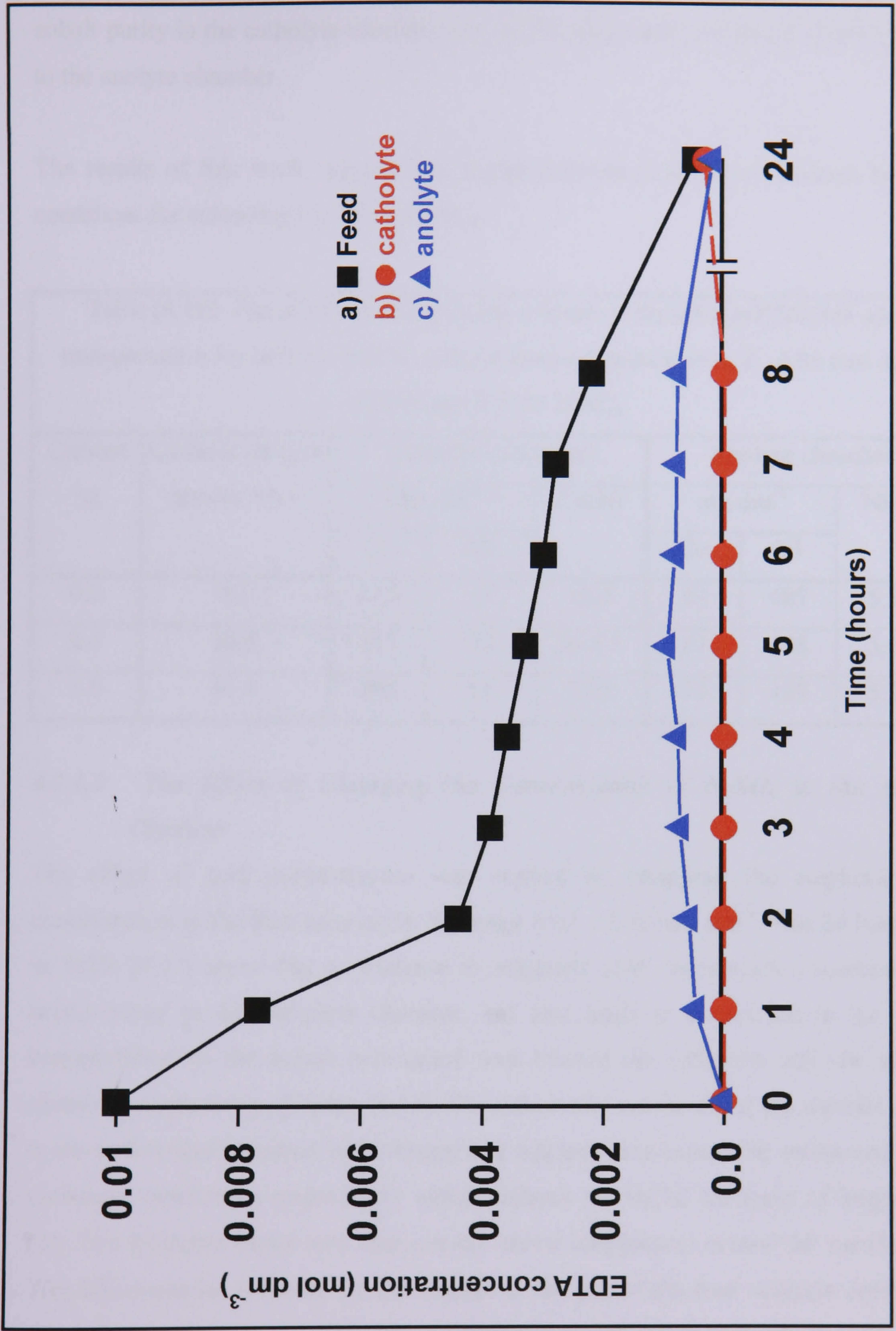


Figure [4.12]: The determination of the EDTA concentration at a) feed chamber, b) catholyte chamber, c) anolyte chamber using a HPLC system



in the vicinity of the anion exchange membrane. This will result in an increase of the cobalt purity in the catholyte chamber and, at the same time, increased cobalt transfer to the anolyte chamber.

The results of this work suggest that higher currents (e.g. 1.0A) produce the best conditions for achieving Co-Ni separation.

Table [4.10]: The effect of changing the current on the total purification and transportation for both Co and Ni using a three-compartment cell, 0.01 mol dm <sup>-3</sup> EDTA and 0.01M H <sub>2</sub> SO <sub>4</sub> .							
Current °A	Cathode current density A/m <sup>2</sup>	Catholyte chamber			Anolyte chamber		
		Mg dm <sup>-3</sup>		Co:Ni	mg dm <sup>-3</sup>		Ni:Co
		Co	Ni		Co	Ni	
0.2	8.3	416	13	32:1	84	487	5.8:1
0.5	20.8	413	12	34.4:1	87	488	5.6:1
1.0	41.5	406	11	37:1	93	489	5.2:1

#### 4.1.1.2 The Effect of Changing the Concentration of H<sub>2</sub>SO<sub>4</sub> in the Middle Chamber

The effect of acid concentration was studied by changing the sulphuric acid concentration in the feed solution in the range 0.01 - 0.05 mol dm<sup>-3</sup>. The 24 hour data in Table [4.11] show that an increase in sulphuric acid concentration increases the cobalt purity in the catholyte chamber, but also leads to a decrease in the initial transportation of the cobalt and nickel ions toward the catholyte and the anolyte chambers respectively, [Figure [4.13]]. The initial decrease in metal ion transfer is due to the preferential transport of hydrogen and sulphate ions across the cation and anion exchange membranes respectively which reduces the initial transport of larger ions (the free hydrated metal ions and anionic metal complexes) across the membranes. This effect can be followed by the change in the pH of the feed solution during the electrolysis processes. The pH changed from 1.8 to 3.9 and from 1.1 to 3.1 after 24 h in 0.01 and 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solutions respectively. Increasing the acid concentration results in a slight decrease in the total nickel transferred to the catholyte chamber and gives a significant increase in the cobalt ratio.

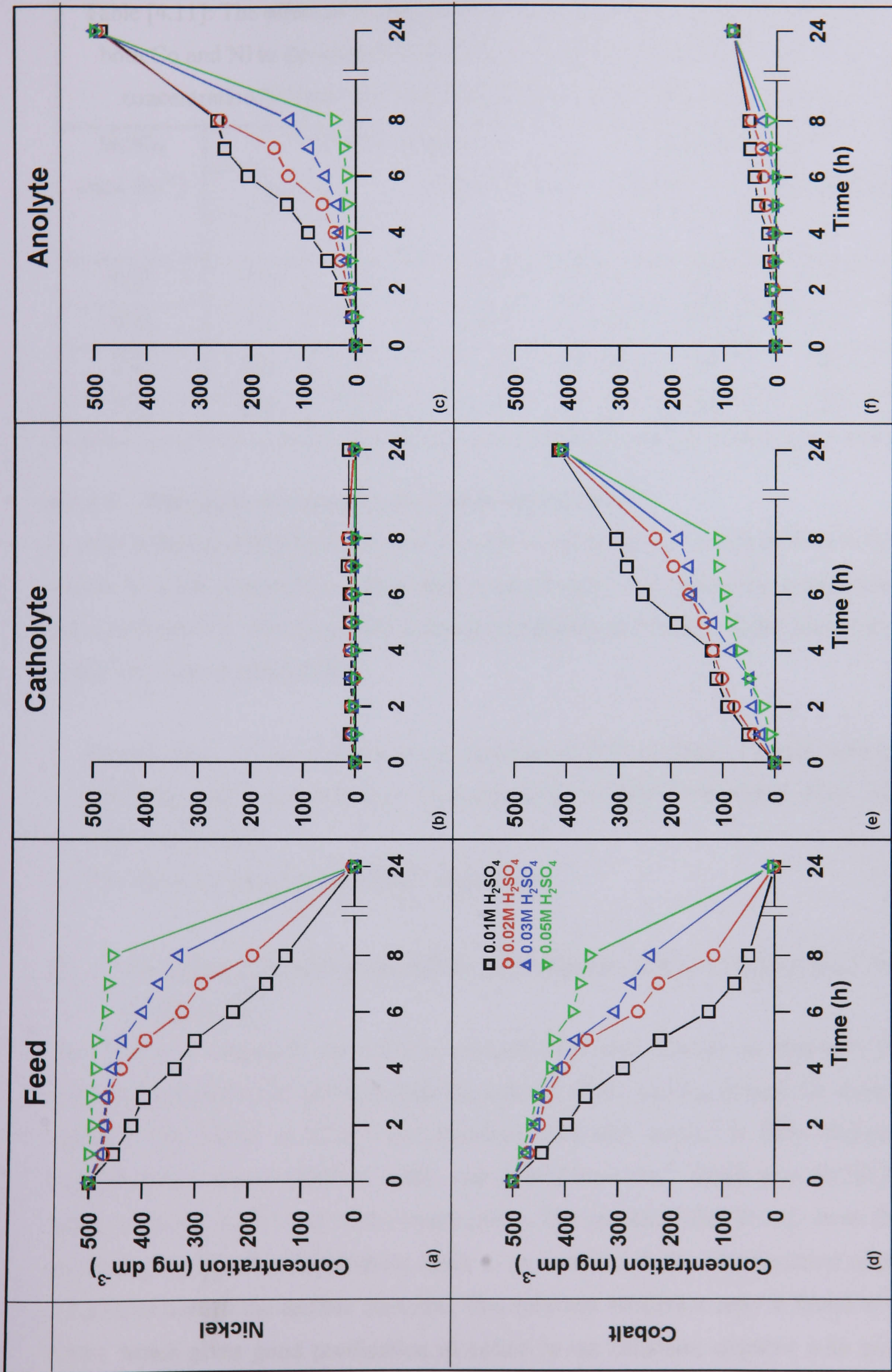


Figure [4.13]: Effect of  $H_2SO_4$  concentration on the separation of nickel-cobalt mixture using a three-compartment electrolysis cell.

Table [4.11]: The effect of H<sub>2</sub>SO<sub>4</sub> on the purification and total transportation for both Co and Ni to the catholyte and anolyte chamber respectively, the EDTA concentration 0.01 mol dm<sup>-3</sup> and current 0.2A, after 24 hours electrolysis.

H <sub>2</sub> SO <sub>4</sub> (mol dm <sup>-3</sup> )	Catholyte chamber			Anolyte chamber		
	mg dm <sup>-3</sup>		ratio of Co to Ni	Mg dm <sup>-3</sup>		ratio of Ni to Co
	Co	Ni		Co	Ni	
0.01	416	13	32:1	84	487	5.7:1
0.02	412	2	206:1	85	494	5.7:1
0.03	405	0	∞	86	500	5.8:1
0.05	410	0	∞	85	500	5.9:1

#### 4.1.1.3 The Effect of Changing the Cobalt-Nickel Ratio

In most hydrometallurgical leach solutions the concentration of nickel in the Co-rich stream is small compared to the cobalt concentration. The following experiments were performed to investigate the optimum conditions to separate small amounts of nickel ions from cobalt solution.

1. Identification of the optimum concentration of EDTA using a Co:Ni ratio of 500:50mg dm<sup>-3</sup> and different concentrations of EDTA (0.00075, 0.01 and 0.00125mg dm<sup>-3</sup>).
2. The effect of changing the cobalt / nickel ratio.

##### (I) The effect of changing the EDTA concentration with Co=500mg dm<sup>-3</sup> and Ni=50mg dm<sup>-3</sup>

The effect of changing the EDTA concentration was studied to optimise the maximum amount of Ni and minimise the amount of Co moving toward the anolyte chamber. The effect of EDTA (as disodium salt) was studied at three different concentrations namely 0.00075, 0.001 and 0.00125mol dm<sup>-3</sup> which give Ni:EDTA ratios of 1.13:1, 0.85:1 and 0.68:1 respectively. The results (Table [4.12]) show that increasing the EDTA concentration leads to an increase in the transportation of the cobalt ions toward the anolyte chamber. The optimum Ni:EDTA ratio is found to be 0.85:1 which gives good purification of cobalt in the catholyte chamber with good

separation for nickel from cobalt in the anolyte chamber (Ni:Co = 26.7:1).

Table [4.12]: The effect of changing the EDTA concentration on the total purification and transportation for both Co and Ni, using three-compartment cell, current 0.2A, acid 0.01M H <sub>2</sub> SO <sub>4</sub> and Co:Ni 500:50 mg dm <sup>-3</sup> , after 24 hours electrolysis							
EDTA (mol dm <sup>-3</sup> )	Ni:EDTA	Catholyte			Anolyte		
		mg dm <sup>-3</sup>		Co:Ni	Mg dm <sup>-3</sup>		Ni:Co
		Co	Ni		Co	Ni	
0.00075	1.13:1	489.7	15.8	3:1	10.3	34.2	3:1
0.001	0.85:1	482.7	3.2	15:1	17.3	46.3	26.7:1
0.00125	0.68:1	470	3.0	15.6:1	27	46.6	17:1

*(II) The effect of changing the cobalt / nickel ratio*

The effect of the cobalt:nickel ratio was investigated by: a) changing the cobalt concentration (500-2000 mg dm<sup>-3</sup>), at a constant nickel concentration of 50 mg dm<sup>-3</sup> and b) changing the cobalt concentration (500-2000 mg dm<sup>-3</sup>), at a constant nickel concentration of 25 mg dm<sup>-3</sup> and a constant EDTA:Ni ratio of 1:0.85.

The results in Figures [4.14-159] show that an increase in the cobalt concentration, reduces the initial transportation of nickel complex toward the anolyte chamber, but after 24 hours a nearly complete transfer of the Ni-EDTA complex to the anolyte chamber is achieved [graphs c]. The 24 hour data in Tables [4.13] and [4.14] show that increasing the cobalt concentration in the feed compartment leads to a slight increase in the concentration of cobalt ions entering the anolyte chamber. The better separation of nickel from cobalt in the anolyte chamber are at lower cobalt concentrations. This is reflected by the Ni:Co ratios in the anolyte chamber. The best cobalt purifications are, however, obtained at the higher cobalt concentrations.

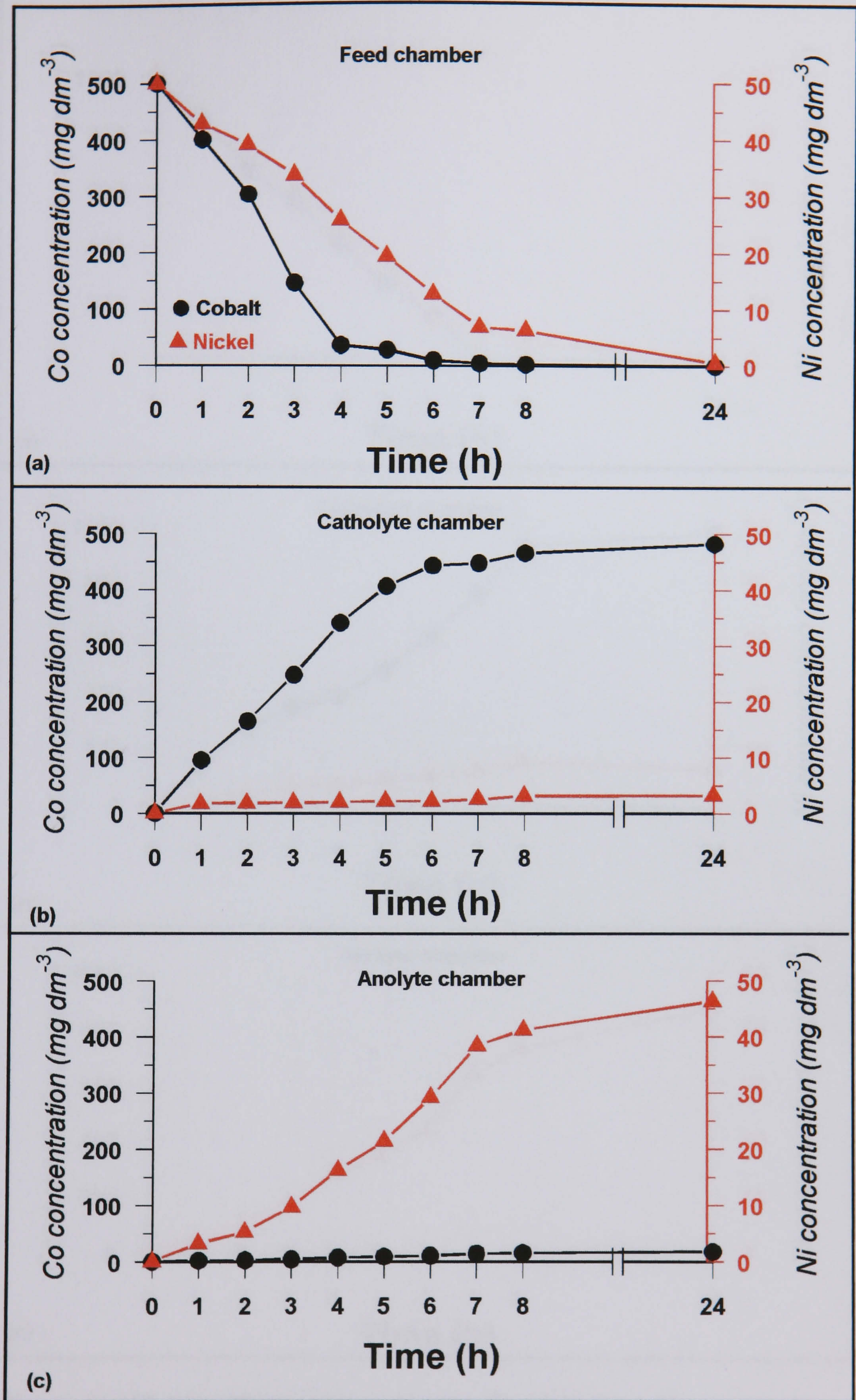


Figure [4.14]: The effect of changing the Co:Ni ratio in the separation process using a three-compartment cell and Co:Ni=500:50.

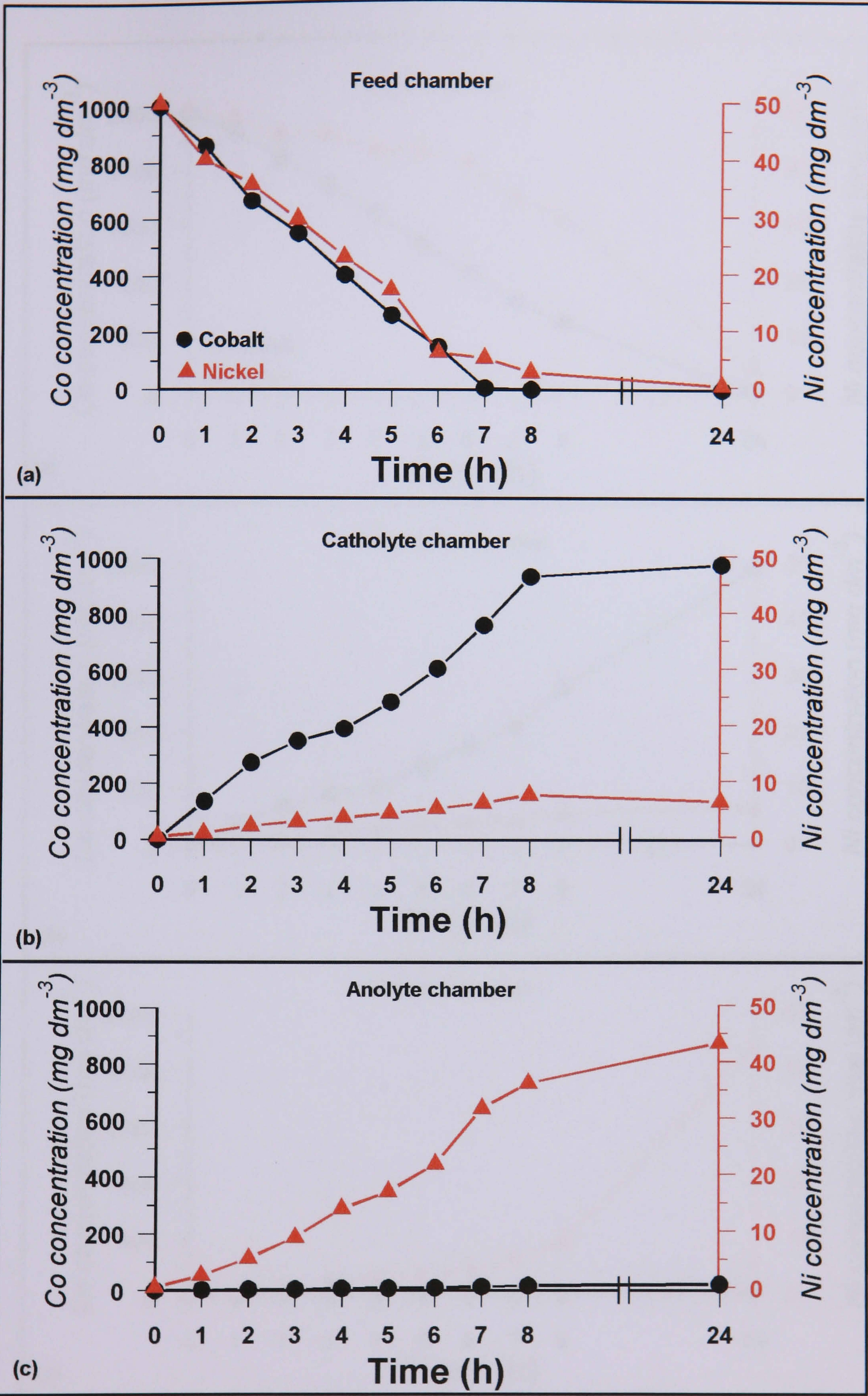


Figure [4.15]: The effect of changing the Co:Ni Ratio in the separation process using a three-compartment cell and Co:Ni=1000:50ppm.

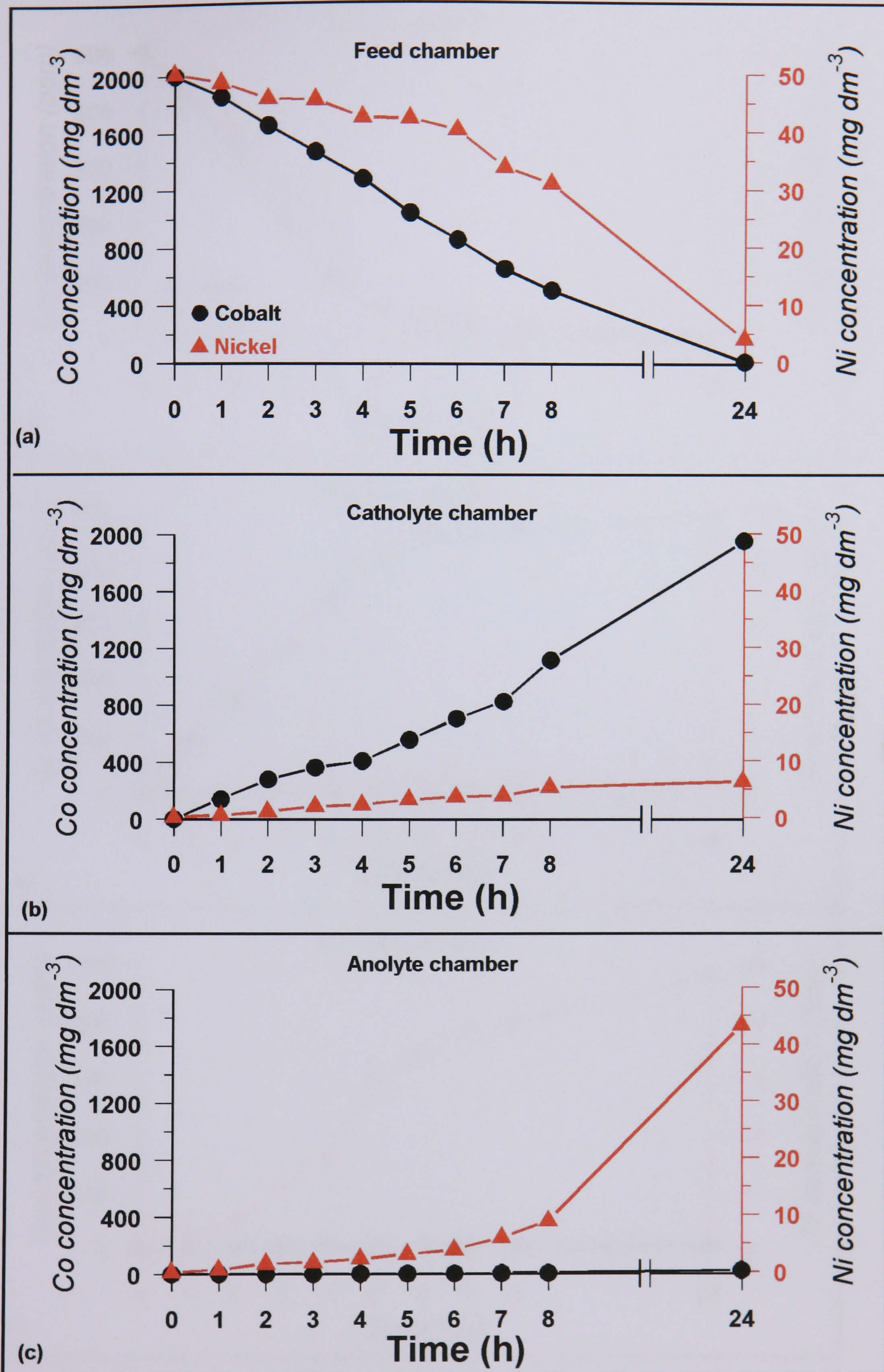


Figure [4.16]: The effect of changing the Co:Ni ratio in the separation process using a three-compartment cell and Co:Ni=2000:50.

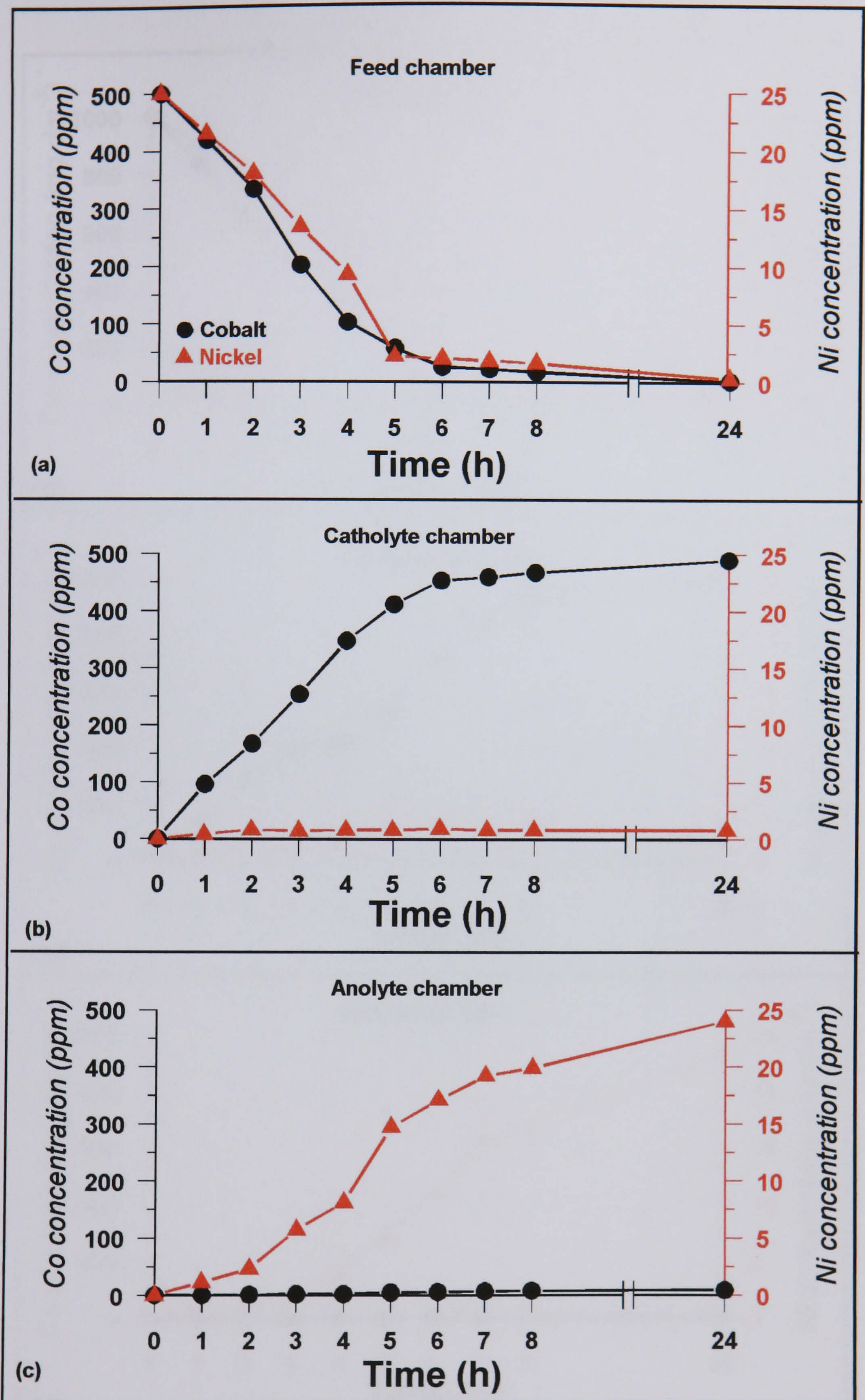


Figure [4.17]: The effect of changing the Co:Ni ratio in the separation process using a three-compartment cell and Co:Ni=500:25.



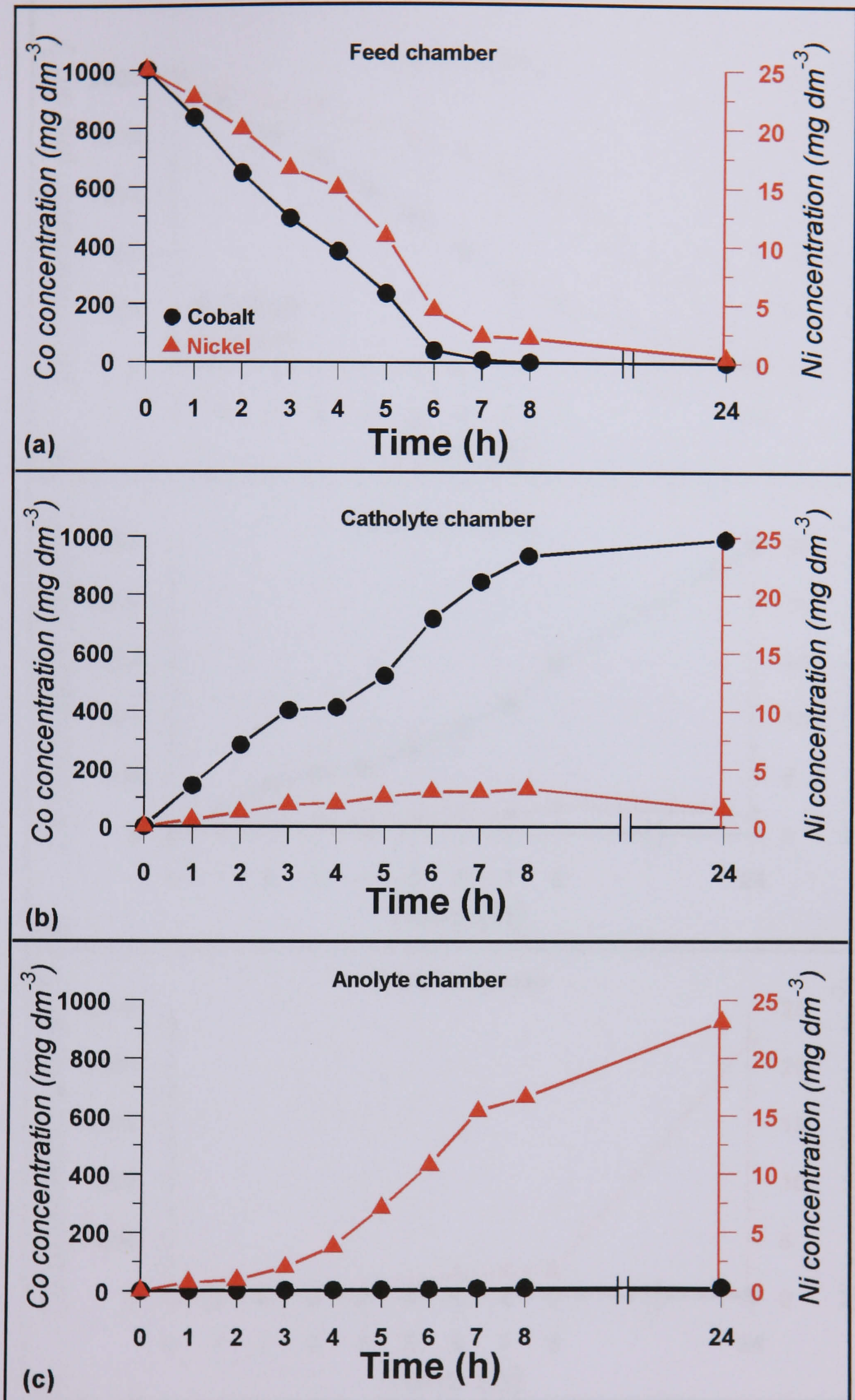


Figure [4.18]: The effect of changing the Co:Ni ratio in the separation process using a three-compartment cell and Co:Ni=1000:25.

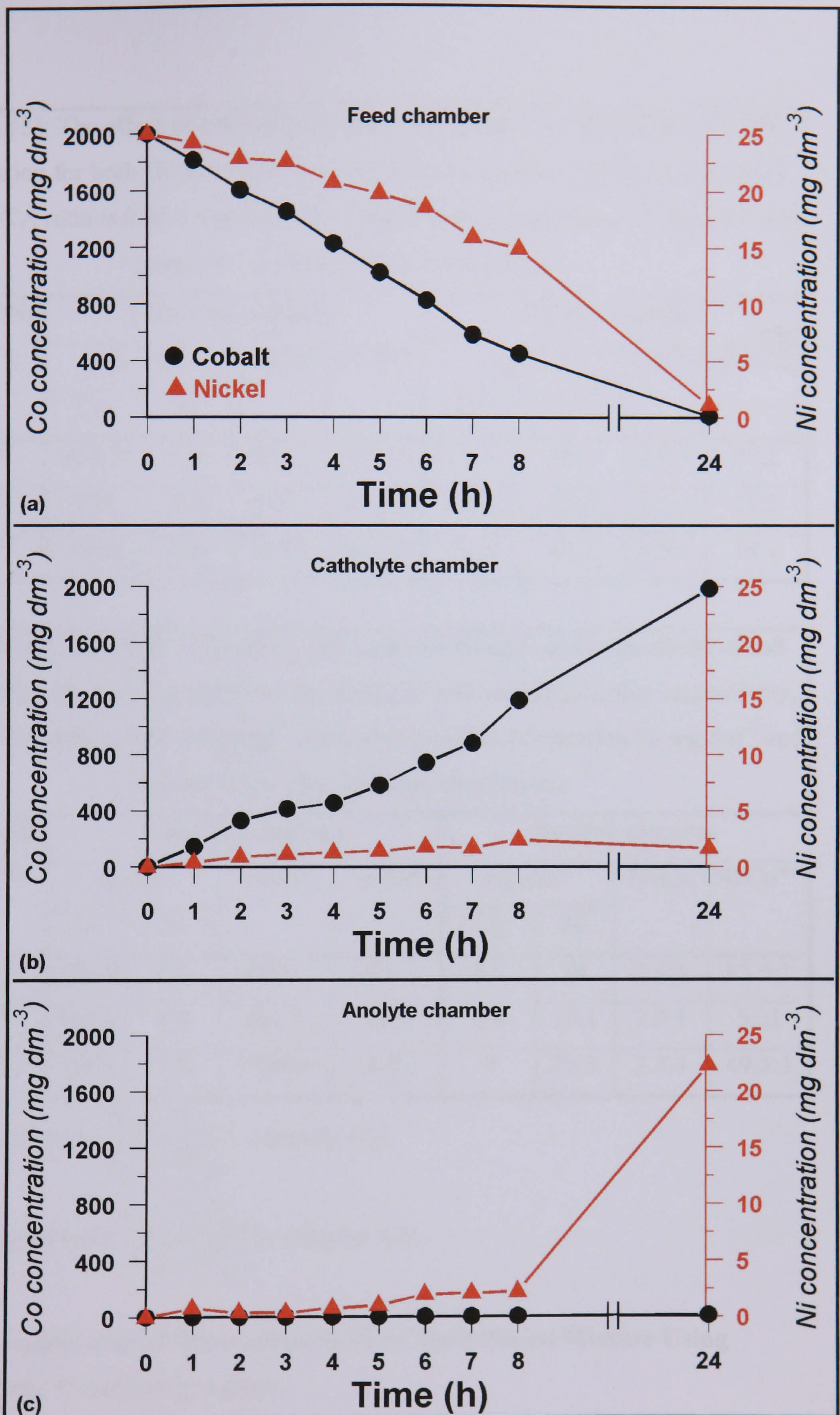


Figure [4.19]: The effect of changing the Co:Ni ratio in the separation process using a three-compartment cell and Co:Ni=2000:25.

Table [4.13]: The effect of changing the initial Co:Ni ratio on the purification and transportation for both Co and Ni to the catholyte and anolyte chamber respectively, the Ni:EDTA ratio is 0.85:1 mg dm<sup>-3</sup>, the initial nickel concentration 50 mg dm<sup>-3</sup> and current 0.2A, after 24 hours electrolysis.

Initial Co:Ni (mg dm <sup>-3</sup> )	Catholyte chamber				Anolyte chamber			
	mg dm <sup>-3</sup>		Co/Ni	Co:Ni*	mg dm <sup>-3</sup>		Ni/Co	Ni:Co **
	Co	Ni			Co	Ni		
500:50	482.7	3.2	151:1	15.1:1	17.3	46.3	2.7:1	27:1
1000:50	979	6.3	155:1	15.5:1	20.4	43.3	2.1:1	21:1
2000:50	1962	6.3	311:1	31.1:1	22.9	43.3	1.9:1	19:1

Table [4.14]: The effect of changing the initial Co:Ni ratio on the purification and transportation for both Co and Ni to the catholyte and anolyte chamber respectively, the Ni:EDTA ratio is 0.85:1 mg dm<sup>-3</sup>, the initial nickel concentration 25 mg dm<sup>-3</sup> and current 0.2A, after 24 hours electrolysis.

Initial Co:Ni (mg dm <sup>-3</sup> )	Catholyte chamber				Anolyte chamber			
	mg dm <sup>-3</sup>		Co/Ni	Co:Ni*	mg dm <sup>-3</sup>		Ni/Co	Ni:Co**
	Co	Ni			Co	Ni		
500:25	489.8	0.8	612:1	30.6:1	8.2	24	2.9:1	85.5:1
1000:25	991.6	1.5	661:1	33:1	8.4	23.1	2.7:1	55:1
2000:25	1983	1.6	1239:1	61.9:1	9	22.3	2.4:1	49.5:1

\* Applying formula  $\frac{C_{Co^{++}} / C_{Ni^{++}}}{C_{Co^{++}}^0 / C_{Ni^{++}}^0}$  (section 4.6).

\*\* Applying formula  $\frac{C_{NiY^{2-}} / C_{CoY^{2-}}}{C_{Ni^{++}}^0 / C_{Co^{++}}^0}$  (section 4.6).

#### 4.1.1 The Application of Electrodialysis of a Cobalt-Nickel Mixture Using Different Complexing Agents

The electrodialysis of Co-Ni mixtures in the presence of complexing agents other than EDTA was performed using the three-compartment cell described in experimental section. The complexing agents used were citric acid, salicylaldoxime, acetic acid, and hydrochloric acid under the stated conditions.

(I) Using citric acid as a complexing agent

In this experiment citric acid ( $0.01 \text{ mol dm}^{-3}$  concentration) was in the feed chamber as a complexing agent for both Co and Ni ( $500 \text{ mg dm}^{-3}$  each) in  $0.01 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$ . The results in Table [4.15] show that no separation can be achieved, although small variations in the metal ratios crossing the cation membrane are observed. The small variation is not promising in terms of obtaining a complete separation and no metal ions were transferred to the anolyte chamber after 8 hours. It is clear that the stability constants of the cobalt and nickel complexes<sup>30</sup>:



are too similar to permit a separation by electro dialysis.

Table [4.15]: The effect of citric acid as a complexing agent on the transportation for both Co and Ni to the catholyte and anolyte chamber respectively with time. The Ni: citric acid ratio is  $0.85:1 \text{ mg dm}^{-3}$ , the initial Ni and Co concentration in the feed chamber  $500 \text{ mg dm}^{-3}$  and current  $0.2\text{A}$ .

Time (h)	Cobalt ( $\text{mg dm}^{-3}$ )		Nickel ( $\text{mg dm}^{-3}$ )	
	Catholyte	Anolyte	Catholyte	Anolyte
2	293	0	242	0
4	471	0	455	0
6	498	0	490	0
8	499	0	495	0

(II) Using salicylaldoxime as a complexing agent

Salicylaldoxime is a well-known selective complexing agent in the analytical chemistry of nickel<sup>23</sup>. However, using  $0.01 \text{ mol dm}^{-3}$  of salicylaldoxime in the electro dialysis process of both Co and Ni ( $500 \text{ mg dm}^{-3}$  each) in  $0.01 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$ , again shows no evidence of separation. The metal ions cross the cation membrane in the same ratio. Increasing the pH or the concentration of salicylaldoxime does not improve the separation. There is no evidence for the transportation of the metal ions to the anolyte chamber.

(III) Using acetic acid as a complexing agent

In these studies, a relatively high concentration of acetic acid ( $1 \text{ mol dm}^{-3}$ ) was used in the feed solution. The results in Table [4.16] show that no separation of Co and Ni is achieved and that there is only a small variation in the ratios of the metals crossing the cation membrane.

Table [4.16]: The effect of acetic acid as a complexing agent on the transportation for both Co and Ni to the catholyte and anolyte chamber respectively with time. The acetic acid concentration $1 \text{ mol dm}^{-3}$ , the initial Ni and Co concentration in the feed chamber $500 \text{ mg dm}^{-3}$ and current $0.2 \text{ A}$ .				
Time (h)	Cobalt ( $\text{mg dm}^{-3}$ )		Nickel ( $\text{mg dm}^{-3}$ )	
	Catholyte	Anolyte	Catholyte	Anolyte
2	270	0	272	0
4	387	0	377	0
6	445	0	430	0
8	464	0	448	0

(IV) Using hydrochloric acid as a complexing agent

It is known that cobalt forms the stable negatively charged complex species with chloride ions  $[\text{CoCl}_4]^{2-}$  in high HCl concentrations, whereas nickel does not form such a complex and remains in solution as hydrated  $\text{Ni}^{2+}$  ions. This difference has been used in cation exchange separation of the metals<sup>31</sup>. Applying the same principle to the separation of both Co and Ni ( $500 \text{ mg dm}^{-3}$  each) using a three-compartment electro dialysis cell and  $8 \text{ mol dm}^{-3}$  of HCl as a complexing agent in the feed solution, no evidence was found for metal transportation to the catholyte or anolyte chambers. This may be because of the preferential transport of the  $\text{Cl}^-$  and  $\text{H}_3\text{O}^+$  ions to the anolyte and the catholyte chamber respectively.

**4.1.1 The Effect of Other Metal Impurities**

The fate of any other metal (M) impurities on the Ni-Co system will depend upon the stability constants of the Co-EDTA, Ni-EDTA and M-EDTA complexes (Table [4.1]). If the stability constant is similar to nickel then there will be competition

between the migration of Ni-EDTA and M-EDTA complexes towards the anolyte chamber. In this case the separation can be optimised by changing the EDTA concentration in the feed solution. If the M-EDTA complex is similar to Co-EDTA complex then the metal impurity will have no effect on the separation of nickel from the cobalt in the mixture but the impurity metals will be transferred to the catholyte chamber with the Co.

#### **4.1.2 The Application of Electrodialysis to Different Metal Mixtures**

The electrodialysis system of a three-compartment cell described in the experimental section was used in studies of the separation processes of Co from each of the following metals: Cu, Zn, Fe and Pd.

The results show differences in the separation rate in each metal mixture arising from different stability constants of the metal-EDTA complexes which are being formed. These differences lead to different amounts of metal ions and metal-EDTA complexes transferring towards the catholyte and anolyte chambers respectively.

##### ***4.1.2.1 Electrodialysis of Co-Cu Mixture in the Presence of EDTA:***

An experiment was performed to determine the possible separation of 500 mg dm<sup>-3</sup> of both Co and Cu from a feed compartment containing 0.01 mg dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 0.01 mg dm<sup>-3</sup> EDTA (as disodium salt). The initial catholyte and anolyte solutions were 0.01 mol dm<sup>-3</sup> sulphuric acid.

The copper ion behaved in a similar manner to the nickel ions described in section [4.7.2] and the results (Figure [4.20]) show that separation of Co and Cu can be achieved. The concentration of metals transferred to the anolyte chamber [Figure 4.20, c] after 4 hours is 16 mg dm<sup>-3</sup> for Co and 30 mg dm<sup>-3</sup> for Cu. This increases to 85 and 253 mg dm<sup>-3</sup> after 8 hours for Co and Cu respectively. The total amount of metal ion transfer to the anolyte chamber after 24 hours is 152 and 484 mg dm<sup>-3</sup> for Co and Cu respectively. These values of metal ion transportation give values for the Cu:Co ratios of 1.9:1, 2.8:1, and 3:1 after 4, 8, and 24 hours of reaction time respectively.

In the catholyte chamber (Figure [4.20, b]), the metal ion concentration after 4 hours is  $86 \text{ mg dm}^{-3}$  for cobalt and  $3 \text{ mg dm}^{-3}$  for copper. This increased to 277 and  $10 \text{ mg dm}^{-3}$  after 8 hours for Co and Cu respectively. The total amount of metal ions transferred to the catholyte chamber after 24 hours is 335 and  $12 \text{ mg dm}^{-3}$  for Co and Cu respectively giving Co:Cu ratios of 28.9:1 27.7:1 and 27.9:1 after 4, 8 and 24 hours respectively.

#### **4.1.2.2 *Electrodialysis of Co-Zn Mixture in the Presence of EDTA:***

Experiments were performed to determine the possible separation of Co and Zn from a solution containing  $500 \text{ mg dm}^{-3}$  of both metals. These proved unsuccessful because of the precipitation of the metal hydroxide on the cation membrane which inhibited the movement of any ions through the membrane. To try to overcome this problem the middle chamber was acidified using  $\text{H}_2\text{SO}_4$  but this was also unsuccessful, because of the preferential transport of hydrogen and sulphate ions across the membranes.

It was found that when a higher concentration of cobalt was used compared to zinc there was no evidence of fouling of the membrane with metal hydroxide. An experiment was performed using metal concentrations of  $\text{Co}=500 \text{ mg dm}^{-3}$  and  $\text{Zn}=50 \text{ mg dm}^{-3}$  in  $0.01 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  and  $0.001 \text{ mol dm}^{-3} \text{ EDTA}$  as disodium salt. The initial catholyte and anolyte solutions were  $0.01 \text{ mol dm}^{-3}$  sulphuric acid. The results (Figure [4.21]) show that the behaviour of zinc ions was similar to that of the cobalt ions, and separation of Co and Zn was not achieved using this electrodialysis system. The metal ion concentrations in the anolyte chamber (Figure [4.21, c] after 4 hours are  $34 \text{ mg dm}^{-3}$  for cobalt and  $6.3 \text{ mg dm}^{-3}$  for Zn, increasing to 69 and  $9 \text{ mg dm}^{-3}$  after 8 hours for cobalt and zinc respectively. These ion transportations give Zn:Co values of 1.8:1 and 1.3:1 after 4 and 8 hours respectively.

In the catholyte chamber (Figure [4.21, b]), the metal ion concentrations after 4 hours were  $305.2 \text{ mg dm}^{-3}$  for cobalt and  $27 \text{ mg dm}^{-3}$  for zinc increasing to 360 and  $31 \text{ mg dm}^{-3}$  after 8 hours for Co and Zn respectively. These metal ion transportations gave a same Co:Zn value of 1.1:1 after 4 and 8 hours.

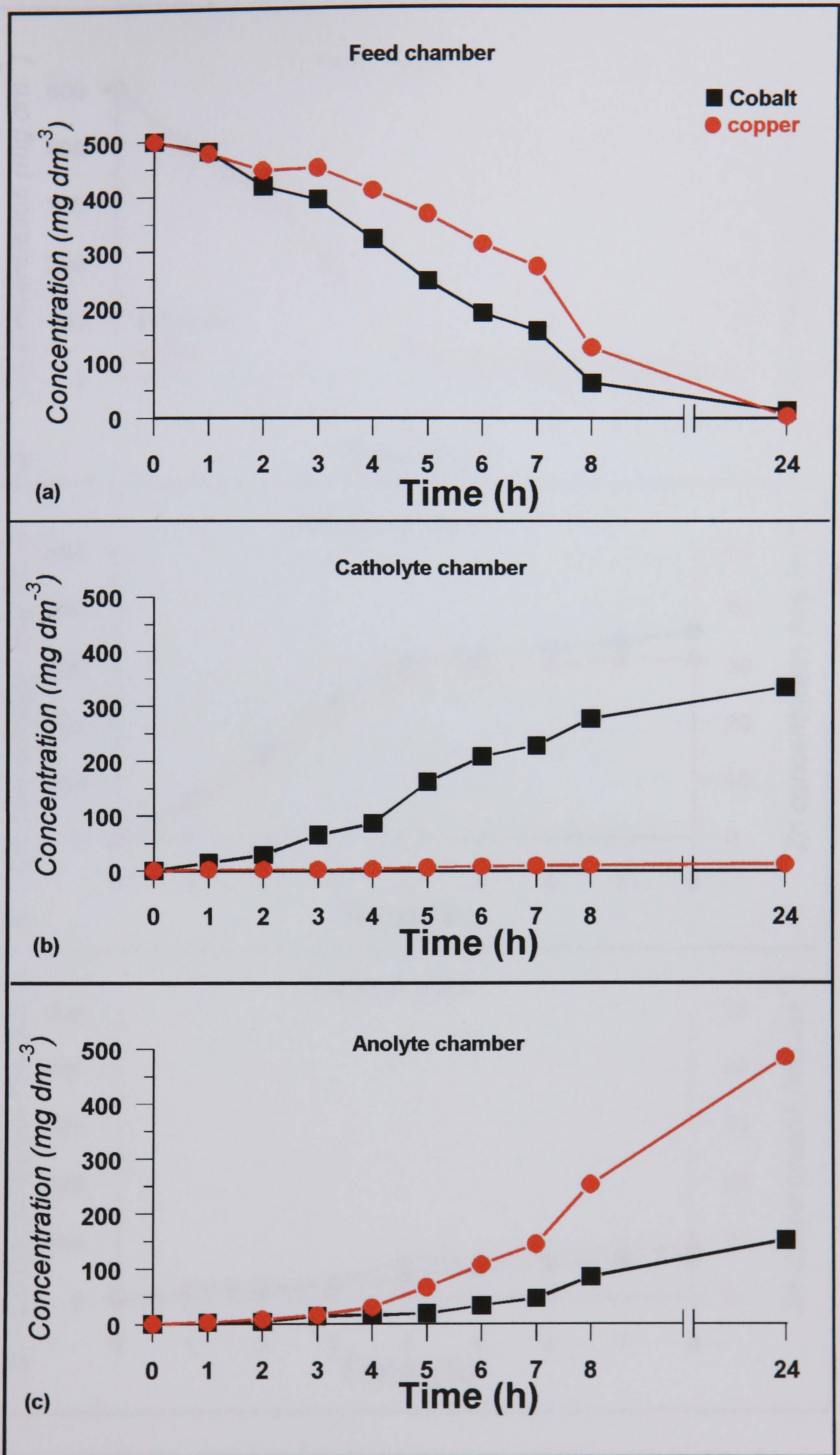


Figure [4.20]: The effect of presence of EDTA in the electro dialysis of Co-Cu using a three-compartment cell.



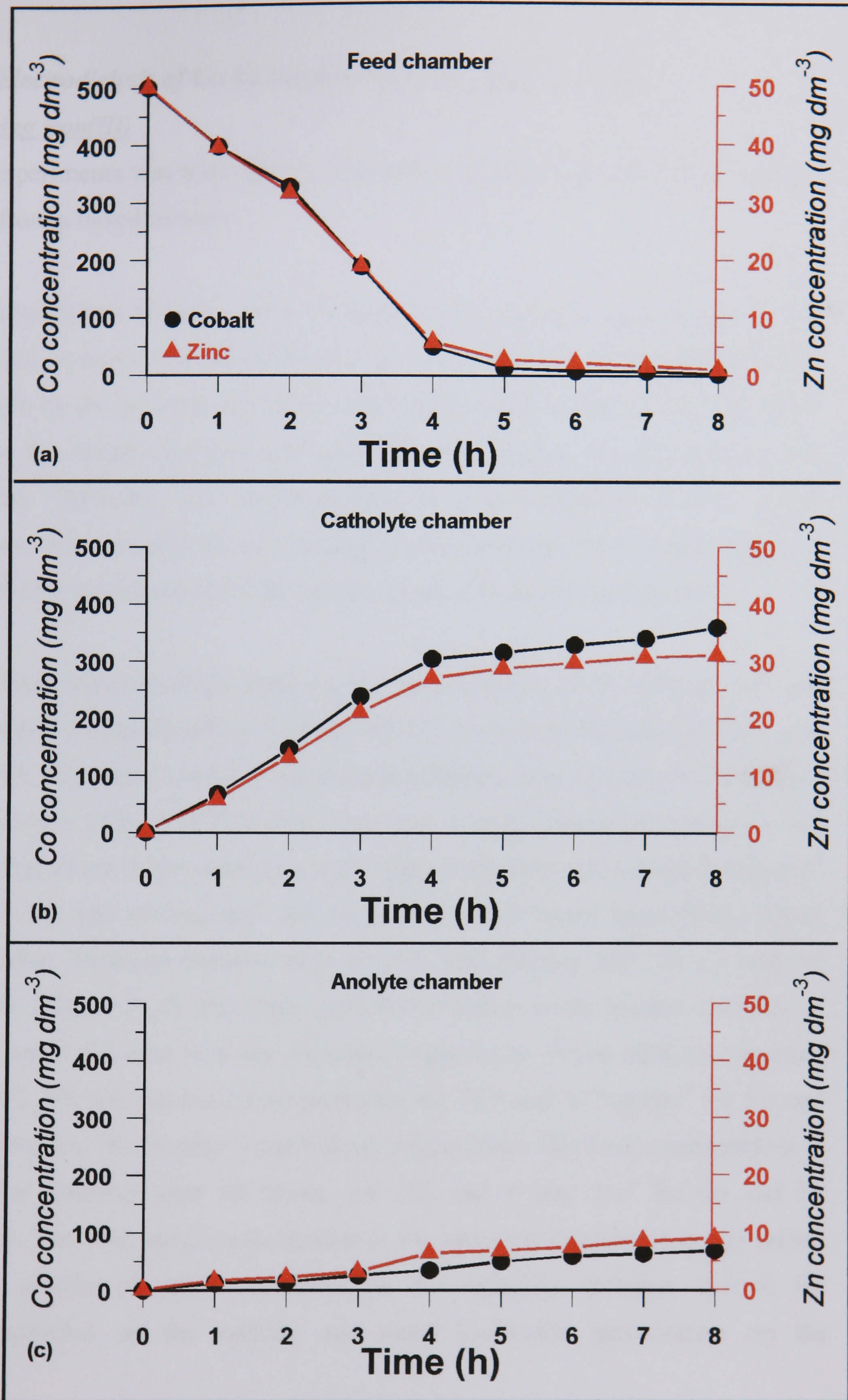


Figure [4.21]: The change of cobalt and zinc concentration in electro dialysis system using a three-compartment cell.

#### **4.1.2.3 Electrodialysis of Co-Fe Mixture in the Presence of EDTA:**

##### **(I) Using iron(III)**

A set of experiments was undertaken to determine whether Co and Fe(III) could be separated from a mixed solution.

Equal concentrations ( $500\text{mg dm}^{-3}$ ) of both ions in solution were placed in the electrodialysis system. The separation did not occur because of membrane failure caused again by the precipitation of the metal hydroxides on the cation membrane. Once again the middle chamber was acidified using  $\text{H}_2\text{SO}_4$ , but this proved to be unsuccessful. Reducing the concentration of iron compared to the cobalt concentration did not result in total fouling of the membrane but a small degree of metal hydroxide was observed on the membrane after 24 hours reaction time.

An experiment was performed using metal concentrations of  $\text{Co}=500\text{mg dm}^{-3}$  and  $\text{Fe}=50\text{mg dm}^{-3}$  as sulphate salts in  $0.01\text{mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  and  $0.001\text{mol dm}^{-3}$  EDTA as disodium salt. The initial catholyte and anolyte solutions were  $0.01\text{mol dm}^{-3}$  sulphuric acid. The results (Figure [4.22]) show that only a small degree of separation was achieved. The values of the metal ions in the anolyte chamber are  $2.5$  and  $8.1\text{mg dm}^{-3}$  for Co and  $3.4$  and  $16.7\text{mg dm}^{-3}$  for Fe after 4 and 8 hours respectively. These increased after 24 hours reaction time to  $21.2$  and  $38.2\text{mg dm}^{-3}$  for Co and Fe respectively, (Figure [4.22, c]). These give Fe:Co values in the anolyte chamber of 1.3:1, 2:1, and 1.8:1 after 4, 8 and 24 hours respectively. In the catholyte chamber (Figure [4.22, b]), the metal ion concentrations are  $54.8$  and  $157\text{mg dm}^{-3}$  for Co and  $1.8$  and  $3.9\text{mg dm}^{-3}$  for Fe after 4 and 8 hours respectively. The total concentrations in the catholyte chamber after 24 hours, are  $162$  and  $4.1\text{mg dm}^{-3}$  for Co and Fe respectively. The final metal concentration in the catholyte chamber does not reflect the actual amount of metal transferred to the catholyte chamber, due to the electroprecipitation on the cathode and metal hydroxide precipitation on the membrane.

##### **(II) Using iron(II)**

A set of experiments was performed to determine whether Co and Fe(II) could be separated from a mixed solution. By using the sulphate salt of the metal ions, it was

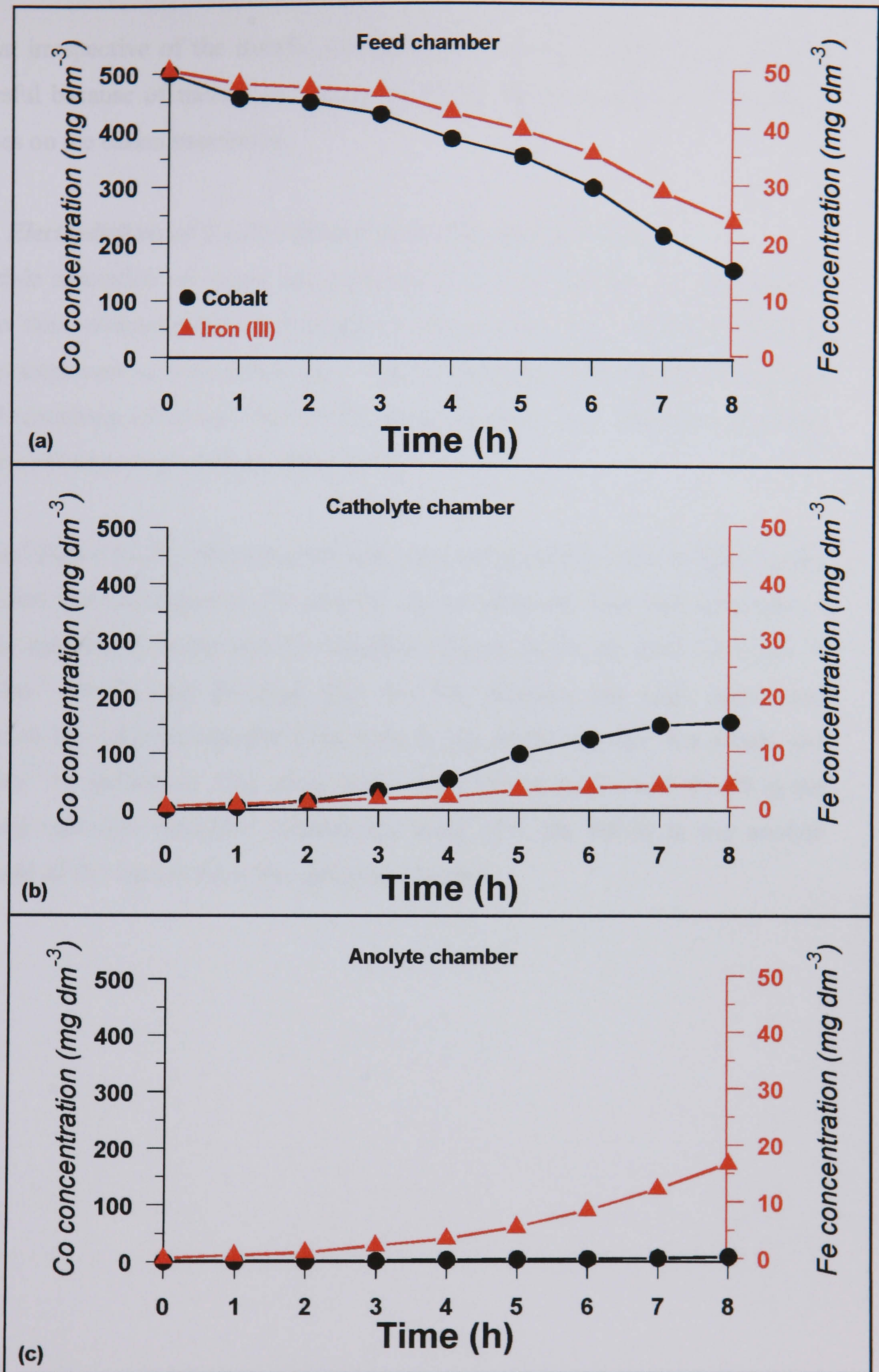


Figure [4.22]: The change of cobalt and iron (III) concentration in electro dialysis system using a three-compartment cell.

found that irrespective of the iron(II) concentration, the electro dialysis process was unsuccessful because of membrane failure caused by the precipitation of the metal hydroxides on the cation membrane.

#### ***4.1.1.1 Electrodialysis of Co-Pd Mixture in the Presence of EDTA:***

The possible separation of cobalt and palladium ions in a mixture was investigated using the three-compartment electro dialysis system. The feed solution contained equal concentrations of both metals ( $\text{Co} = \text{Pd} = 250\text{mg dm}^{-3}$ ) as chloride in  $0.01\text{mol dm}^{-3}$  HCl containing  $0.005\text{mol dm}^{-3}$  EDTA as the disodium salt. The initial catholyte and anolyte solutions were  $0.01\text{mol dm}^{-3}$  HCl.

The results (Figure [4.23]) show that the behaviour of palladium ion is similar to that of nickel and that separation of Co and Pd can be achieved. The total amounts of metal ions transferred to the anolyte chamber (Figure [4.23, c]) after 24 hours is  $6.25\text{mg dm}^{-3}$  for Co and  $231.4\text{mg dm}^{-3}$  for Pd, whereas, the total metal ions transferred to the catholyte chamber (Figure [4.23, b]) are  $244\text{mg dm}^{-3}$  for cobalt and  $18.4\text{mg dm}^{-3}$  for palladium. This gives high values for the Pd:Co and Co:Pd in the anolyte and catholyte chambers respectively being 37:1 for Pd:Co in the anolyte chamber and 13.2:1 for Co:Pd in the catholyte chamber.

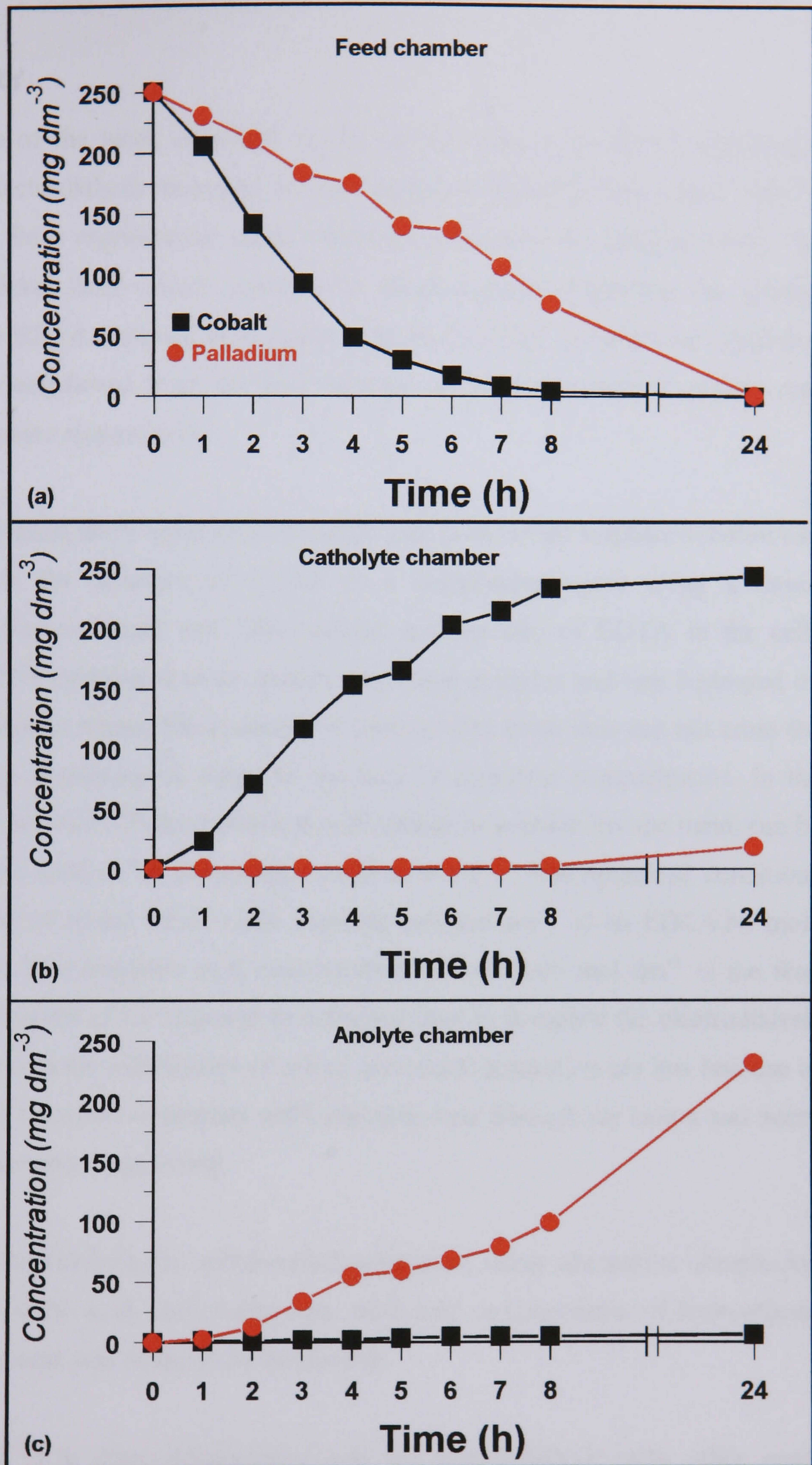


Figure [4.23]: The effect of presence of EDTA in the electro dialysis of Co-Pd using a three-compartment cell.

## 4.2 SUMMARY

The main aim of the work described in this chapter was to develop a technology based on an electrodialysis technique for the separation of nickel from cobalt without a requirement for a regenerating agent. Optimum conditions are determined for the removal of nickel from cobalt solution by electrodialysis exploiting the greater stability of the EDTA complex with nickel. The Ni-(EDTA)<sup>2-</sup> complex and hydrated Co<sup>2+</sup> ions are transferred from the feed solution to the electrodialysis anolyte and catholyte chambers respectively.

The results obtained show separation of nickel ions from cobalt sulphate solution can be achieved in the presence of EDTA as a complexing agent using a three-compartment electrodialysis cell. The transfer and the fate of EDTA in the cells shows that EDTA transferred to the anolyte as a metal complex and was destroyed on the anode surface to release the hydrated Ni ions but that these ions can not cross the anion exchange membrane to return to the feed or catholyte compartments. In the catholyte chamber most of the cobalt ions will remain in solution but the metal can be deposited on the cathode by increasing the pH to 4-4.5<sup>(12)</sup>. The optimised conditions for the removal of nickel from cobalt sulphate solution are : a) an EDTA:Ni mole ratio of 1:0.85, b) a sulphuric acid concentration of 0.03-0.05 mol dm<sup>-3</sup> in the feed chamber, c) a current of 1.0 amp and d) sufficient time to complete the electrodialysis separation. The current efficiencies of cobalt and nickel separation are low because of the competitive transport of protons and hydroxide ions through the cation and anion exchange membranes respectively.

The use of electrodialysis for cobalt-nickel separation using alternative complexing agents such as citric acid, salicylaldoxime, high acid concentration of hydrochloric acid, and acetic acid was found to be ineffective.

Use of EDTA in a three-compartment cell for electrodialysis with other metal mixtures, such as Co-Cu, and Co-Pd, also gave good separations because of differences in the stability constants of the complexes. No significant separation of zinc or iron from cobalt could, however, be achieved using EDTA as complexing agent in the three-compartment cell.

### 4.3 REFERENCES

- [1] J. D. Donaldson, S. M. Grimes and S. J. Clark, "Cobalt in Chemistry the Monograph series", published by The Cobalt Development Institute, 1986.
- [2] L. Rosato, G.B. Harris and R.W. Stanley, *Hydrometallurgy*, (1984) **13**, 34.
- [3] B. K. Tait, *Hydrometallurgy*, (1993) **32**, 365.
- [4] Li Longquan, Wang Cheng and Li Yadong, *Journal of Membrane Science*, 1997, **135**, 173-177.
- [5] M. Labbe, J. Fenyo and E. Selegny, *Separation Science*, 1975, **10** (3), 307-322.
- [6] Abstract of: B. N. Laskorin, D. D. Slesareva and E. V. Zharova, USSR. Zh. Prikl. Khim(Leningrad), 1975, **48**(7), 1442-1447.
- [7] Abstract of: F.I Brouchek, Sh.P. Gotsiridze and E.A. Kochiashvili, "Separation of Cobalt and Nickel from Accompanying Elements by Using the Fluoride and EDTA forms of Anion Exchangers", Akad. Nauk Gruz. SSR, (1972), **66**(3), 593-596.
- [8] M. Kubal, T. Machula and N. Strnadova, *Separation Science and Technology*, 1998, **33** (13), 1969-1980.
- [9] M.V. Rozhkova, V.A. Shaposhnik, I.P. Strygina, and L.V. Artemova, *Russian Journal of electrochemistry*, 1996, **32**(2), 237-240.
- [10] Yu. V. Karlin and V. N. Kropotov, *Russian Journal of Electrochemistry*, 1994, **30**(3), 362-363.
- [11] A.T. Cherif, A. Elmidaoui and C. Gavach, *Journal of Membrane science*, 1993, **76**, 39-49.
- [12] J. D. Donaldson, Ullmann's, "Encyclopaedia of Industrial Chemistry, Cobalt and Cobalt Compounds", Fifth edition, vol. A7, 1986.
- [13] N.N. Greenwood and A. Earnshaw, "Chemistry of the Elements", Pergamon Press, 1984.
- [14] J. D. Donaldson, S. J. Clark and S. M. Grimes, "Cobalt in Medicine, Agriculture and the Environment", The Monograph Series, Published by the Cobalt Development Institute, 1986.
- [15] R. A. Goyer, C. D. Klaassen and M. P. Waalkes, "Metal Toxicology", Academic Press, 1995.

- [16] F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, "Advanced Inorganic Chemistry", 6th edition, A Willey-Interscience Publishers. 1999.
- [17] D. Nicholls, "Complexes and First-Row Transition Elements", Macmillan Education LTD, 1986.
- [18] A.R. Burkin, "Extractive Metallurgy of Nickel; Critical Reports on Applied Chemistry", Vol 17. Society of Chemical Industry, John Wiley and Sons LTD, 1987.
- [19] A.G. Sharpe, "Inorganic Chemistry", third edition, Longman Scientific & Technical, 1992.
- [20] D. G. Crosby, "Environmental Toxicology and Chemistry", Oxford University Press, 1998.
- [21] T. S. West, "Complexometry with EDTA and Related Reagents", BDH Chemicals LTd, 1969.
- [22] R. Pribil, "Analytical Applications of EDTA and Related Compounds", Pergamon Press, 1972.
- [23] Revised by: G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, "Vogel's, Textbook of Quantitative Chemical Analysis", Fifth Edition, Longman Scientific & Technical, 1989.
- [24] K. Scott, "Electrochemical Processes for Clean Technology", The Royal Society of Chemistry, 1995, UK.
- [25] R. Eliot Stauffer, "Techniques of Organic Chemistry, Volume III, Chapter V, Dialysis and Electrodialysis", Interscience Publishers LTD., London, 1950.
- [26] J. D. Norton and M.F. Buehler, *Separation Science and Technology*, 1994, **29** (12), 1553-1566.
- [27] Y. Osada and T. Nakagawa, "Membrane Science and Technology", Marcel Dekker, Inc. 1992.
- [28] G.F. Grot, "Nafion as a Separator in Electrolytic Cells", Du Pont Company, USA, 1986.
- [29] Information provided from Solvay company.
- [30] D. D Perrin, "Stability Constants of Metal-ion Complexes, Part B, Organic



Ligands", IUPAC Chemical Data Series-No. 22, Pergamon Press, 1979.

[31] M. A. Jan, Ph. D. Thesis, Brunel University, London, UK, 1996.

## CHAPTER FIVE

### A NOVEL COMBINATION OF ADSORPTION AND ELECTROLYTIC PROCESSES FOR THE REMOVAL OF DYE FROM AQUEOUS SOLUTION

5.1	INTRODUCTION .....	197
5.2	WHAT IS A DYE? .....	197
5.2.1	<i>Classification of Dyes:</i> .....	198
5.2.1.1	Classification According to Constitution.....	198
5.2.1.2	Classification According to Application:.....	198
5.2.2	<i>Characteristics of Dye Industrial Effluent</i> .....	200
5.2.3	<i>General Health and Environmental Problems Associated with Dye Use and Disposal</i> .....	202
5.3	DYE TREATMENT METHODS.....	202
5.3.1	<i>Adsorption</i> .....	203
5.3.2	<i>Degradation of Dyes in Aqueous Solution Supersaturated with Oxygen by Irradiation with High Energy Electron Beams</i> .....	204
5.3.3	<i>Ozonation</i> .....	204
5.3.4	<i>Degradation of Dyes by Fenton's Oxidation</i> .....	204
5.3.5	<i>Photocatalytic Oxidation</i> .....	205
5.3.6	<i>Electrochemical Treatment</i> .....	205
5.3.6.1	Electrocoagulation .....	205
5.3.6.2	Electro-oxidation .....	206
5.3.6.3	Theory of Electro-oxidation Process .....	208
5.4	ACTIVATED CARBON .....	209
5.5	DETERMINATION OF THE DYE CONCENTRATIONS.....	210
5.6	EXPERIMENTAL.....	214
5.7	RESULTS AND DISCUSSION .....	214
5.7.1	<i>Anodic Oxidation</i> .....	214
5.7.1.1	Electrolysis of Dye Materials.....	215
5.7.1.2	The Effect of the Electrolyte Concentration on the Electrolysis of Reactive Dyes .....	217
5.7.1.3	The Effect of the Current Input on the Electrolysis of Reactive Blue 2 .....	220
5.7.2	<i>The Identification of the Intermediate Compound Formed During the Electrolysis of Methylene Blue</i> .....	222
5.7.2.1	HPLC Study of Methylene Blue Derivatives:.....	233
5.7.3	<i>Combination of Electrolysis and Adsorption for the Destruction of Different Dye Solutions.</i> .....	235
5.7.3.1	The Study of Combined Electrolysis and Adsorption on the Destruction of Methylene Blue .....	236
5.7.3.2	Electrolysis of Methylene Blue Using Configuration (1) .....	237
5.1.1.1	Electrolysis of Methylene Blue Using Configuration (2) .....	246
5.1.1.2	Electrolysis of Methylene Blue Using Configuration (3) .....	246

5.1.1.1	The Study of Combined Electrolysis and Adsorption on the Destruction of Acid Blue 25	257
5.1.1.1	The Study of Combined Electrolysis and Adsorption on the Destruction of Reactive Blue 2 and Reactive Blue 15.....	263
5.1.1.2	Reactive Blue 2 .....	263
5.1.1.1	Reactive Blue 15 .....	268
5.1.1.1	Industrial Trial.....	273
5.2	DISCUSSION .....	276
5.3	REFERENCES.....	283

## 5.1 INTRODUCTION

Dyeing and finishing steps have become an integral part of the textile manufacturing process. These steps involve treating the fibres to the desired permanent colour and processing into commercial products. However, these processes produce a considerable amount of wastewater that is released into the environment. The effluents are high in colour, chemical oxygen demand, pH, and suspended solids<sup>1</sup>, properties that can make the wastewater dangerous to aquatic life. Increasingly stringent regulations on wastewater have changed the priority for the textile industry to achieve removal of potentially toxic pollutants before discharge into the environment<sup>2</sup> and this includes minimising the chemical oxygen demand in the effluent<sup>3</sup>. Textile wastewater is usually treated to reduce its pollution load after the water leaves the textile plant. However, certain types of pollution, such as colour, heavy metals and electrolytes, are not easily removed by conventional biological waste treatment methods. This is not surprising because dyestuff manufacturers recently have been aiming at the development of dyestuffs that are as stable as possible<sup>4</sup>.

In this work, the main objective is to study electrochemical oxidation as a method for the decolourisation of model dye solutions.

## 5.2 WHAT IS A DYE?

Dyes<sup>5</sup> are individual organic chemical compounds, which are coloured and ionised in appropriate solvents. Dissolved dyes absorb light of wavelengths covering the range 400-800nm. Dye molecules contain groups responsible for the colour (chromophores). Chromophores include nitro (-NO<sub>2</sub>), nitroso (-NO), azo (-N=N-), ethylene (-CH=CH-) and carbonyl (-COO-) groups. Most dyes also include basic groups such as -NH<sub>2</sub>, -NH(Me), -N(Me)<sub>2</sub> as cations (= <sup>+</sup>N Me Cl<sup>-</sup>) or weakly acidic groups -SO<sub>3</sub>H, -OH, -COOH as anions (-O<sup>-</sup>, -SO<sub>3</sub><sup>-</sup>).

### 5.2.1 Classification of Dyes:

There are different ways to classify dyes and pigments according to their structure or to the method of application to a substrate. Neither system of classification is really satisfactory. The same chromophoric system may be present in dyes differing widely in structure and application because they have different solubilising groups. A brief description of both the classifications is now presented.

#### 5.2.1.1 Classification According to Constitution

The Colour Index<sup>6</sup> classifies dyes on chemical structure or on the chromophoric system. The most common structure types of this classification are summarised in Figure [5.1]<sup>7</sup>.

#### 5.2.1.2 Classification According to Application:

Dyes may be classified by fibre type, such as dyes for nylon, cotton, polyester or by their method of application to the substrate including for example<sup>7-8</sup>:

1. **Basic dyes:** sometimes called the cationic dyes, which are usually hydrochlorides or salts of organic bases. They give high tinctorial strength but low fastness to light and are applied to wool, silk and tannin-mordant cotton, and used in the manufacture of colour paper, printing inks and cosmetics. An example is methylene blue.
2. **Acid dyes:** are sodium salts usually of sulphonic acid, but in a few cases of carboxylic acids. They are applied mainly to protein and polyamide fibres. An example is acid blue.
3. **Direct dyes:** resemble acid dyes in being sodium salts, but they have a direct affinity for cellulosic fibres.
4. **Mordant dyes:** have no natural affinity for textiles, but are applied to cellulosic or protein fibres which have been pre-treated with a metallic compound such as sodium dichromate.
5. **Sulphur dyes:** Little is known about the chemical structure of these dyes. They are complex organic compounds containing sulphur and are used in processes in which the initial products are baked at temperatures above 200°C.
6. **Azo dyes:** are used for dyeing cellulosic fibres. They are insoluble pigments and build up within the fibre by padding with a soluble coupling component and then

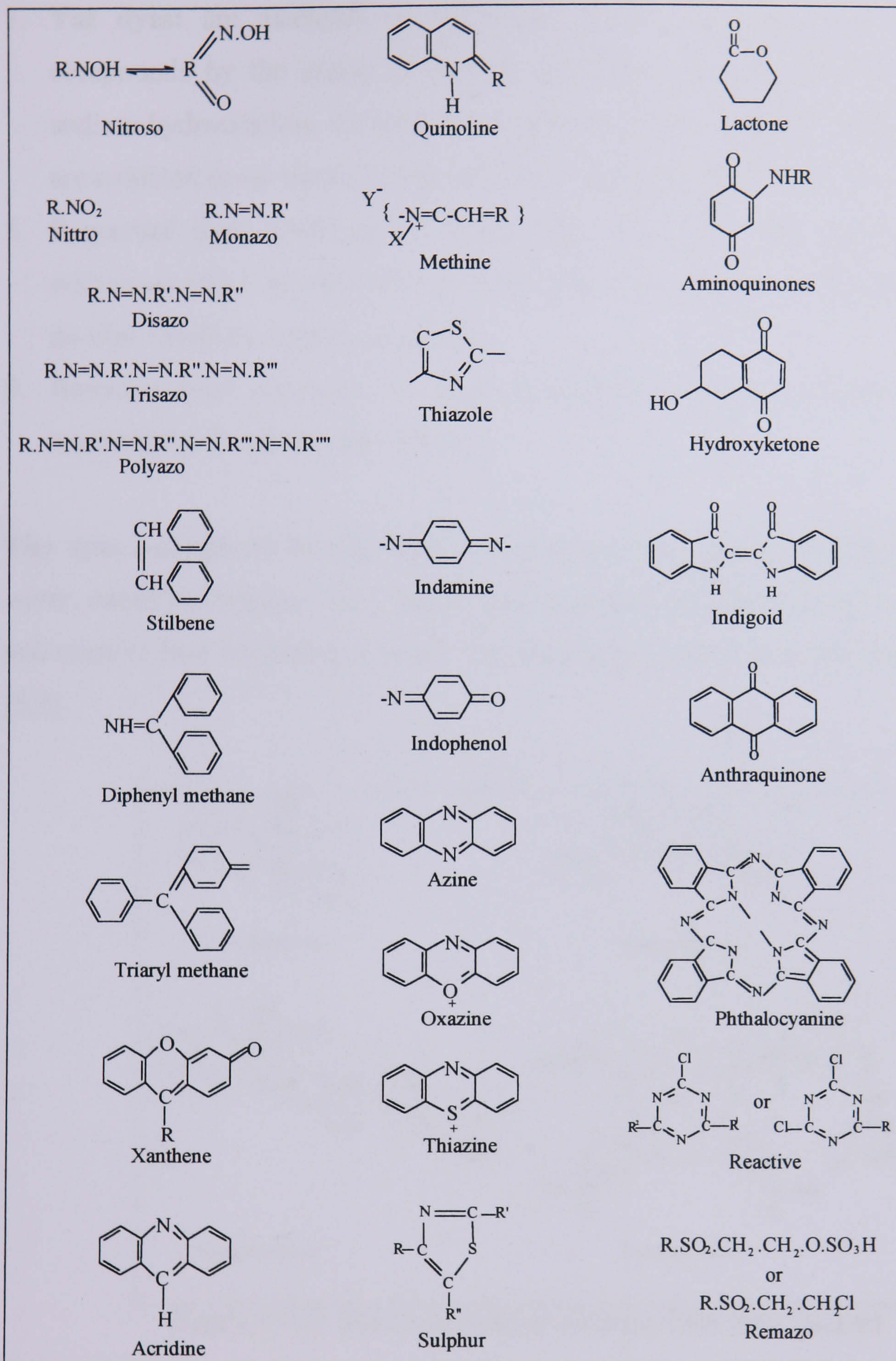


Figure [5.1]: The groups and the typical structure units according to the constitution classification

treating with a diazotized base.

7. **Vat dyes:** are insoluble in water but can be converted into soluble leuco compounds by the action of sodium hydroxide and a reducing agent such as sodium hydrosulphite. Cellulose has an affinity for these leuco compounds, which are oxidized to an insoluble pigment after being absorbed by the fibre.
8. **Dispersed dyes:** Hydrophobic fibres often dye better with insoluble dyes than with those which are dissolved in water. Dispersed dyes are suspensions of finely-divided insoluble organic pigments.
9. **Reactive dyes:** can enter into chemical combination with cellulose and include: reactive blue 2 and reactive blue 15.

The dyes considered in this study are of three types chosen for their solubility in water, namely methylene blue (basic dye), acid blue 25 (acidic dye), reactive blue 2 and reactive blue 15 (reactive dyes). The structures of these dyes are shown in Figure [5.2].

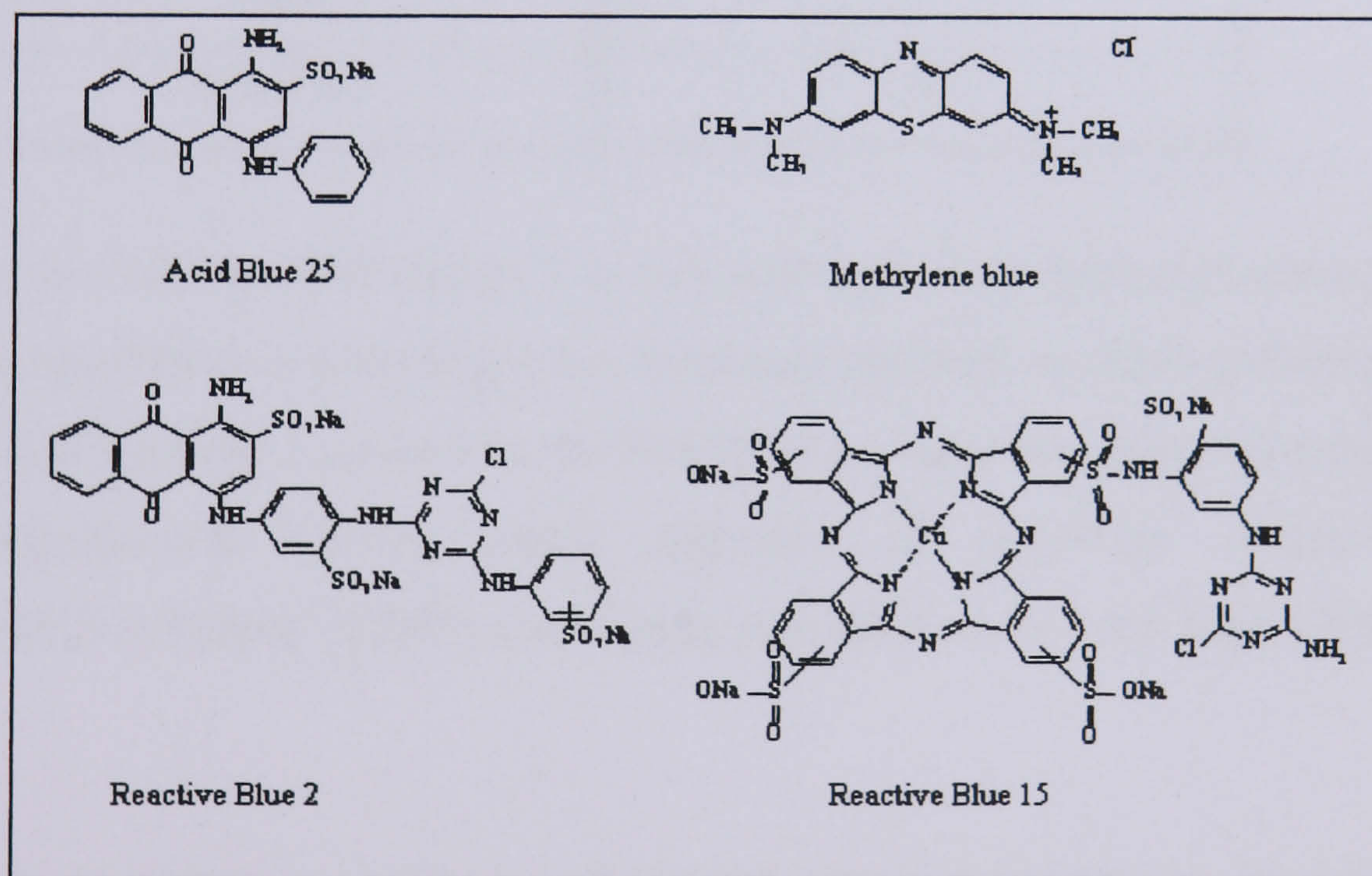


Figure [5.2]: The molecular structures of the dyes studied.

### 5.2.2 Characteristics of Dye Industrial Effluent

As the major components of the effluent are organic, bacteria in the water will try to utilise the compounds as a nutrient source by breaking them down. This will affect the Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) leaving less dissolved oxygen available for other organisms<sup>2</sup>.

Table [5.1] shows the typical percentages of dyes present in textile wastewater<sup>2</sup>. The water insoluble dyes (disperse, vat, sulphur, azo dyes) are removed in a primary settling treatment, whereas, water soluble dyestuffs, basic and direct dyes, are almost all removed by bioelimination, as are most (but not all) acid dyes. For reasons that are not understood, reactive dyes are not removed by conventional biomasses to any great degree (maximum of 30%, and only 10% average) and about 90% of a reactive dye is discharged to the river systems<sup>4</sup>.

Table [5.1] : Dye concentration of different dye classes in textile wastewaters.	
Dye	Waste dye (%)
Direct	10
Disperse	5
Basic	2
Acid	5
Reactive	30

Fluctuation in COD and pH (range 2 to 12) and high rinse water temperatures (up to 90<sup>0</sup>C) cause problems in choosing a dye treatment method. Another pollution problem associated with dyeing is caused by the formulations used for sizing man-made fibres. These formulations include small amounts of polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC) and starch and leads to a very high COD in rinse water.

The final textile effluent, which has often stable physically and chemically properties, is classified under three main areas, depending on the COD levels:

- 1- High strength wastewater which has COD exceeding 1600 mg/l with strong dark colour and very low transparency.
- 2- Medium strength wastewater which has COD between 800 and 1600 mg/l.
- 3- Low strength wastewater which has COD of less than 800 mg/l.

Table [5.2] summarises the characteristics of typical textile wastewaters<sup>1</sup>.



Table [5.2]: <i>Characteristics of typical textile wastewaters.</i>							
Type	BOD (mg/l)	COD (mg/l)	pH	Suspended Solid (mg/l)	Temperature (°C)	Oil (mg/l)	Conductivity (µS)
High	500	1500	10	250	28	50	2900
Medium	270	970	9	137	28	21	2500
Low	100	460	10	91	31	10	210

### 5.2.3 General Health and Environmental Problems Associated with Dye Use and Disposal<sup>9</sup>

All dyes lead to common health and environmental problems. The majority are irritants, some are suspected carcinogens and possibly toxins, although their toxicology, in general, has not been studied thoroughly. The main pathways of entry into the body are inhalation, ingestion or absorption through the skin. The target organs affected by exposure to the dyes are generally the eyes, mucous membranes, lungs, nasal passages and the upper respiratory tract.

As most of the dyes are based on aromatic compounds they will have inherent effects on the environment. The greatest effect is probably persistence because benzene-derived structures are so stable and resistant to degradation by bacterial means. In water, the problem is immense not only in terms of effects on wildlife, but also on the aesthetic quality of waterways.

## 5.3 DYE TREATMENT METHODS

Dyeing manufacturers are using various processes to try and reduce the impact of wastewater. These processes consist of traditional methods, which are constantly being modified as new technology is being introduced. Many of the dyes are, however, difficult to remove, as they are stable to light and heat and are biologically non-degradable.

The concept of re-use is an extremely important one in the waste management hierarchy. Most of the processes that have been studied have been focused on cleaning

the water to the levels stipulated by regulatory bodies. This is indeed important but with the demands on the water resource growing all the time more resources should be devoted to developing processes that permit material and water reuse. The conventional methods used to purify dye wastewater before being released into the environment or prior to discharge to an aerobic biological treatment are based on physical or physicochemical processes. Although chemical treatments can be used problems do occur because of the large variability in wastewater composition and the possibility of generating other pollution problems associated with the chemicals used<sup>9</sup>. All the methods in use have specific advantages and disadvantages and are now described briefly.

### **5.3.1 Adsorption**

Adsorption seems to be the most popular technique due to its ease of operation, but there are drawbacks. The vast majority of adsorbents used are relatively expensive and they tend to be effective for some dyes and not for others<sup>10</sup>. An ideal adsorbent would be one that has a short contact time, high ratio of dye to adsorbent, effective over a large range of dyes, with easy regeneration and, perhaps the most important, low cost. Most work, however, seems to have been on the use of waste products as adsorbents, (e.g. woolwaste, activated alumina, molecular sieve, and sawdust, etc)<sup>10-11</sup>. This is fine in theory but unless it can be utilised by industry in a practicable and large-scale way it serves no purpose. The main problems with the adsorption technique is that it produces a sludge or suspension that requires further treatment and that it does not break down the potentially toxic compounds present in the effluent.

It can be assumed that the dye would be transferred into the adsorbent material in the following three ways<sup>11</sup>:

- Diffusion of dye molecules in aqueous phase to the adsorbent surface.
- Adsorption of dye on the outer surface of the solid
- Penetration and fixation of dye molecules in pores distributed throughout the whole interior of the solid.

The first adsorption stage usually takes place when the concentration gradient within the particles is high enough to allow for rapid transfer of the dye molecules to the outer surface of the adsorbant. The second stage occurs when water molecules

penetrate into pores of the solid.

### **5.3.2 Degradation of Dyes in Aqueous Solution Supersaturated with Oxygen by Irradiation with High Energy Electron Beams**

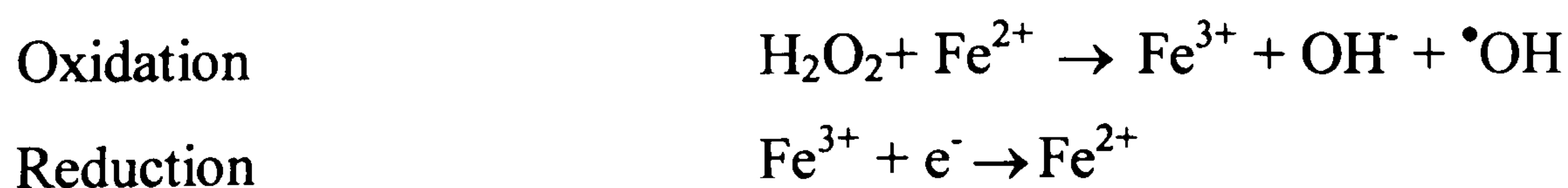
A method<sup>12</sup> that has been used in recent years for wastewater treatment involves irradiation with a high-energy electron beam. This method involves rapid consumption of the dissolved oxygen which has to be supplied during the process. This has been achieved in methods described by Kawakami et al<sup>13</sup>, Suzuki et al<sup>14</sup> and Hashimoto et al<sup>15</sup> using a dual-tube oxygen bubbling reactor in which the sample circulates at high oxygen pressure from the bottom of the reactor. In this way, high dissolved oxygen concentration is maintained for a short period after the pressure is reduced to atmospheric level, during which the sample solution can be irradiated by the electron beam. In order for this method to be successful, the sample has to be first pressurised with oxygen up to 0.3Mpa to increase the dissolved oxygen concentration. Not all dyes, however, can be destroyed by this method and it is expensive to operate.

### **5.3.3 Ozonation**

One method that has been proposed in recent years is ozonation. This involves feeding dried ambient air into an ozone generator to give a product containing approximately 1% ozone. The ozone/air mixture from the generator is then mixed with the dye effluent in an aspirator to the effluent reactor. Results from this method have shown it to be quite effective in the removal of dyes from wastewater but it has also been proven to be expensive and further development is needed<sup>16</sup>.

### **5.3.4 Degradation of Dyes by Fenton's Oxidation**

Fenton's reagent,  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ , is a method that has been used in the textile industry to remove colour from dye effluent. Studies have shown that the oxidative catalytic system  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  is very good for the destruction and decolourisation of industrial wastewater<sup>17</sup>. In this process there is a continuous oxidation / reduction cycle:



The  $\cdot\text{OH}$  radical can catalyse the destruction of the organic materials<sup>2</sup>.

### **5.3.5 Photocatalytic Oxidation.**

There is a growing interest in the photocatalytic degradation of certain kinds of organic pollutants using UV light, in combination with  $\text{H}_2\text{O}_2$  and in the presence of heterogeneous semiconductor catalysts such as  $\text{TiO}_2$  and  $\text{SnO}_2$ . In this process the irradiation enhances the production of electrons on the surface of the semiconductor at the conduction band, and positive holes are formed in the valence band. The negative electrons and positive holes can be either recombined and produce thermal energy, or can interact with other molecules, which results in the oxidation of complex organic compounds. It was found that COD could be simultaneously reduced by this method of removing the colour from sewage. The process is dependent upon pH, wavelength, light intensity and molecular structure<sup>18-20</sup>.

### **5.3.6 Electrochemical Treatment**

Electrochemical methods of two types have been tested for colour removal:

- 1- Electrocoagulation.
- 2- Electro-oxidation.

#### **5.3.6.1 Electrocoagulation**

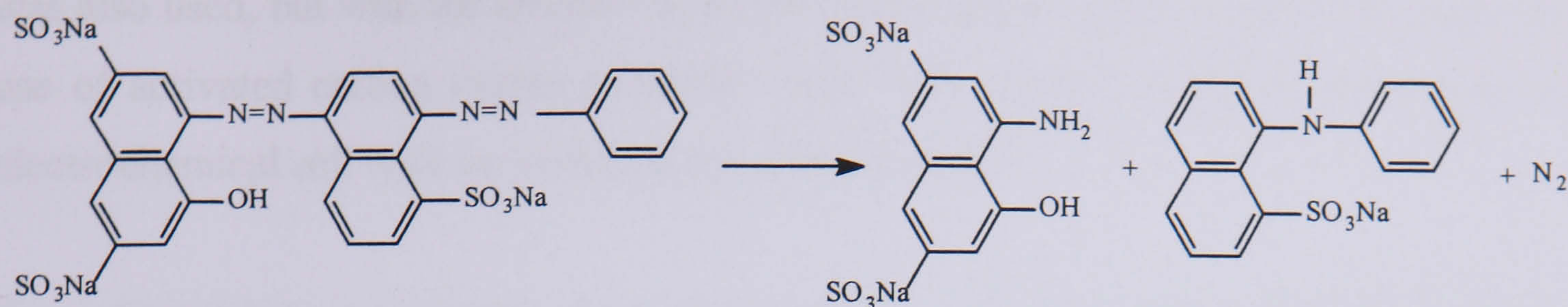
In general the cell used for electrocoagulation consists of a sacrificial anode made of iron or aluminium<sup>21</sup>. In the case of a sacrificial iron anode, the ferrous ions generated at the anode react with hydroxide ions resulting from water decomposition at the cathode and precipitate as hydroxide. If aluminium electrodes are used aluminium hydroxides are formed<sup>9</sup>. The dye molecules are reduced in the electrochemical cell to small organic molecules which are captured by the hydroxide precipitate which is then removed by sedimentation or by hydrogen flotation<sup>1, 22</sup>. Good decolourisation of textile wastewater has been achieved by this method, especially with the addition of a coagulant such as polyaluminium chloride (PAC)<sup>(1)</sup>. The drawbacks of using this method lie in the disposal of the hydroxide precipitates and the fact that different pH adjustment is required for each individual dye<sup>21</sup>. The method has been extended using bipolar packed beds with steel rings as bipolar electrodes<sup>23</sup> isolated from each other by a non-conductive material. A bipolar packed bed reactor is particularly convenient

in achieving high mass transfer because it has a large electrode surface area. By applying the voltage across the bipolar cell, one side of each particle becomes cathodic and the other side anodic. Although the process is effective and can be used in the treatment of textile wastewaters the drawbacks of hydroxide precipitate and pH adjustment still exist.

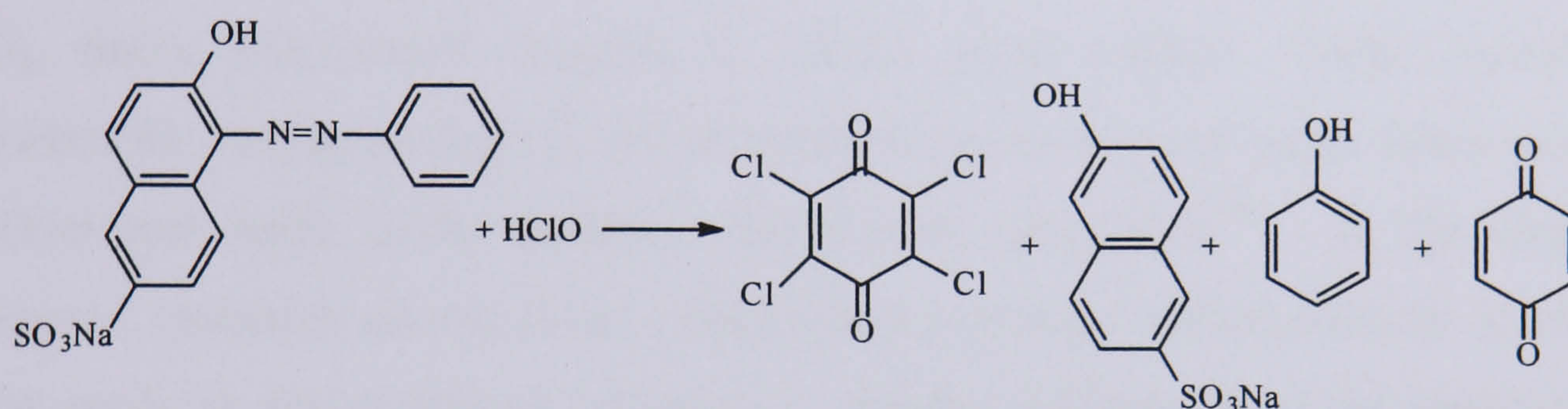
### **5.3.6.2 Electro-oxidation**

Anodic oxidation is a method of achieving the destruction of dye molecules in dye manufacturing and textile effluent<sup>24-27</sup>. This method was introduced in the early seventies and has been applied to treatment of wastewater from the textile and related industries. In electro-oxidation treatment, the pollutants are destroyed by direct anodic oxidation or by an indirect oxidation processes, converting all of the carbon and hydrogen atoms of the dye to carbon dioxide and water. In order to obtain a high destruction efficiency many different anodes and electrolyte solutions have been investigated for different dyes. M. S. E. Abdo et al<sup>26</sup>, used a lead sphere anode and sodium sulphate electrolyte to destroy direct dyes but suggested that decolourisation was due to the formation of colourless compounds obtained upon rupturing the dye molecule. Y. A. Borovskii et al<sup>27</sup> used platinized platinum, lead dioxide supported by graphite and, to a limited extent, ruthenium oxide-titanium anodes to destroy direct azo dyes from different media. They established that lead dioxide supported by graphite has the highest electrocatalytic activity and an acceptable corrosion stability. They also found that, during the electro-oxidation process, only the chromophore conjugated system in the visible region disappears which points to the fact that the molecule is only partially decomposed to colourless compounds. It is clear that more information is required to understand the mechanisms of anodic electro-oxidation.

A number of researchers have studied the mechanism of anodic oxidation of dyes, for example the synthetic acidic-dye (blue 2K) is decomposed according to the following reaction<sup>28</sup>:



It has been reported that in the presence of sodium chloride, as an electrolyte, there is evidence for the formation of chlorinated organic products<sup>24</sup>. Another acidic dye, light orange (6), for example, is oxidized in the presence of hypochlorite in the following way<sup>24</sup>:



Since these intermediates, and particularly the chlorinated compounds, may be more harmful to the aqueous environment than the dye molecules from which they are formed, it is necessary to identify the nature of the intermediates.

In the present work, results of studies on the compounds that are formed in the early stages of the electro-oxidation of methylene blue are reported and the crystal structure of one of the major products described. Furthermore, in order to eliminate the products, which were found, i.e. chlorinated compounds, a combination of an adsorption process and electrochemical process has also been developed. This combination was studied by Zhou et al<sup>29</sup> using a packed electrochemical cell filled with activated carbon mixed with mica and silica as isolator. They compared the decolourising of dyeing effluent using the bipolar system with and without applying an electric field. They found that the decolourising in the presence of an applied field is more effected than that with carbon only.

In the present work the combination of adsorption and the electrochemical process was also used, but with the absence of an isolator (mica or silica). This is because the use of activated carbon (semiconductor) alone was found to conduct current in an electrochemical cell with no evidence for a short-circuit.

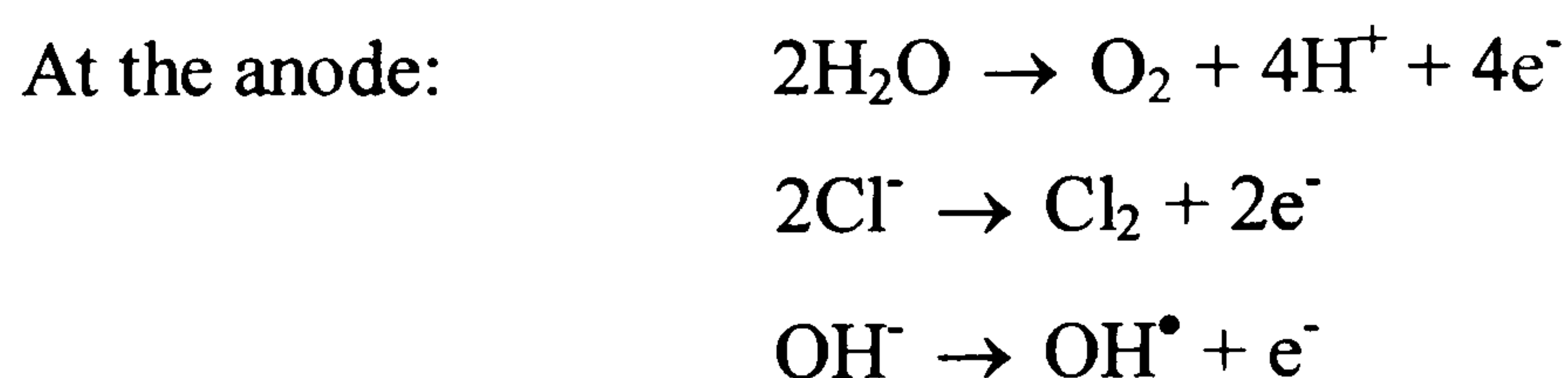
To understand the mechanism of anodic oxidation and of the adsorption taking place, a brief description of the theory of both techniques is now presented.

### 5.3.6.3 Theory of Electro-oxidation Process

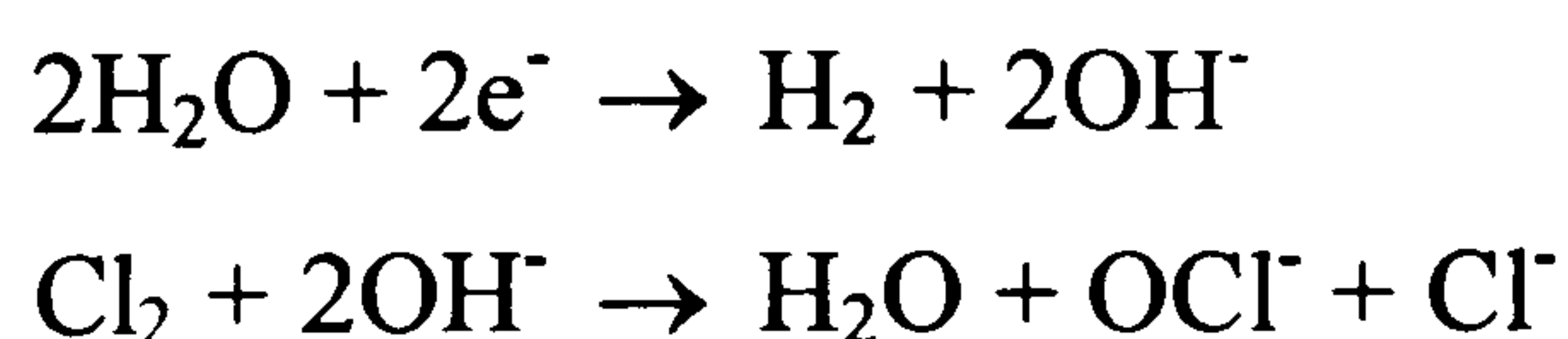
In this type of process, the electrochemical cell requires electrodes (mesh or plate) usually a cathode consisting of mild steel or titanium and a non-sacrificial anode with high oxygen evolution (usually platinised titanium (Pt/Ti), graphite, Pb, Pb-alloy, PbO<sub>2</sub>, SnO<sub>2</sub>, IrO<sub>2</sub>-coated titanium or mixed metal oxides). These anodes allow considerable voltage savings in the electrolysis processes and make them more cost-efficient and stable under technical electrolysis conditions<sup>30-31</sup>. In the electrolysis processes, reduction occurs at the cathode and oxidation occurs directly or indirectly at the anode so that undesired inorganic or organic compounds in the wastewater can be destroyed by electrolytic treatment. This process achieves the oxidation of organic compounds effectively with little consumption of chemicals and very little or no sludge production. Previous investigations have shown sodium chloride to be an effective electrolyte for this method for the removal of colour from wastewater. Three factors are responsible for the decolourisation at the anode in a NaCl electrolyte<sup>23</sup>:

- Active chlorine formation (Cl<sub>2</sub>, HOCl, OCl<sup>•</sup>)
- Oxygen evolution
- Dye destruction

The reaction that takes place at the electrodes in this experiment when sodium chloride is used are:



The corresponding cathode reactions are:



Previous work has shown that the most important of these factors is the formation of hypochlorite and free chlorine which act as oxidising agents<sup>23</sup>.

## 5.4 ACTIVATED CARBON

Activated carbon is an amorphous form of elemental carbon with high-surface-area and high-porosity. The raw materials for active carbons are usually sawdust, coconut shells, wood, black ash, charcoal or petroleum coke. The manufacture of activated carbons involves two main steps: the carbonisation of the carbonaceous raw material at temperatures below 800°C in the absence of oxygen, and the activation of the carbonised product. The methods of activation most commonly used are broadly divided into two main types: chemical activation and physical activation (the activated carbon products are called chemical carbons and physical carbons respectively). In the chemical activation process, the carbonisation and activation are performed in a single step by carrying out thermal decomposition (in the temperature range from 200 to 650°C) of the raw material impregnated with chemical agents (such as  $\text{H}_3\text{PO}_4$ ,  $\text{ZnCl}_2$  or  $\text{H}_2\text{SO}_4$ ). The common feature of these activating agents is that they are dehydrating agents which influence the pyrolytic decomposition and inhibit the formation of tar, acetic acid, methanol, etc., and enhance the yield of carbon. Physical activation involves gasification of the char in the mass of the active carbon by oxidation with water vapour, carbon dioxide, air or any mixture of these gases in the temperature range 850-1100°C. Oxygen is never used in the process as the oxidising gas because its reaction with the carbon surface is too rapid and violent.

The surface area of activated carbons is extremely high, ranging from 800 to over 1500  $\text{m}^2/\text{g}$  with different pore structures. These pores vary and can be divided into three categories:

- Micropores (diameters below 2nm).
- Mesopores (diameter between 2 and 50 nm).
- Macropores (diameters are larger than 50 nm).

Micro- and mesopores give the carbon its adsorptive capacity, whereas, granular activated carbons have also macropores. These allow a rapid access (throughout the particle) to the meso- and micropores, where the actual adsorption takes place. The pore size distribution in a given carbon depends on the type of the raw material and



the method of manufacture of the carbon<sup>32-33</sup>.

In this work a highly porous granular activated carbon of particle size 0.85-1.70mm supplied by BDH was used.

The key characteristic sought in this work for the combined electrochemical and adsorption methods is bipolarity which should give rise to high efficiency and low energy consumption. Applying an electric current to a solution containing activated carbon particles polarises the particles, forming micro-anodes and micro-cathodes at their two extremities, thus creating an infinite number of microelectrolytic cells in series. The effective number of cells created enhances the oxygen and hydrogen evolution and also enhances the adsorption properties of the activated carbon particles<sup>29</sup>.

## 5.5 DETERMINATION OF THE DYE CONCENTRATIONS

The quantitative determination of methylene blue, acid blue 25, reactive blue 2 and reactive blue 15 was by colorimetric methods using a Perkin-Elmer Lambda 9 UV/Visible/NIR spectrometer.

The spectra of these four dyes show absorption in two regions, the visible region and the ultra violet (UV) region. The intensity of the spectral lines is concentration-dependent and obeys the Beer Lambert Law.

Lambert's law expresses the relationship between incident ( $I_0$ ) and absorbed radiation [the transmitted light intensity ( $I$ )] at a given wavelength by the equation<sup>34</sup>:

$$I = I_0 e^{-Kd} \quad \text{Equation [5.1]}$$

Where:  $K$  = absorption constant and  $d$  = thickness in centimetres.

When concentration is considered, the Lambert-Beer law applies :

$$e = -\log I_0 / I = \epsilon c t \quad \text{Equation [5.2]}$$

Where: ( $e$ ) = known as absorption or optical density or 'extinction', ( $\epsilon$ ) = the molecular extinction coefficient, ( $c$ ) = concentration of solution in moles per litre and ( $t$ ) = thickness of the solution in centimetres.

The absorbance was measured using 1cm quartz cells, at the wavelength range from 750 to 200 nm, using distilled water as a reference material. The experimental spectrometer settings that were used are given in Table [5.3].

Slit	2 nm	Peak threshold	0.02 A
Scan Speed	60 nm min <sup>-1</sup>	Response	0.5 sec
Lamp	332.8 nm	Cycle/time	1/0.05 min

Different standard concentrations of dye solutions were prepared in the concentration range 2 to 50 ppm (1 to 10ppm, for methylene blue because concentrations above this range give saturated spectra). Table [5.4] shows the absorptions for different dye concentrations within the visible and UV regions. The calibration graphs were produced for the visible range peaks and found to be linear over the range studied. The spectra and the calibration curves, are shown in Figure [5.3] and [5.4] respectively.

Concentration mg dm <sup>-3</sup>	Absorbance							
	methylene blue		acid blue 25		reactive blue 2		reactive blue 15	
	UV range	Visible range	UV range	Visible range	UV range	Visible range	UV range	Visible range
1	0.1	0.2	--	--	--	--	--	--
2	0.2	0.43	0.035	0.035	0.04	0.03	0.049	0.049
3	0.25	0.59	--	--	--	--	--	--
5	0.5	0.9	0.12	0.07	0.14	0.06	0.19	0.09
10	1.05	1.8	0.28	0.14	0.4	0.12	0.49	0.19
30	--	--	0.92	0.41	1.39	0.31	1.62	0.59
50	--	--	1.45	0.62	2.1	0.53	2.26	0.98

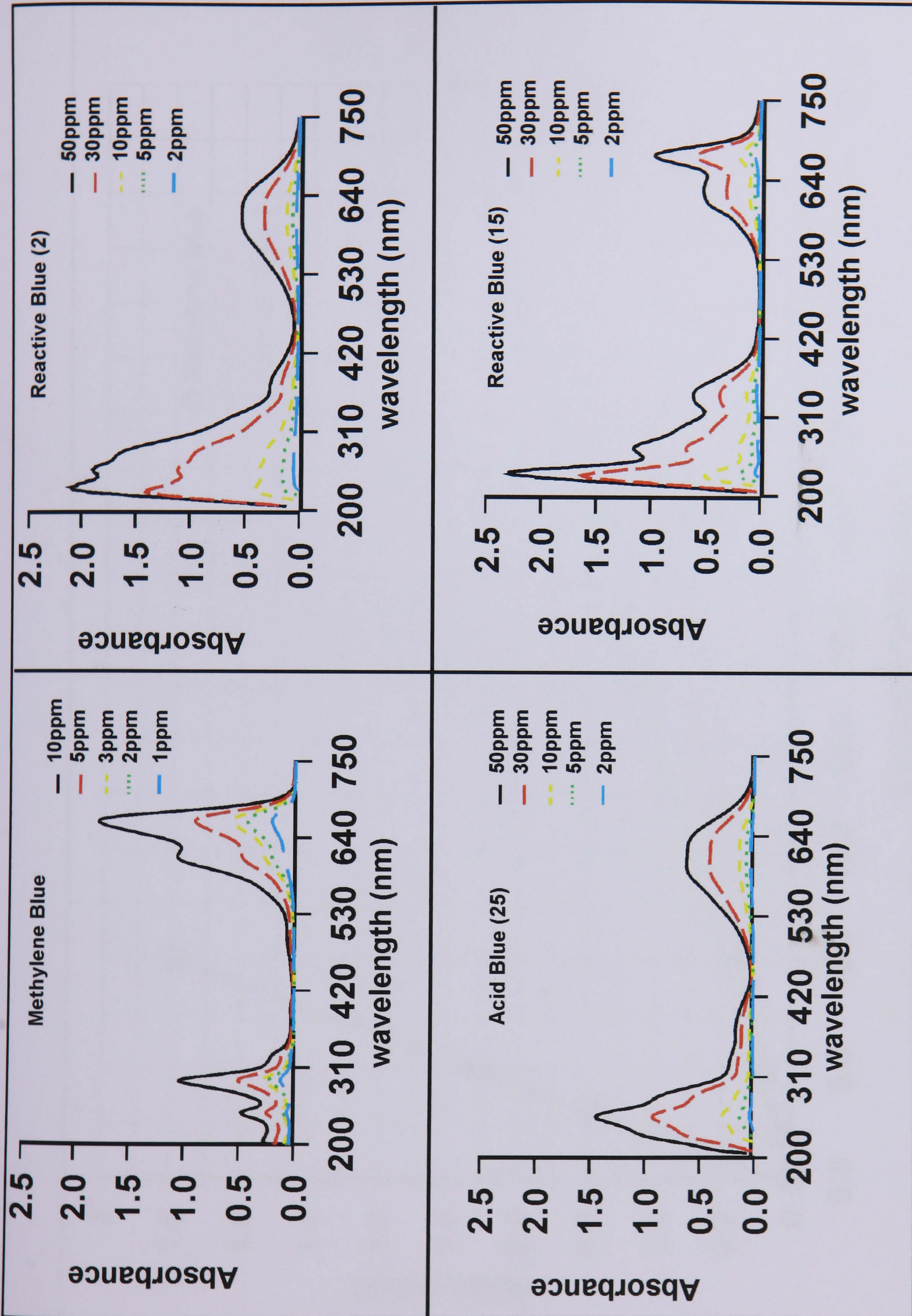


Figure [5.3]: UV/Visible spectra of Methylene Blue, Acid Blue 25, Reactive Blue 2 and Reactive Blue 15 at standard different concentrations

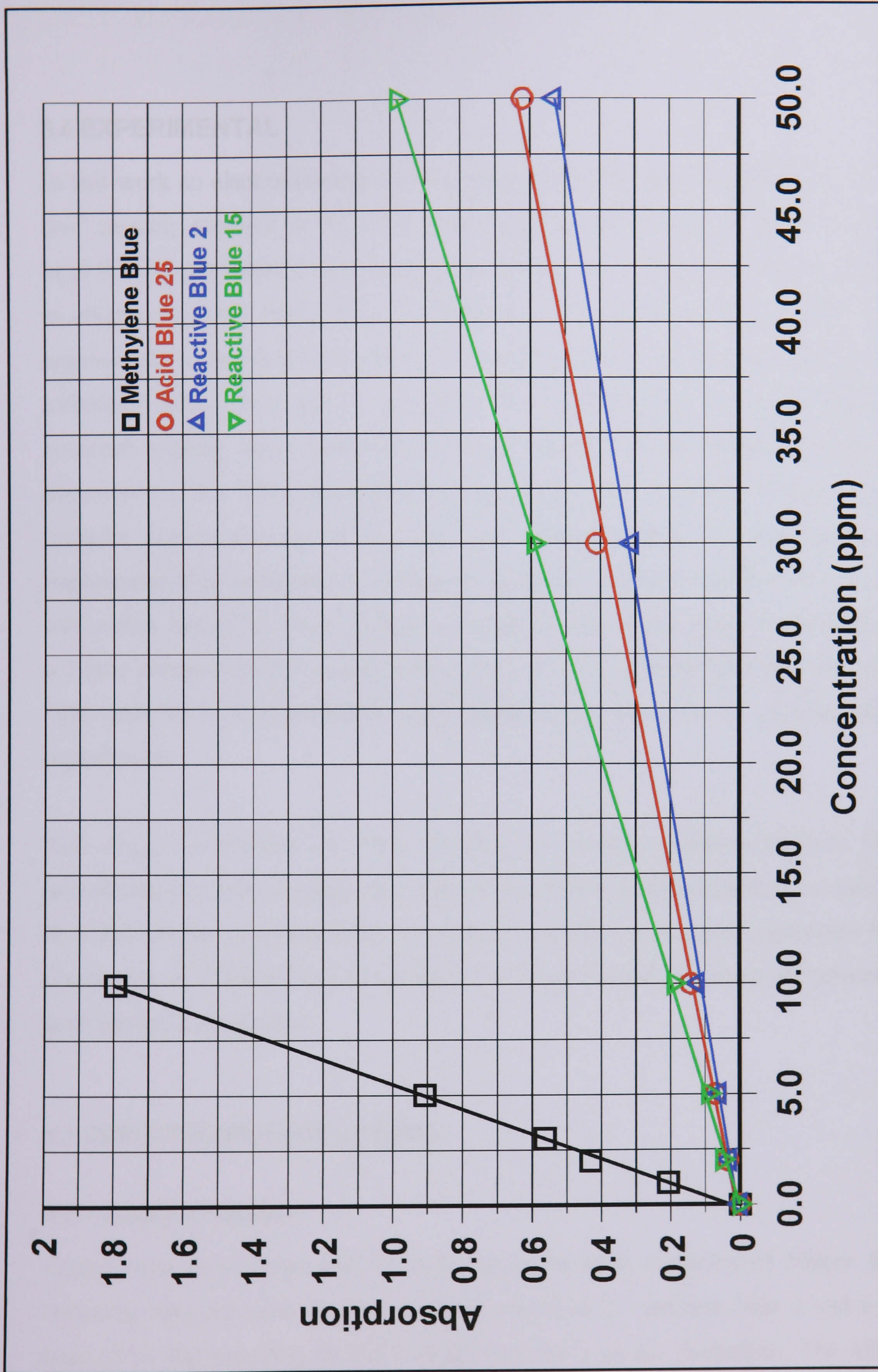


Figure [5.4]: Standard concentration line for Methylene Blue, Acid Blue 25, Reactive Blue 2, and Reactive Blue 15

## 5.6 EXPERIMENTAL

In this work an electrochemical cell, originally designed as a fluidised bed cell of 5 dm<sup>3</sup> capacity supplied by BEWT (Water Engineers Ltd) was used, without the glass bead fluidising material. The schematic diagram of this cell was shown in Figure [2.2] in chapter 2 of this thesis with the dimensions of the electrolysis chamber and the reservoir set to be 13.5x9x30 and 13.5x18.5x27cm respectively. The electrolyte was circulated with a flow rate of 3.5 l/min. Two mixed metal oxide mesh (chloride resistant) anodes were used with a single titanium mesh cathode of the same dimensions (7.5 x 12.8 cm<sup>2</sup>) and surface area (0.02 m<sup>2</sup>). A current of 1.5A to give a cathodic current density of 75 A/m<sup>2</sup> was applied unless otherwise stated. The experiments were conducted at ambient temperature and the electrolyte was circulated with a flow rate of 5.0 l/min. Samples of solution were taken every 15 minutes during a 2 hour period, only the sample time is recorded. The samples were also analysed by TOC and HPLC measurements. Experiments were performed in replicate and are reproducible.

This chapter is divided into three sections, (1) anodic oxidation of dyes, (2) the identification of intermediate compounds formed during the electrolysis of methylene blue and (3) the combination of electrolysis and electroadsorption processes for the destruction of different dyes in solution. The experimental processes are presented in each section individually.

## 5.7 RESULTS AND DISCUSSION

### 5.7.1 Anodic Oxidation

Experiments were performed to study the electrolytic oxidation of 50ppm for the following dye materials: methylene blue, acid blue 25, reactive blue 2 and reactive blue 15 in the presence of NaCl (0.03 mol dm<sup>-3</sup>) as an electrolyte. The effect of electrolyte concentration was studied on reactive blue 2 and reactive blue 15 and the effect of current was studied on reactive blue 15.

### 5.7.1.1 Electrolysis of Dye Materials

The UV/Visible spectra of the degraded dye solutions over 2 hours are shown in Figure [5.5] and the corresponding single run TOC data are in Table [5.5].

In the case of methylene blue, if the treated solution is stored for a further 24h period, a dark blue-black precipitate is formed. The colour of the acid blue 25 solution changed from dark blue to light pink after 15 minutes and the pink colour was found to disappear after 60 minutes. The solution of reactive blue 2 changed colour from dark blue to colourless immediately on applying the current. Reactive blue 15 solution showed no colour degradation over 2 hours electrolysis but storing the samples at room temperature for 24 hours resulted in colourless solutions. The stored samples were characterised by UV and TOC analysis.

Although the visible colours of dye solutions in the electrolytes were completely discharged after 1h, under the conditions of electro-oxidation used, absorptions in the UV-region show that organic material remains in the solutions. TOC results show slight decreases over the 2 hour electrolysis period.

Time (minutes)	TOC (ppm)			
	Methylene blue	Acid blue 25	Reactive blue 2	reactive blue 15
0	25.1	27.9	20.89	19.22
15	25.1	27.3	20.2	19.00
30	24.9	26.3	19.8	18.84
45	23.4	26.3	19.6	18.60
60	21.8	25.1	19.4	18.42
120	19.4	23.6	17.2	17.86

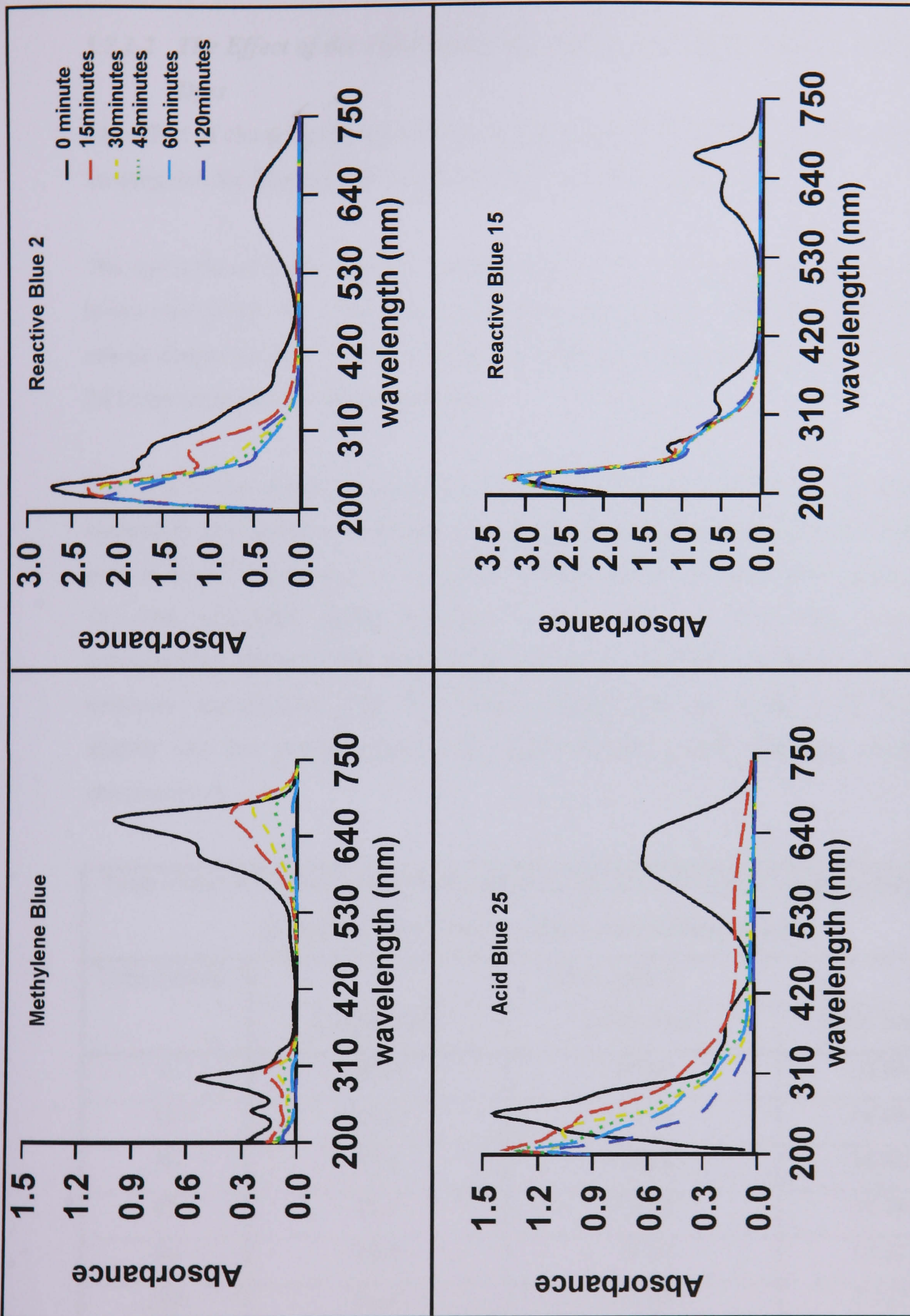


Figure [5.5]: UV/Visible spectra of the Methylene Blue, Acid Blue 25, Reactive Blue 2 and Reactive Blue 15, following electrolytic oxidation over 2 hours.

### 5.7.1.2 The Effect of the Electrolyte Concentration on the Electrolysis of Reactive Dyes

The effect of changing the electrolyte (NaCl) concentration (0.05, 0.1 and 0.2 M) was investigated for 50ppm of each reactive blue 2 and reactive blue 15.

The dye solution in the case of reactive blue 15 showed no colour removal after 2 hours electrolysis but extending the experimental time to 4 hours showed that the colour disappears after 3 hours. Storing the samples at room temperature for a further 24 hours results in colourless solutions.

The UV/Visible spectra (Figure [5.6] and Figure [5.7]) show that increasing the electrolyte concentration enhances the organic break-down to produce an additional peak in the UV region at a wavelength of 300nm for reactive blue 2 and reactive blue 15. The additional peaks increased in intensity with increasing electrolyte concentration showing that there is intermediate compound formation in the dye molecule degradations. The TOC values (Table [5.6] and Table [5.7]) decrease slightly and the general trend is for slight increases with increasing electrolyte concentration.

Table [5.6]: The effect of NaCl concentration on the TOC values in the degradation of reactive blue 2 using control electrochemical cell.			
Time (hours)	TOC (ppm)		
	0.05M NaCl	0.1M NaCl	0.2M NaCl
0	20.84	20.86	20.94
15	20.02	19.94	19.84
30	19.6	19.14	18.86
45	18.8	18.42	18.18
60	18.0	17.94	17.54
120	16.4	15.92	15.22



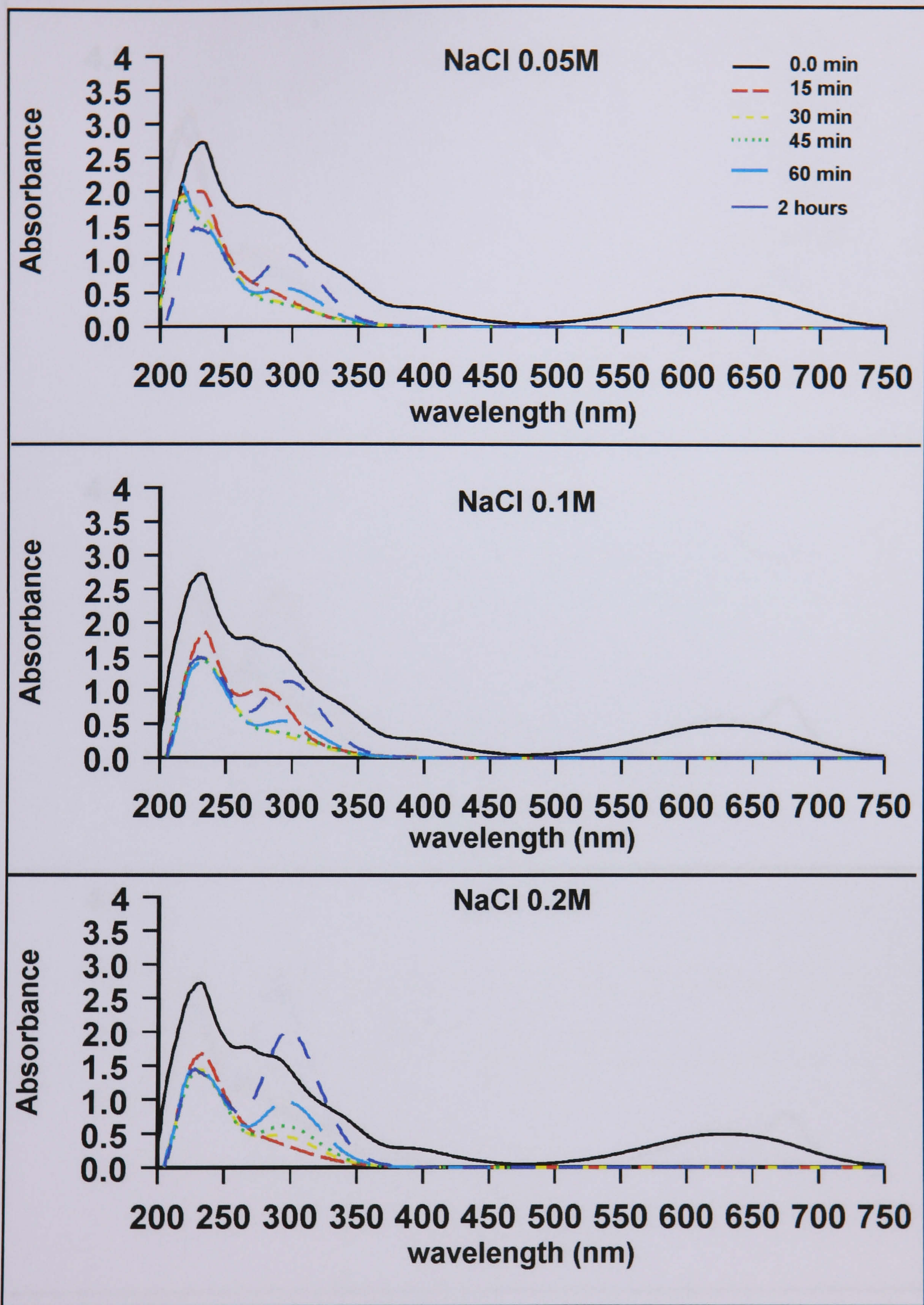


Figure [5.6]: UV/Visible spectra of reactive blue 2 following electrolytic oxidation. The effect of changing the electrolyte (NaCl) concentration.

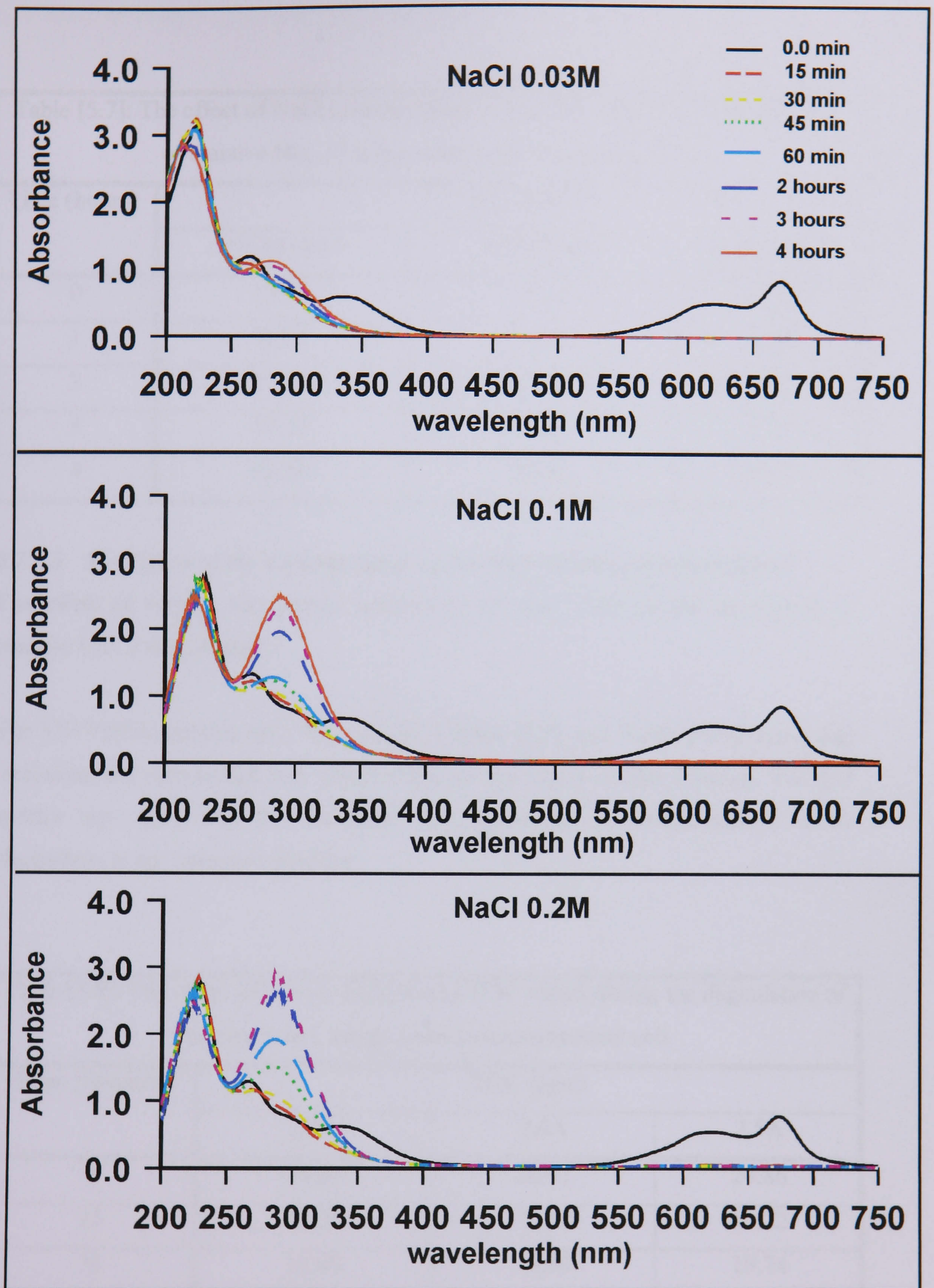


Figure [5.7]: UV/Visible spectra of reactive blue 15 following electrolytic oxidation. The effect of changing the NaCl concentration

Table [5.7]: The effect of NaCl concentration on the TOC values in the degradation of reactive blue 15 using control electrochemical cell.			
Time (hours)	TOC ppm		
	0.03M NaCl	0.1M NaCl	0.2M NaCl
0	19.22	19.18	19.16
1	18.42	18.34	18.28
2	17.86	17.66	17.58
3	17.22	17.10	17.02
4	16.96	16.82	16.64

### 5.7.1.3 The Effect of the Current Input on the Electrolysis of Reactive Blue 2

The effect of varying the current input (1.5, 2.0 and 2.5A) on the electrolysis of reactive blue 2 was studied.

The UV/Visible spectra and TOC results (Figure [5.8] and Table [5.8]) show that increasing the current has only small effect on the extent of dye removal. The UV spectra also show that the additional peak appearing at 300nm after 2 hours electrolysis is not current-dependent.

Table [5.8]: The effect of current input on the TOC values during the degradation of reactive blue 2 using control electrochemical cell.			
Time (minutes)	TOC (ppm)		
	1.5A	2.0A	2.5A
0	20.89	20.92	20.86
15	20.20	20.18	20.22
30	19.80	19.66	19.74
45	19.60	19.56	19.54
60	19.40	19.52	19.50
120	17.20	17.00	17.08

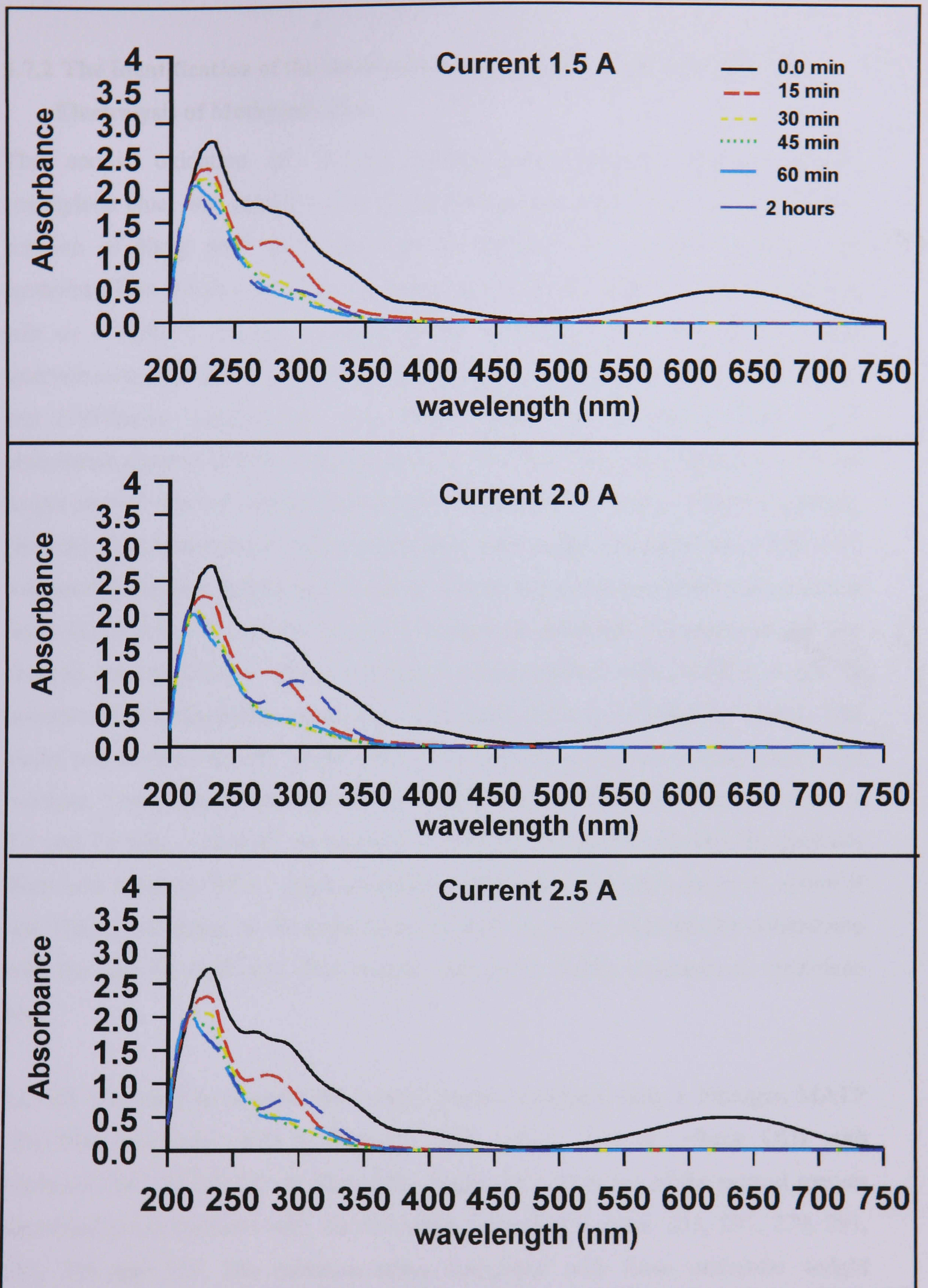


Figure [5.8]: UV/Visible spectra of reactive blue 2 following electrolytic oxidation. The effect of changing the current input.

### 5.7.2 The Identification of the Intermediate Compound Formed During the Electrolysis of Methylene Blue

The anodic oxidation of [3,7-bis (dimethylamino)phenothiazinium] chloride (methylene blue) was carried out in the electrochemical cell. The electrolyte was a solution of 50mg dm<sup>-3</sup> methylene blue in 0.03mol dm<sup>-3</sup> sodium chloride. The methylene blue solution used gave a single narrow HPLC peak at retention time 3.8 min on a PLRP-S column. Samples of the electrolyte were taken at 15 minute intervals over a period of 2 hours for analysis of the intermediate products by HPLC and UV/Visible spectroscopy. The HPLC eluate was monitored using a UV absorbance detector (Cecil 1100) operated at 290 nm. This was coupled to a 15 cm length and 4.5 mm o.d column packed with Pinnacle ODS 5 μm, a silica C<sub>18</sub> packing (Restek). A reversed-phase eluent, containing pH3 buffer and methanol (15:85 v/v), was used to separate neutral intermediates. Seven neutral intermediates with retention times of 6.6, 4.8, 3.7, 3.2, 2.8, 2.6 and 2.4 min were identified and characterised. For charged intermediates a 15cm × 4.5mm column packed with PLRP-S 5 μm (a polystyrene-divinylbenzene copolymer) was used with an ion-pairing eluent. The eluent was acetonitrile:pH3 buffer (50:50 v/v) containing 8 g/l tetramethylammonium bromide. Two charged intermediates were identified by HPLC with retention times of 5.4 and 7.6 min. A detector wavelength of 290 nm was used to identify the products from both columns. HPLC chromatographs of the dye compounds Azure A, Azure B and Thionin subjected to the electrolysis process were also obtained for comparison with the data for methylene blue because they have similar structures to methylene blue.

LC-MS was used to separate the neutral phases obtained using a Finnigan MATP SSQ7000 instrument with a Hypersil ODS column (10 cm ×3mm OD) with methanol:H<sub>2</sub>O (80:20 v/v) as the mobile phase. LC separation of the neutral species identified seven fractions with the following molecular weights: 215, 297, 279, 291, 311, 291 and 325. The retention times associated with these molecular weight fractions are 34, 69, 75, 90, 99, 104 and 162 seconds respectively. LC-MS chromatograms of the electrolyte sample and the peaks retention times (minutes) are shown in Figure [5.9], while the associated m/z (molecular weight) values for each eluated peak are shown in Figure [5.10].

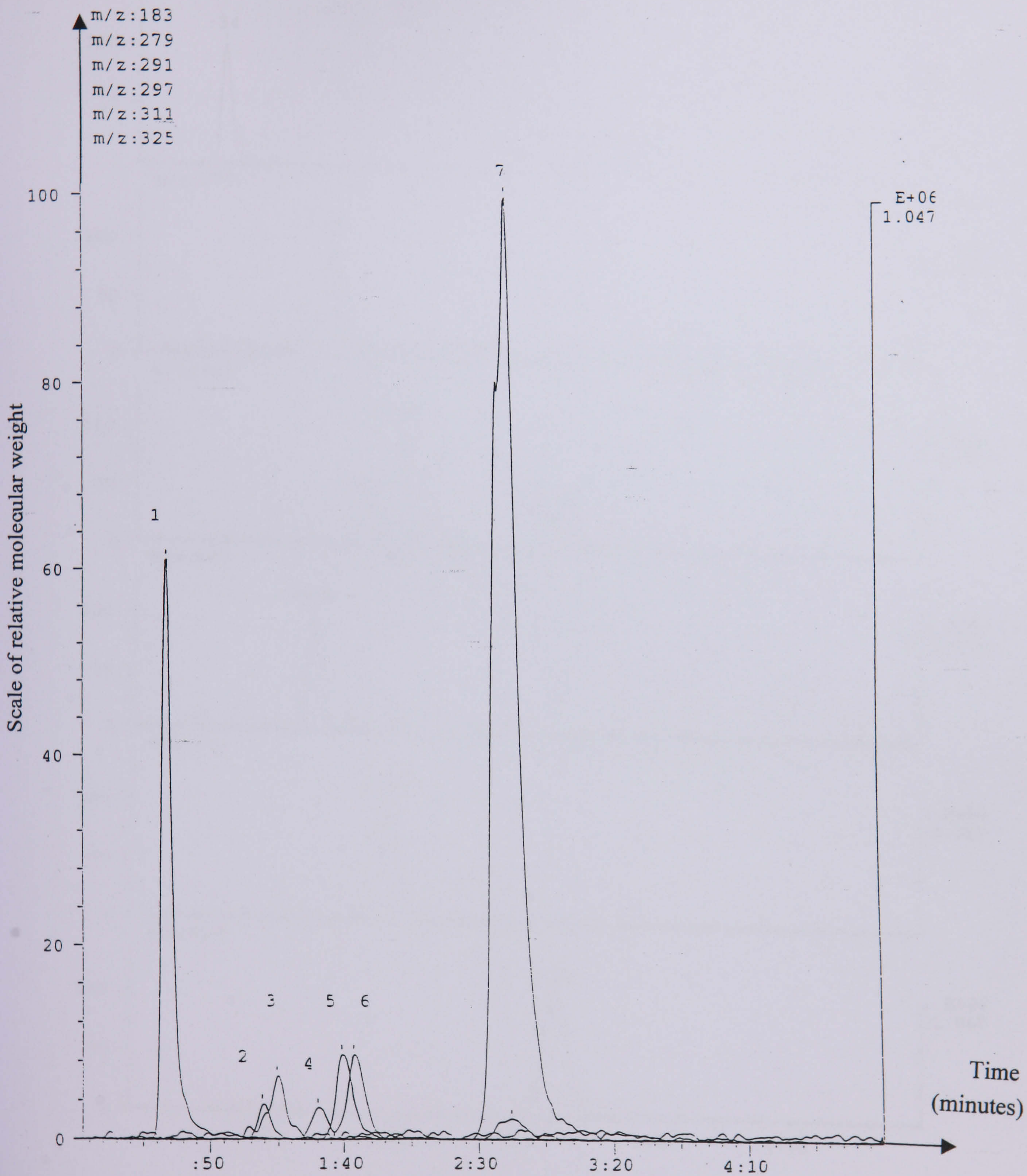


Figure [5.9]: The retention time of the eluted methylene blue sample after 15 minutes electrolysis using LC-MS.

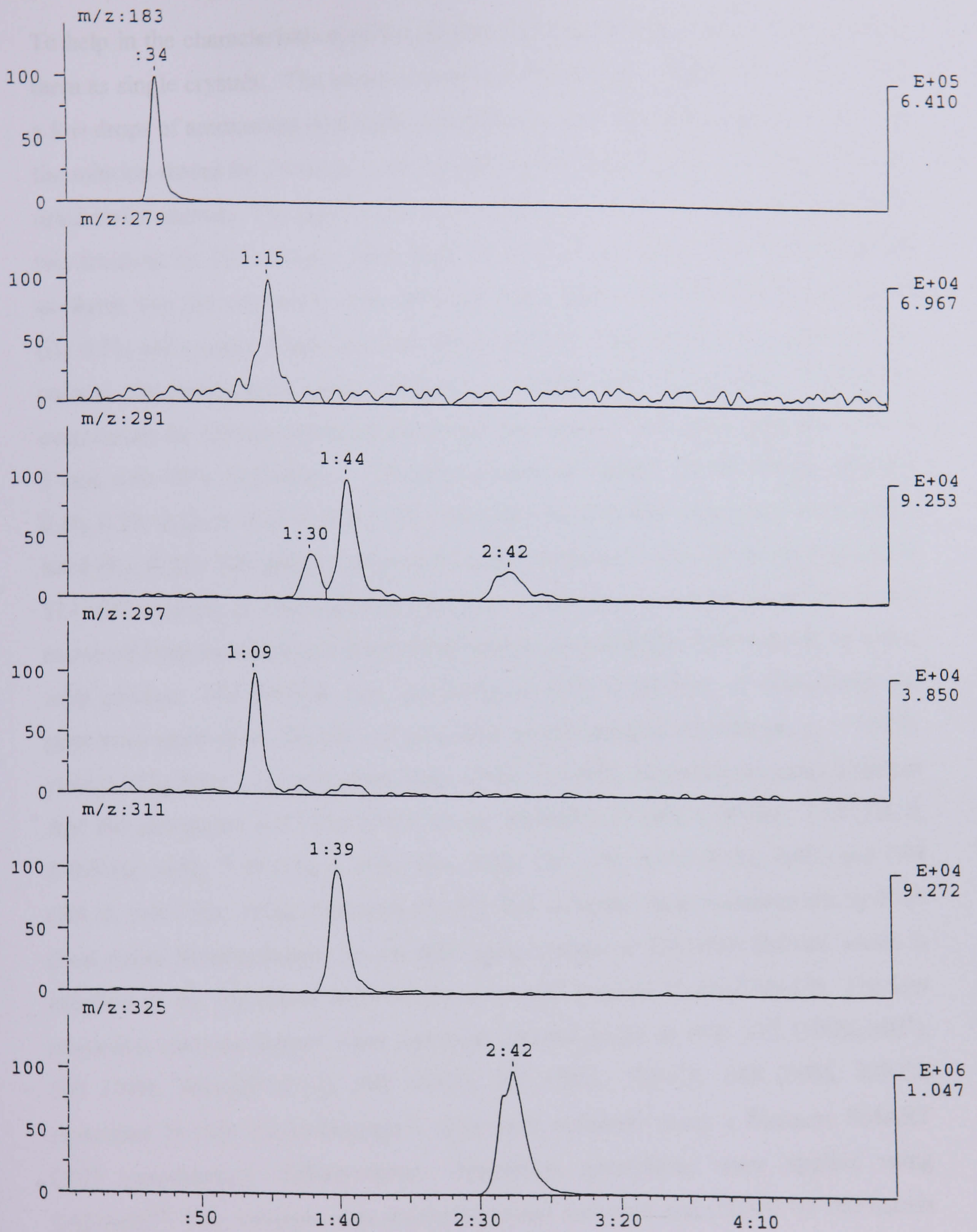
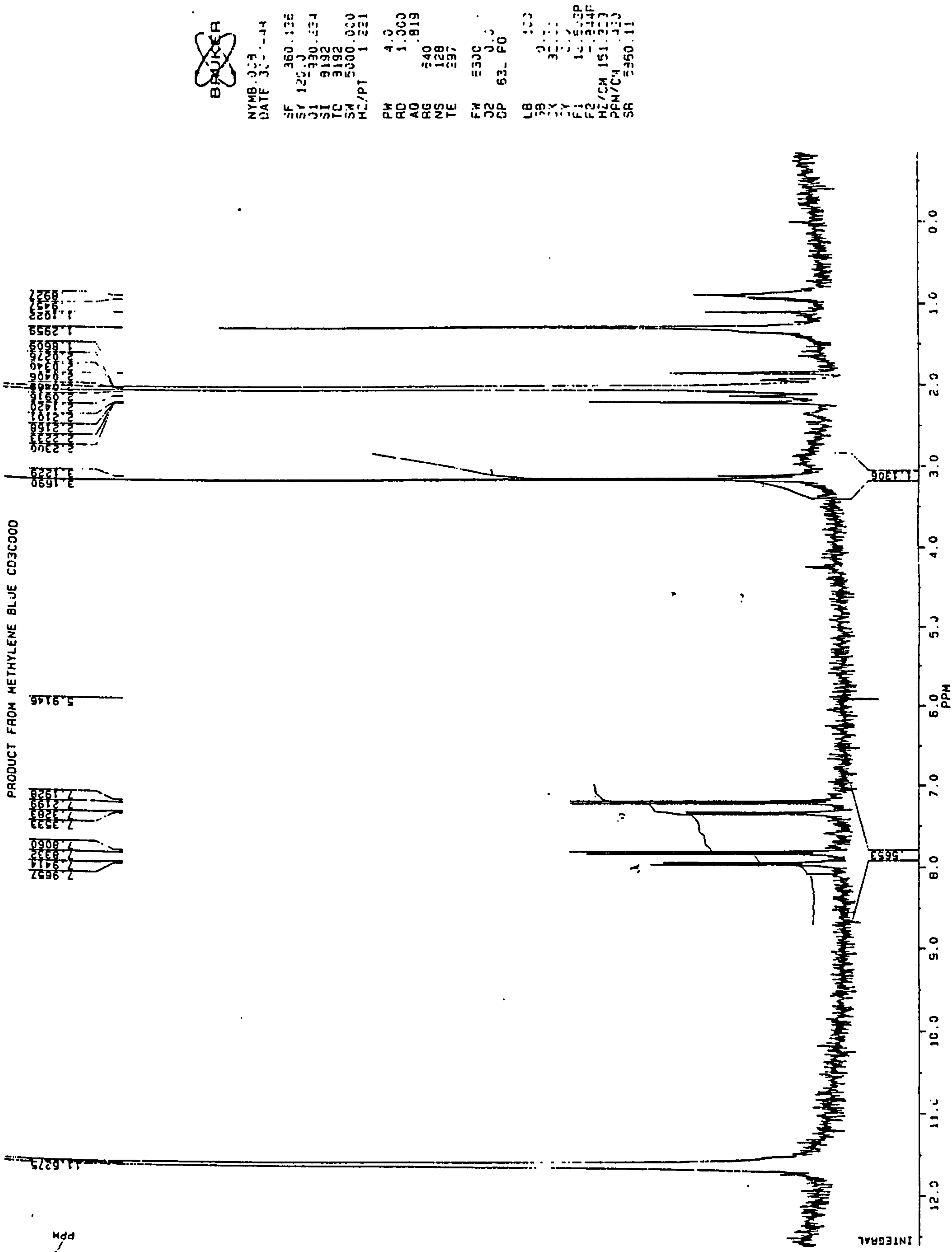


Figure [5.10]: Molecular weight (m/z) values for the eluted peaks of methylene blue sample after 15 minutes electrolysis using LC-MS analysis.

To help in the characterisation of the neutral products, attempts were made to obtain them as single crystals. The electro-oxidation reaction was stopped after 15 minutes, a few drops of ammonium hydroxide was added to raise the pH to greater than 7, and the solution stored for 24 hours to give a black precipitate which was filtered off and dried under vacuum. The precipitate was redissolved in methanol and separated into two fractions by TLC using a glass plate (9×3cm) coated with silica. With methanol as eluent, two discrete bands were observed, viz: a wide blue band fraction centred at ( $R_f$ : 0.23) and a major purple fraction ( $R_f$ : 0.77). The latter fraction was separated by column chromatography using methanol as eluent and the product obtained by evaporating the solvent separated into seven fractions by TLC using a glass plate (9 x 3 cm) with 99% chloroform + 1% ethyl acetate as eluent. The  $R_f$  values are 0.15, 0.16, 0.19, 0.22, 0.45, 0.58 and 0.79. The major band in this separation was a purple band ( $R_f$ : 0.22). The purple compound in this band was collected using preparative TLC (20 x 20 cm on silica-gel layer thickness 1000  $\mu\text{m}$ ) using the same solvent and extracted from the silica into chloroform prior to evaporating off the solvent, to give a solid product. The product was recrystallised from a mixture of chloroform and petroleum spirit (b.pt. 80-100) to give dark purple acicular crystals (m.p. > 300°C, yield 0.017g from 0.1g methylene blue, 17%).  $^1\text{H}$  NMR data obtained using a Bruker AM 360 instrument and  $\text{CD}_3\text{COOD}$  solvent showed 3.17 (6H, s,  $\text{NMe}_2$ ), 7.19 (1H, d,  $J=9.8$  Hz, ArH), 7.33 (1H, d,  $J=9.0$  Hz, ArH), 7.81 (1H, d,  $J=9.8$  Hz, ArH), and 7.94 (1H, d,  $J=8.7$  Hz, ArH) (Spectrum [5.11]). The accurate mass measurement by FAB (Fast Atom Bombardment) on the  $\text{MH}^+$  gave a mass of 324.9969 Daltons which is identical to the calculated mass of the molecular formula  $\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{N}_2\text{OS}$ . The low resolution electron impact mass spectrum showed peaks at  $m/z$ : 325 (100%,  $\text{MH}^+$ ), 309 (74%,  $\text{MH}-[\text{H}+\text{CH}_3]$ ), 282 (63%), 275 (58%, 282-Cl), 248 (30%, 309-Cl) (spectrum [5.12]). Crystallographic data were collected using a Siemens SMART CCD area-detector diffractometer. Absorption corrections were applied using SADABS<sup>35</sup>. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  for all data using SHELXL 97<sup>(36)</sup>. The compound was identified as 4,6-dichloro-7-dimethylamino-3*H*-phenothiazin-3-one [abbreviated as (A)].

The crystal data and structure refinement are in Table [5.9], atomic co-ordinates of





~~BRUKER~~  
 NYMB.009  
 DATE 30--84  
 SF 360.128  
 SY 120.0  
 J1 990.234  
 SI 9192  
 TD 9192  
 SM 5000.000  
 HL/PT 1.221  
 PW 4.0  
 RD 1.000  
 AQ .819  
 RG 540  
 NS 128  
 TE 297  
 FM 5300  
 J2 0.0  
 CP 63.00  
 LB 100  
 GB 0.00  
 EX 30.00  
 SY 12.00  
 F1 12.00  
 F2 12.00  
 HZ/CM 151.223  
 PPM/CM 1.000  
 SR 3950.11

Figure [5.11]: <sup>1</sup>H NMR spectrum of the dark purple crystal (A) using CD<sub>3</sub>COOD as solvent.

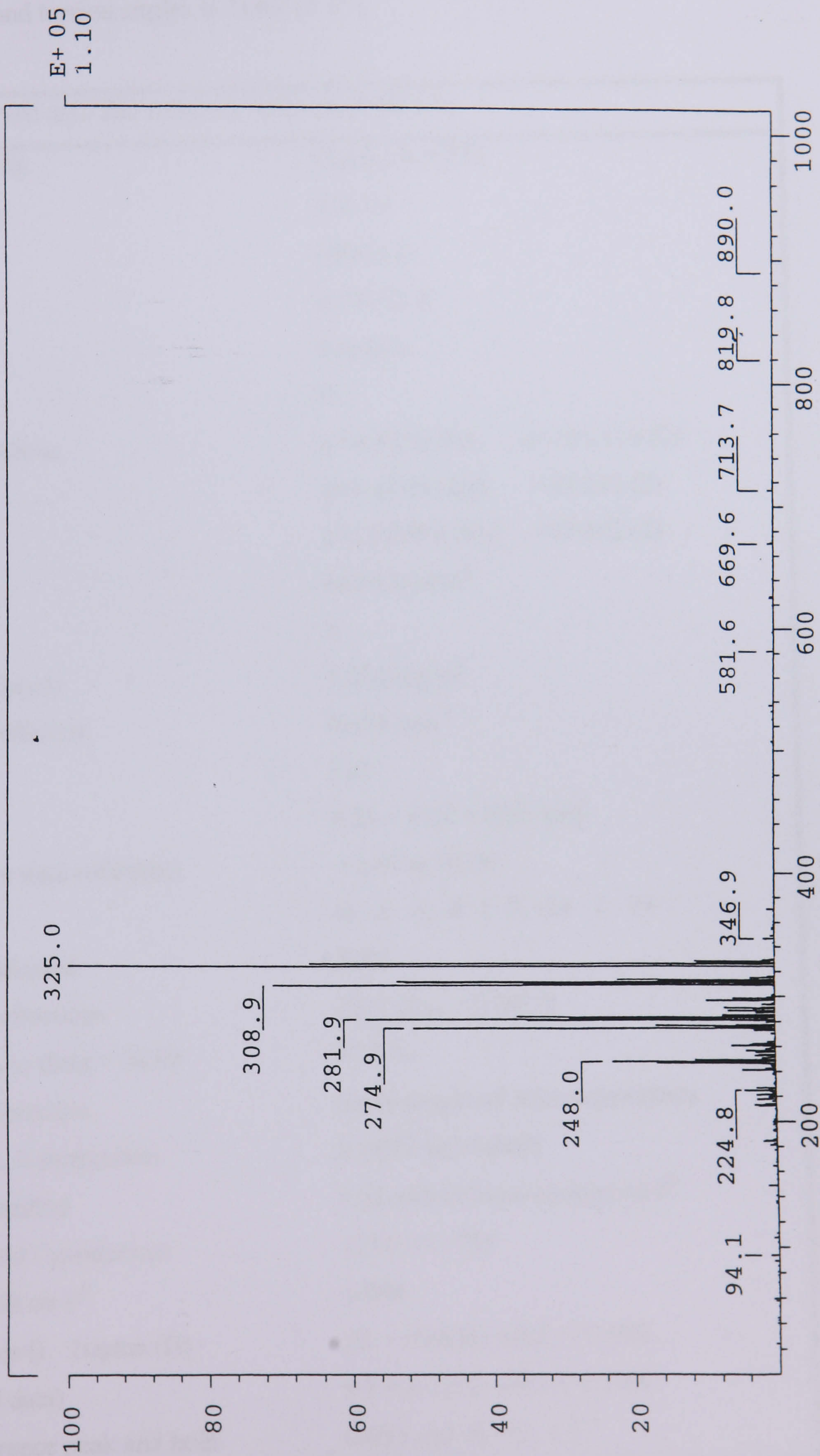


Figure [5.12]: The low resolution electron impact mass spectrum of the dark purple crystal (A).

this novel compound (A) in Table [5.10], selected bond distances and angles in Table [5.11], isotropic displacement parameters and isotropic displacement factor are shown in Table [5.12] and torsion angles in Table [5.13].

Table [5.9]: Crystal data and structure refinement for (A).	
Empirical formula	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> OS
Formula weight	325.20
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a=6.8756(9)\text{Å}$ $a=101.119(2)$ $b=7.8328(10)\text{Å}$ $=99.210(2)$ $c=12.6593(16)\text{Å}$ $=97.842(2)$
Volume	650.42(14)Å <sup>3</sup>
Z des/cm <sup>3</sup>	2
Density (calculated)	1.660 mg/m <sup>3</sup>
Absorption coefficient	0.654 mm <sup>-1</sup>
<i>F</i> (000)	332
Crystal size	0.22 × 0.20 × 0.02 mm <sup>3</sup>
Theta range for data collection	=1.67 to 24.99
Index ranges	-8 <i>h</i> 6, -8 <i>k</i> 9, -14 <i>l</i> 14
Reflections collected	3346
Independent reflections	2231 [R <sub>int</sub> = 0.0417]
Completeness to theta = 24.99	97.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9870 and 0.8695
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2231 / 0 / 183
Goodness of fit on F <sup>2</sup>	1.098
Final R indices [I ≥ 2sigma (I)]	R1 = 0.0836, wR2 = 0.1942
R indices (all data)	R1 = 0.1251, wR2 = 0.2309
Largest difference peak and hole	0.653 and -0.722 e Å <sup>-3</sup>

Table [5.10]: Atomic coordinates [ $\times 10^4$ ] for (A).

	X	Y	Z	U(eq)
S5	2414 (3)	3451 (2)	9830 (1)	27 (1)
Cl (1)	3182 (3)	6779 (2)	11652 (2)	38 (1)
Cl (2)	1432 (3)	2658 (2)	7364 (2)	35 (1)
N (10)	2705 (8)	73 (7)	10804 (4)	25 (1)
N (11)	1545 (8)	-1161 (7)	6229 (4)	25 (1)
O (1)	4037 (8)	6178 (7)	13876 (4)	41 (1)
C (1)	3336 (10)	1581 (10)	12658 (6)	30 (2)
C (2)	3720 (11)	3081 (10)	13426 (6)	33 (2)
C (3)	3718 (10)	4815 (10)	13172 (6)	31 (2)
C (4)	3284 (11)	4797 (9)	12003 (6)	29 (2)
C (6)	1914 (10)	917 (9)	7994 (5)	24 (2)
C (7)	1799 (10)	-792 (9)	7352 (5)	24 (2)
C (8)	1879 (10)	-2163 (9)	7939 (6)	29 (2)
C (9)	2156 (10)	-1830 (9)	9058 (5)	26 (2)
C (11)	2968 (9)	1582 (9)	11488 (5)	24 (2)
C (12)	2946 (10)	3304 (9)	11200 (5)	24 (2)
C (13)	2239 (10)	1276 (9)	9144 (5)	24 (2)
C (14)	2393 (10)	-121 (9)	9688 (5)	24 (2)
C (15)	2740 (11)	-53 (10)	5654 (6)	33 (2)
C (16)	904 (11)	-2982 (9)	5626 (6)	32 (2)

Table [5.11]: Bond lengths [Å] and angles [°] for (A).

S(5)-C(13)	1.73 (7)	S(5)-C(12)	1.742 (7)
Cl(1)-C(4)	1.702 (7)	Cl(2)-C(6)	1.750 (7)
N(10)-C(11)	1.295 (8)	N(10)-C(14)	1.370 (8)
N(11)-C(7)	1.373 (8)	N(11)-C(16)	1.453 (9)
N(11)-C(15)	1.482 (9)	O(1)-C(3)	1.221 (9)
C(1)-C(2)	1.337 (10)	C(1)-C(11)	1.462 (9)
C(2)-C(3)	1.455 (11)	C(3)-C(4)	1.459(10)
C(4)-C(12)	1.360 (9)	C(6)-C(13)	1.403 (9)
C(6)-C(7)	1.411 (9)	C(7)-C(8)	1.421 (10)
C(8)-C(9)	1.367 (10)	C(9)-C(14)	1.394 (9)
C(11)-C(12)	1.465 (9)	C(13)-C(14)	1.408 (9)
C(13)-S(5)-C(12)	102.2 (3)	C(11)-N(10)-C(14)	123.7 (6)
C(7)-N(11)-C(16)	119.0 (6)	C(7)-N(11)-C(15)	121.3 (6)
C(16)-N(11)-C(15)	113.4 (5)	C(2)-C(1)-C(11)	121.7 (7)
C(1)-C(2)-C(3)	123.2 (7)	O(1)-C(3)-C(2)	123.0 (7)
O(1)-C(3)-C(4)	122.4 (7)	C(2)-C(3)-C(4)	114.6 (7)
C(12)-C(4)-C(3)	123.7 (6)	C(12)-C(4)-Cl(1)	119.3 (5)
C(3)-C(4)-Cl(1)	117.0 (5)	C(13)-C(6)-C(7)	122.6 (6)
C(13)-C(6)-Cl(2)	117.0 (5)	C(7)-C(6)-Cl(2)	120.2 (5)
N(11)-C(7)-C(6)	123.5 (6)	N(11)-C(7)-C(8)	120.8 (6)
C(6)-C(7)-C(8)	115.7 (6)	C(9)-C(8)-C(7)	122.0 (6)
C(8)-C(9)-C(14)	121.8 (6)	N(10)-C(11)-C(1)	117.4 (6)
N(10)-C(11)-C(12)	126.1 (6)	C(1)-C(11)-C(12)	116.6 (6)
C(4)-C(12)-C(11)	120.0 (6)	C(4)-C(12)-S(5)	119.5 (5)
C(11)-C(12)-S(5)	120.4 (5)	C(6)-C(13)-C(14)	119.4 (6)
C(6)-C(13)-S(5)	117.6 (5)	C(14)-C(13)-S(5)	123.0 (5)
N(10)-C(14)-C(9)	117.1 (6)	N(10)-C(14)-C(13)	124.4 (6)
C(9)-C(13)-C(14)	118.4 (6)		

Table [5.12]: Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for (A). The anisotropic displacement factor takes the form:

$$-2^2 [h^2 a^{*2} U^{11} + \dots + 2hka^* b^* U^{12}]$$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
S(5)	33(1)	23(1)	23(1)	1(1)	5(1)	7(1)
Cl(1)	42(1)	34(1)	39(1)	6(1)	9(1)	9(1)
Cl(2)	44(1)	32(1)	31(1)	9(1)	6(1)	14(1)
N(10)	21(3)	30(3)	23(3)	6(3)	3(2)	5(2)
N(11)	22(3)	29(3)	22(3)	0(2)	4(2)	-1(2)
O(1)	47(4)	42(3)	28(3)	-2(3)	9(2)	2(3)
C(1)	24(4)	35(4)	32(4)	4(3)	7(3)	10(3)
C(2)	24(4)	45(5)	29(4)	8(4)	2(3)	8(3)
C(3)	21(4)	36(4)	32(4)	1(3)	8(3)	1(3)
C(4)	26(4)	27(4)	32(4)	1(3)	9(3)	4(3)
C(6)	23(4)	27(4)	22(3)	7(3)	6(3)	5(3)
C(7)	18(3)	30(4)	27(4)	5(3)	8(3)	8(3)
C(8)	26(4)	26(4)	30(4)	-3(3)	4(3)	7(3)
C(9)	26(4)	24(4)	26(4)	6(3)	4(3)	1(3)
C(11)	16(3)	32(4)	27(4)	6(3)	6(3)	7(3)
C(12)	17(3)	28(4)	25(3)	4(3)	6(3)	2(3)
C(13)	17(3)	26(4)	26(4)	2(3)	1(3)	2(3)
C(14)	20(3)	29(4)	25(3)	9(3)	4(3)	5(3)
C(15)	31(4)	38(4)	32(4)	8(3)	12(3)	7(3)
C(16)	34(4)	34(4)	24(4)	-2(3)	6(3)	3(3)

C(11)-C(1)-C(2)-C(3)	2.8(11)	Cl(1)-C(4)-C(12)-C(11)	-178.2(5)
C(1)-C(2)-C(3)-O(1)	178.7(7)	C(3)-C(4)-C(12)-S(5)	179.3(5)
C(1)-C(2)-C(3)-C(4)	-0.7(11)	Cl(1)-C(4)-C(12)-S(5)	-0.1(8)
O(1)-C(3)-C(4)-C(12)	179.2(7)	N(10)-C(11)-C(12)-C(4)	-178.7(7)
C(2)-C(3)-C(4)-C(12)	-1.4(11)	C(1)-C(11)-C(12)-C(4)	0.8(10)
O(1)-C(3)-C(4)-Cl(1)	-1.4(10)	N(10)-C(11)-C(12)-S(5)	3.3(10)
C(2)-C(3)-C(4)-Cl(1)	178.0(5)	C(1)-C(11)-C(12)-S(5)	-177.2(5)
C(16)-N(11)-C(7)-C(6)	-163.3(6)	C(13)-S(5)-C(12)-C(4)	177.1(6)
C(15)-N(11)-C(7)-C(6)	46.3(10)	C(13)-S(5)-C(12)-C(11)	-4.9(6)
C(16)-N(11)-C(7)-C(8)	14.0(9)	C(7)-C(6)-C(13)-C(14)	-2.2(10)
C(15)-N(11)-C(7)-C(8)	-136.4(7)	Cl(2)-C(6)-C(13)-C(14)	172.4(5)
C(13)-C(6)-C(7)-N(11)	-177.9(6)	C(7)-C(6)-C(13)-S(5)	178.3(5)
Cl(2)-C(6)-C(7)-N(11)	7.7(9)	Cl(2)-C(6)-C(13)-S(5)	-7.1(8)
C(13)-C(6)-C(7)-C(8)	4.7(10)	C(12)-S(5)-C(13)-C(6)	-176.8(5)
Cl(2)-C(6)-C(7)-C(8)	-169.7(5)	C(12)-S(5)-C(13)-C(14)	3.7(6)
N(11)-C(7)-C(8)-C(9)	179.2(6)	C(11)-N(10)-C(14)-C(9)	179.3(6)
C(6)-C(7)-C(8)-C(9)	-3.3(10)	C(11)-N(10)-C(14)-C(13)	-2.7(10)
C(7)-C(8)-C(9)-C(14)	-0.6(11)	C(8)-C(9)-C(14)-N(10)	-178.6(6)
C(14)-N(10)-C(11)-C(1)	-178.4(6)	C(8)-C(9)-C(14)-C(13)	3.2(10)
C(14)-N(10)-C(11)-C(12)	1.1(10)	C(6)-C(13)-C(14)-N(10)	-179.9(6)
C(2)-C(1)-C(11)-N(10)	179.8(7)	S(5)-C(13)-C(14)-N(10)	-0.4(10)
C(2)-C(1)-C(11)-C(12)	-2.8(10)	C(6)-C(13)-C(14)-C(9)	-1.8(10)
C(3)-C(4)-C(12)-C(11)	1.2(11)	S(5)-C(13)-C(14)-C(9)	177.6(5)

### 5.7.2.1 HPLC Study of Methylene Blue Derivatives:

In an attempt to aid the characterisation of the products formed when methylene blue is subjected to electrolysis, the analogous compounds azure A, azure B, and thionin were subjected to electrolysis followed by HPLC. The structures of dyes chosen for this study are shown in Figure [5.13] and differ from methylene blue only in the number of methyl groups on the nitrogen atoms. The HPLC studies were performed on the initial solutions and on the dye solutions following 15 minutes of electrolysis, with (PLRP-S) (polystyrene packing) column [condition 1] and PINNACLE ODS (silica C<sub>18</sub> packing) column [condition 2]. The HPLC chromatograms are showing in appendix 3.

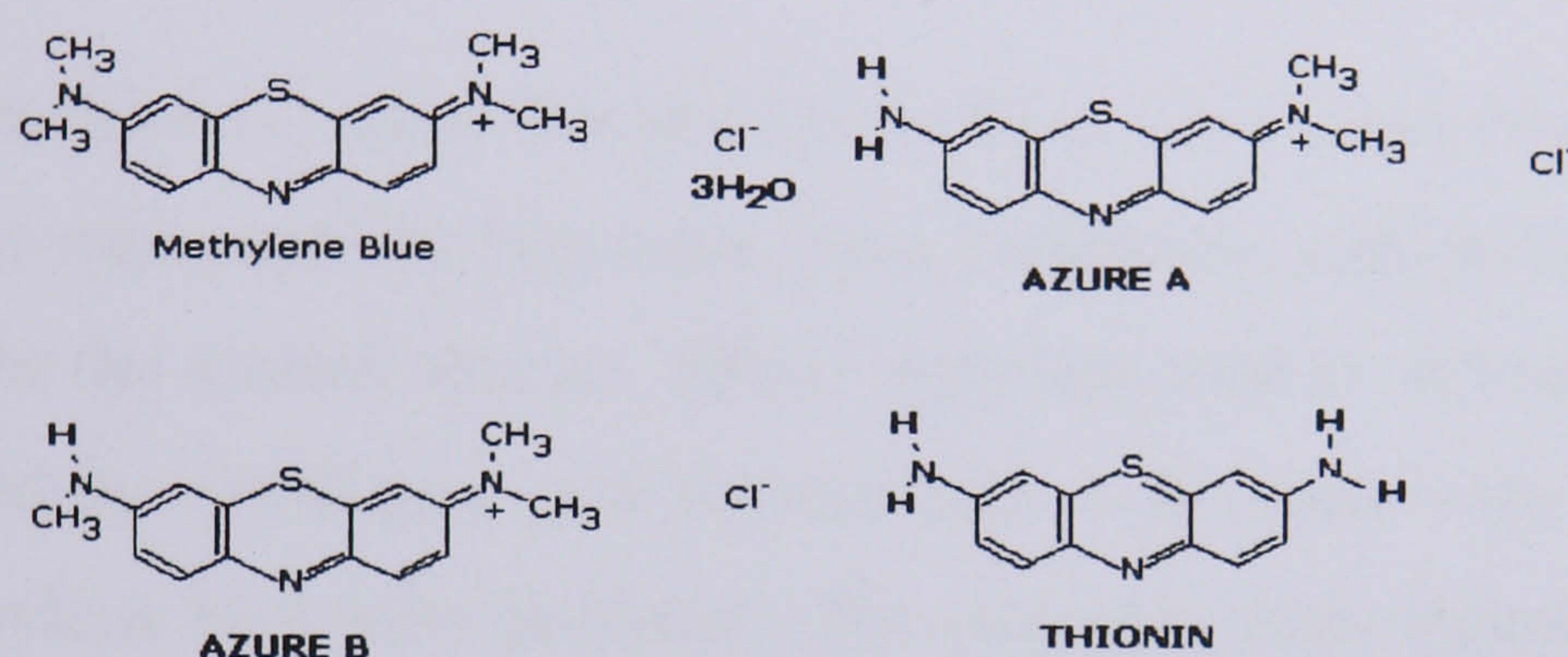


Figure [5.13]: The structure formula of the methylene blue derivatives Azure A, Azure B and Thionin.

Using condition (1), Methylene blue, Azure B and Thionin gave single peaks when initially run under these conditions, suggesting that they are single component samples. Azure A, however, was shown to be a mixture of components. Electrolysis produced components with longer retention times (RT) than the original peaks observed (Table [5.14]) which shows that:

- 1- Methylene blue and Azure B produce a common break-down product with a retention time 5.4 minutes.
- 2- Methylene blue produces a well-defined break-down product of retention time 7.6minutes, which is also found in Azure A.



Table [5.14]: HPLC results of pre-electrolysis and electrolysed dye solution under condition(1) using PLRP-S column.		
Material	RT (minutes) of dyes before electrolysis.	RT (minutes) of additional peaks in dyes following 15 min electrolysis.
Methylene blue	3.8	5.4, 7.6
Azure A	2.7, 3.2, 3.6	5.4, 7.6
Azure B	3.4	5.4
Thionin	2.4	-----

Results from condition (2) show that methylene blue, azure B and thionin gave single very broad peaks when initially run under these conditions, indicating that the column is not suitable for the ionised species. HPLC was then used to determine non-charged species produced by electrolysis and showed that compounds with shorter retention times than methylene blue were produced. The retention times measured for each dye before and after electrolysis are in Table [5.15] and the results indicate that:

- 1- Azure A is a mixture of dyes.
- 2- Methylene blue produces well-defined breakdown products of retention times 4.8, 6.6 minutes, which may be the same breakdown products as found with azure A (but may be a result of impurities within this sample). These breakdown products are not found with azure B.

Analysis of products after 2hours electrolysis shows no HPLC peaks, indicating that none of these structures remain in the solution.

Table [5.15]: HPLC results of pre-electrolysis and electrolysed dye solution under condition(2) using PINNACLE ODS column.		
Material	Starting RT(minute)	Addition peaks (after electrolysis) RT(minute)
Methylene blue	10.8	2.4, 2.6, 2.8, 3.2, 3.7, 4.8, 6.6
Azure A	4, 5.8, 9.2	4.6, 6.4
Azure B	7.6	9.2
Thionin	2.9	-----

Storing the samples of the electrolysed dyes for a period of 24 hours after electrolysis resulted in a dark blue-black precipitate. HPLC characterisation of the precipitates dissolved in methanol using condition (2) is shown in Table [5.16] and indicates that only Azure A and Azure B have a common peak (at 6 minutes retention time). The precipitate from methylene blue is the only dye which results in one major peak (RT. 6.6); this in the presence of other insignificant peaks (RT. 2.4, 2.6, 2.8, 3.2, 3.7 and 4.8). All other dye precipitates following electrolysis are more complicated mixtures, since up to three major peaks are identified by HPLC.

Table [5.16]: HPLC results of precipitates obtained following electrolysis under condition(2) using PINNACLE ODS column.	
Materials	RT (minute)
Methylene blue precipitate	6.6
Azure A precipitate	3, 4.6, 6
Azure B precipitate	2.4, 6, 7.4
Thionin precipitate	2.3, 2.7

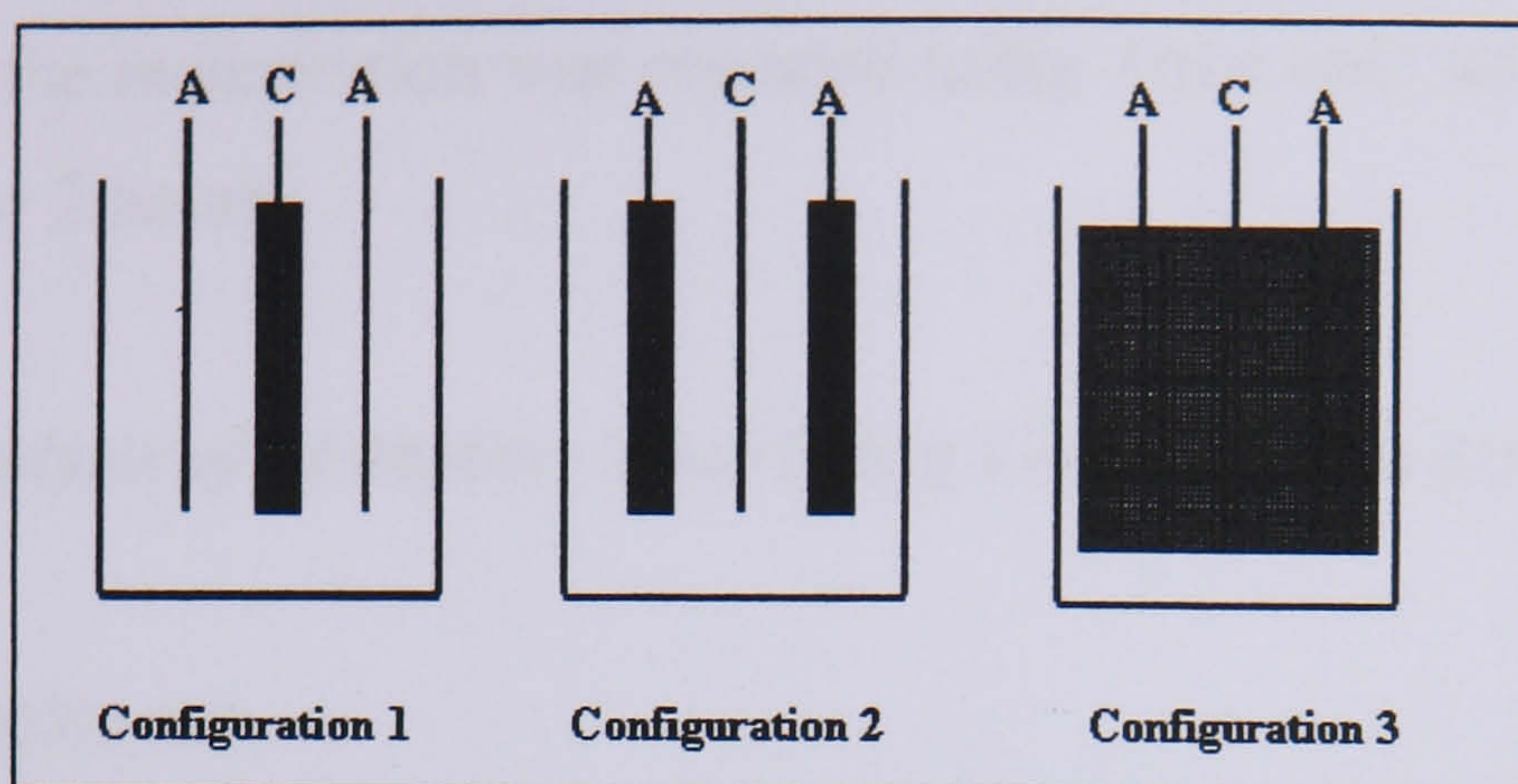
### 5.7.3 Combination of Electrolysis and Adsorption for the Destruction of Different Dye Solutions.

In order to eliminate the intermediate compounds formed during electrolysis of the dye solution, and to achieve optimum efficiency with minimal chemical consumption, time and manpower, the electrolyte chamber in the electrochemical cell used in the previous work was modified by including activated carbon granules in the system. The modification was made in three configurations (Figure 5.14)

- 1- Activated carbon granules surrounding the cathode.
- 2- Activated carbon granules surrounding the two anodes.
- 3- Activated carbon granules occupying the entire electrolysis chamber.

The study included a comparison of the performance of the three configurations with that of a normal electrochemical cell (control) using the following dyes: methylene blue, acid blue 25, reactive blue 2 and reactive blue 15. The results for each dye are

given in detail in the following sections.



A = Anode    C = Cathode

Figure [5.14]: Basic configurations of the electrolyte chamber in the electrochemical cell.

### 5.7.3.1 *The Study of Combined Electrolysis and Adsorption on the Destruction of Methylene Blue*

To study the effect of activated carbon in configuration (1) and (2) a comparison with the control condition was made using 50ppm of methylene blue in 0.03M NaCl solution. Successive run experiments were performed, using the original dye solution of 50ppm for 8 hours, and topping up with 0.25g methylene blue dissolved in 50 ml water every 2 hours to return the concentration to 50ppm in the 5 litre cell. For configuration 1, the effects of electrolyte (NaCl) concentration, of changing the electrolyte to  $\text{CaCl}_2$  and of current input were also studied.

Successive run experiments using the configuration 3 cell were made using 200ppm of dye solution in 0.03M NaCl over 10 hours topping up with 50 ml of a solution containing 1.0gr of methylene blue in 50ml water every hour. Data for a successive run without current input and on the regeneration of the activated carbon were also collected.

The regeneration of activated carbon, solutions of NaCl (0.03M) or HCl (1M) was achieved by applying a current of 1.5A for two hours. The cell after the regeneration procedure was washed with water until the pH of the washing water remained constant to ensure that no salt or acid remain adsorbed on the activated carbon granules. After regeneration the performance of the cell was tested for 200ppm of dye

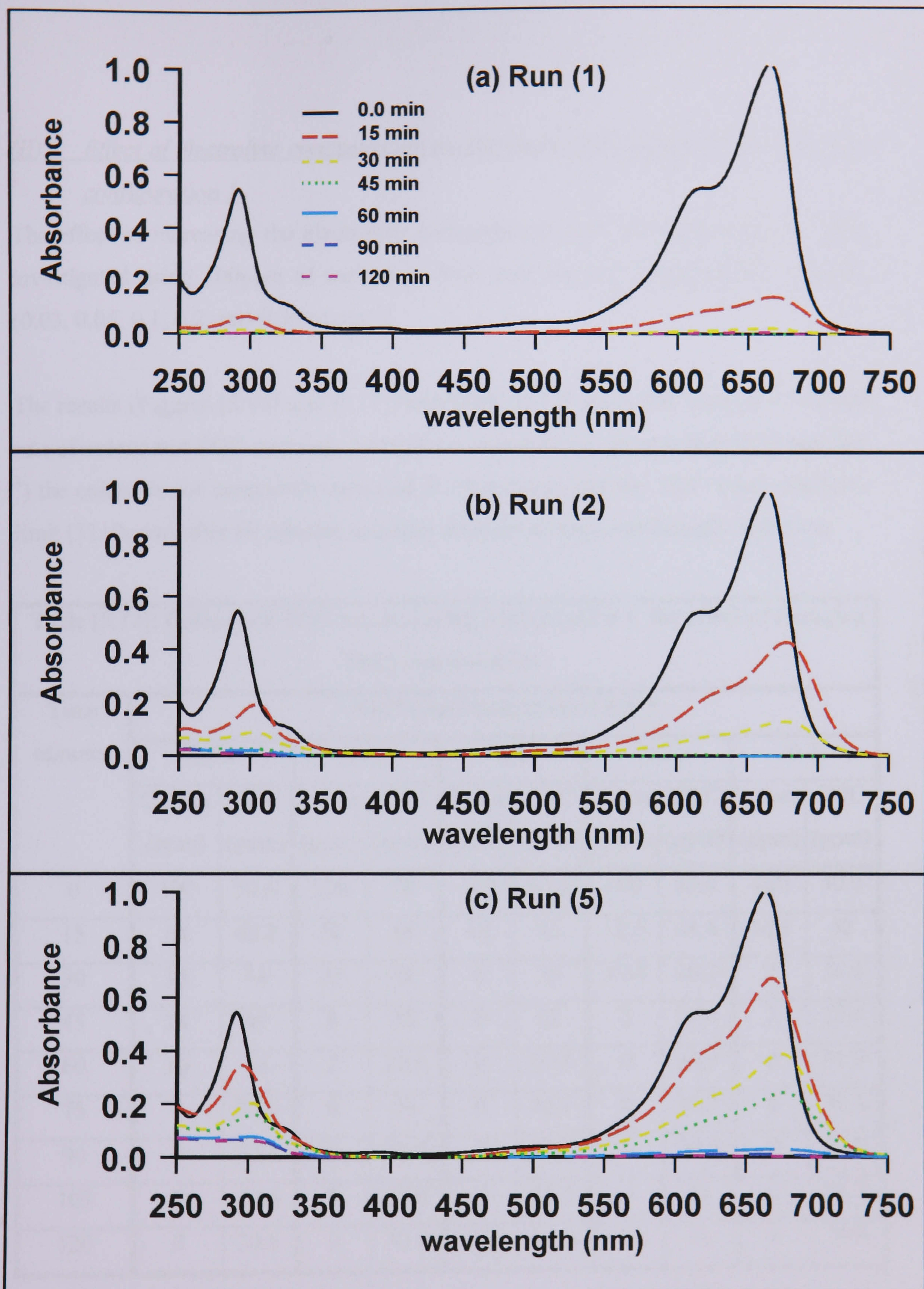
solution in 0.03M NaCl, in three successive 10 hour experiments, topping up the solution every 1 hour to return the concentration to 200ppm. At the end of each successive run the regeneration was repeated using  $1\text{ mol dm}^{-3}$  HCl, applying a 1.5 A current input for 2 hours.

### ***5.7.3.2 Electrolysis of Methylene Blue Using Configuration (1)***

#### ***(I) Successive run***

In successive experiments, 5 consecutive runs were carried out. Figure [5.15] shows the UV/Visible spectra for the resulting samples in the first run (graph [5.15, a]), second run (graph [5.15, b]) and fifth run (graph [5.15, c]). From these results it can be seen that the colour concentration decreased in run 1 gradually to reach concentration of 6.5 after 15 minutes, and the colour disappears completely after 30 minutes electrolysis. The efficiency of this configuration decreases on increasing the run time. The concentration only reduces to 21.7 and 33.6ppm after 15 minutes in runs 2 and 5 respectively. The colour does, however, disappear after 60, and 90 minutes of reaction time in runs 2 and 5 respectively.

Examination of the resulting samples using HPLC condition 2 shows a decrease in the formation of the chloroorganic compounds in the electrolyte. No peaks were observed during the first run. However, very small peaks were observed only after 15 minutes of run 2. These peaks disappeared in the later samples. In run 5 the HPLC peaks were showing the same trend obtained using control conditions [Section 5.7.2].



The dye samples diluted  
10ml in 50ml water

Figure [5.15]: UV/Visible spectra for methylene blue removal using cell-configuration (1), successive run.

*(II) Effect of electrolyte concentration on the electrolysis of methylene blue using configuration 1*

The effect of increasing the electrolyte concentration used in configuration (1) was investigated using 100ppm of methylene blue with varying concentrations of NaCl (0.03, 0.05, 0.1, 0.2, and 0.3mol dm<sup>-3</sup>).

The results (Figures [5.16] and [5.17]) and Table [5.17] show that there is a constant rate of colour and TOC removal. At higher concentrations (greater than 0.05 mol dm<sup>-3</sup>) the colour is not completely removed in 30 minutes and the TOC value reaches a limit (31±2ppm) after 60 minutes and then does not change significantly with time.

Table [5.17]: Colour and TOC removal using configuration 1, the effect of changing NaCl concentration.										
Time minutes	NaCl concentration (mol dm <sup>-3</sup> )									
	0.03		0.05		0.1		0.2		0.3	
	Colour (ppm)	TOC (ppm)	Colour (ppm)	TOC (ppm)	Colour (ppm)	TOC (ppm)	Colour (ppm)	TOC (ppm)	Colour (ppm)	TOC (ppm)
0	100	50.6	100	50	100	50.6	100	50.8	100	50.0
15	68	48.2	50	46	10	46	12.6	44.4	16.1	42
30	38	44	34	42	6	36	4.34	36.2	2	36.4
45	24	40	8	38	0	32	0	31.4	2	32.6
60	10	36	2	32.6	0	30.8	0	30.9	0	31.9
75	4	30.6	0	31	0	30.8	0	31.2	0	31.6
90	2	30.4	0	30.8	0	31.2	0	30.9	0	31.2
105	0	30.6	0	30.6	0	31.2	0	31	0	30.6
120	0	30.8	0	30.8	0	31.0	0	31	0	30.8

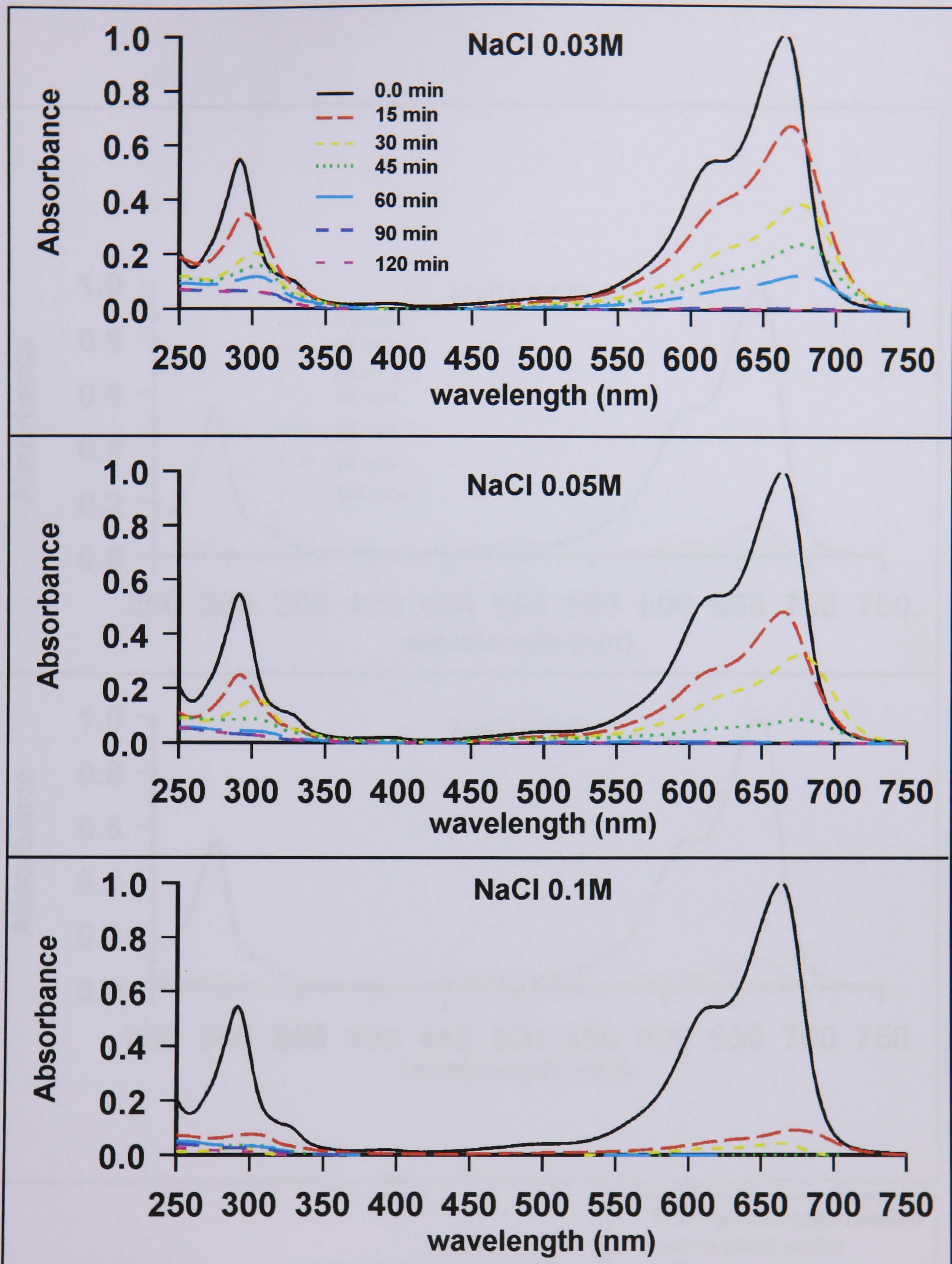
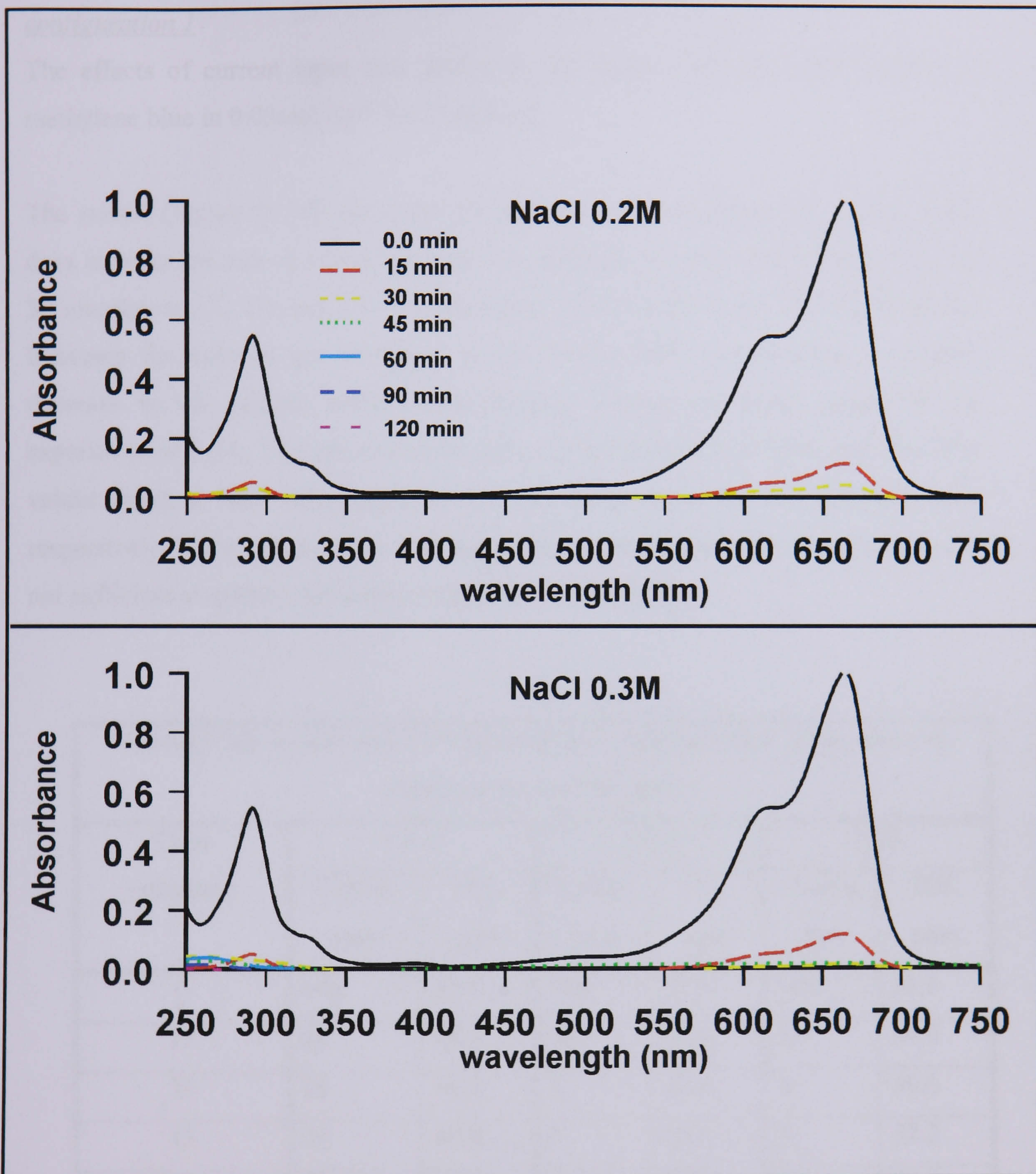


Figure [5.16]: UV/Visible spectra for methylene blue following electrolytic destruction using cell configuration (1), the effect of changing the concentration of NaCl.



The dye samples diluted  
5ml in 50ml water

**Figure [5.17]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (1), the effect of changing the concentration of NaCl.**

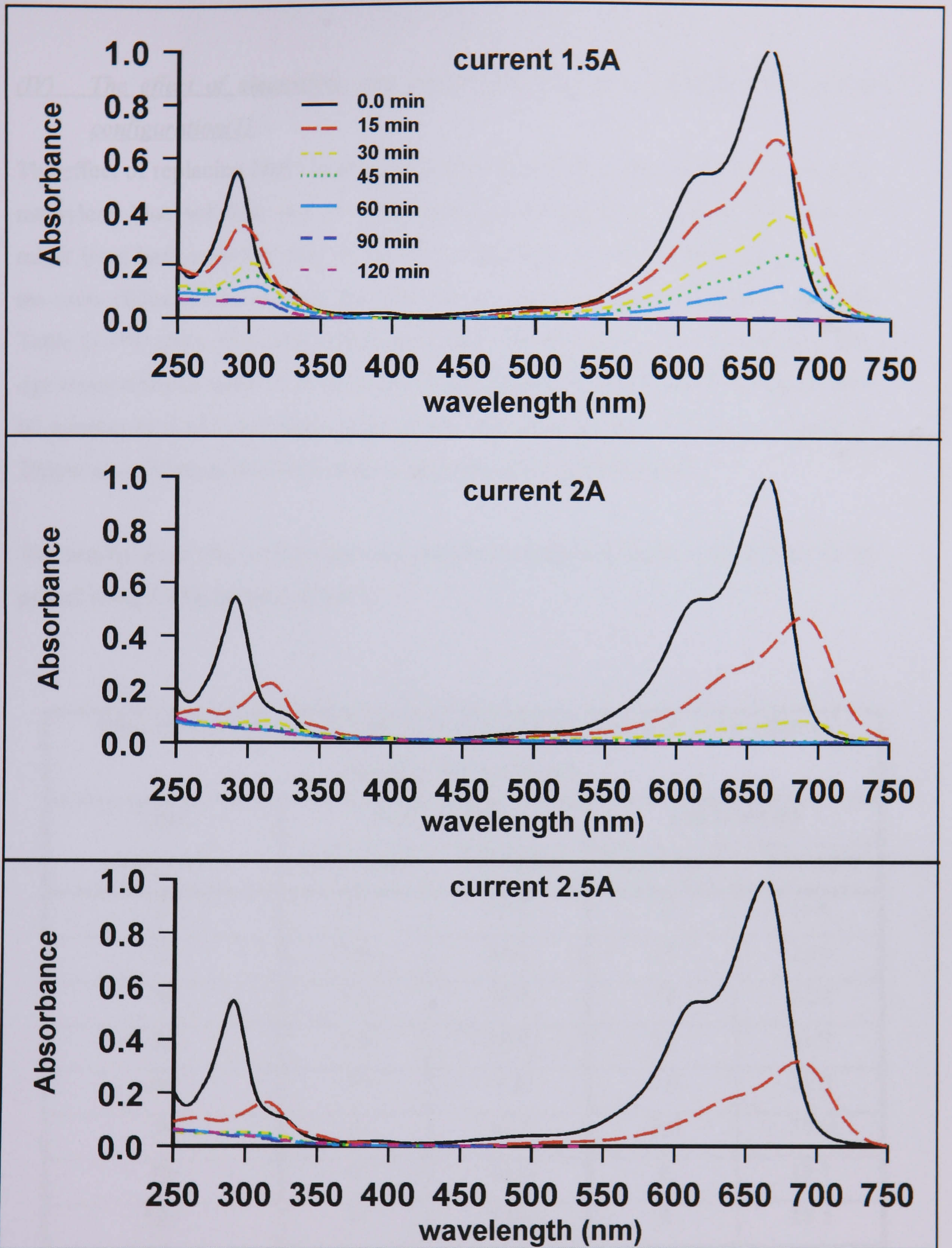


(III) The effect of current input on the electrolysis of methylene blue using configuration 1

The effects of current input was studied in the range 1.5-2.5A using 100ppm of methylene blue in 0.03mol dm<sup>-3</sup> NaCl solution.

The results (Figure [5.18] and Table [5.18] show that increasing the current input does increase the rate of colour removal. The solution becomes clear after 75, 45 and 30 minutes at 1.5, 2.0 and 2.5 A respectively. An increase in the current, however, increases the chlorine gas evolution at the anode. TOC studies show a constant decrease in the organic carbon concentration during the initial stages of the experiment at 1.5A. The rate increases with current from 2.0 to 2.5A, but the TOC values reach a limit (30±2ppm) at 75, 60, 45 minutes for 1.5, 2.0 and 2.5A respectively. These results show that increasing current input with configuration 1 is not sufficient to achieve dye removal under these conditions.

Time (minutes)	1.5 A		2.0A		2.5A	
	Colour ppm	TOC ppm	Colour ppm	TOC ppm	Colour ppm	TOC ppm
0	100	50.6	100	51.2	100	50.8
15	68	48.2	48	46.4	32	46.0
30	38	44.0	8	42.4	0	40.6
45	24	40.0	2	38.0	0	32.2
60	10	36.0	0	32.6	0	30.4
75	4	30.6	0	30.8	0	30.8
90	2	30.4	0	31.6	0	30.6
105	0	30.6	0	31.2	0	31.2
120	0	30.8	0	31.2	0	30.8



The dye samples diluted 5ml in 50ml water

Figure [5.18]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (1), the effect of changing the current.

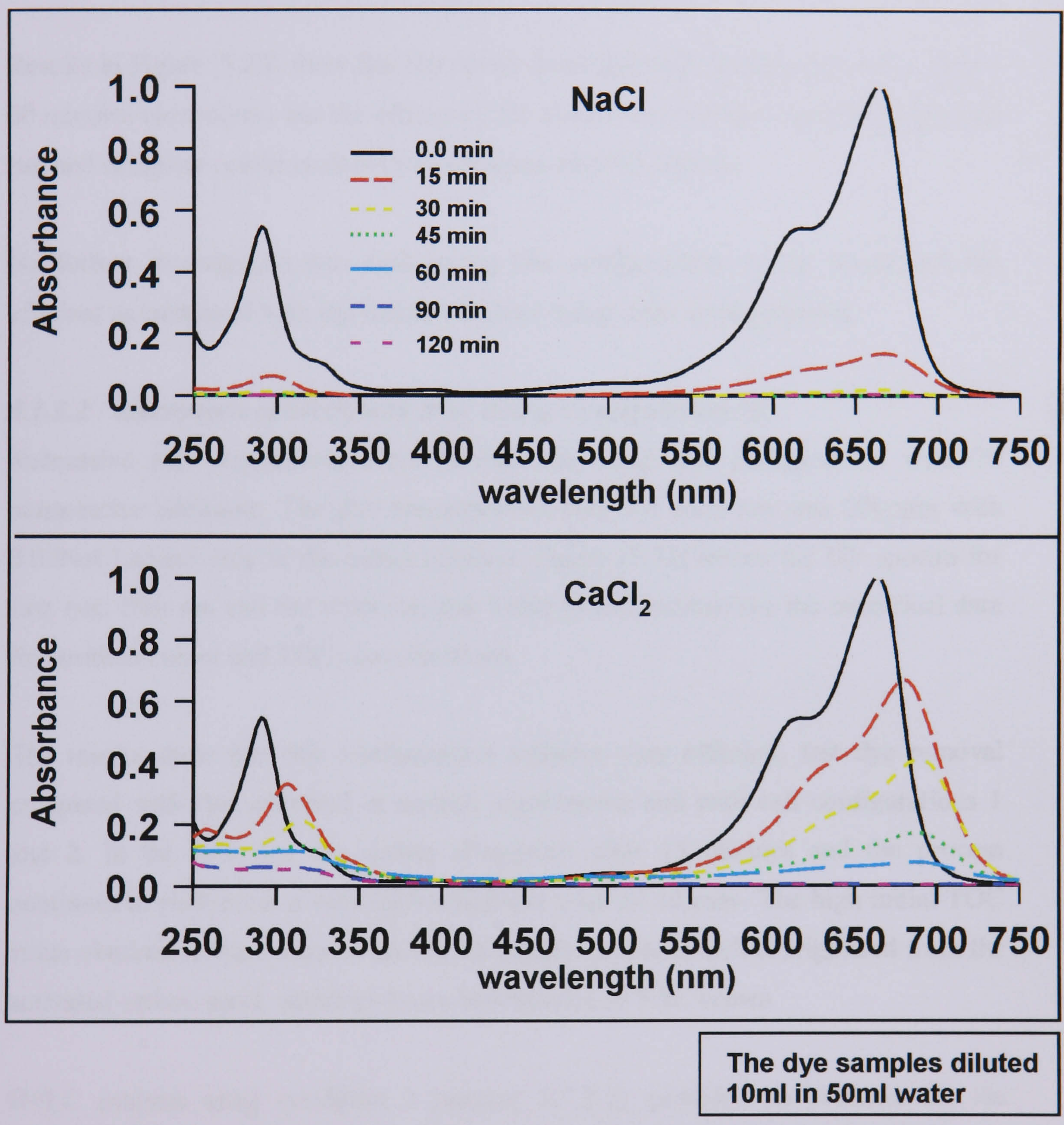
(IV) The effect of electrolyte type on the electrolysis of methylene blue using configuration(1)

The effect of replacing NaCl in the electrolyte with CaCl<sub>2</sub> was studied with a 50ppm methylene blue solution and all other experimental details remaining the same. It might have been expected that the rate of colour removal would be increased due to the extra chlorine ions present, but this was not the case. Results (Figure [5.19] and Table [5.19]) show that with CaCl<sub>2</sub> the colour removal occurs at a slower rate. The dye concentrations after 15 minutes are 34 and 7ppm decreasing to 4 and 0ppm after 60 minutes for CaCl<sub>2</sub> and NaCl respectively. The TOC using CaCl<sub>2</sub> shows a value of 20ppm after 75 minutes which is more than that observed with NaCl.

The results show that under these experimental conditions there is no benefit to be gained using CaCl<sub>2</sub> instead of NaCl.

Time (minuets)	NaCl 0.03M		CaCl <sub>2</sub> 0.03M	
	Colour ppm	TOC ppm	Colour ppm	TOC ppm
0	55	25.6	55	25.6
15	7.0	24.3	34	23.1
30	1.5	19.5	22	22.2
45	1.0	19.8	9.5	21.9
60	0	7.4	4.0	21.0
75	0	16.1	1.0	20.0
90	0	14.3	0	19.1
105	0	15.6	0	18.5
120	0	15.1	0	18.6

5.1.1.1 Electrolysis of Methylene Blue using Cell-configuration (1)  
 Successive run studies were carried out by changing the electrolyte type and the electrolyte concentration after the removal of the electrolyte from the cell. The effect of changing the electrolyte type on the electrolysis of methylene blue is shown in Figure 5.19.



**Figure [5.19]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (1), the effect of changing the electrolyte types.**

#### ***5.1.1.1 Electrolysis of Methylene Blue Using Configuration (2)***

Successive run studies were made using this configuration. The experiments were stopped after the second run, because the colour reduction was very slow as compared to other configurations (1 and 3).

Results in Figure [5.20] show that the colour decreased and disappeared in run 1 after 60 minutes electrolysis, but the efficiency for colour removal decreased in the second run and complete colour removal was obtained after 90 minutes.

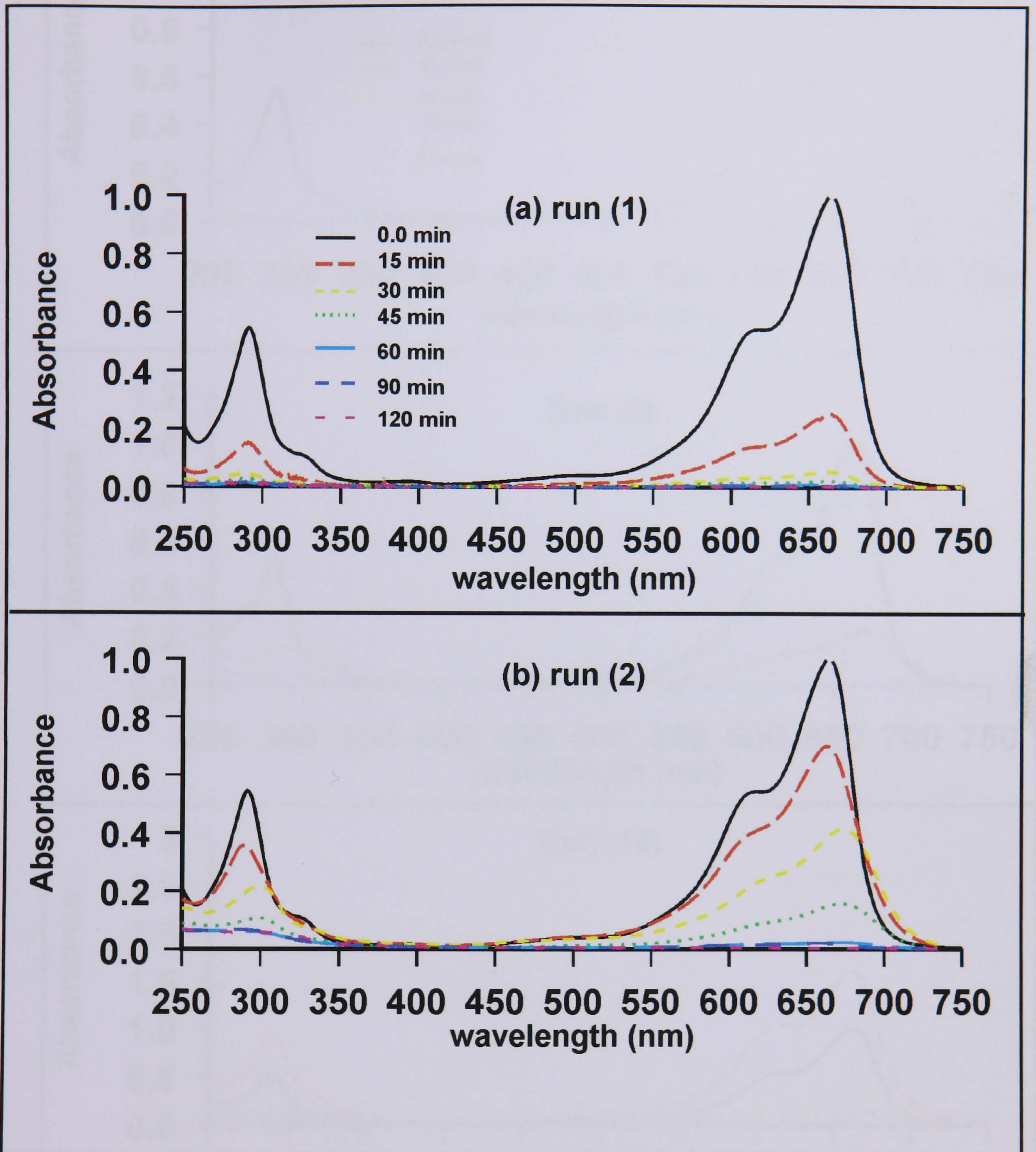
No further investigation was made using this configuration, as the results are not efficient as compared with the results obtained using other configurations.

#### ***5.1.1.2 Electrolysis of Methylene Blue Using Configuration (3)***

Successive run experiments were carried out using this configuration with 10 consecutive additions. The dye concentration used for each run was 200ppm with 0.03NaCl added only in the initial solution. Figure [5.21] shows the UV spectra for first run, fifth run and the tenth run and Table [5.20] summarises the numerical data for residual colour and TOC concentrations.

The results show that this configuration achieves very efficient, fast dye removal compared with that achieved in control experiments and with cell configurations 1 and 2. In the first run, the colour disappears after 15 minutes and the process continues to perform at a very high efficiency over all 10 runs. The high initial TOC value obtained in run 1 may be due to the organic carbon which is originated from the activated carbon itself, which gives an interference in TOC values.

HPLC analysis using condition 2 (section 5.7.2.1), provided no evidence for the formation of chloroorganic compounds (Section [5.7.2]). No peaks were observed in the chromatograms of all runs.



The dye samples diluted 10ml in 50ml water

Figure [5.20]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (2), successive run.

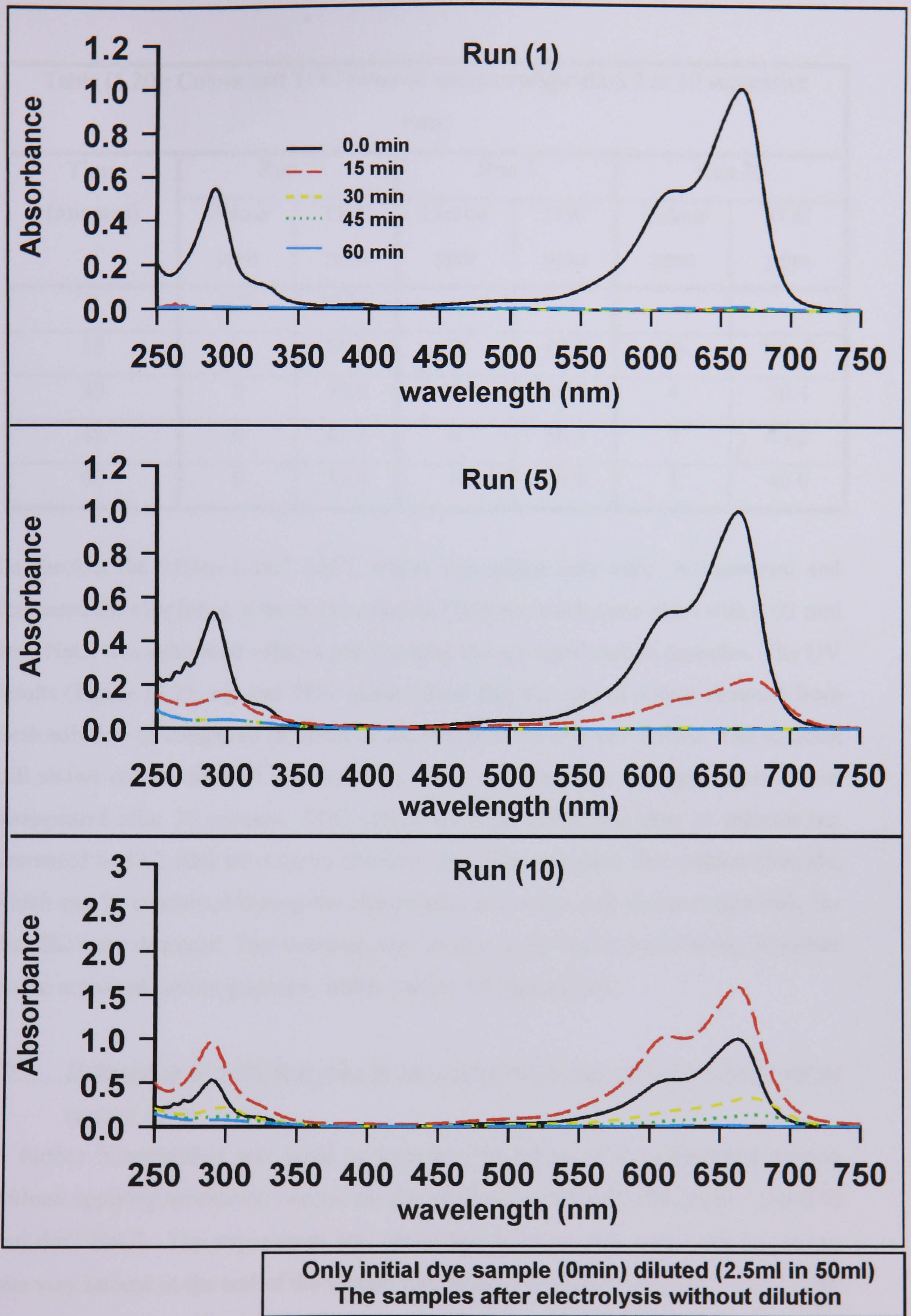


Figure [5.21]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (3), successive run experiment.

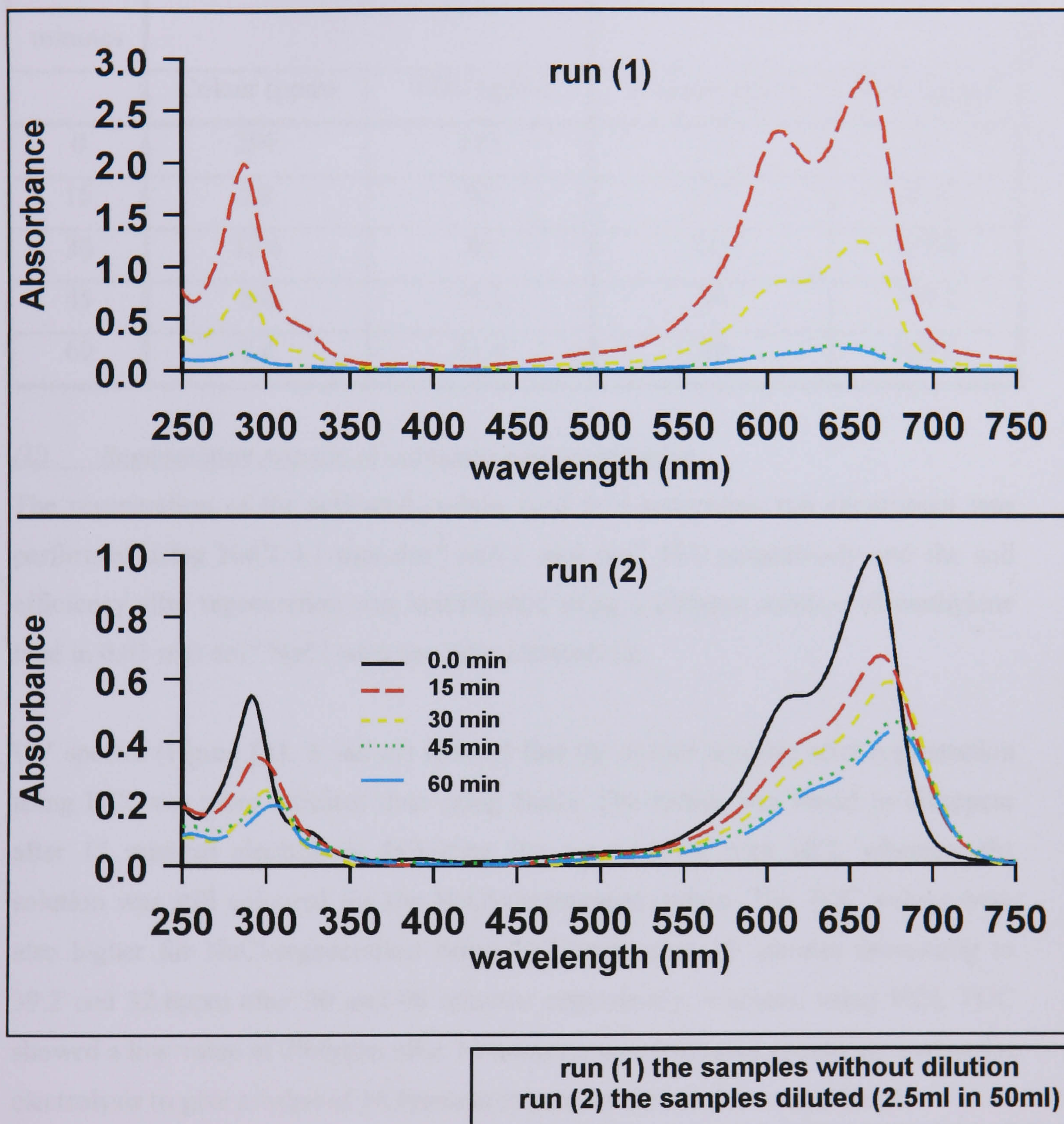
Table [5.20]: Colour and TOC removal using configuration 3 in 10 successive runs.						
Time (minutes)	Run 1		Run 5		Run 10	
	Colour ppm	TOC ppm	Colour ppm	TOC ppm	Colour ppm	TOC ppm
0	200	127.6	---	---	---	---
15	0	76.0	2	48.8	16	124.8
30	0	45.6	0	36.8	4	50.4
45	0	43.2	0	36.4	2	45.2
60	0	38.4	0	36.0	1	40.0

To check if the  $0.03 \text{ mol dm}^{-3}$  NaCl, which was added only once, is consumed and decreased the efficiency, a fresh dye solution (200ppm methylene blue) with  $0.03 \text{ mol dm}^{-3}$  NaCl was examined without pre-washing the activated carbon granules. The UV results (Figure [5.23, a]) and TOC values show that the rate of colour removal from fresh solution as compared to result in the run10 previously are similar. The solution still shows colour after 15 minutes with a dye concentration of 5ppm. This colour disappeared after 30 minutes. TOC values are high 120.8ppm, after 15 minutes but decreased to 39.2 after 60 minutes reaction time. This indicates that sodium chloride, which can be consumed during the electrolysis, is not the only factor responsible for the efficiency decrease. This decrease may be due to the dye material being absorbed on the activated carbon granules, which need to be regenerated.

(I) Destruction of methylene blue in successive run using configuration 3 without current input.

A further investigation was made to examine the effect of the adsorption process without applying an electric current for the solution containing 200ppm dye and  $0.03 \text{ mol dm}^{-3}$  NaCl. The experiment was performed only for two runs since the colour was very intense at the end of the second run. Results (Figure [5.22] and Table [5.21]) show that the adsorption process only occurs efficiently in the first run, the colour and TOC rapidly reduced, whereas, in the second run the colour and TOC removal are poor in the absence of the applied electric current.





**Figure [5.22]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (3) in successive run without current input.**

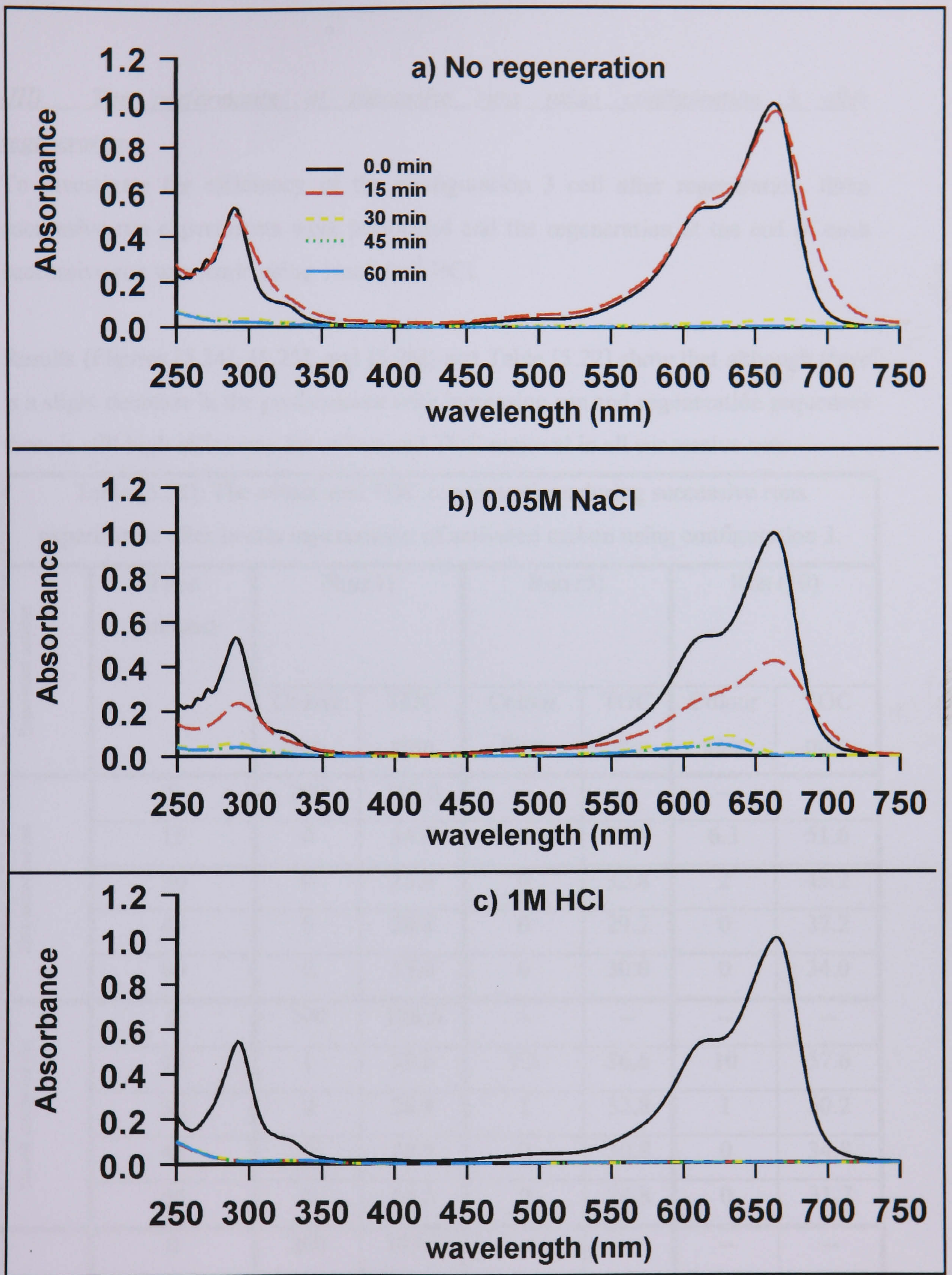
Table [5.21]: The change of colour and TOC concentration using successive run without current input.				
Time minutes	Run 1		Run 2	
	Colour (ppm)	TOC (ppm)	Colour (ppm)	TOC (ppm)
0	200	112	---	---
15	28	92	137	112
30	12.6	80	115	108.8
45	2.6	73.2	94	107.2
60	2.4	61.6	89	104.2

*(II) Regeneration process of activated carbon granules.*

The regeneration of the activated carbon used in a successive run experiment was performed using NaCl  $0.1 \text{ mol dm}^{-3}$  and  $1 \text{ mol dm}^{-3}$  HCl respectively and the cell efficiency after regeneration was investigated using a 200ppm solution of methylene blue in  $0.03 \text{ mol dm}^{-3}$  NaCl with one hour electrolysis.

UV spectra (Figure [23, b and c]) showed that the colour removal after regeneration using HCl was more efficient than using NaCl. The colour was found to disappear after 15 minutes electrolysis following the regeneration with HCl, whereas, the solution was still coloured for the NaCl-regenerated carbon. The TOC values were also higher for NaCl-regeneration being 117.2ppm after 15 minutes decreasing to 39.2 and 32.8ppm after 30 and 60 minutes respectively, whereas, using HCl, TOC showed a low value of 29.6ppm after 15 minutes, and decreased constantly during the electrolysis to give a value of 14.8ppm at the end of the one hour experiment.

The above results show that 1M HCl gives a better efficiency for regeneration. Therefore, this acid concentration was used for further regeneration experiments.



Only initial dye sample (0min) diluted (2.5ml in 50ml)  
 The samples after electrolysis without dilution

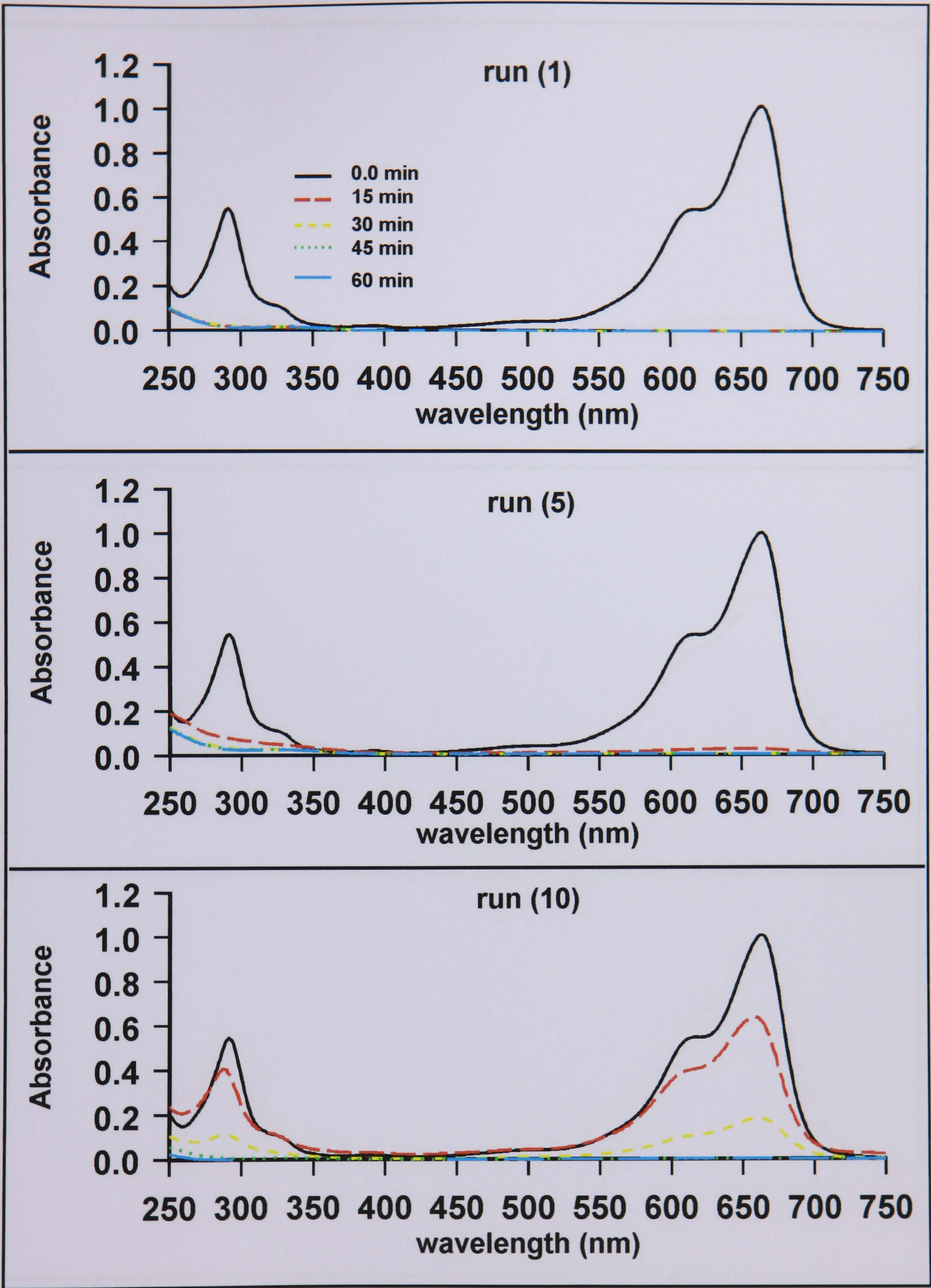
Figure [5.23]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (3) after regeneration with b) 0.05M NaCl, c) 1M HCl and compared with a) fresh solution with no regeneration.

(III) The performance of successive runs using configuration 3 after regeneration.

To investigate the efficiency of the configuration 3 cell after regeneration, three successive run experiments were performed and the regeneration at the end of each successive run was made using  $1\text{ mol dm}^{-3}$  HCl.

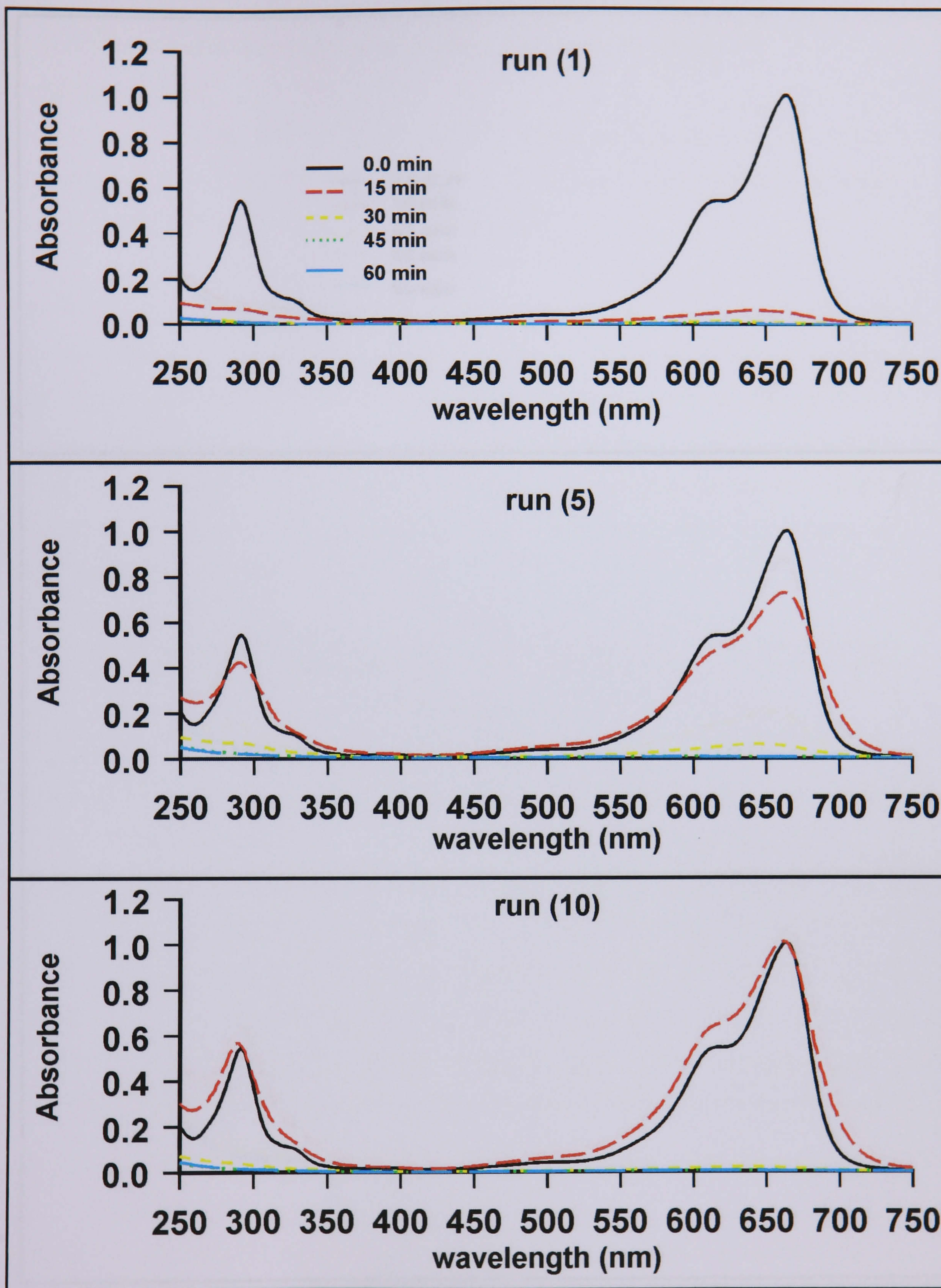
Results (Figures [5.24], [5.25], and [5.26]) and Table [5.22] show that although there is a slight decrease in the performance with increasing run and regeneration sequences there is still high efficiency for colour and TOC removal in all successive runs.

Table [5.22]: The colour and TOC concentrations during successive runs experiments after <i>in-situ</i> regeneration of activated carbon using configuration 3.							
Experiment number	Time (minute)	Run(1)		Run (5)		Run (10)	
		Colour ppm	TOC ppm	Colour Ppm	TOC ppm	Colour ppm	TOC ppm
First successive run	0	200	105.0	--	--	--	--
	15	0	34.0	1	36.8	6.3	51.6
	30	0	25.6	0	32.8	2	45.2
	45	0	20.8	0	29.2	0	37.2
	60	0	15.6	0	30.0	0	34.0
Second successive run	0	200	108.6	--	--	--	--
	15	1	35.6	7.3	36.6	10	57.6
	30	0	28.8	1	32.8	1	50.2
	45	0	20.8	0	30.8	0	34.8
	60	0	14.5	0	24.8	0	31.7
Third successive run	0	200	107.1	--	--	--	--
	15	1	34.0	8.6	40.8	10.5	52.8
	30	0	23.6	2	33.2	1	43.6
	45	0	20.0	0	25.6	0	40.4
	60	0	16.0	0	24.0	0	39.2



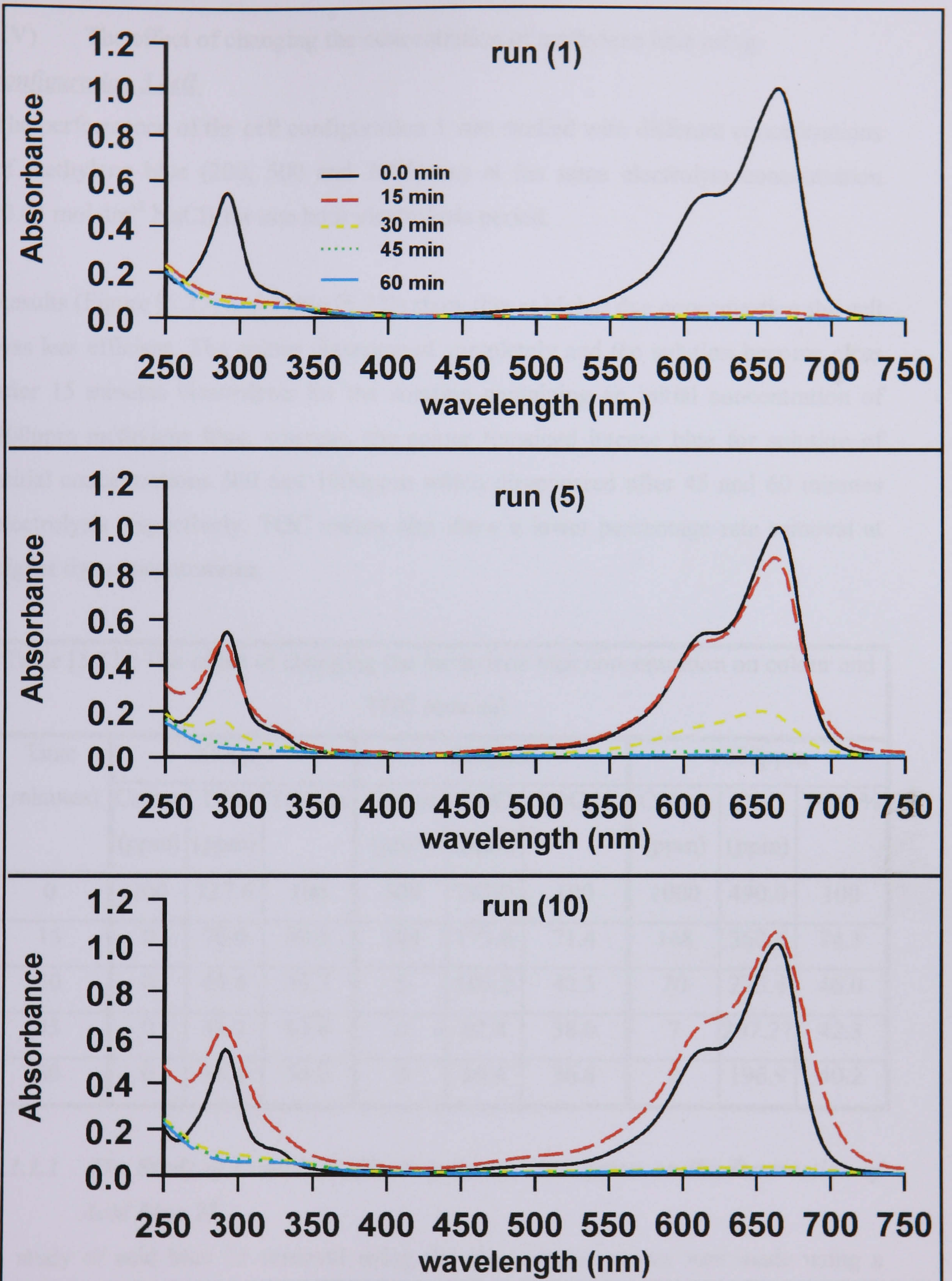
Only initial dye sample (0min) diluted (2.5ml in 50ml)  
 The samples after electrolysis without dilution

Figure [5.24]: UV/Visible spectra for methylene blue following electrolytic destruction using configuration (3), successive run after first regeneration.



Only initial dye sample (0min) diluted (2.5ml in 50ml)  
 The samples after electrolysis without dilution.

Figure [5.25]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (3) successive run after second regeneration.



Only initial dye sample (0min) diluted (2.5ml in 50ml)  
 The samples after electrolysis without dilution

Figure [5.26]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (3), successive run after third regeneration.

(IV) The effect of changing the concentration of methylene blue using configuration 3 cell.

The performance of the cell configuration 3 was studied with different concentrations of methylene blue (200, 500 and 1000ppm) at the same electrolyte concentration (0.03 mol dm<sup>-3</sup> NaCl) for one hour electrolysis period.

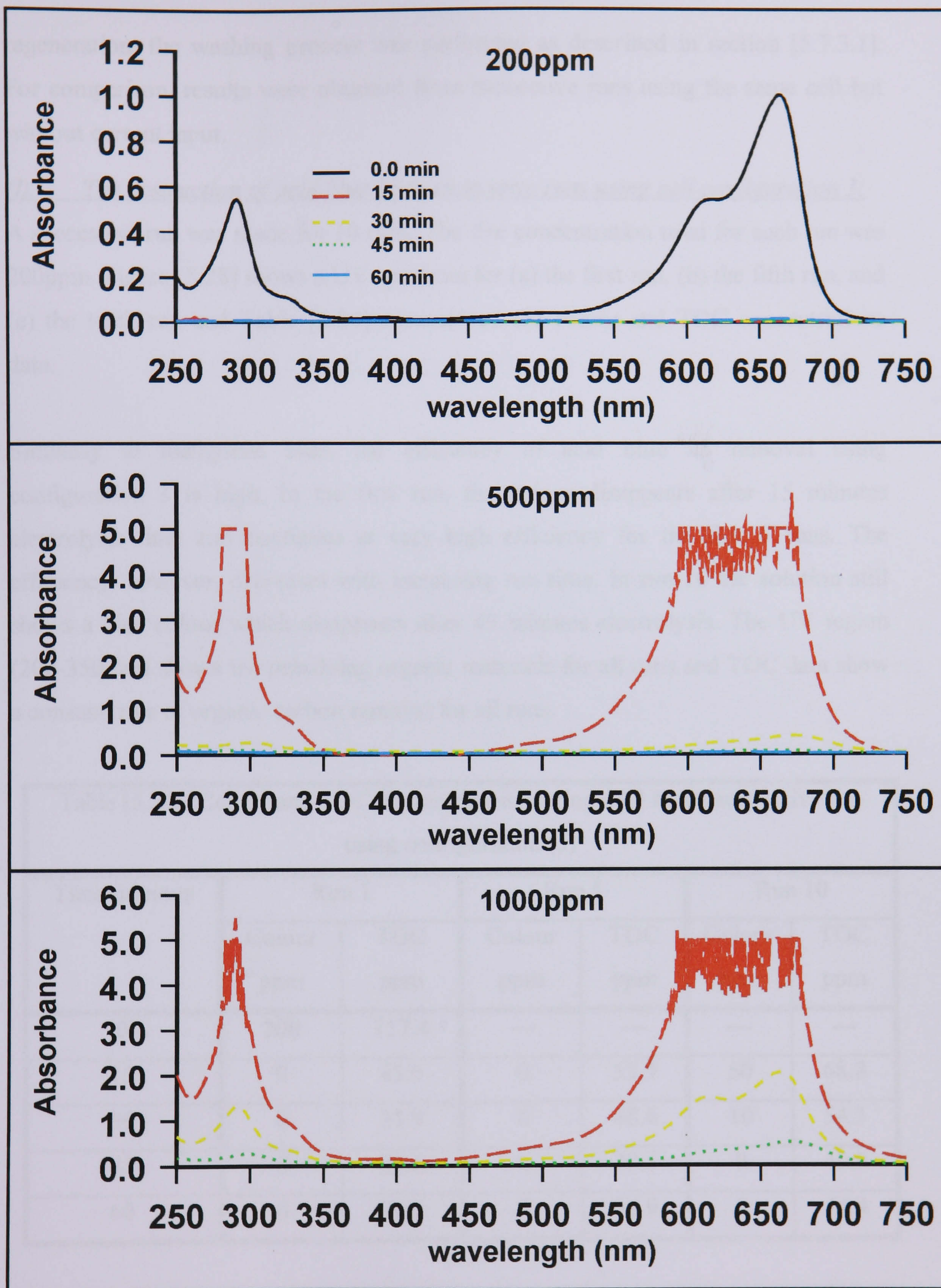
Results (Figure [5.27] and Table [5.23]) show that at higher dye concentration the cell was less efficient. The colour disappeared completely and the solution become clear after 15 minutes electrolysis for the solution containing an initial concentration of 200ppm methylene blue, whereas, the colour remained intense blue for solution of initial concentrations 500 and 1000ppm which disappeared after 45 and 60 minutes electrolysis respectively. TOC values also show a lower percentage rate removal at higher dye concentrations.

Time (minutes)	200ppm			500ppm			1000ppm		
	Colour (ppm)	TOC (ppm)	TOC %	Colour (ppm)	TOC (ppm)	TOC %	Colour (ppm)	TOC (ppm)	TOC %
0	200	127.6	100	500	242.9	100	1000	490.0	100
15	0	76.0	59.5	104	173.6	71.4	168	362.6	74.1
30	0	45.6	35.7	5	103.2	42.5	20	225.4	46.0
45	0	43.2	33.8	0	92.4	38.0	7	207.27	42.3
60	0	38.4	30.0	0	89.4	36.8	0	196.9	40.2

#### ***5.1.1.1 The Study of Combined Electrolysis and Adsorption on the Destruction of Acid Blue 25***

A study of acid blue 25 removal using the electrolysis process was made using a combination of an electrolysis system with activated carbon (configuration 3). The cell was operated for 10 hour successive runs using 200ppm of acid blue 25 in 0.03mol dm<sup>-3</sup> NaCl solution and topping up the solution every hour to return the concentration to 200ppm. After 10 runs, the activated carbon was regenerated by treatment with 1mol dm<sup>-3</sup> HCl and applying a current of 1.5 A for 2 hours. After





Only initial dye sample (0min) diluted (2.5ml in 50ml)  
The samples after electrolysis without dilution.

Figure [5.27]: UV/Visible spectra for methylene blue following electrolytic destruction using cell-configuration (3). The effect of changing the concentration of methylene blue.

regeneration, the washing process was performed as described in section [5.7.3.1]. For comparison, results were obtained from successive runs using the same cell but without current input.

(I) The destruction of acid blue 25 in successive runs using cell configuration 3:

A successive run was made for 10 runs. The dye concentration used for each run was 200ppm. Figure [5.28] shows a UV spectrum for (a) the first run, (b) the fifth run, and (c) the tenth run and Table [5.24] summarised the colour and TOC concentrations data.

Similarly to methylene blue, the efficiency of acid blue 25 removal using configuration 3 is high. In the first run, the colour disappears after 15 minutes electrolysis time and continues at very high efficiency for the first 5 runs. The efficiency, however, decreases with increasing run time. In run 10 the solution still shows a blue colour which disappears after 45 minutes electrolysis. The UV region (200-350 nm) shows the remaining organic materials for all runs and TOC data show a constant rate of organic carbon removal for all runs.

Table [5.24]: Colour and TOC concentrations during a 10 hours successive run using configuration (3)						
Time minutes	Run 1		Run 5		Run 10	
	Colour ppm	TOC ppm	Colour ppm	TOC ppm	Colour ppm	TOC ppm
0	200	117.4	---	---	---	---
15	0	43.6	0	53.9	50	68.8
30	0	31.9	0	48.6	10	54.3
45	0	28.6	0	39.5	0	49.9
60	0	28.2	0	38.9	0	44.4

(II) The destruction of acid blue 25 in successive runs using configuration 3 without current input.

A further investigation was made to examine the effect of the adsorption process without applying an electric current for a 200ppm dye solution in 0.03 mol dm<sup>-3</sup> NaCl. The experiment was performed for two runs only, since the colour observed was

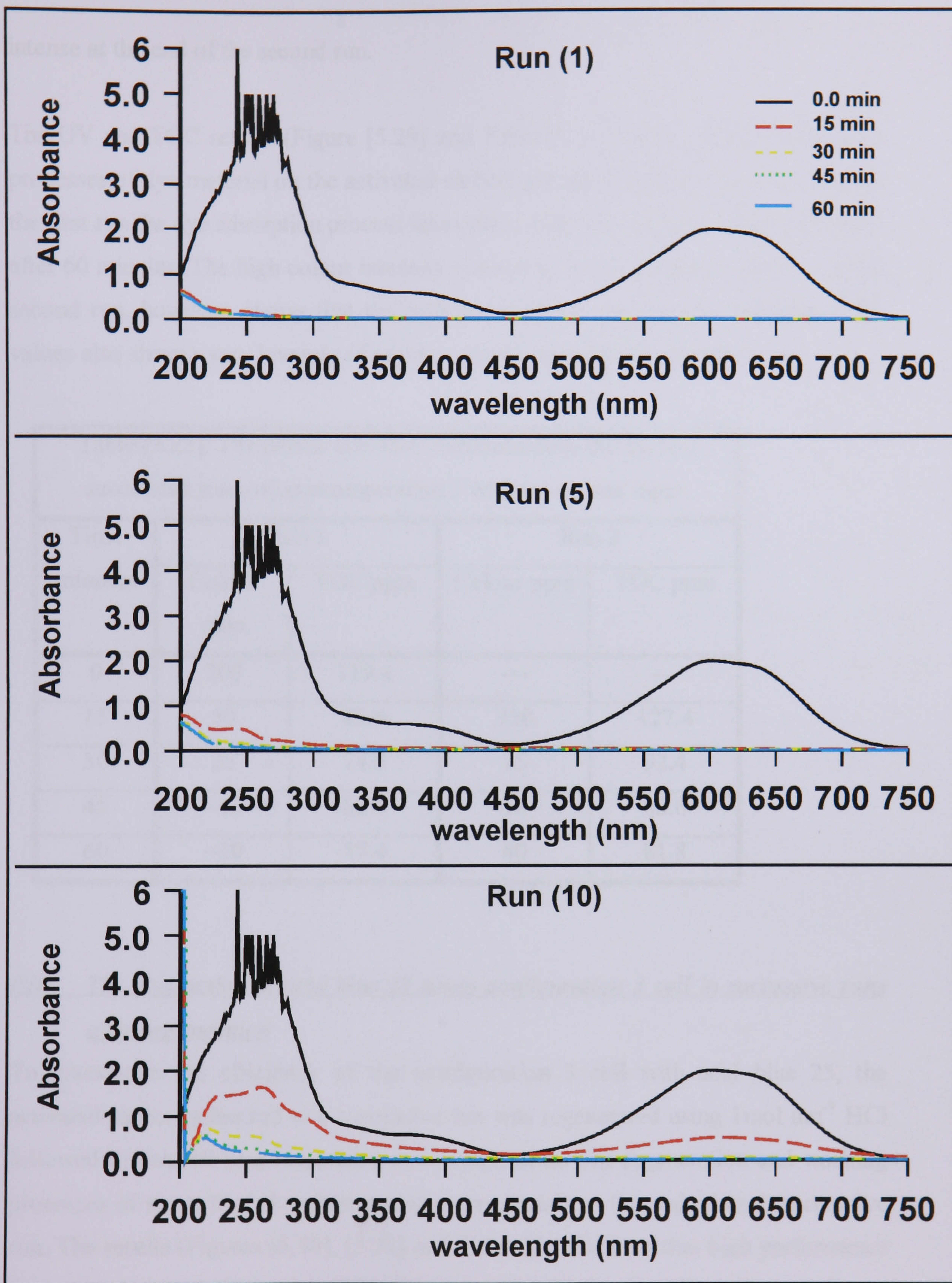


Figure [5.28]: UV/Visible spectra for the electrolytic destruction of acid blue 25 using configuration (3), successive run experiment.

intense at the end of the second run.

The UV and TOC results (Figure [5.29] and Table [5.25]) show that the adsorption processes of dye material on the activated carbon granules occur at a constant rate. In the first run the dye adsorption process takes place with only a slight colour remaining after 60 minutes. The high colour intensity remaining in the solution at the end of the second run, however, shows that the carbon adsorbent has become saturated. TOC values also show a very low rate of organic carbon removal over the two runs.

Table [5.25]: The colour and TOC concentrations during two successive runs using configuration 3 without current input.				
Time minutes	Run 1		Run 2	
	Colour ppm	TOC ppm	Colour ppm	TOC ppm
0	200	119.4	---	---
15	50	81.6	150	127.4
30	25	74.5	75	92.4
45	~12	62.8	50	85.6
60	~10	57.4	40	81.8

(III) The destruction of acid blue 25 using configuration 3 cell in successive runs after regeneration

To investigate the efficiency of the configuration 3 cell with acid blue 25, the activated carbon subjected to a successive run was regenerated using  $1\text{ mol dm}^{-3}$  HCl followed by two 10 hour successive run experiments. The regeneration and washing processes of the activated carbon granules were made at the end of each successive run. The results (Figures [5.30], [5.31] and Table [5.26]) show that high performance for both colour and TOC removal is achieved during both successive runs.

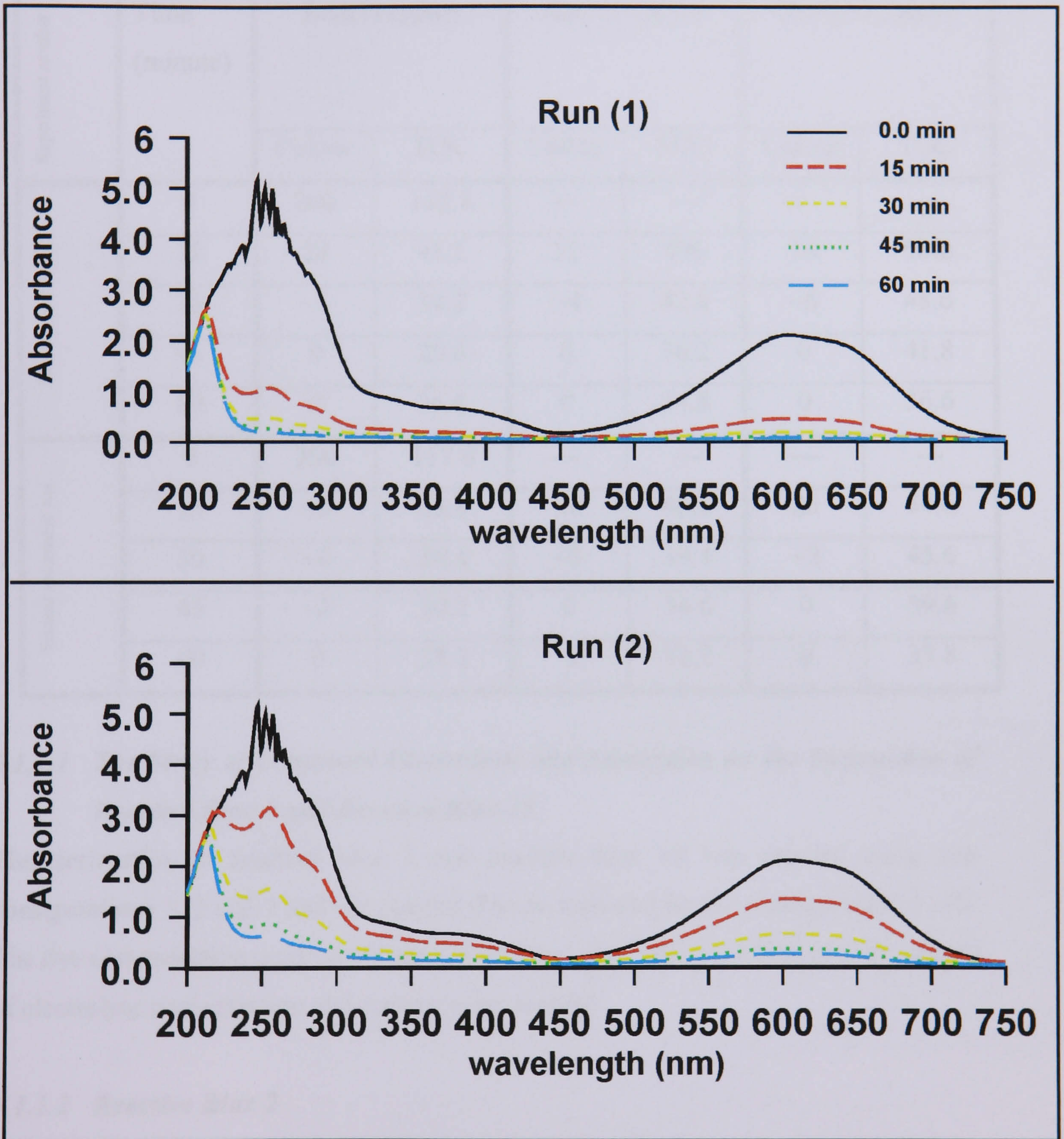


Figure [5.29]: UV/Visible spectra for the destruction of acid blue 25 using configuration (3), continuous run without current input.

Table [5.26]: The colour and TOC change of solution containing acid blue 25 during successive runs experiments after regeneration of activated carbon using configuration 3.							
Experiment number	Time (minute)	Run(1) (ppm)		Run (5) (ppm)		Run (10) (ppm)	
		Colour	TOC	Colour	TOC	Colour	TOC
First successive run	0	200	118.8	---	---	---	---
	15	20	45.2	22	496	18	58.2
	30	~5	34.2	~4	42.8	~6	48.6
	45	0	29.6	0	36.2	0	41.8
	60	0	26.6	0	34.8	0	36.6
Second successive run	0	200	117.6	---	---	---	---
	15	18	43.6	20	46.5	25	54.6
	30	~6	36.4	~5	39.4	~2	45.6
	45	~2	30.2	0	34.6	0	39.6
	60	0	28.5	0	32.2	0	35.8

### 5.1.1.1 *The Study of Combined Electrolysis and Adsorption on the Destruction of Reactive Blue 2 and Reactive Blue 15*

The destruction of reactive blue 2 and reactive blue 15 was studied using cell configurations 1, 2 and 3 and the control system followed by the configuration 3 cell. The dye concentration used was 50ppm in 0.03mol dm<sup>-3</sup> NaCl solution and the effects of electrolyte concentration and current were studied.

### 5.1.1.2 *Reactive Blue 2*

#### (I) *The effect of the different cell configuration on the removal of reactive blue 2*

To study the combination of activated carbon granules with an electrochemical cell on the removal of 50ppm reactive blue 2, the configurations (1, 2, and 3) were used with 0.03mol dm<sup>-3</sup> NaCl as electrolyte.

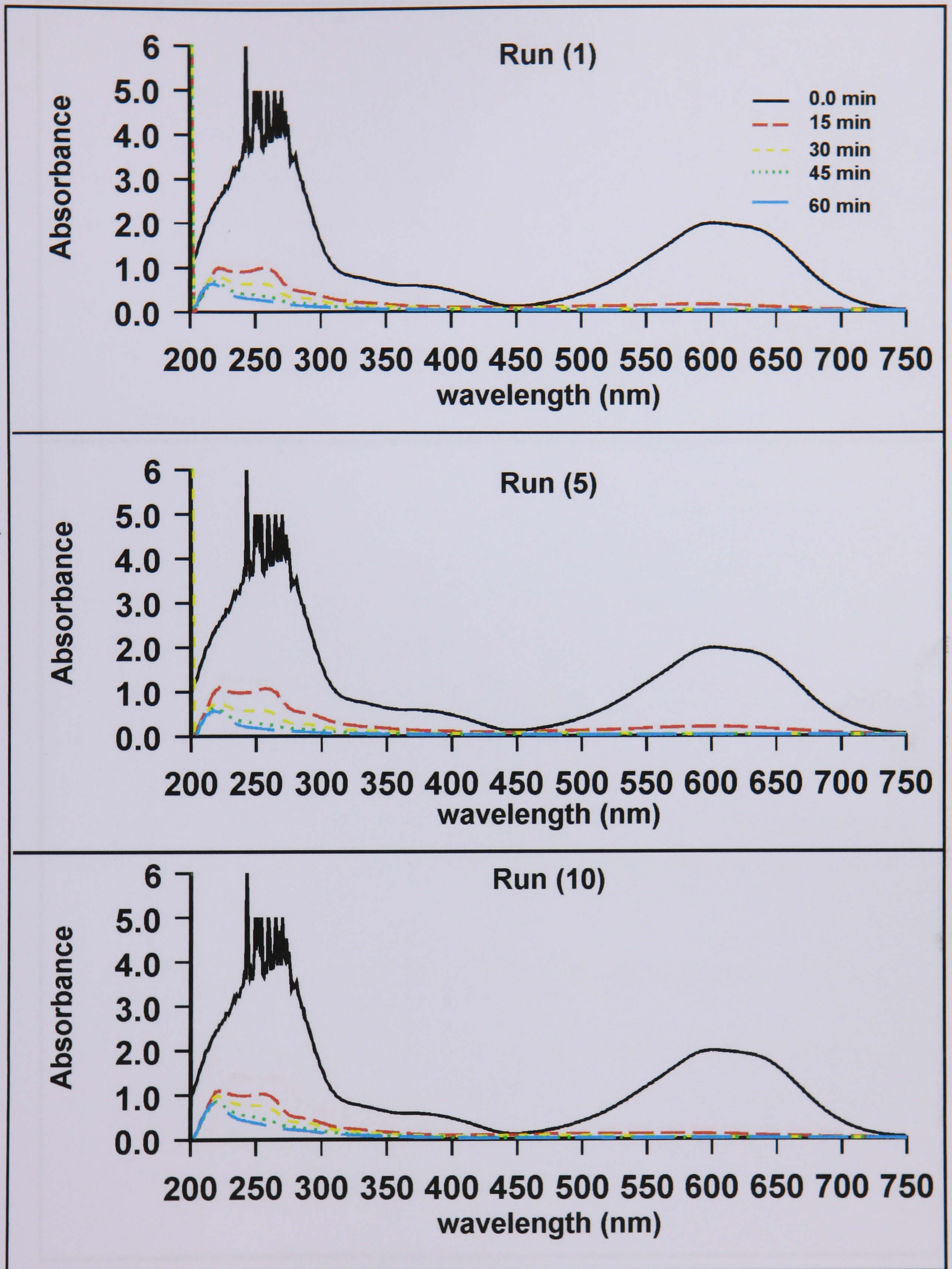


Figure [5.30]: UV/Visible spectra for the electrolytic destruction of acid blue 25 using configuration (3), successive run after first regeneration.

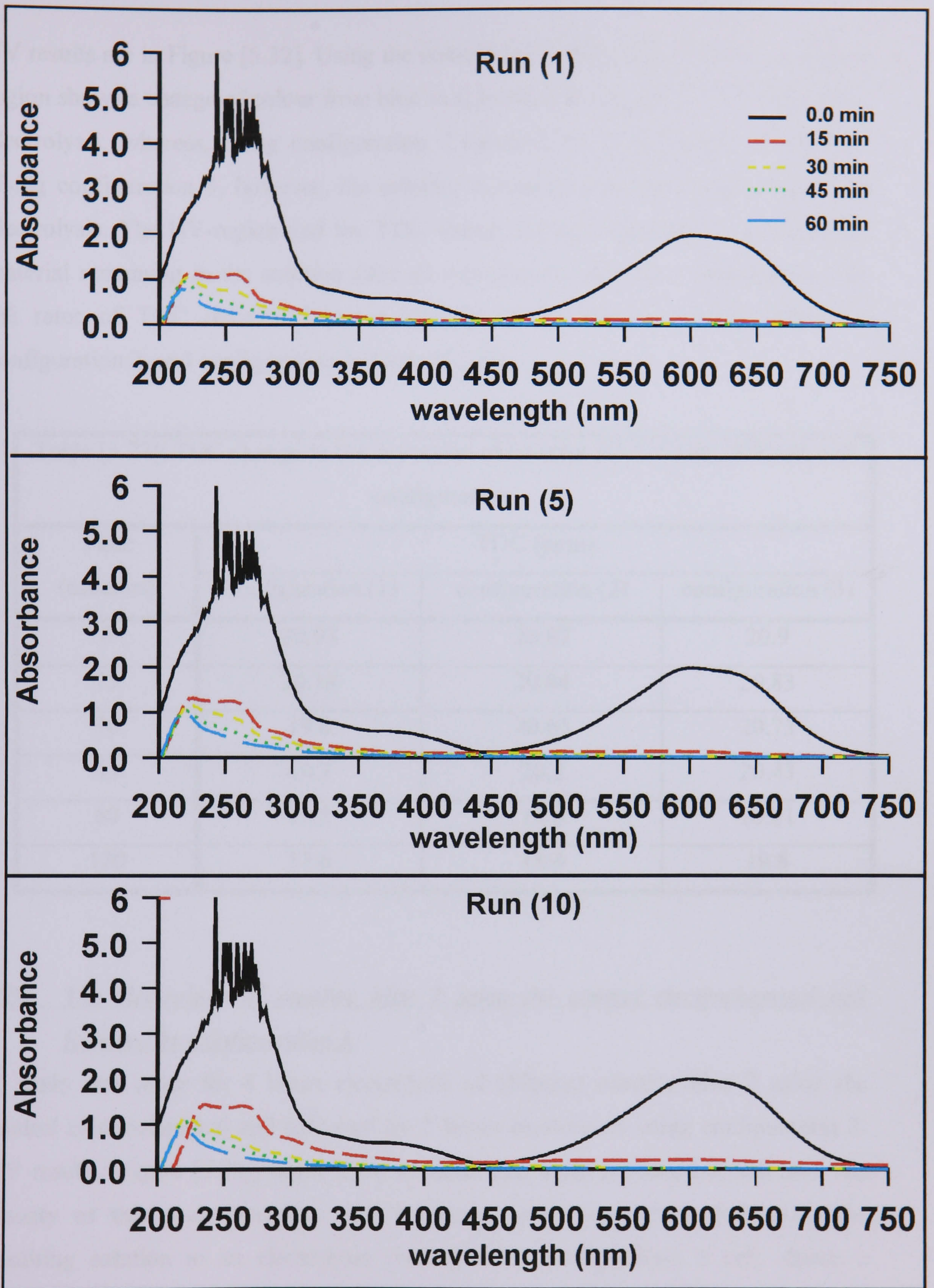


Figure [5.31]: UV/Visible spectra for the electrolytic destruction of acid blue 25 using configuration (3), successive run after second regeneration.



UV results are in Figure [5.32]. Using the control and configuration 1 cells the visible region shows a change of colour from blue to colourless during the first 15 minutes of electrolysis, whereas, using configuration 2 clearing the colour took 30 minutes. Using configuration 3, however, the solution remained blue during the 2 hours of electrolysis. The UV-region and the TOC values indicate that there is still organic material remaining in the solution after all experiments with all configurations, and the rates of TOC removal increase slightly in the sequence configuration 1, configuration 2, and configuration 3 (Table [5.27]).

Table [5.27]: TOC change in the extraction of reactive blue 2 using different cell configuration.			
Time (minutes)	TOC (ppm)		
	Configuration (1)	configuration (2)	configuration (3)
0	20.93	20.87	20.9
15	20.18	20.84	20.83
30	19.8	20.65	20.73
45	19.7	20.2	20.43
60	19.5	19.8	20.21
120	17.6	18.4	19.8

*(II) The electrolysis of reactive blue 2 using the control electrochemical cell followed by Configuration 3.*

A study was made for 4 hours electrolysis of (50ppm) reactive blue 2 using the control electrochemical cell followed by 2 hours electrolysis using configuration 3. UV results (Figure [5.33]) again show an additional peak produced at 300 nm. The density of this peak increases with increasing electrolysis time. Subjecting the resulting solution to an electrolysis process using configuration 3 cell, shows a complete disappearance of the additional peak after 15 minutes electrolysis. The TOC values (Table [5.28]) during the control experiment are reduced slowly and subjecting the resulting solution to electrolysis in the configuration 3 cell leads to further decrease in TOC values.

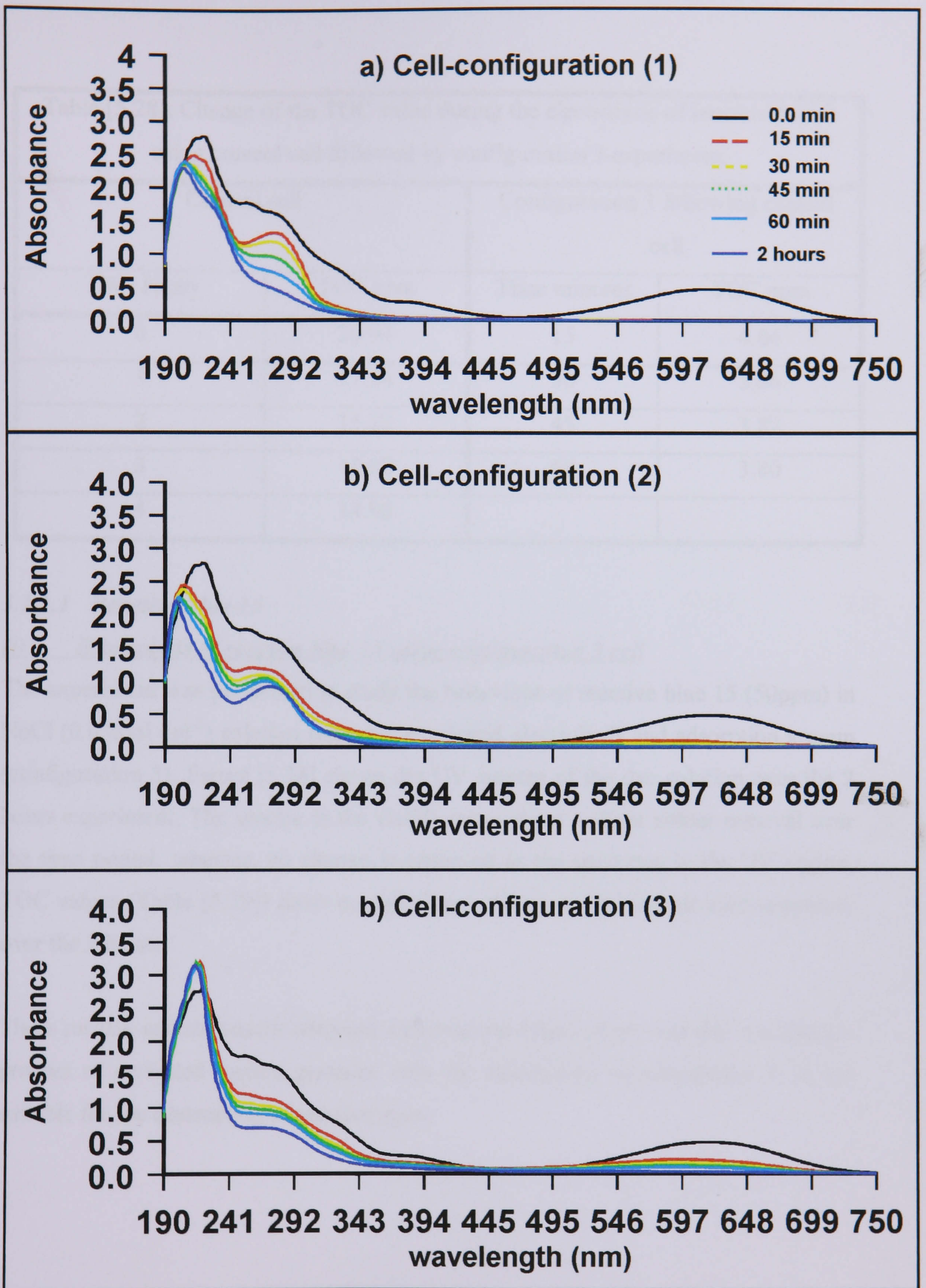


Figure [5.32]: UV/Visible spectra for reactive blue 2 following electrolytic destruction using a) cell-configuration (1), b) cell-configuration (2), and c) cell-configuration (3).

Table [5.28]: Change of the TOC value during the electrolysis of reactive blue 2 using control cell followed by configuration 3 experiment.			
Control cell		Configuration 3 following control cell	
Time hours	TOC ppm	Time minutes	TOC ppm
0	20.94	15	4.06
1	17.54	30	3.86
2	15.22	45	3.82
3	15.02	60	3.80
4	14.96		

### 5.1.1.1 Reactive Blue 15

#### *(I) Electrolysis of reactive blue 15 using configuration 3 cell*

The experiment was performed to study the behaviour of reactive blue 15 (50ppm) in NaCl (0.03mol dm<sup>-3</sup>) solution using the combined electrolysis and adsorption system (configuration 3). Figure [5.34] shows the UV spectra of the dye solution over the 2 hours experiment. The spectra in the visible range show a slight colour removal over the time period, whereas, no change is observed in the spectrum in the UV region. TOC values (Table [5.29]) show no significant change in the organic carbon present over the 2 hours.

These results, and the results obtained with reactive blue 2 show that the combination process of activated carbon granules with the electrolysis (configuration 3) is not suitable for the destruction of reactive dyes.

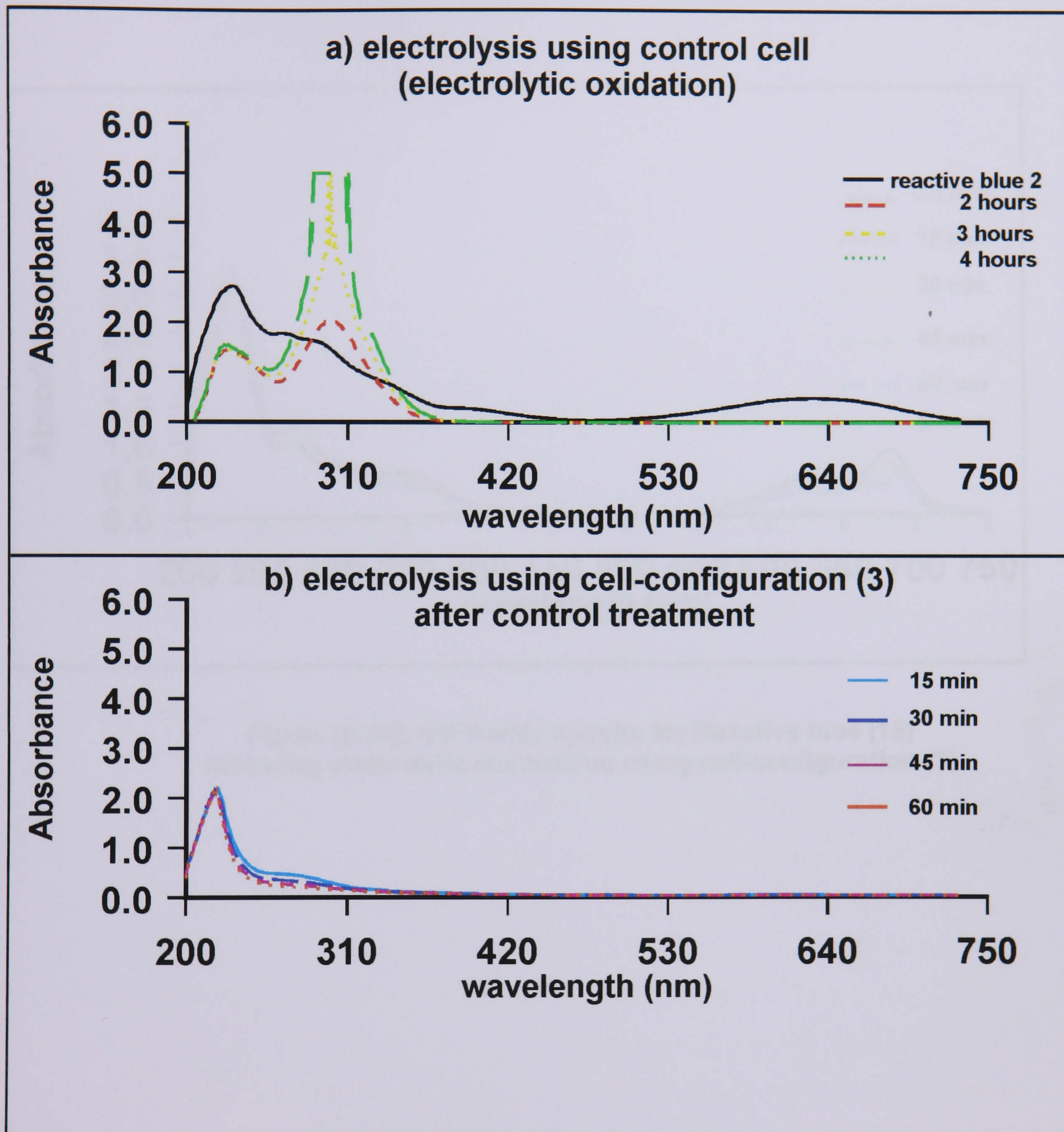
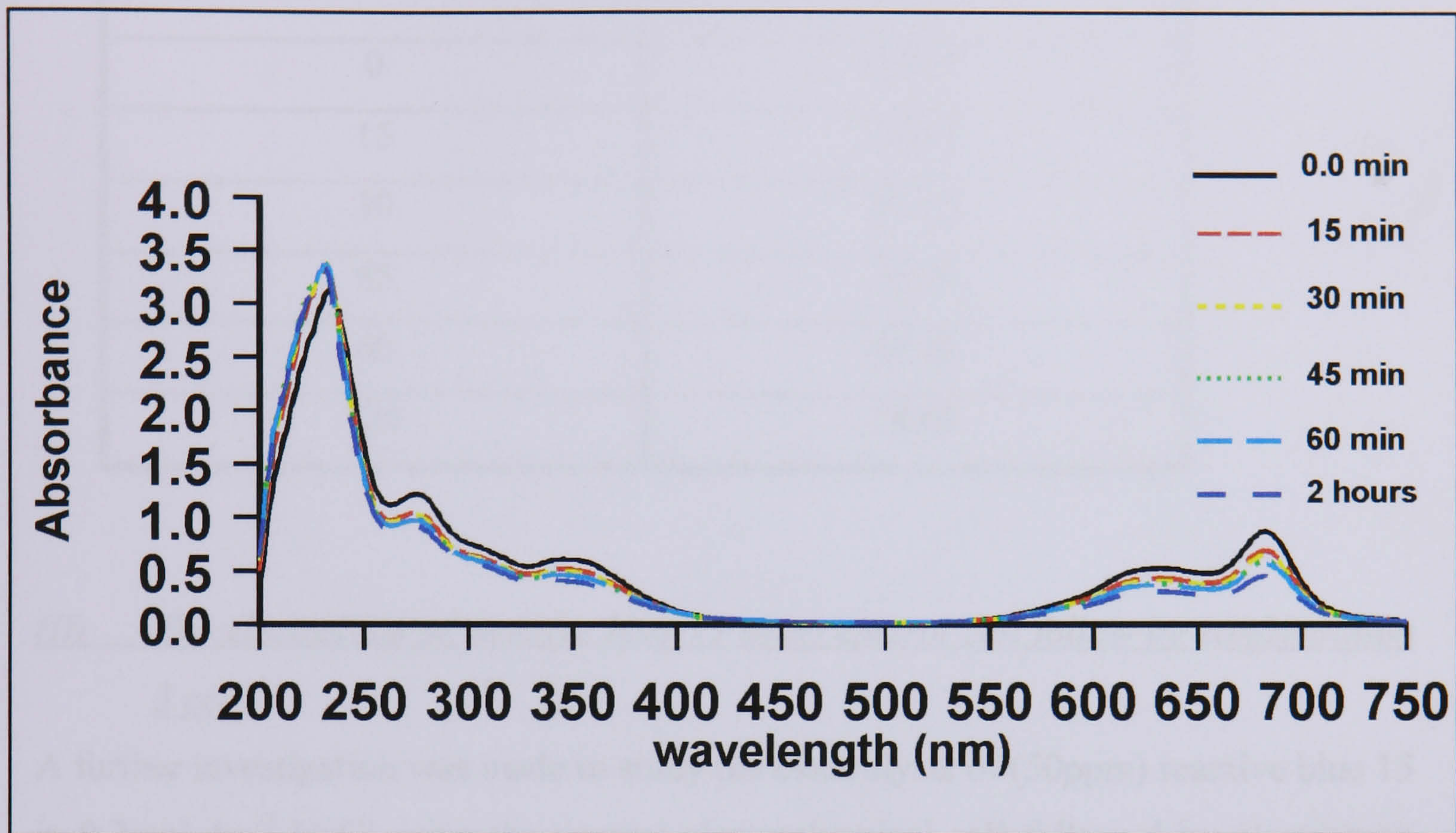


Figure [5.33]: UV/Visible spectra for reative blue 2 after a) electrolytic oxidation followed by b) electrolytic destruction using cell-configuration (3).



**Figure [5.34]: UV/Visible spectra for Reactive blue (15) following electrolytic destruction using cell-configuration (3).**

Table [5.29]: Change of the TOC value during the electrolysis of reactive blue 15 using configuration (3) cell.	
Time minutes	TOC ppm
0	19.16
15	19.12
30	19.06
45	18.98
60	18.80
120	18.62

*(II) The electrolysis of reactive blue 15 using control cell follow by configuration 3 cell.*

A further investigation was made to study the electrolysis of (50ppm) reactive blue 15 in  $0.2\text{mol dm}^{-3}$  NaCl using the control electrochemical cell followed by electrolysis using the configuration 3 cell.

UV results (Figure [5.35]) again show an additional peak produced at 300nm which increased with increasing electrolysis time. Subjecting the resulting solution to electrolysis using configuration 3 cell, shows a complete disappearance of the additional peak after 15 minutes. TOC values (Table [5.30]) show a very slow rate of organic carbon removal during the 4 hour control experiment. The rate of TOC reduction was increased by passing the resulting solution through the configuration 3 cell. These results may be due to breakdown materials which are adsorbed on the activated carbon more than the dye itself.

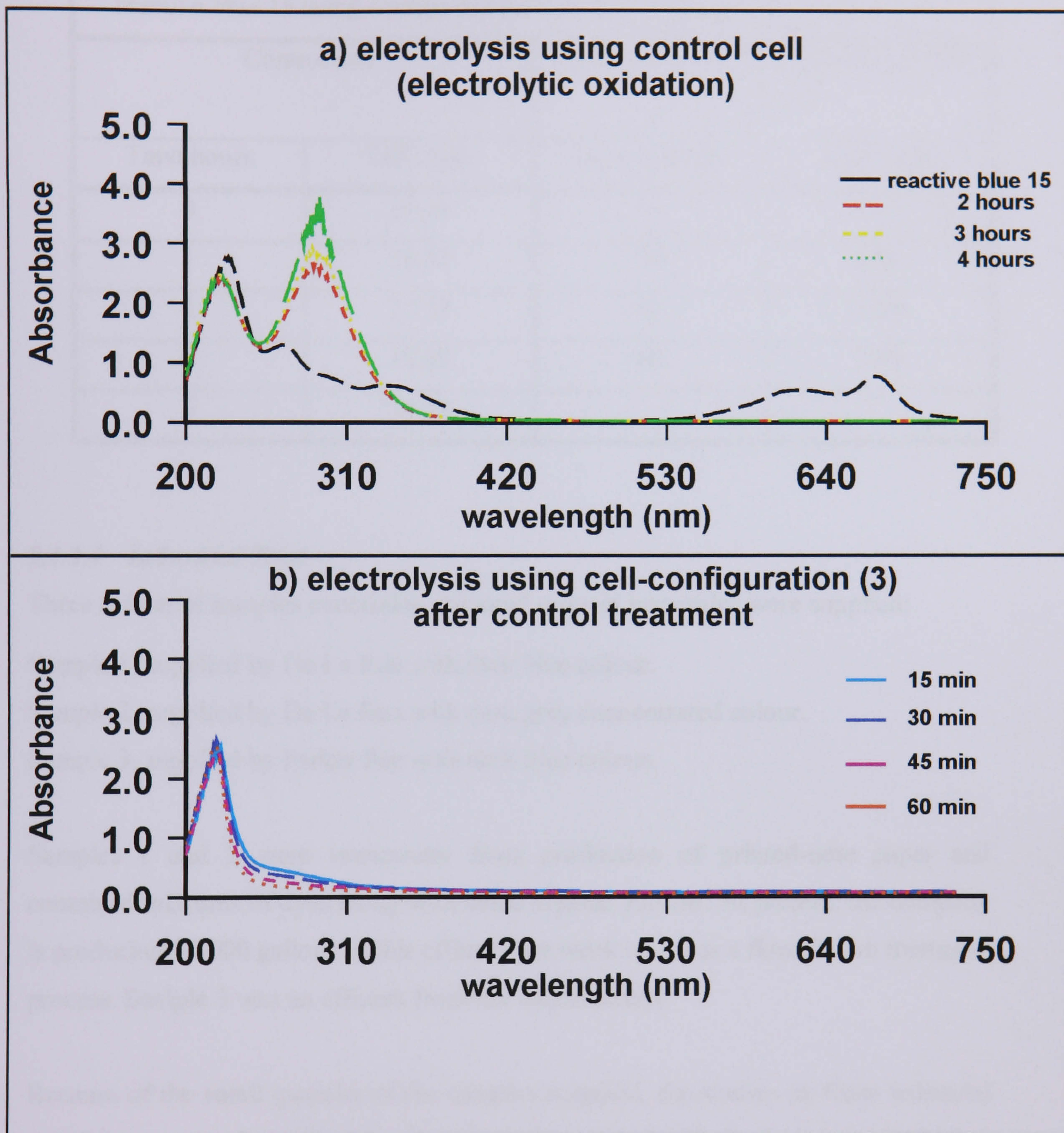


Figure [5.35]: UV/Visible spectra for reactive blue 15 after a) electrolytic oxidation followed by b) electrolytic destruction using cell-configuration (3).

Table [5.30]: Change of the TOC value during the electrolysis of reactive blue 15 using control cell followed by configuration 3 experiment.			
Control cell		Configuration 3 cell following control cell	
Time hours	TOC ppm	Time minutes	TOC ppm
0	19.16	15	4.62
1	18.28	30	4.00
2	17.58	45	3.98
3	17.02	60	3.96
4	16.64		

#### **5.1.1.1 Industrial Trial**

Three industrial samples containing coloured organic impurities were supplied:

Sample 1, supplied by De La Rue with dark blue colour.

Sample 2, supplied by De La Rue with dark grey concentrated colour.

Sample 3, supplied by Parker Pen with dark blue colour.

Samples 1 and 2 were wastewater from production of printed-note paper and contained mixtures of dyes along with some organic solvent. At present, the company is producing 50,000 gallons of this effluent per week and uses a flocculation treatment process. Sample 3 was an effluent from ink manufacture.

Because of the small quantity of the samples supplied, the studies on these industrial solutions were performed using only the configuration 3 cell. In the cases of sample 1 and 2, the experiments were performed on undiluted samples but for sample 3, one litre of sample was diluted to 5 litres.

The combined system i.e. the combination of an electrolytic cell with activated carbon granules (configuration 3) is shown to be successful in treating these industrial samples.



The results (Figure [5.36]) show that in the case of sample 1 [Spectrum 5.36, a], complete removal of the colour was observed after 15 minute treatment and only a small peak remained in the UV region. This remaining peak was not reduced by increasing the treatment time to two hours.

In the case of sample 2 longer time was required to reduce the colour and the organic content but total degradation was achieved in 24 hours. The results [Spectrum 5.36, b] show that only a small peak in the UV region remained after 24 hours treatment.

Sample 3 [Spectrum 5.36, c] shows that after only 15 minutes of treatment time the colour and the organic materials were removed.

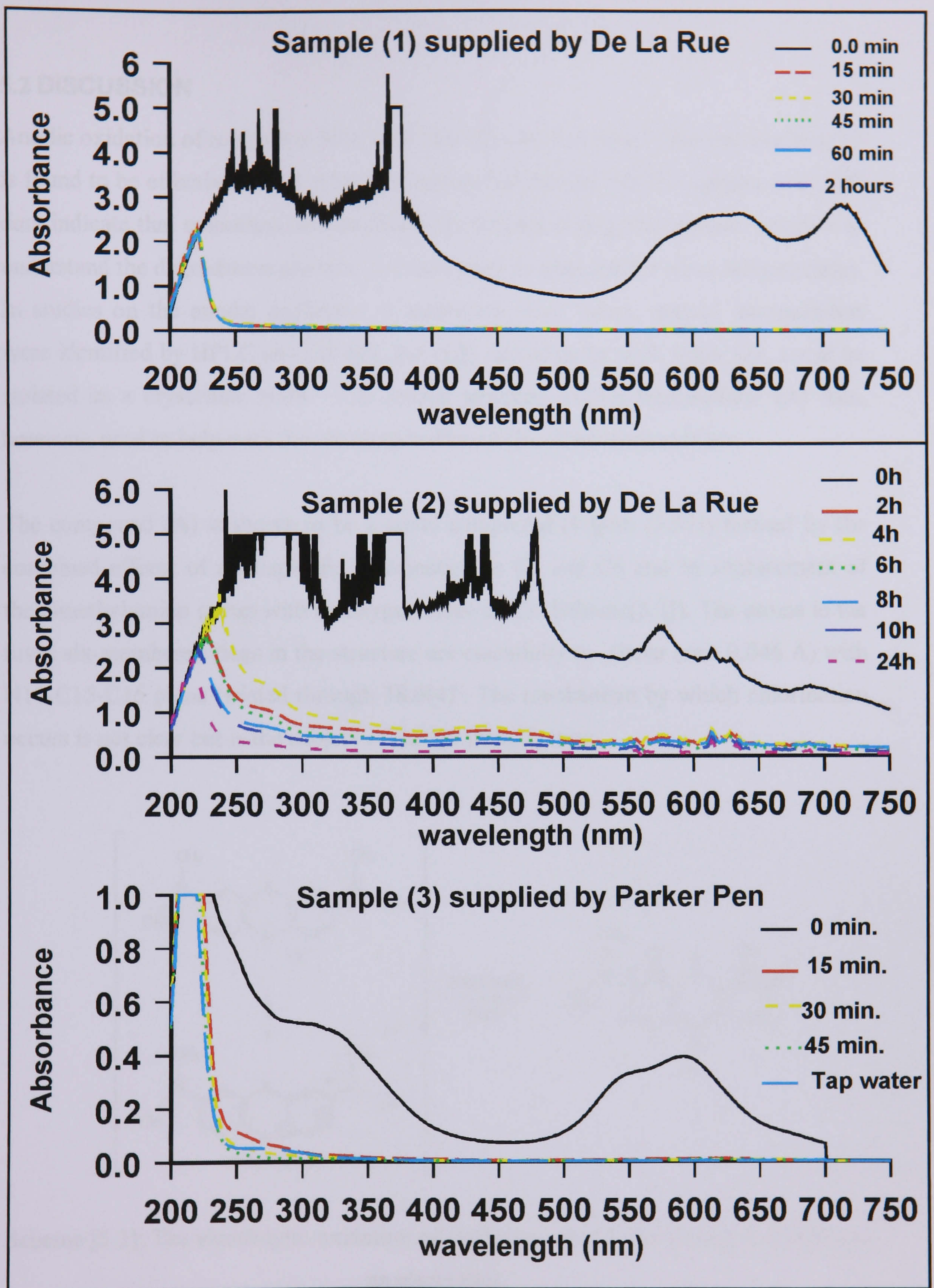
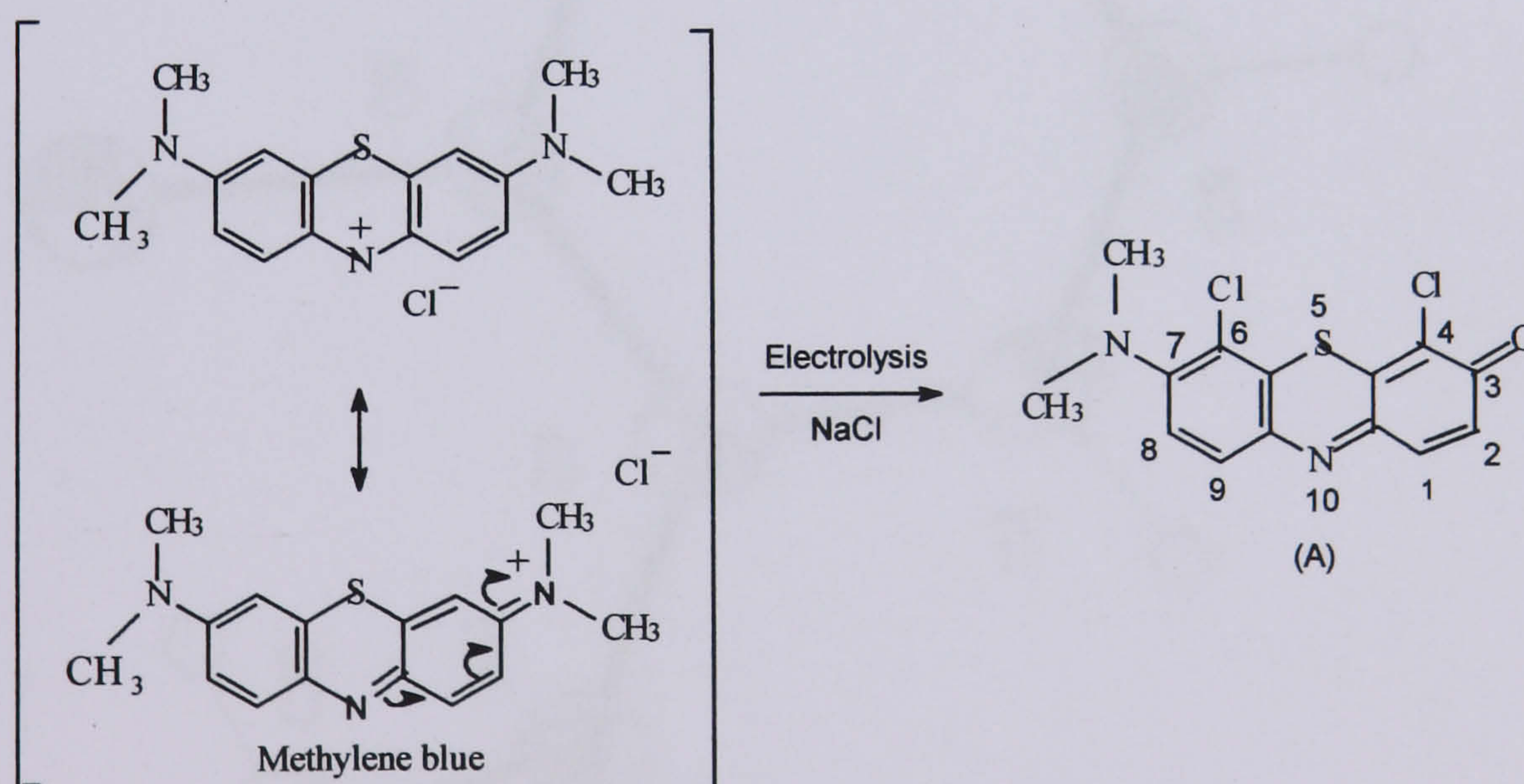


Figure [5.36]: UV/Visible spectra for organic impurities in samples supplied from real industrial samples following electrolytic destruction using cell-configuration (3).

## 5.2 DISCUSSION

Anodic oxidation of methylene blue, acid blue 25, reactive blue 2 and reactive blue 15 is found to be effective in that it leads to colour destruction, but UV spectra and TOC data indicate that colourless intermediates are formed during the process. In order to understand the degradation process, it is necessary to characterise these intermediates. In studies on the anodic oxidation of methylene blue, seven neutral intermediates were identified by HPLC and LC-MS, but only one of them, with mass 324, could be isolated as a crystalline solid. The crystal structure of this intermediate (A) was, however, used to help with the characterization of the other intermediates.

The compound (A) is shown to be a novel compound (Figure [5.37]) formed by the combined effects of regiospecific chlorination at C4 and C6 and by replacement of the dimethylamino group with an oxygen atom at C3 (Scheme[5.3]). The atoms in the fused six-membered rings in the structure are essentially co-planar (rms 0.046 Å) with N11-C15-C16 plane twisted through 38.6(4)°. The mechanism by which chlorination occurs is not clear but is the subject of further investigation.



Scheme [5.3]: The electrolytic oxidation of methylene blue in the presence of NaCl as an electrolyte.

The structure of (A) taken with the mass spectrometry data from LC-MS for the intermediates with  $m/z = 297$  ( $C_{12}H_6Cl_2N_2OS$ ) (Spectrum[5.38]) and 311 ( $C_{13}H_8Cl_2N_2OS$ ) (Spectrum [5.39]) suggests that these compounds have structures (B)

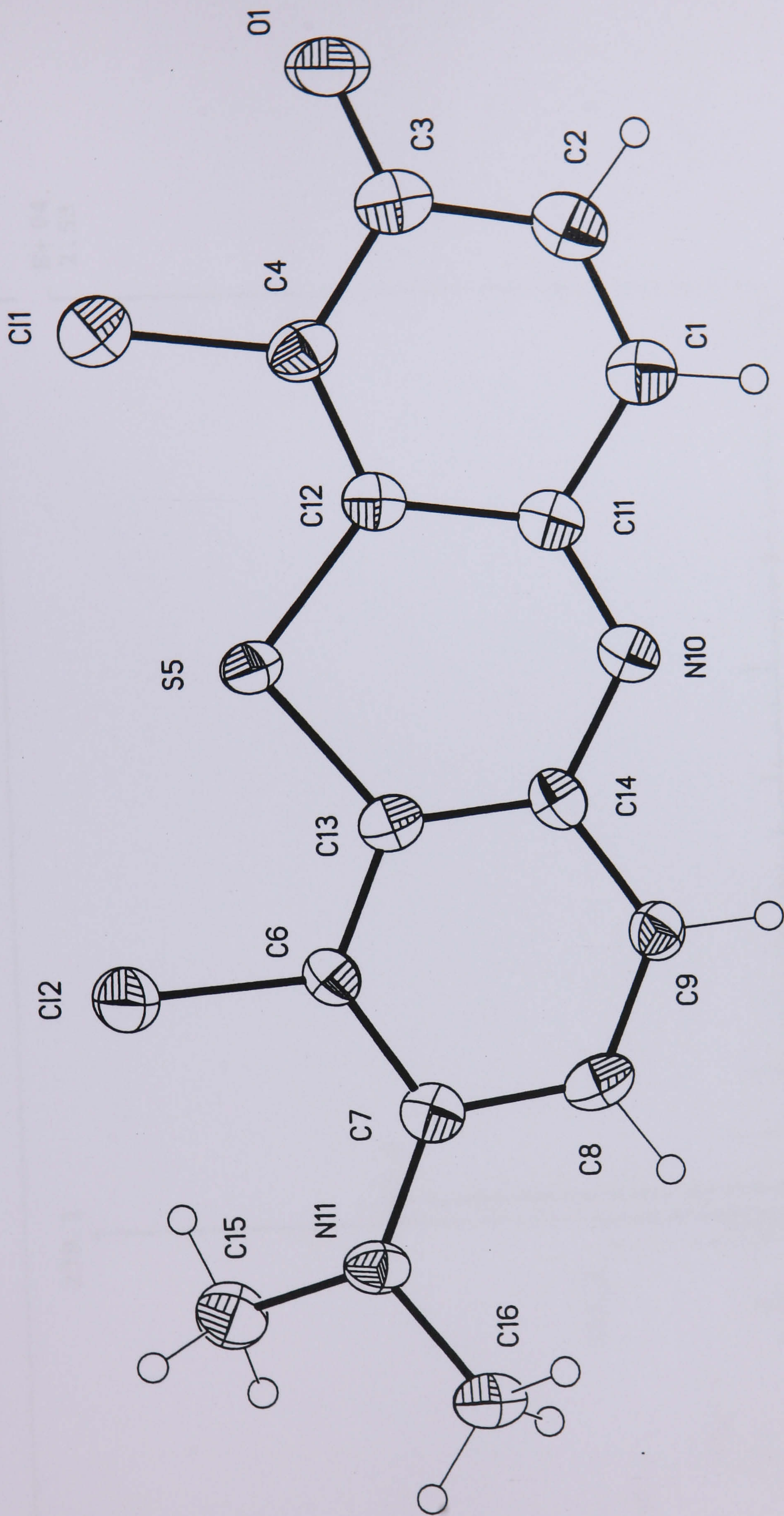


Figure [5.37]: The formula structure of the identified novel compound (A).

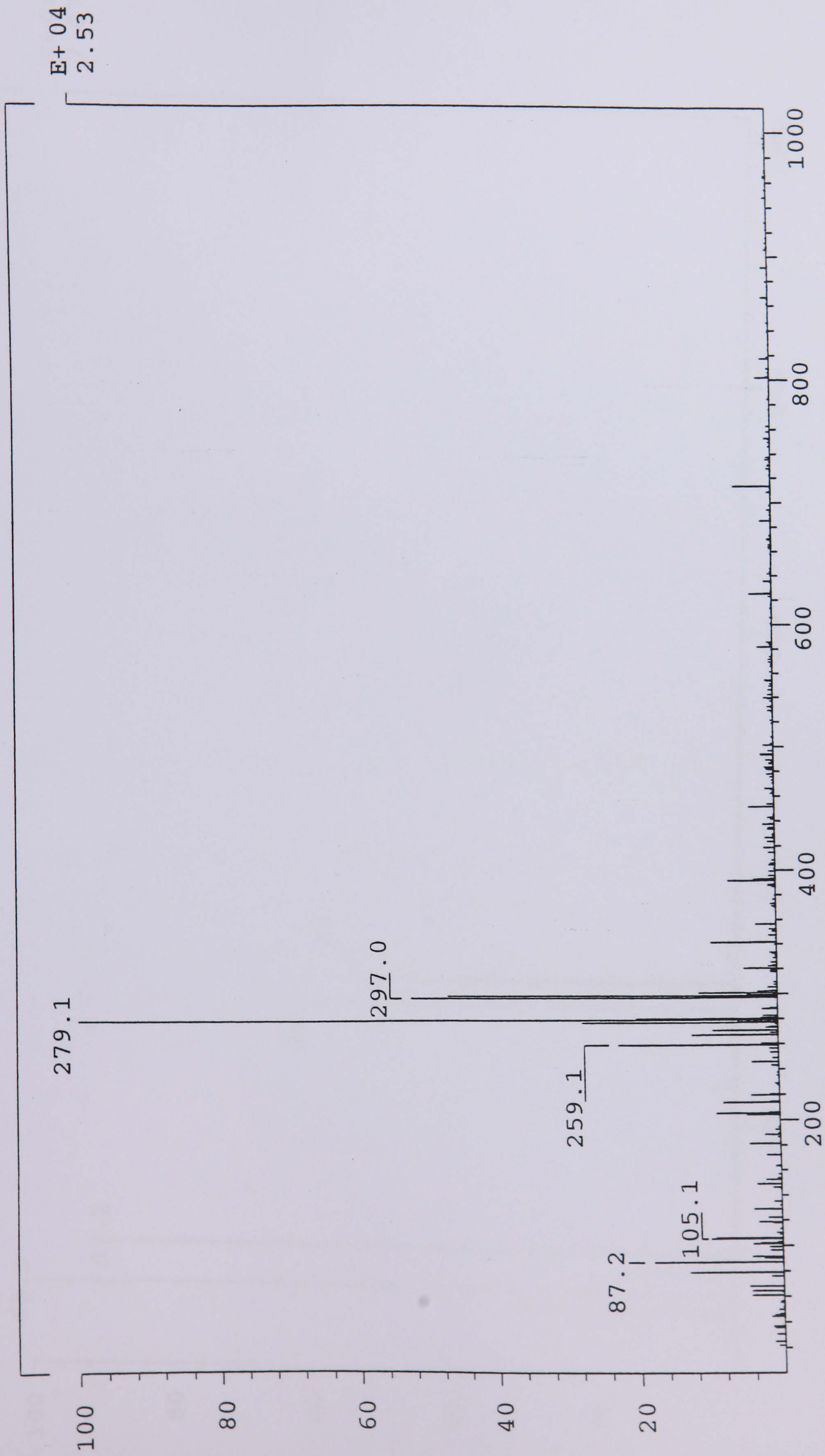


Figure [5.38]: The low resolution electron impact mass spectrum using LC-MS analysis of the compound (B)  $m/z=297$ .

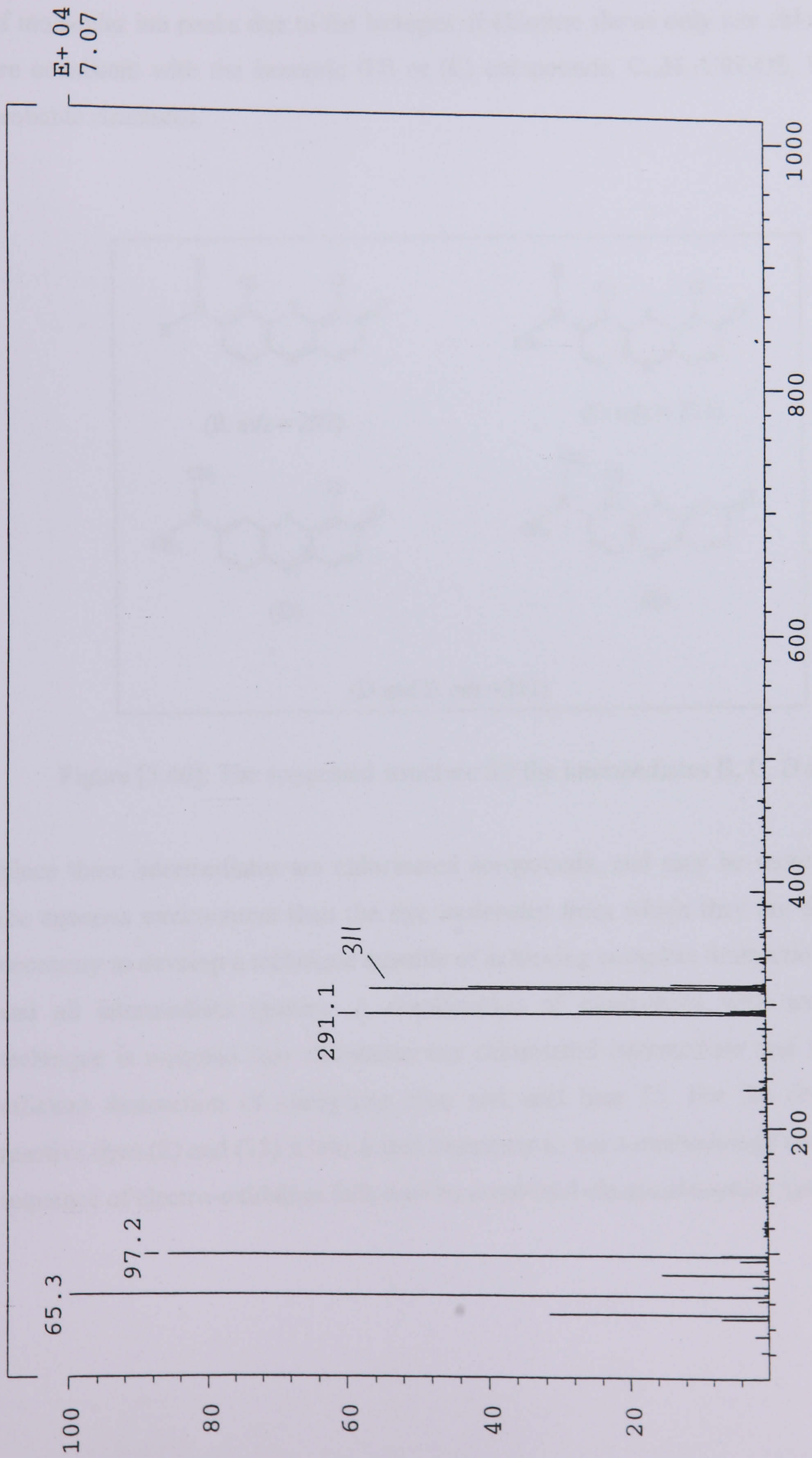


Figure [5.39]: The low resolution electron impact mass spectrum using LC-MS analysis of the compound (C)  $m/z=311$ .

and (C), respectively (Figure [5.40]). The presence of two chlorine atoms in B and C is confirmed by the pattern and ratio of the peaks at MH ( $2 \times {}^{35}\text{Cl}$ ), MH+2 and MH+4. In addition, the two peaks with m/z 291 (Spectrum[5.41] and [5.42]), where the ratio of molecular ion peaks due to the isotopes of chlorine shows only one chlorine atom, are consistent with the isomeric (D) or (E) compounds,  $\text{C}_{14}\text{H}_{11}\text{ClN}_2\text{OS}$ , being their probable structures.

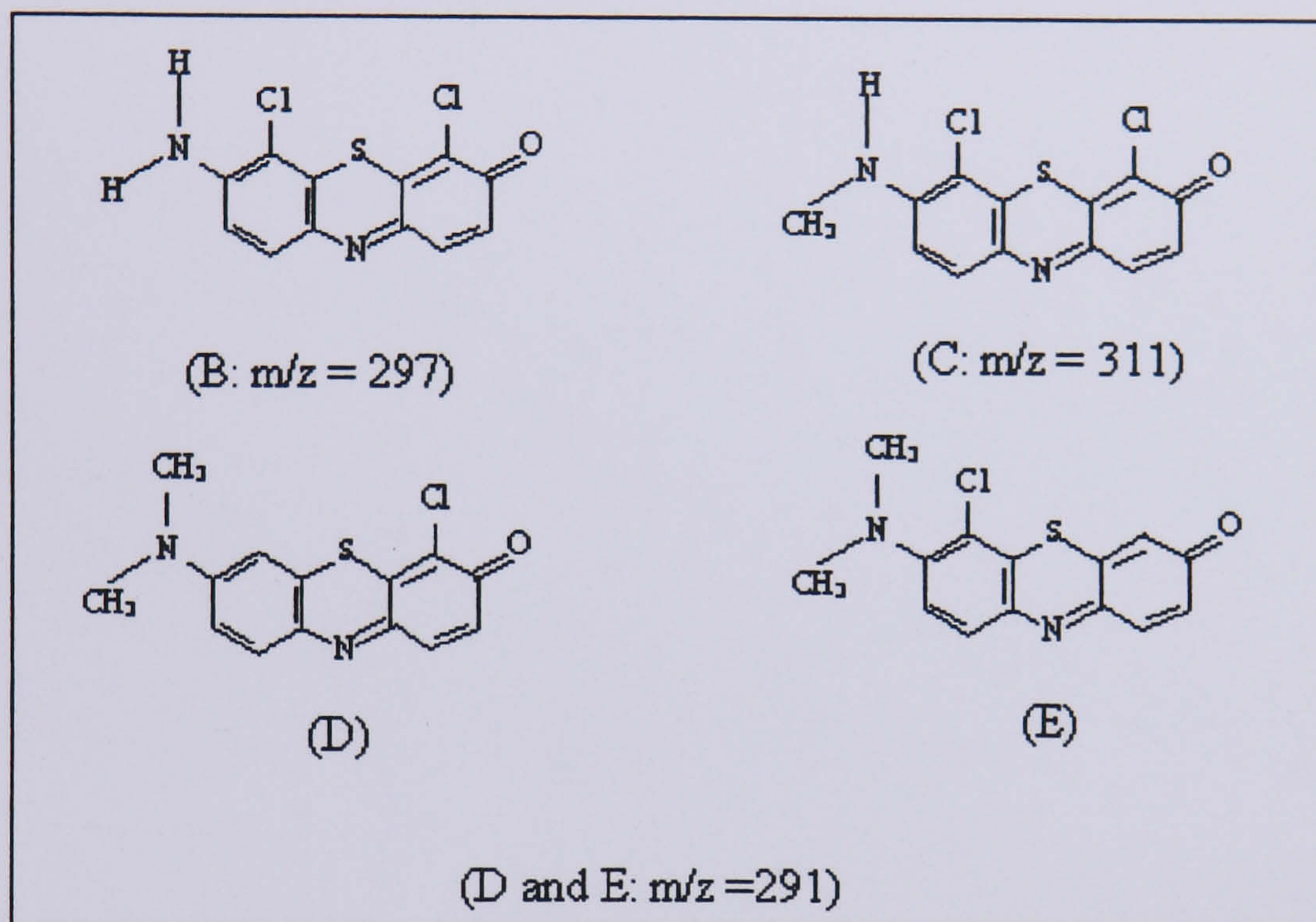


Figure [5.40]: The suggested structure for the intermediates B, C, D and E.

Since these intermediates are chlorinated compounds, and may be more harmful to the aqueous environment than the dye molecules from which they are formed, it is necessary to develop a technique capable of achieving complete destruction of the dye and all intermediate species. A combination of electrolysis with an adsorption technique is reported that eliminates the chlorinated intermediate and leads to the efficient destruction of methylene blue and acid blue 25. For the destruction of reactive dyes (2) and (15) it was found necessary to use a methodology consisting of a sequence of electro-oxidation followed by combined electroadsorption system.

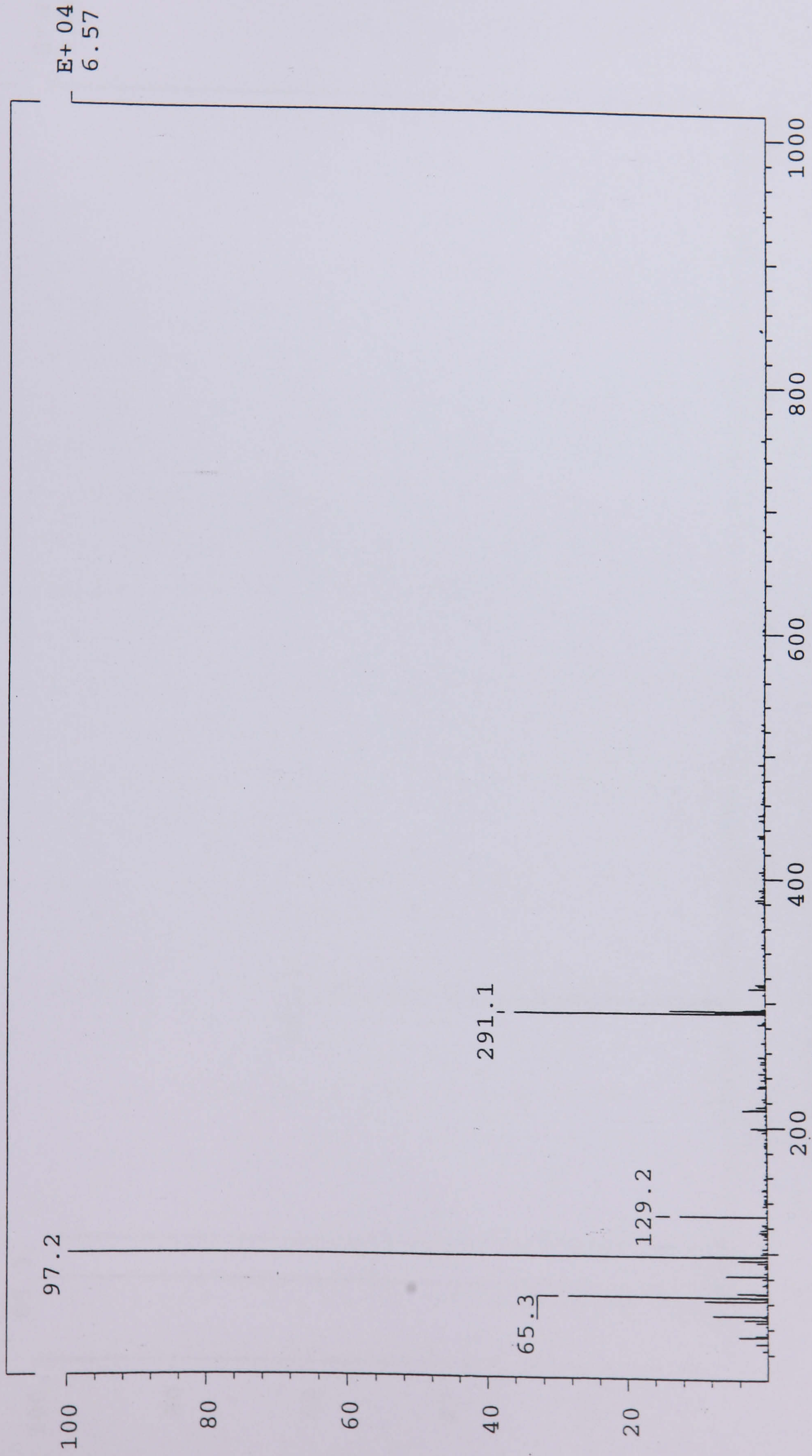


Figure [5.41]: The low resolution electron impact mass spectrum using LC-MS analysis of the isomer (E)  $m/z = 291$ .



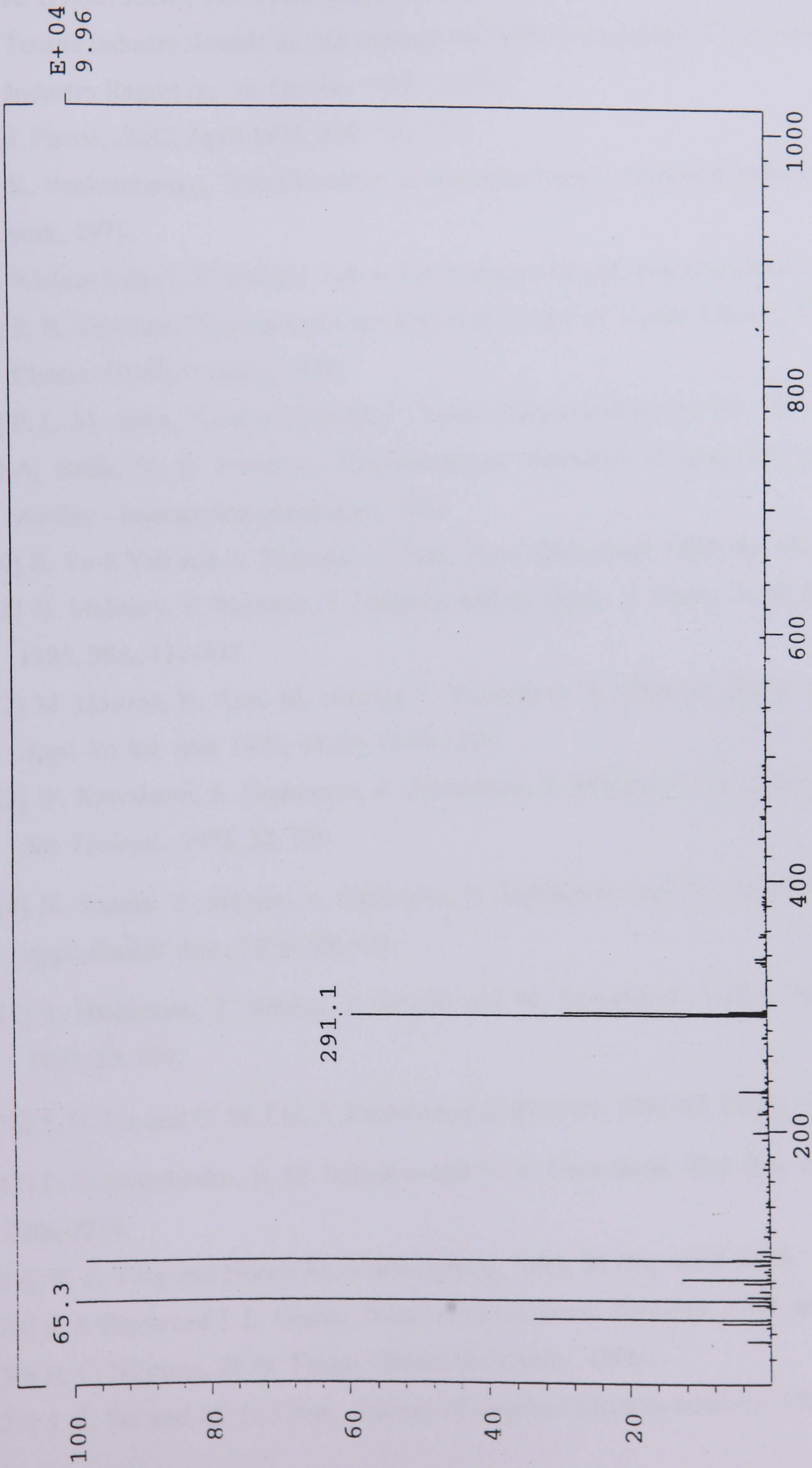


Figure [5.42]: The low resolution electron impact mass spectrum using LC-MS analysis of the isomer (D)  $m/z=291$ .

### 5.3 REFERENCES

- [1] S. H. Lin and C. F. Peng, *Water Research*, 1994, **28** (2), 277-282.
- [2] A. Uygur, *JSDC*, 1997, July/August **113**, 211-217.
- [3] Textile industry threads its way through the effluent challenge. *ENDS report: 225*. Industry Report no. 58. October 1993. 225027.
- [4] J. Pierce, *JSdC*, April 1994, **110**, 131-133.
- [5] K. Venkataraman, "The Chemistry of Synthetic Dyes", Academic Press INC, New York, 1971.
- [6] "Colour Index", 3<sup>rd</sup> Edition, **vol. 4**, The Society of Dyers and Colourists (1971).
- [7] E. R. Trotman, "Dyeing and Chemical Technology of Textile Fibers", 3<sup>rd</sup> Edition, Charles Griffin London, 1964.
- [8] P. L. M. Allen, "Colour Chemistry", Tomas Nelson and Sons LTD, 1971.
- [9] A. Reife, H. S. Freeman, "Environmental chemistry of dyes and pigments", Awiley - interscience publication, 1996.
- [10] R. Yu-li Yeh and A. Thomas, *J. Chem. Tech. Biotechnol.* 1995, **63**, 48-54.
- [11] G. Malmary, F. Perineau, J. Molinier and A. Gaset, *J. Chem. Tech. Biotechnol.*, 1985, **35A**, 431-437.
- [12] M. Hosono, H. Arai, M. Aizawa, I. Yamamoto, K. Shimizu and M. Sugiyama, *Appl. Radiat. Isot.*, 1993, **44** (9), 1199-1203.
- [13] W. Kawakami, S. Hashimoto, K. Nishimura, T. Miyata and N. Suzuki, *Environ. Sci. Technol.*, 1978, **12**, 189.
- [14] N. Suzuki, T. Miyata, A. Sakumoto, S. Hashimoto and W. Kawakami, *Int. J. Appl. Radiat. Isot.*, 1978, **29**, 103.
- [15] S. Hashimoto, T. Miyata. T. Suzuki and W. Kawakami, *Radiat. Phys. Chem.*, 1979, **13**, 107.
- [16] S. H. Lin and C. M. Lin, *J. Environmental Systems*, 1991-92, **21**(2), 143-156.
- [17] E. G. Solozhenko, N. M. Soboleva and V. V. Goncharuk, *Wat. Res.* 1995, **29** (9), 2206-2210.
- [18] W. Z. Tang and Huren An, *Chemosphere*, 1995, **31** (9), 4157-4170.
- [19] R. J. Davis and J. L. Gainer, *Water Environmental Research*, 1994, **66**, 50-53.
- [20] H. C. Ngwang, Ph.D. Thesis, Brunel University, 1996.
- [21] J. S. Do and M. L. Chen, *Journal of Applied Electrochemistry*, 1994, **24**, 785-

790.

- [22] S. H. Lin and C. F. Peng, *Wat. Res*, 1996, **30** (3), 587-592.
- [23] U. B. Ogutveren and S. Koparal, *Intern. J. Environmental Studies*, 1992, **42**, 41-52.
- [24] J. Naumczyk, L. Azyrkowicz and F. Z. Grandi, *Wat. Sci. Tech*, 1996, **34** (11), 17-24.
- [25] K. Oeher, *J. Wat. Pollut. Control Fed*, 1978, **50**, 286-289.
- [26] M. S. E. Abdo and R. S. Al-Ameeri, *J. Environ. Sci. Health*, 1987, **A22** (1), 27-45.
- [27] Y. A. Borovskii, T. M. Grishina and G. A. Bogdanovskii, *Russian Journal of Applied Chemistry*, 1994, **67** (8), part 2, 1217-1219.
- [28] Krasnobodko, 1988, side in [J. Naumczyk, L. Azyrkowicz and F. Z. Grandi, *Wat. Sci. Tech*, 1996, **34** (11), 17-24.]
- [29] Z. Ding, C. W. Min and W. Q. Hui, *Wat. Sci. Tech*, 1987, **19**, Rio, 391-400.
- [30] R. Kotz, S. Stucki and B. Carcer, *Journal of Applied Electrochemistry*, 1991, **21**, 14-20.
- [31] K. Scott, "Electrochemical Processes for Clean Technology", Royal Society of Chemistry, 1995.
- [32] R. C. Bansal, J. B. Donnet and F. Stoeckli, "Active Carbon", Marcel Dekker, INC. 1988.
- [33] K. Kinoshita, "Carbon Electrochemical and Physicochemical Properties", John Wiley & Sons, Inc, 1988.
- [34] C. N. R. RAO, "Ultra-violet and Visible Spectroscopy", Third Edition, Butterworthy LTD, 1975.
- [35] G. M. Sheldrick, SADABS, "Program for Absorption Corrections", University of Göttingen, 1996.
- [36] G. M. Sheldrick, SHELXL 97, "Program for Crystal Structure Refinement", University of Göttingen, 1997.

## CHAPTER SIX

### CONCLUSION

The work described in this thesis is concerned with the application of electrochemical methods to the solution of environmental problems:

- to remove toxic metals from dilute solution.
- to separate metals from mixed metal solutions to facilitate recovery and recycle.
- to achieve the destruction of organic contaminants in water.

The work has led to the development of technology to achieve:

- the removal of metals from solution using novel concentrator electrodes.
- the use of complexing agents to achieve the electrochemical separation of tin, indium and lead from solutions containing ions of all three metals.
- the separation of nickel from cobalt using membrane technology and electro dialysis.
- the destruction of dye molecules in effluents.

The work on dye solutions also led to the development of a methodology to study the nature of the intermediates formed in the degradation of dye molecules and to the identification of previously unknown compounds in the degradation of methylene blue.

#### **Removal of Toxic Metals from Solution**

The use of electrolysis for heavy metal removal and recovery has limitations when dilute solutions are involved. In concentrated solutions there is sufficient ion transport to the cathode to ensure that deposition of the metal is a favoured reaction. In dilute solutions, however, the concentration of metal ions in the vicinity of the electrode may be too low to achieve metal removal by electrodeposition. The problems associated with dilute solutions have been overcome in this work by using concentrator cells. The basic concept of the concentrator cell is to capture metal ions on a concentrator

medium close to an electrode as they move towards an electrode under the driving force of an electric potential. When the concentrator medium becomes saturated, the metals are released into a small volume of electrolyte close to the electrode improving the efficiency of the relevant cathodic reduction or anodic oxidation processes.

In this work the efficiency of concentrator cells containing either (1) an ion-exchange material close to but not in contact with the cathode or (2) carbon cloth as the concentrator medium attached to a metal cathode, is demonstrated for the removal of lead and cadmium from dilute solution. For both lead and cadmium, maximum efficiency in metal removal is achieved using the ion-exchange concentrator cell with 90% of the lead is been deposited from an 0.01 molar solution in a nitrate medium in 1 hour compared with only 46% using a standard mesh cathode. The corresponding figures for cadmium removal from a 0.01 molar nitrate solution are 89 and 0% respectively.

A further, and very important, advantage of the ion-exchange concentrator cell is that the ion-exchange material is regenerated *in-situ* by the electrode reaction producing  $\text{H}_3\text{O}^+$  within the cell thus eliminating the need for pH adjustment

### **Use of Complexing Agents to Facilitate the Electrochemical Separation and Recovery of Metals from Mixed-metal Solutions.**

Two separation and recovery systems were considered *viz.* (1) the tin : lead : indium system and (2) the cobalt : nickel system.

Tin lead and indium are often found together in wastes produced from the mining and application of these metals. The results obtained show that their removal and separation can be achieved electrochemically and that the efficiency of separation depends on the acidity of the solutions and the presence of complexing agents.

All three metals are co-deposited from an acetic acid medium, which is surprising in view of the differences in the strengths of the complexes that they form with acetate ions. Selective deposition of Pb can, however, be achieved from solutions containing 0.1 to 0.5 mol dm<sup>-3</sup> of nitric acid and from solutions containing greater than 0.1 mol

$\text{dm}^{-3}$  perchloric acid.

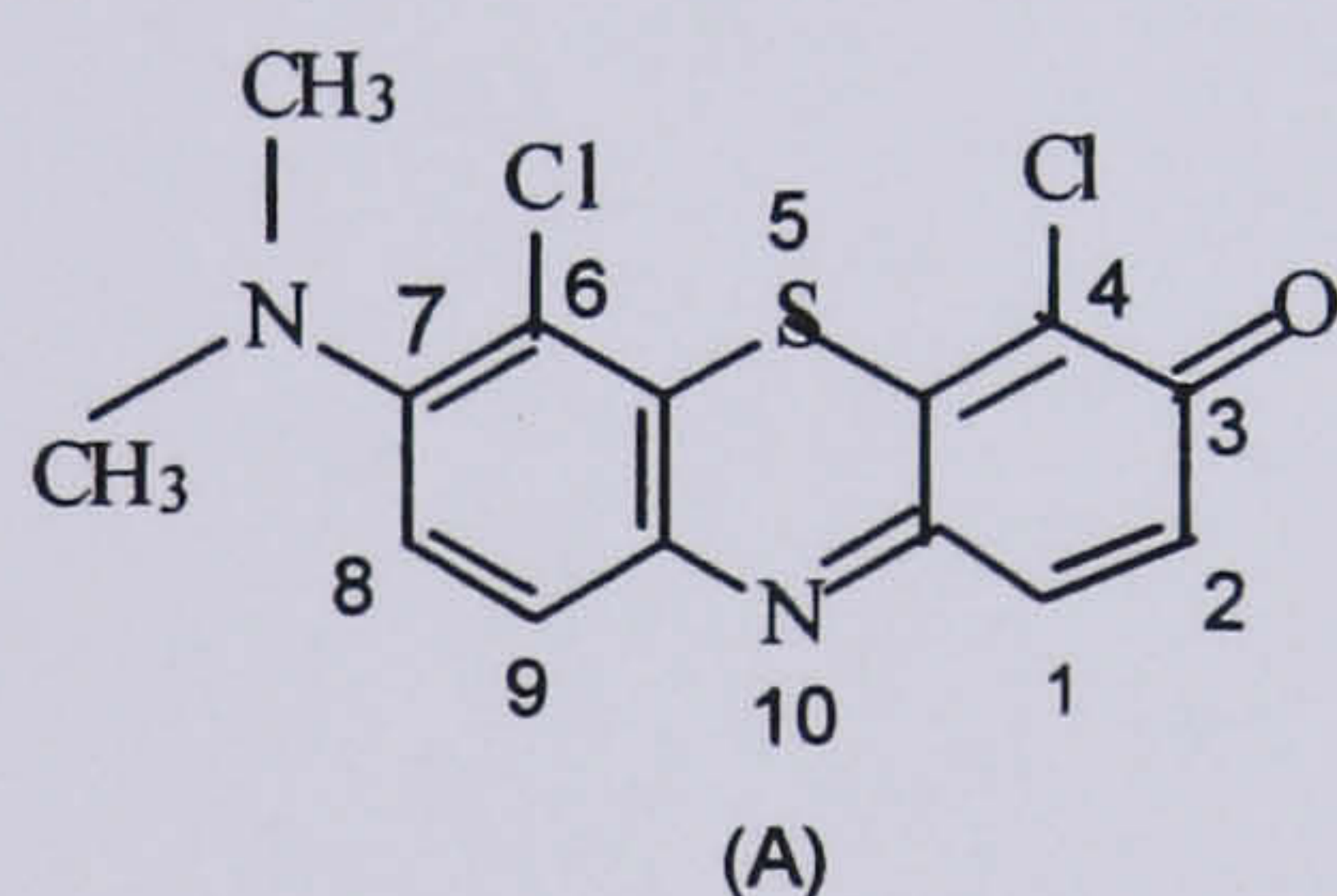
Following selective separation of lead, tin and indium separation can be achieved whereby tin is deposited in the presence of thiocyanate as complexing agent from  $0.1 \text{ mol dm}^{-3} \text{ HNO}_3$  leaving indium in solution. This separation depends upon the greater strength of the indium(III) - thiocyanate complex in comparison with the tin(II) complex as evidenced by the fact that, in the presence of an excess of thiocyanate, the indium is deposited at the anode, presumably from the  $\text{In}(\text{CNS})_6^{3-}$  complex.

A major part of any recovery process for cobalt is concerned with its separation from other elements. Because of the similarities in the chemical behaviour of cobalt and nickel the separation of these two elements from one another is often the most difficult purification stage. A major aim of the present research was to develop technology based on electrodialysis for the separation of nickel from cobalt using less energy and without a requirement for a regenerating agent. Optimum conditions are determined for the removal of nickel from cobalt solution by electrodialysis using a three compartment electrodialysis cell to exploit the greater stability of the EDTA complex with nickel. The  $\text{Ni}(\text{EDTA})^{2-}$  complex and hydrated  $\text{Co}^{2+}$  ions are transferred from a feed chamber to the anolyte and catholyte chambers respectively. The EDTA is transferred to the anolyte chamber as a nickel complex is destroyed on the anode surface to release the hydrated Ni ions but these ions cannot cross the anion exchange membrane to return to the feed or catholyte compartments. In the catholyte chamber most of the cobalt ions remain in solution. but the metal can be deposited on the cathode by increasing the pH in the catholyte chamber to 4-4.5. The cobalt solution in the catholyte chamber, however, also provides an excellent starting material for the recovery of the metal as added-value chemicals rather than metal.

Use of EDTA in a three-compartment cell for electrodialysis with other metal mixtures, such as Co-Cu, and Co-Pd, also gave good separations. No significant separation of zinc or iron from cobalt could, however, be achieved using EDTA because of the similarities in the stabilities of the EDTA complexes with cobalt, zinc and iron.

## Electrochemical Destruction of Organic Molecules

The presence of organic contaminants can pose problems for water reuse. A particular current concern arises from the presence of coloured materials in solution and for this reason the destruction of dye molecules by electrochemical methods was studied. Anodic oxidation of dye materials is found to be effective in that it leads to the removal of colour, but UV spectra and TOC data indicate that colourless organic intermediates are formed during the process. In order to obtain a complete understanding of the degradation process it was, therefore, necessary to characterise these intermediates. In studies on the anodic oxidation of methylene blue, seven neutral intermediates were identified by HPLC and LC-MS, but only one of them, with mass 324, could be isolated as a crystalline solid. The crystallised material was found to be the previously unknown compound (A) and its structure was determined by a combination of single-crystal X-ray diffraction and accurate mass spectrometry data.



From a knowledge of the structure of (A) it is possible to suggest the formulae of four of the other intermediates. Since these chlorinated intermediates may be more harmful to the aqueous environment than the dye molecules from which they are formed, it is necessary to develop a technique capable of achieving complete destruction of the dye and all intermediate species. A combination of electrolysis with adsorption (electroadsorption) was developed that lead to the complete removal of all of the original and intermediate phases present. A characteristic of the methodology developed for combined electrolysis and adsorption is bipolarity which gives rise to high efficiency. Applying an electric current to a solution containing activated carbon particles polarises the particles, forming micro-anodes and micro-cathodes, thus creating a very high number of microelectrolytic cells in series. The effective number of cells created enhances the adsorption properties of the activated carbon particles. This method leads to the efficient direct destruction of methylene blue and acid blue while a

sequence of electro-oxidation followed a combined electrochemical -adsorption step is required for the destruction of reactive dyes.

The work described in this thesis shows the potential for the exploitation of various aspects of electrochemistry in the control of environmental problems and, in the case of the studies on the intermediates formed in the destruction of dyes, opportunities for the electrosynthesis of new compounds.



## APPENDIX 1

### Technical specifications for Activated Carbon Cloth

- 1- The typical dry weight of the product shall be in the range 190 to 230 grams per square metre (gsm).
- 2- The thickness shall be in the range 1.2 to 1.4 mm.
- 3- Air permeability shall not be less than  $55 \text{ cm}^2/\text{cm}^2/\text{sec}$  at 10 mm water gauge pressure drop.
- 4- Tensile breaking strength, in either warp or weft direction, shall not be less than 20 Newtons per centimetre ( $\text{N cm}^{-1}$ ).
- 5- The uptake of carbon tetrachloride vapour in dry air shall not be less than 55% w/w.
- 6- The time to penetrate chlorobenzene vapour shall not be less than 30.0 minutes under the prescribed conditions of test.
- 7- The heat of wetting in silicone 2 cp fluid shall not be less than 25 joules per gram ( $\text{J g}^{-1}$ ).

## APPENDIX 2

The energy consumption and the current efficiency for lead, tin and indium recovery from single metal ion solution.

The effects of nitric acid concentration on the value of current efficiency and energy consumption for 50ppm of each lead, tin and indium recovery from a single metal ion solution are shown in Figure Appendix [1] and [2] respectively. Current efficiency is used as a measure of how effectively each amp of current is used in the electrolysis process, and therefore gives an indication of the efficiency of the process. In order to calculate the current efficiency the electrochemical equivalent based on 100 per cent current efficiency (Table Appendix 1) for each metal is used in the following equation:

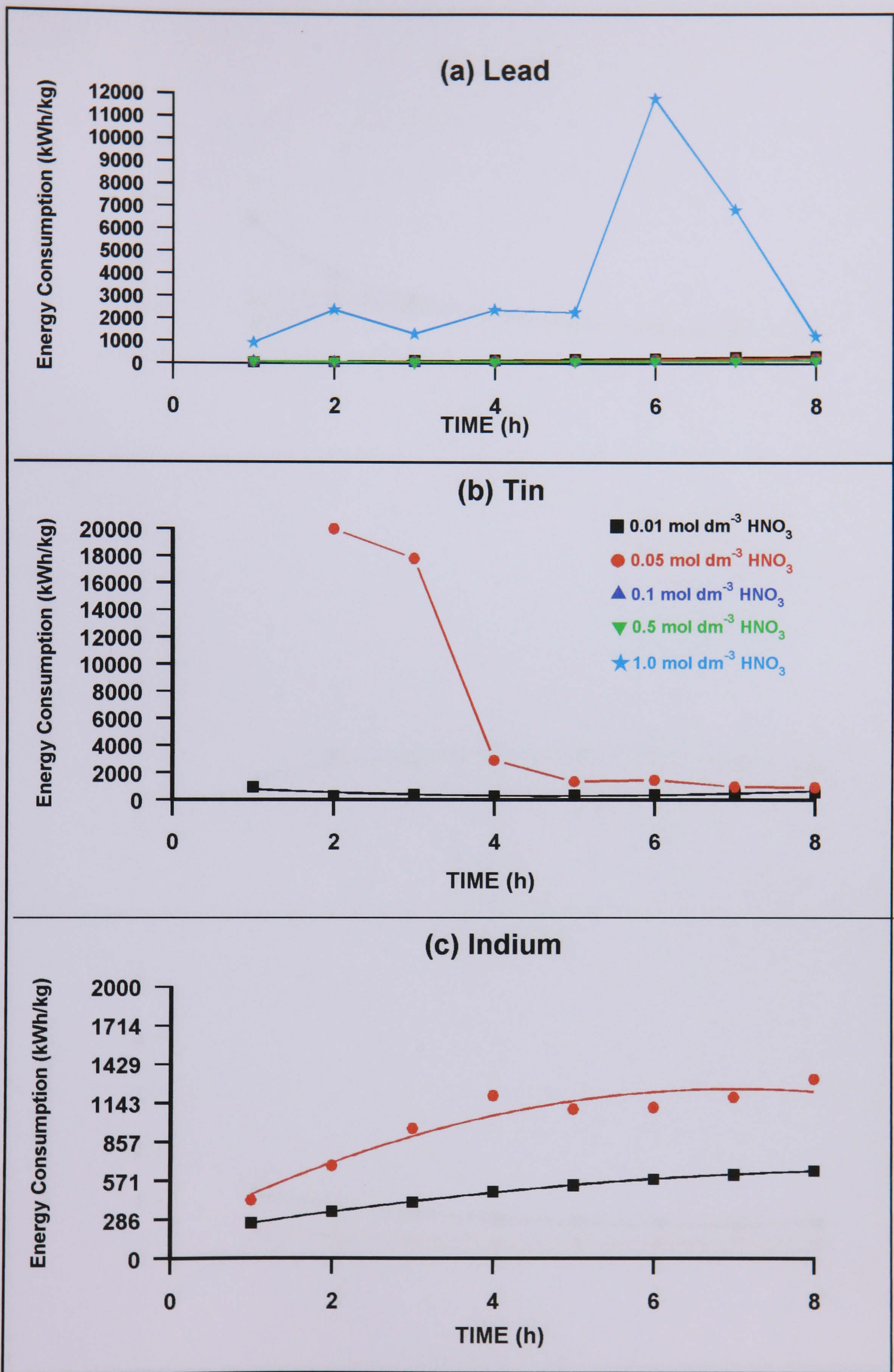
$$\eta(\%) = \frac{\text{actual deposit}(g)}{\text{theoretical deposit}(g)} \times 100$$

In the calculation of the energy consumption values, the electrochemical equation used are explained in the experimental section of chapter 2.

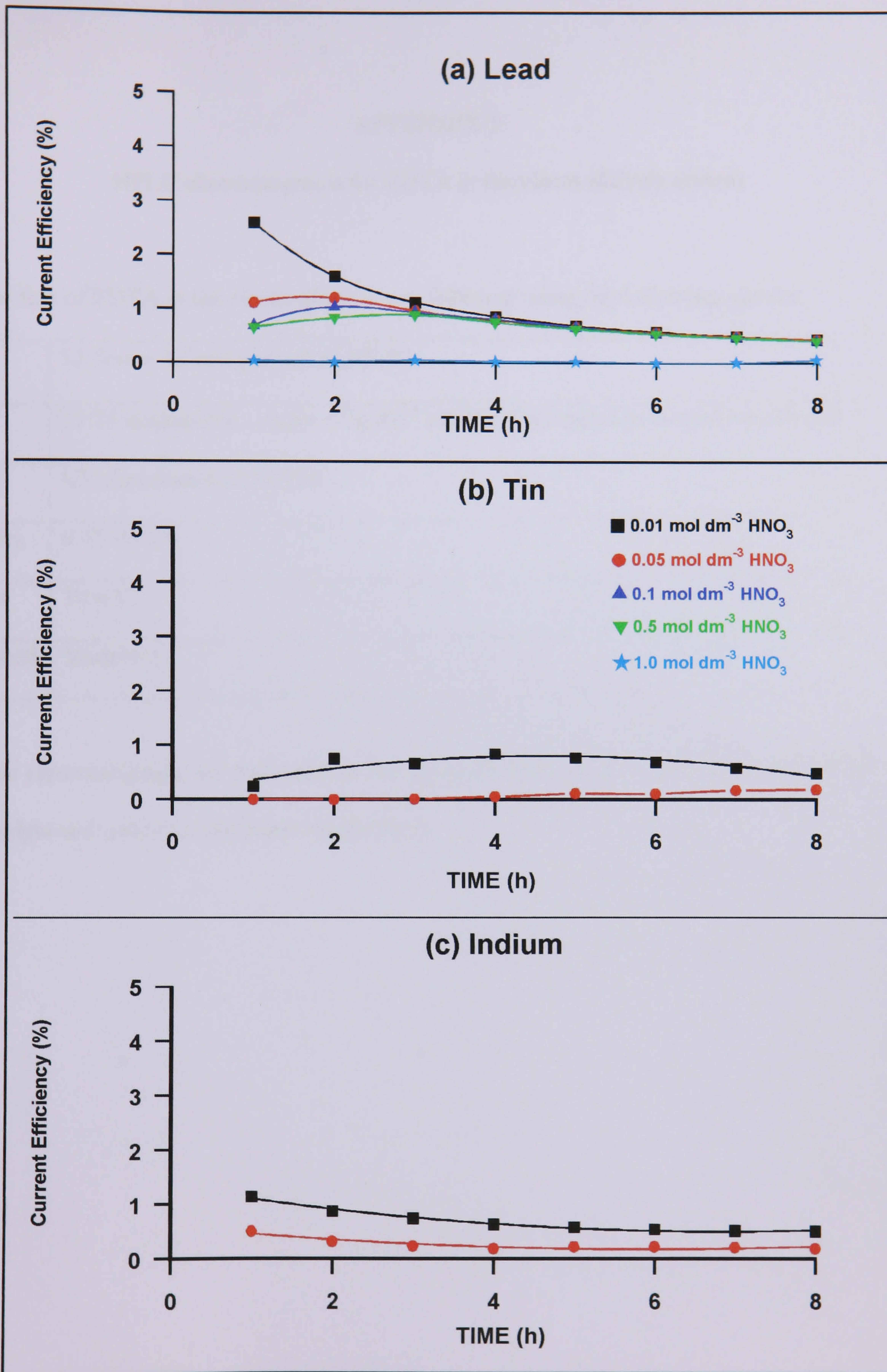
In general, the value of current efficiency was found to be very low and the energy consumption relatively high. This is because of the competitive hydrogen evolution reaction at the cathode surface with no agitation and the use of low metal ion concentrations in the electrolyte solution studied.

Appendix Table [1]

Metal	Weight of deposit (ampere hour)	
	Ounce	Grams
Lead(II)	0.1360	3.865
Tin(II)	0.0780	2.214
Indium(III)	0.0502	1.428
Cadmium(II)	0.0740	2.100



Appendix Figure [1]: The effect of nitric acid concentration on the energy consumption for (A) lead, (b) tin and (c) indium recovery from 50ppm single metal ion solutions.



Appendix Figure [2]: The effect of nitric acid concentration on the current efficiency for (A) lead, (b) tin and (c) indium recovery from 50ppm single metal ion solutions.

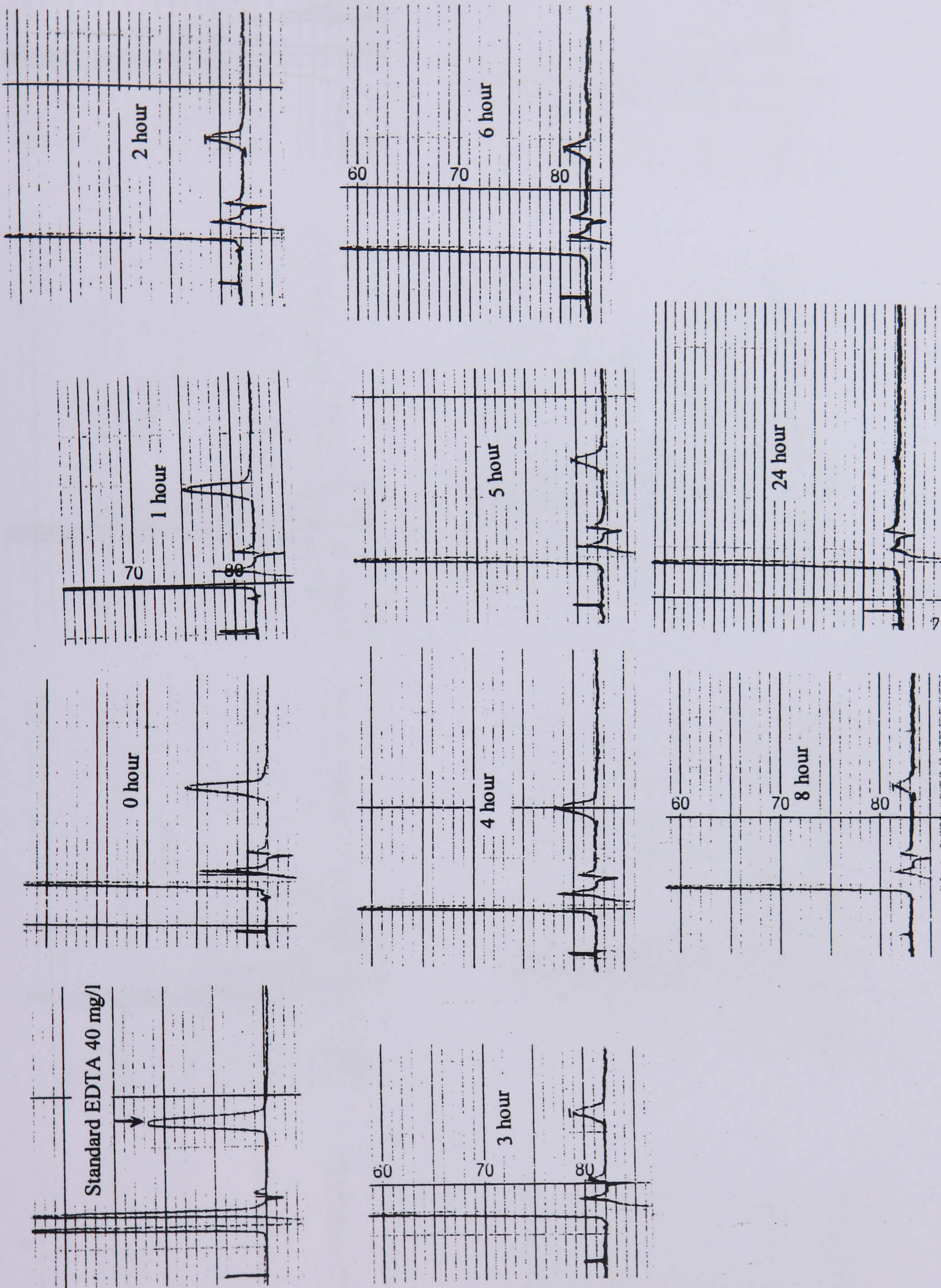
### APPENDIX 3

#### HPLC chromatograms for EDTA in the electro dialysis system

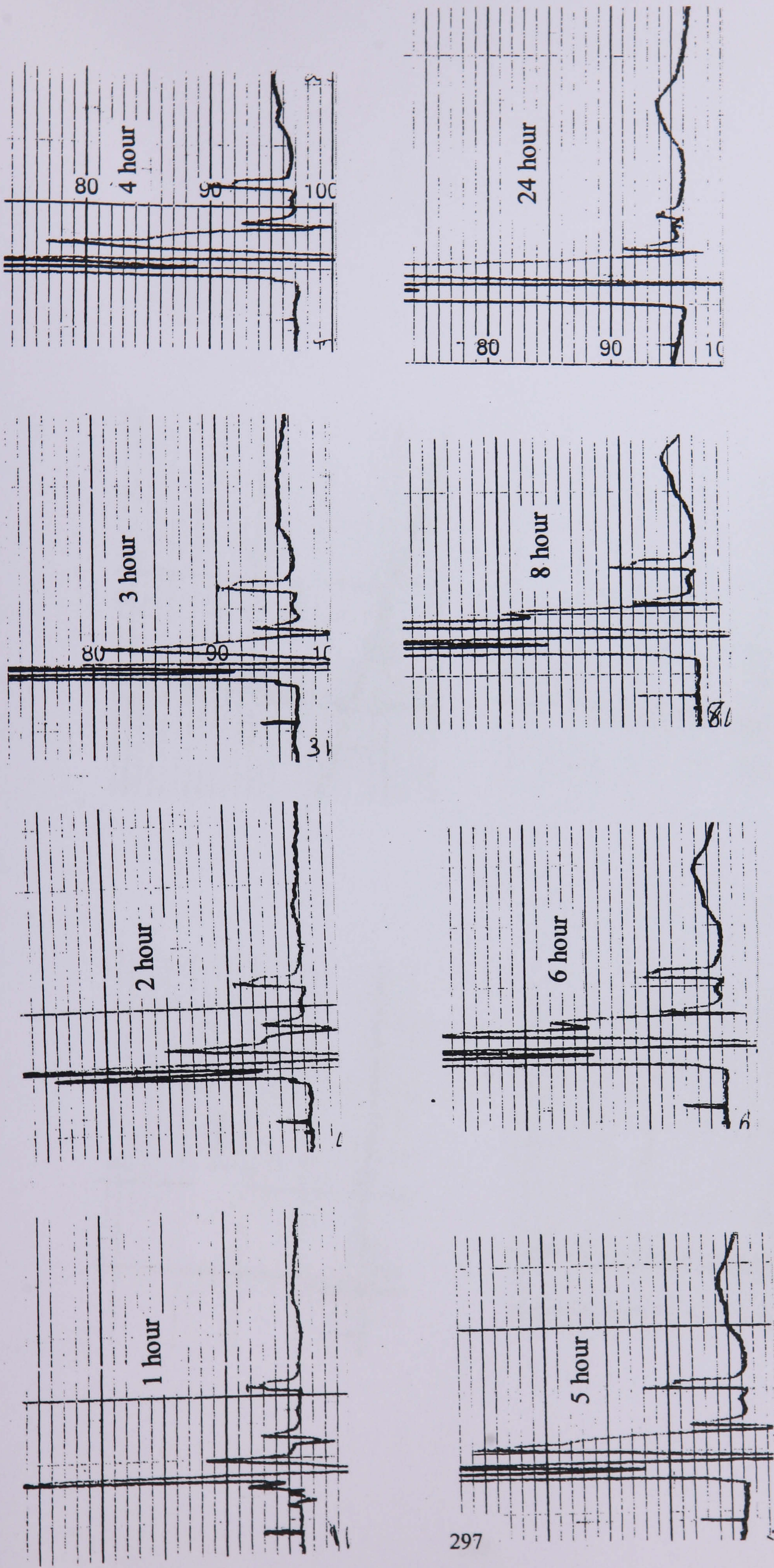
The fate of EDTA in the electro dialysis was followed using the following system:

Column	12.5cm × 4.5mm packed PLRP-S5
Eluent	25:75 acetonitrile : water + 3g dm <sup>-3</sup> tetrabutyl ammonium bromide at pH 6.0
Detector	UV absorbance at 300nm
Sensitivity	0.01 AUFS
Recorder	10 mV.
Chart speed	5mm/min

The chromatograms are presented in the appendix Figures [3, 4 and 5] for the middle, anolyte and catholyte chambers respectively.

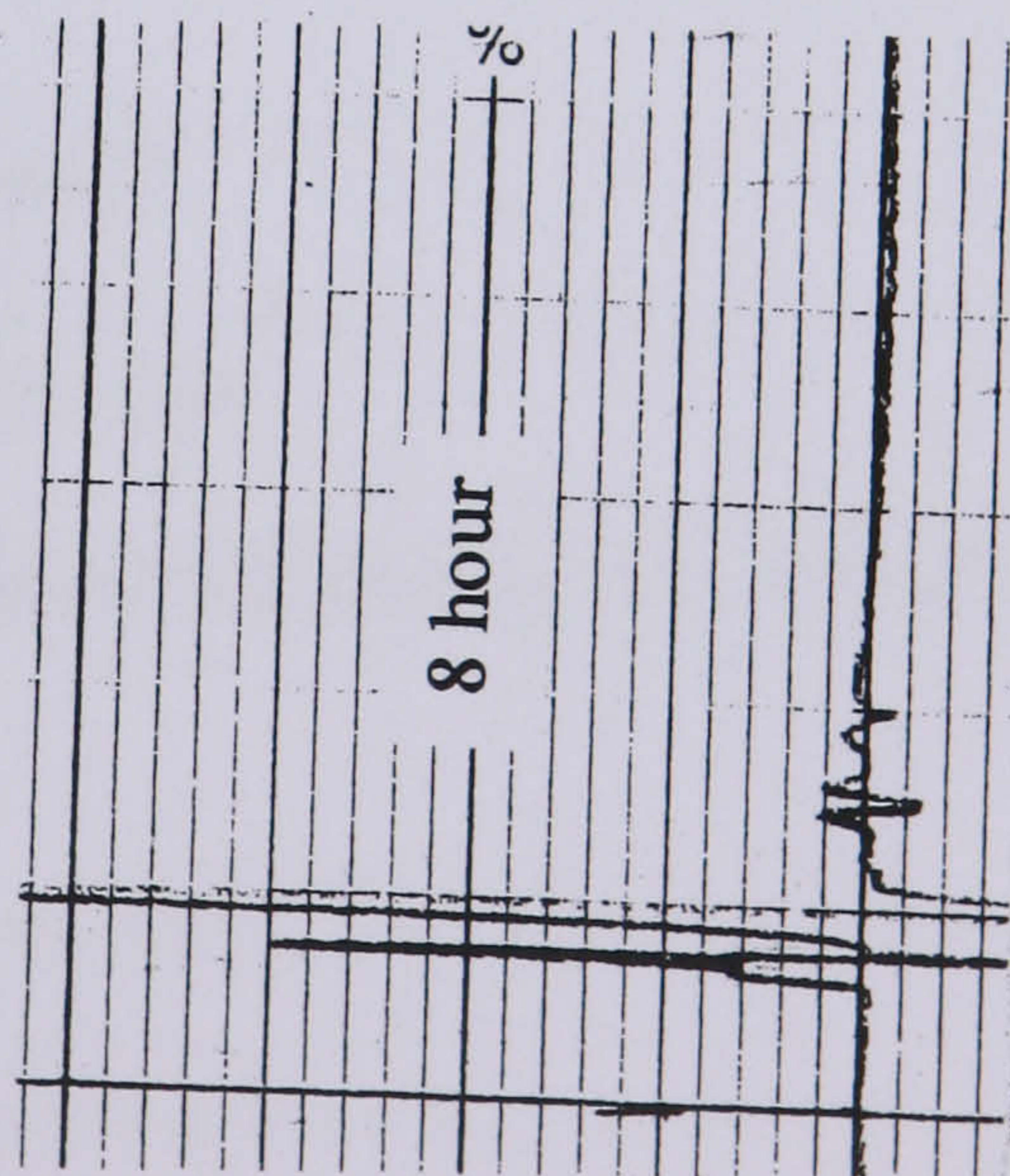
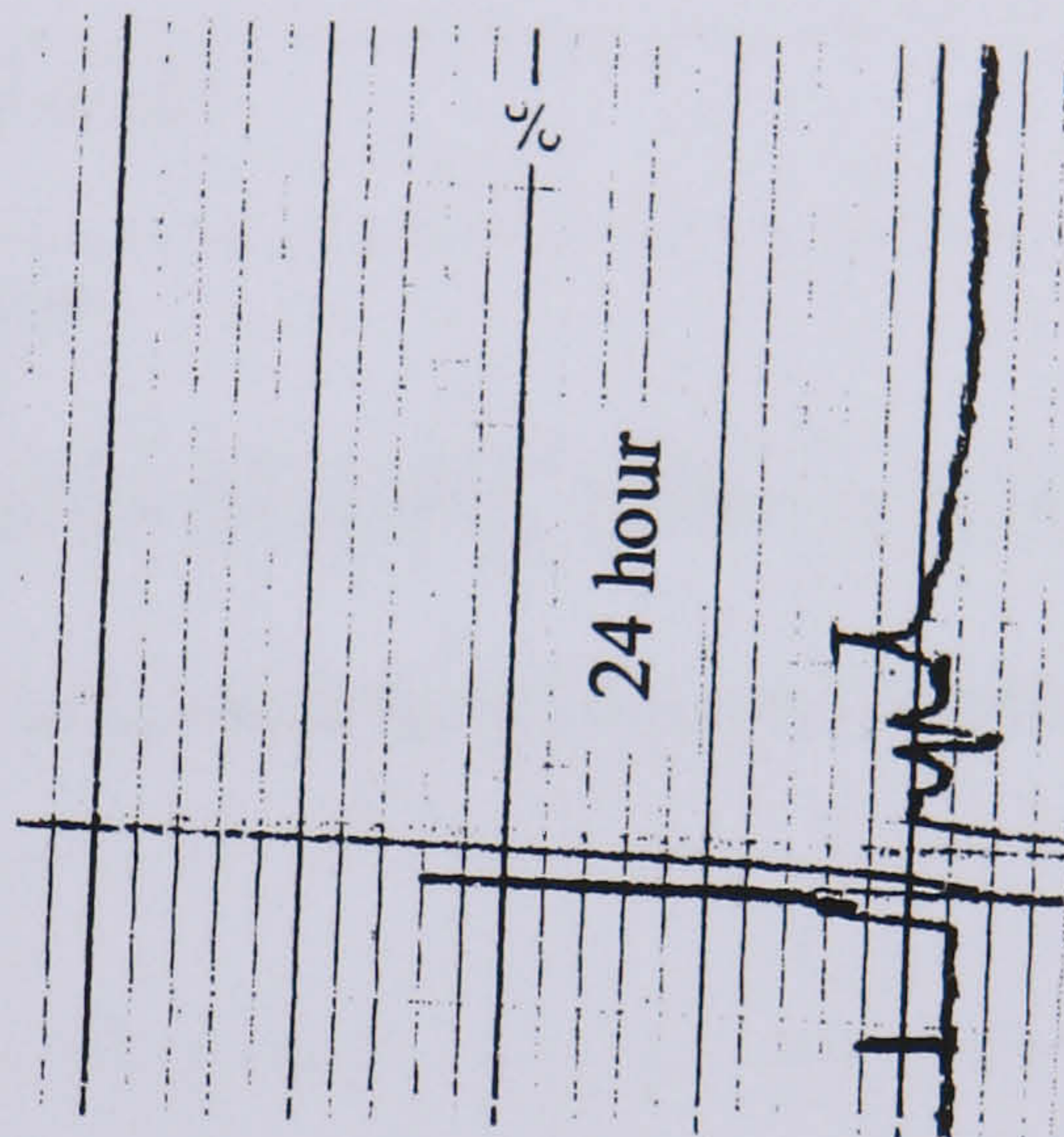
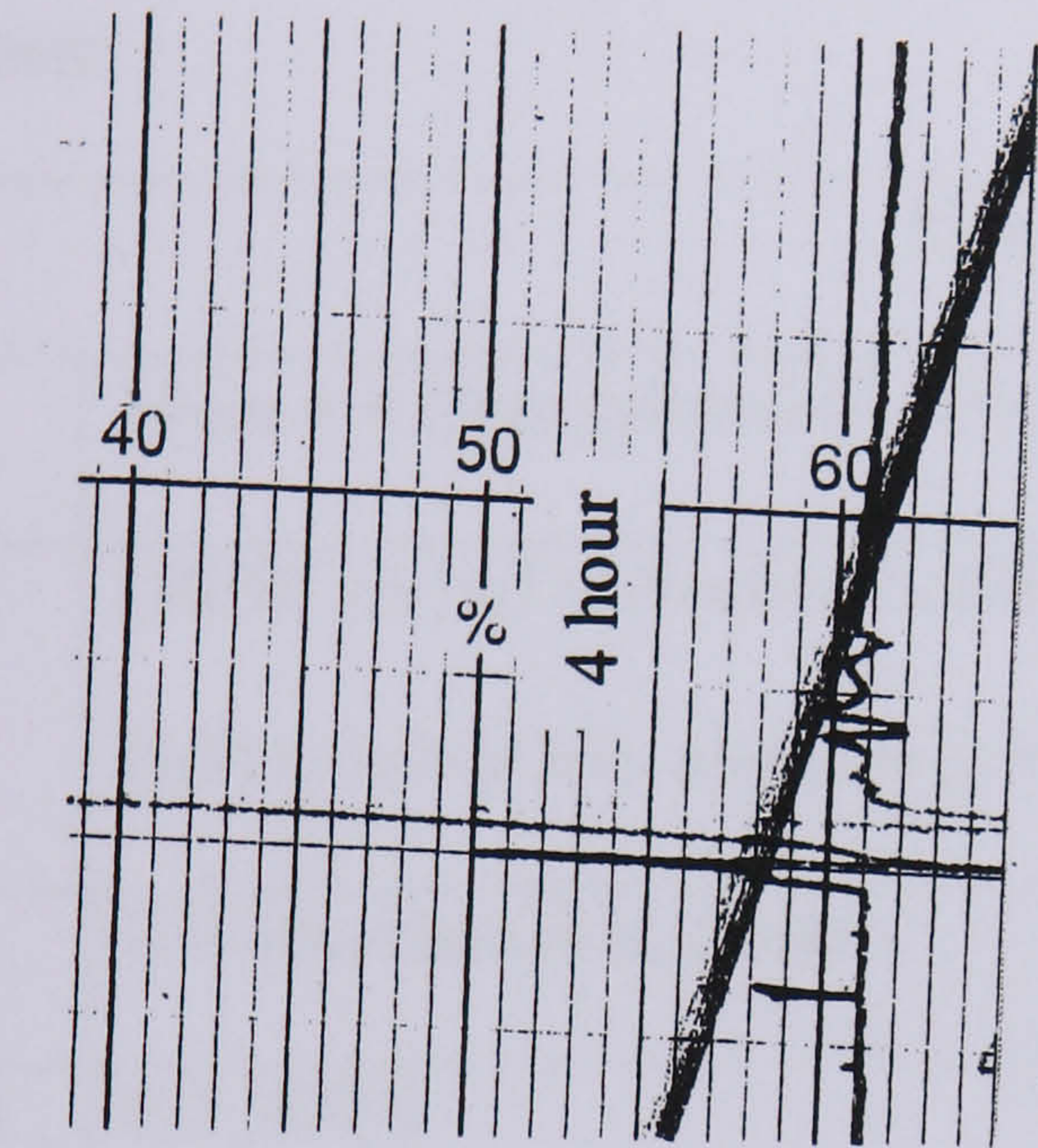


Appendix Figure [3]: The HPLC chromatogram for the middle chamber.



Appendix Figure [4]: The HPLC chromatogram for the analyte chamber.





Appendix Figure [5]: The HPLC chromatogram for the catholyte chamber.

## APPENDIX 4

### HPLC chromatograms for dye samples

The HPLC chromatograms of dye solution and 15 minutes electrolysed dye solution of methylene blue, azure B, azure A and thionin were performed using the following two systems:

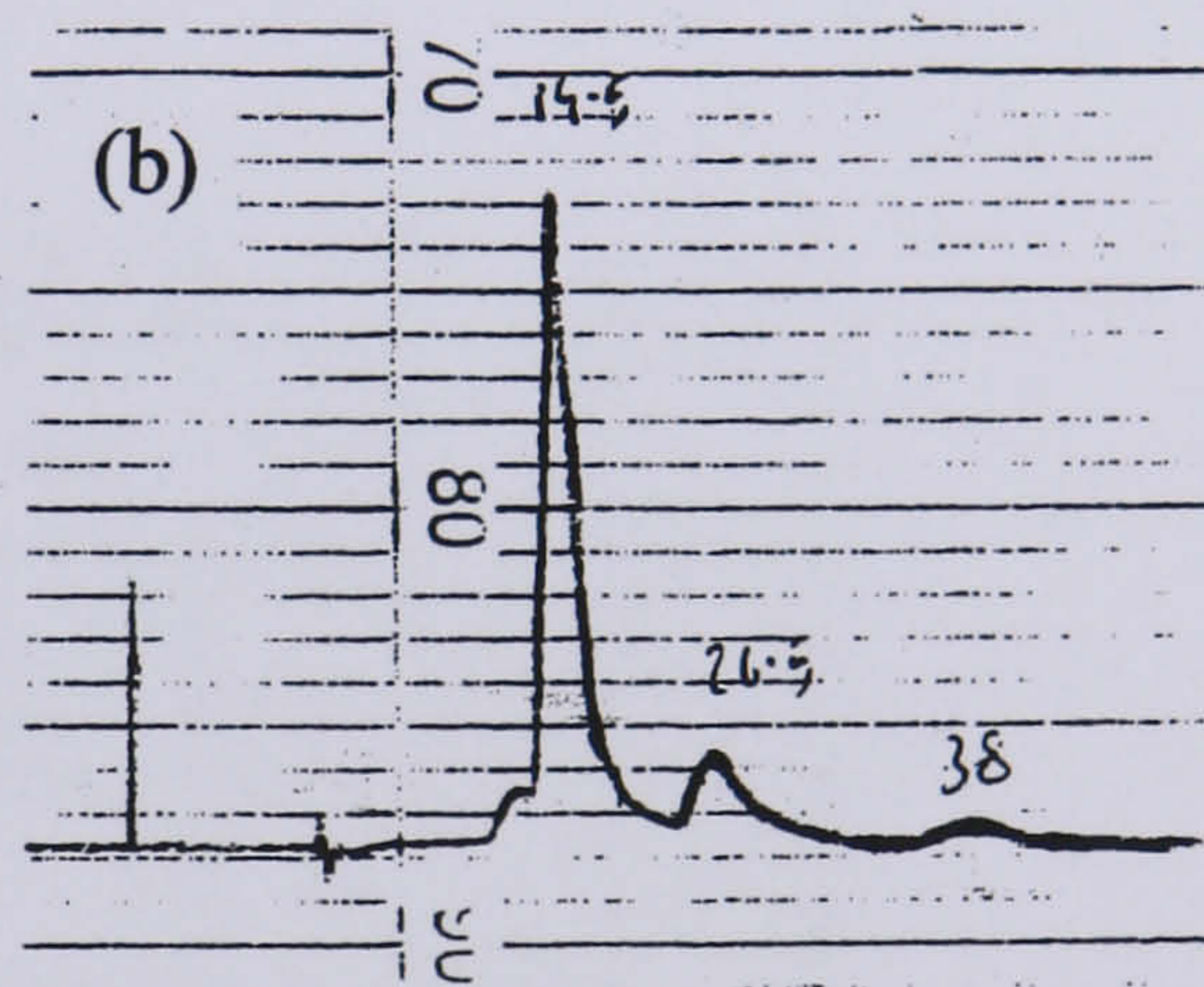
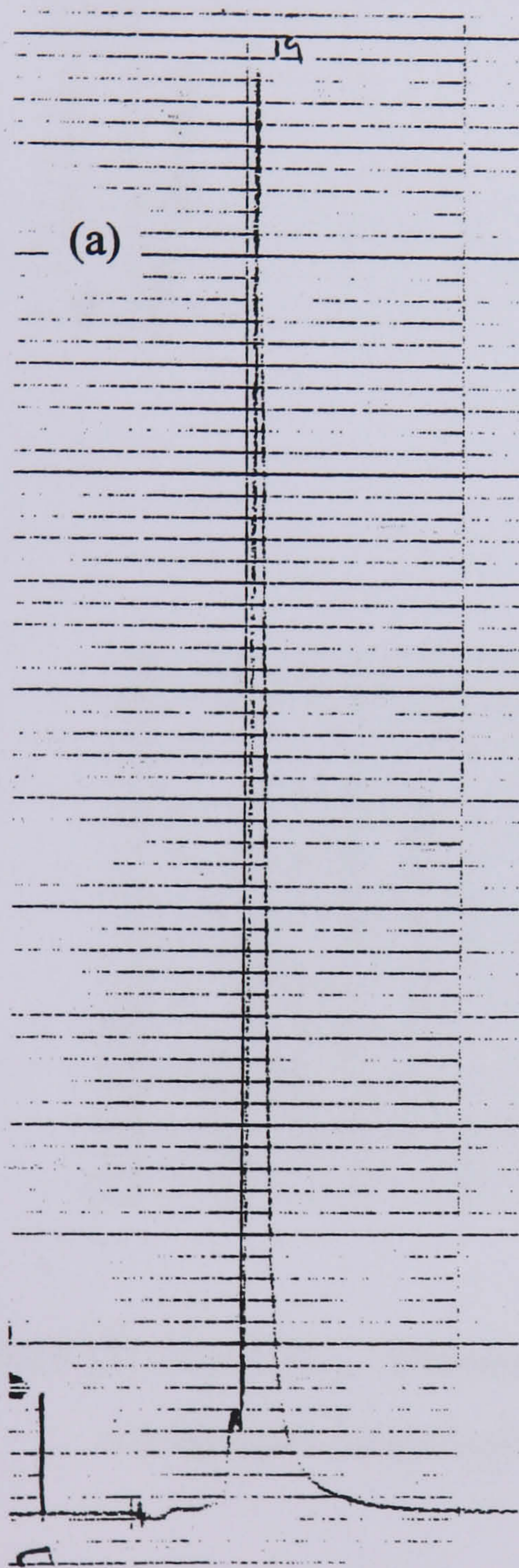
#### Condition (1)

Column	15cm × 4.5mm packed PLRP-S 5 $\mu$ m
Eluent	(50:50 v/v) of acetonitrile : pH3 buffer (NaH <sub>2</sub> PO <sub>4</sub> 1g/litre adjusted with H <sub>3</sub> PO <sub>4</sub> or NaOH) containing 8 g/l tetramethylammonium bromide
Detector	UV absorbance at 290nm
Sensitivity	0.2 AUFS
Recorder	10 mV
Chart speed	5mm/min

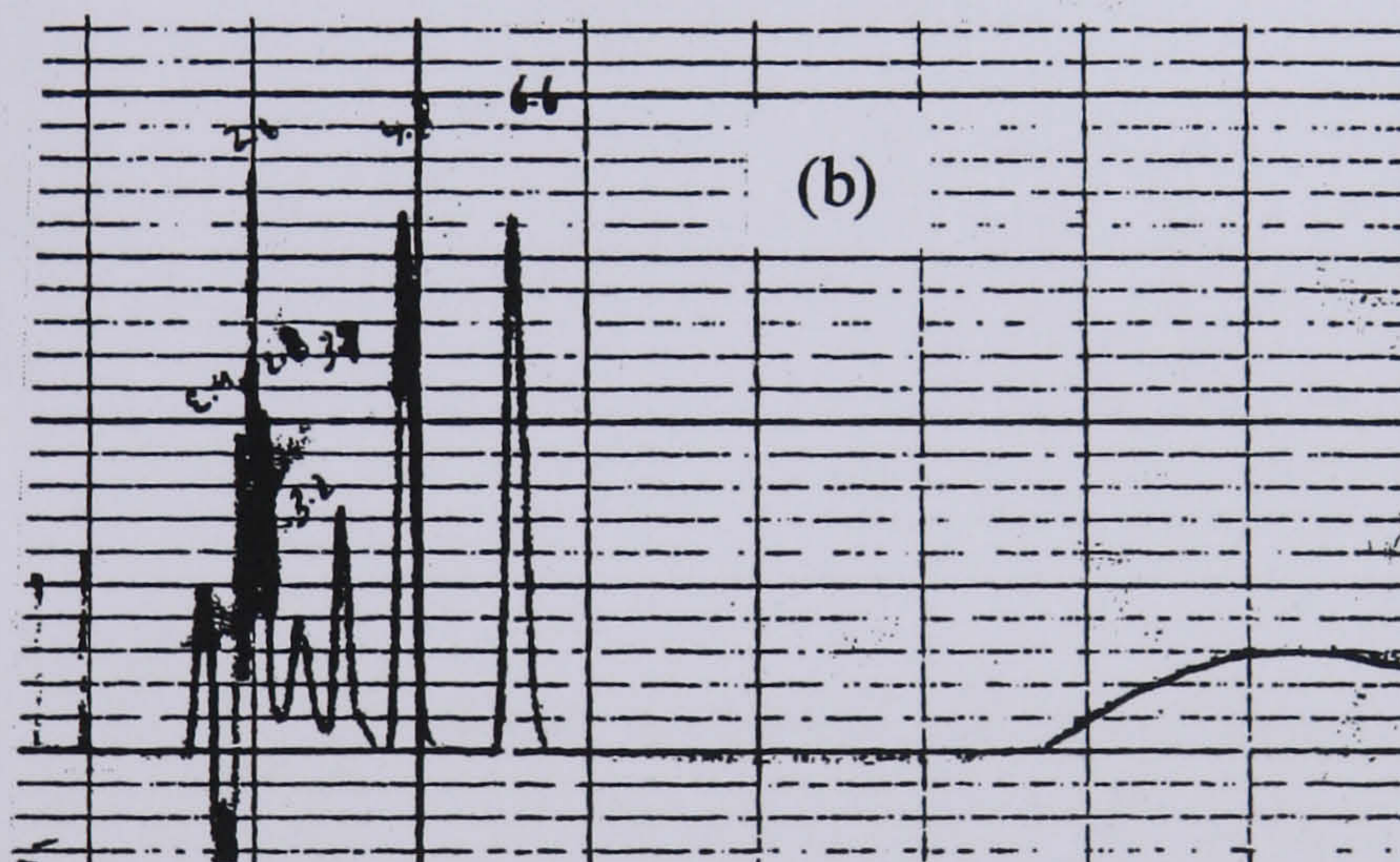
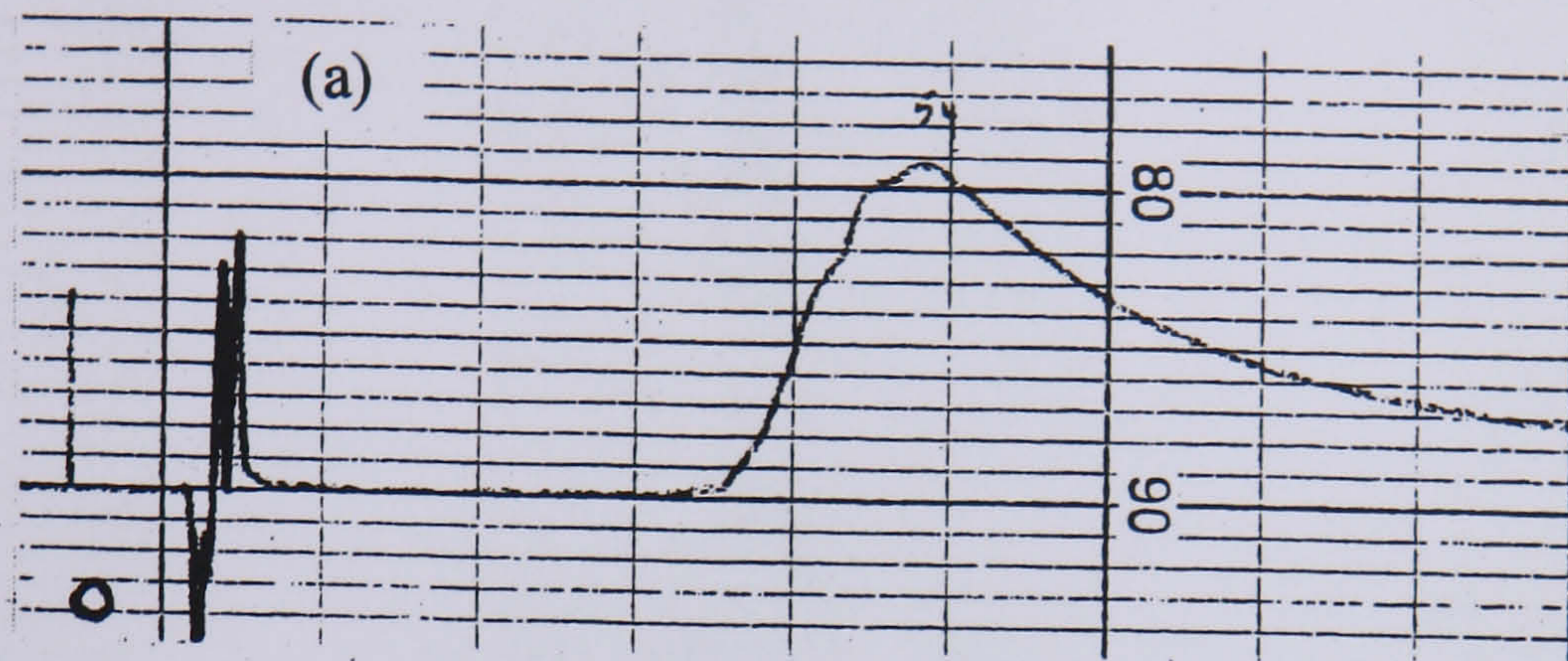
#### Condition (2)

Column	15cm × 4.5mm packed Pinnacle ODS 5 $\mu$ m
Eluent	(85:15 v/v) of methanole : pH3 buffer (NaH <sub>2</sub> PO <sub>4</sub> 1g/litre adjusted with H <sub>3</sub> PO <sub>4</sub> or NaOH)
Detector	UV absorbance at 290nm
Sensitivity	0.1 AUFS
Recorder	10 mV
Chart speed	5mm/min

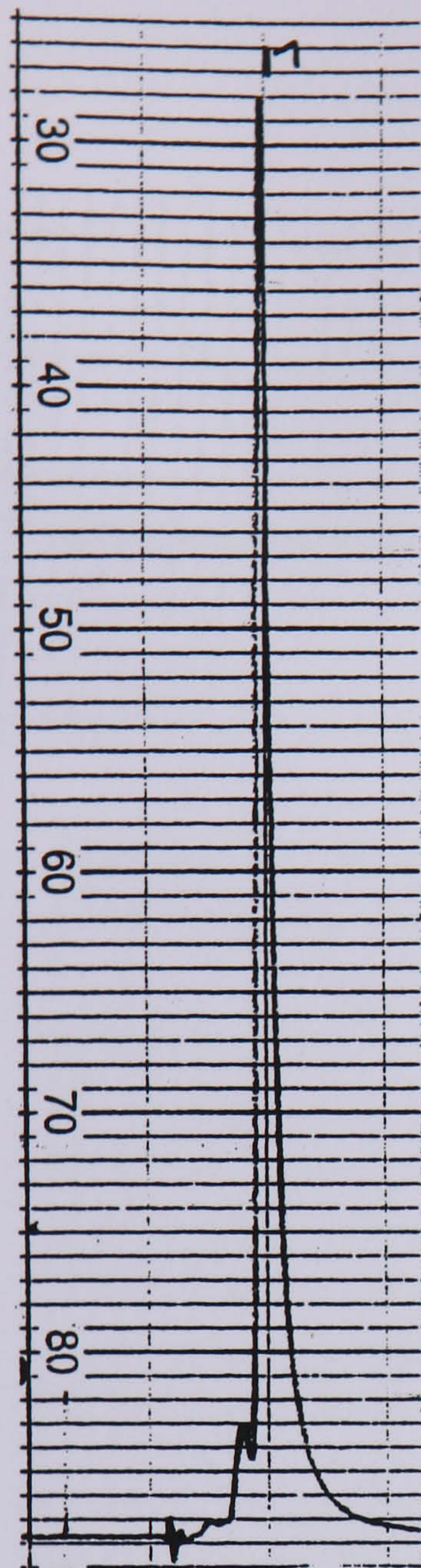
Appendix Figures [4 and 5] show the HPLC chromatograms for methylene blue solutions in the condition (1) and (2) respectively. Appendix Figure [6] shows the HPLC chromatograms of azure B, azure A and thionin solutions and 15 minutes electrolysed solutions of these dyes using condition (1), whereas, appendix Figure [7] shows the HPLC chromatograms of these dye solutions and 15 minutes electrolysed solutions using condition (2).



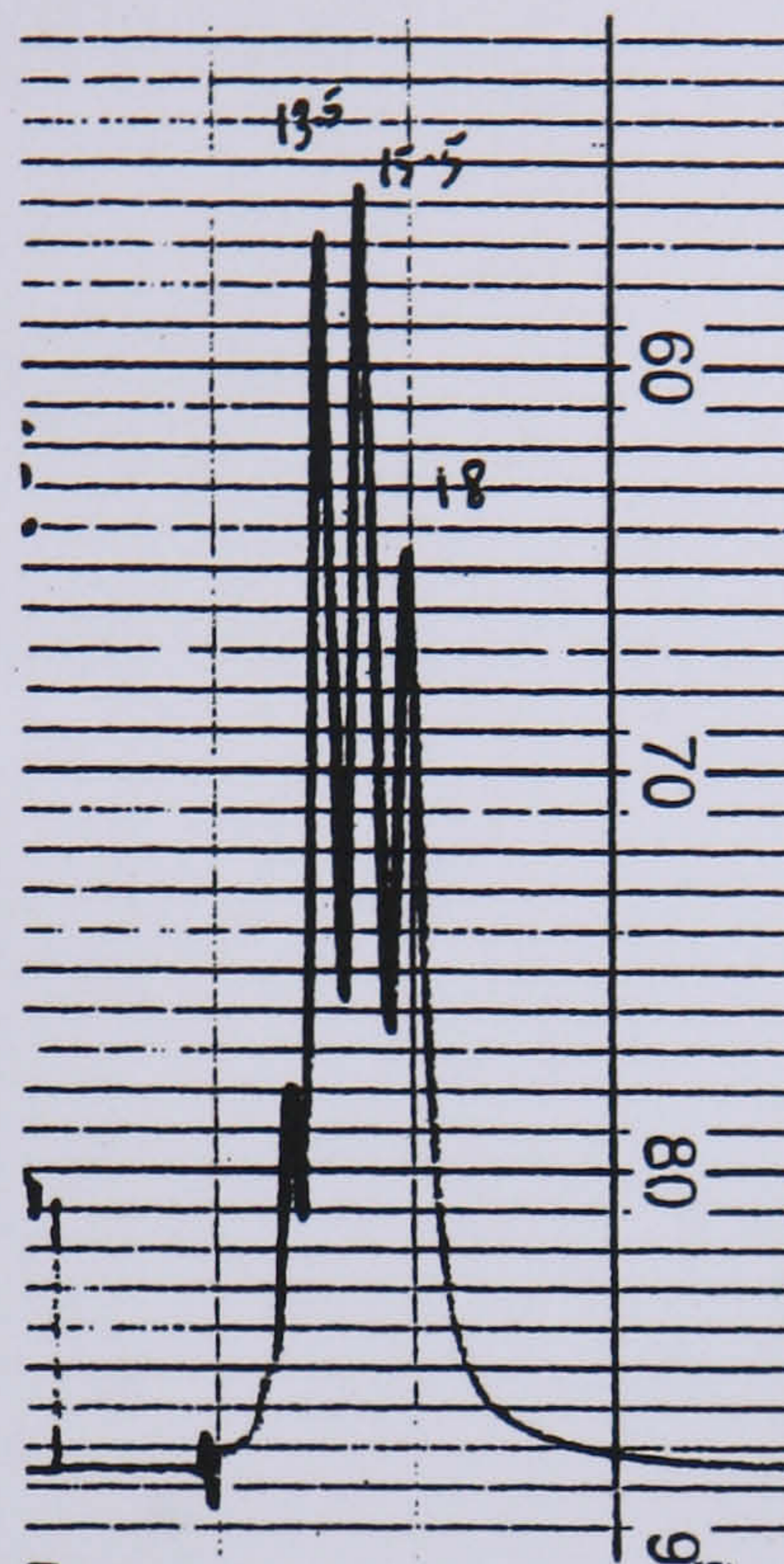
Appendix Figure [6]: The HPLC chromatogram using condition (1) for a) methylene blue solution and b) electrolysed methylene blue solution.



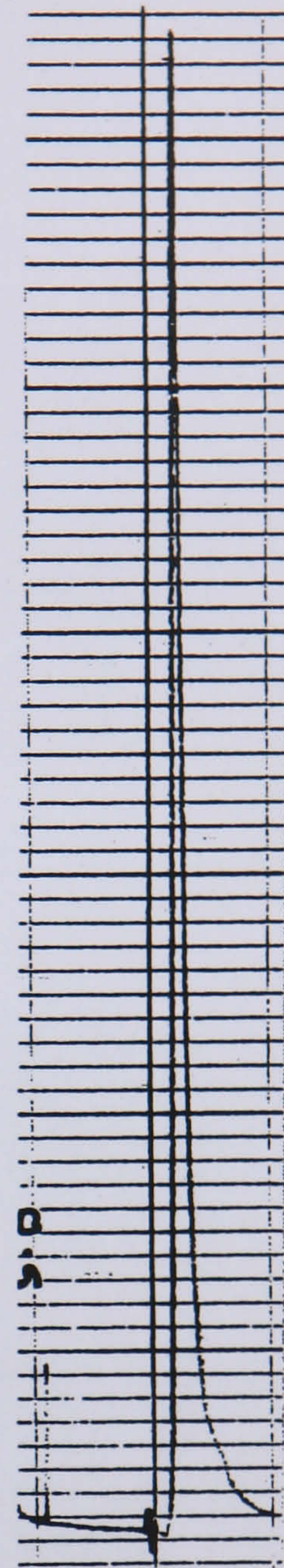
Appendix Figure [7]: The HPLC chromatogram using condition (2) for a) methylene blue solution and b) electrolysed methylene blue solution.



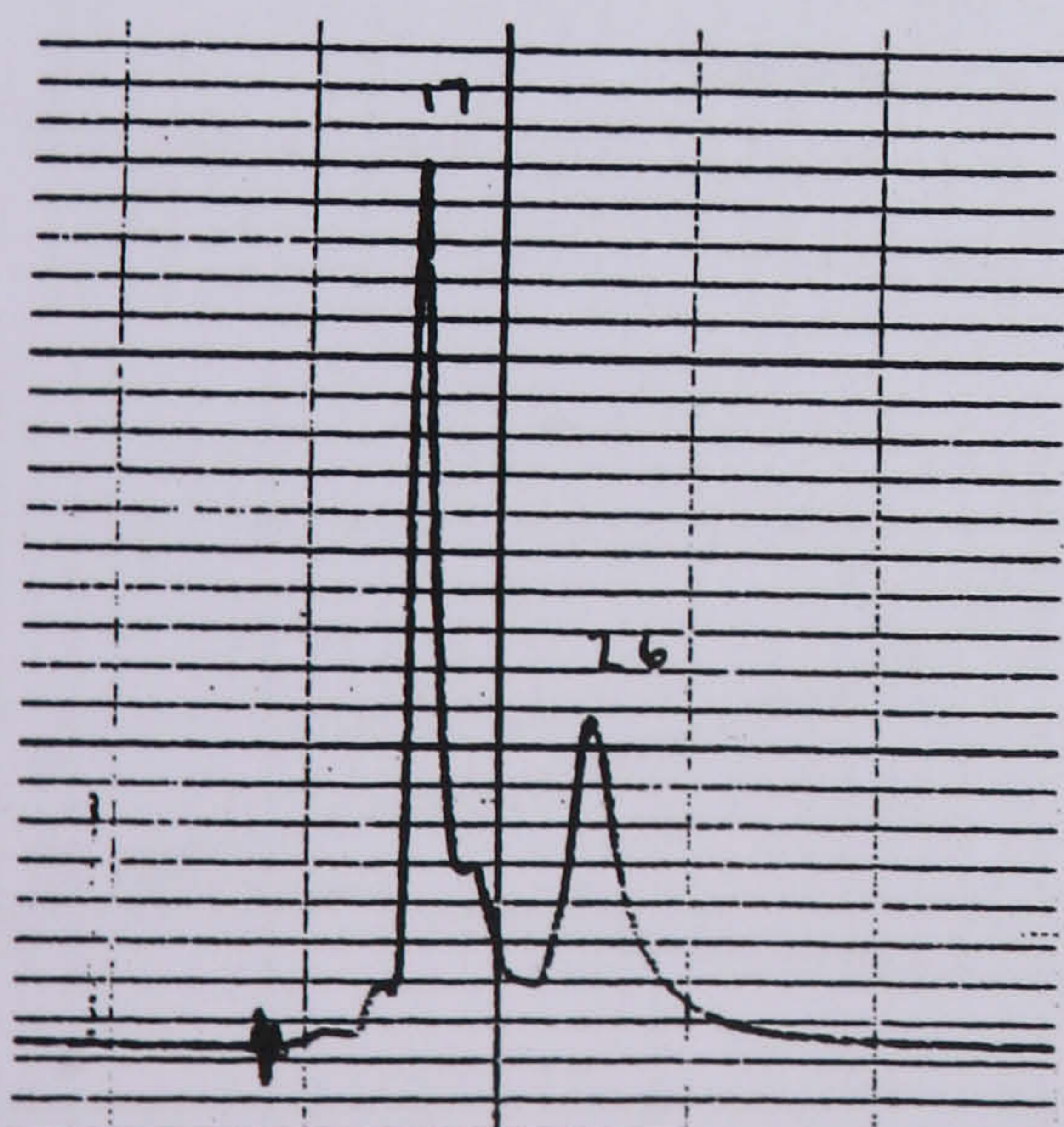
Azure B solution



Azure A solution

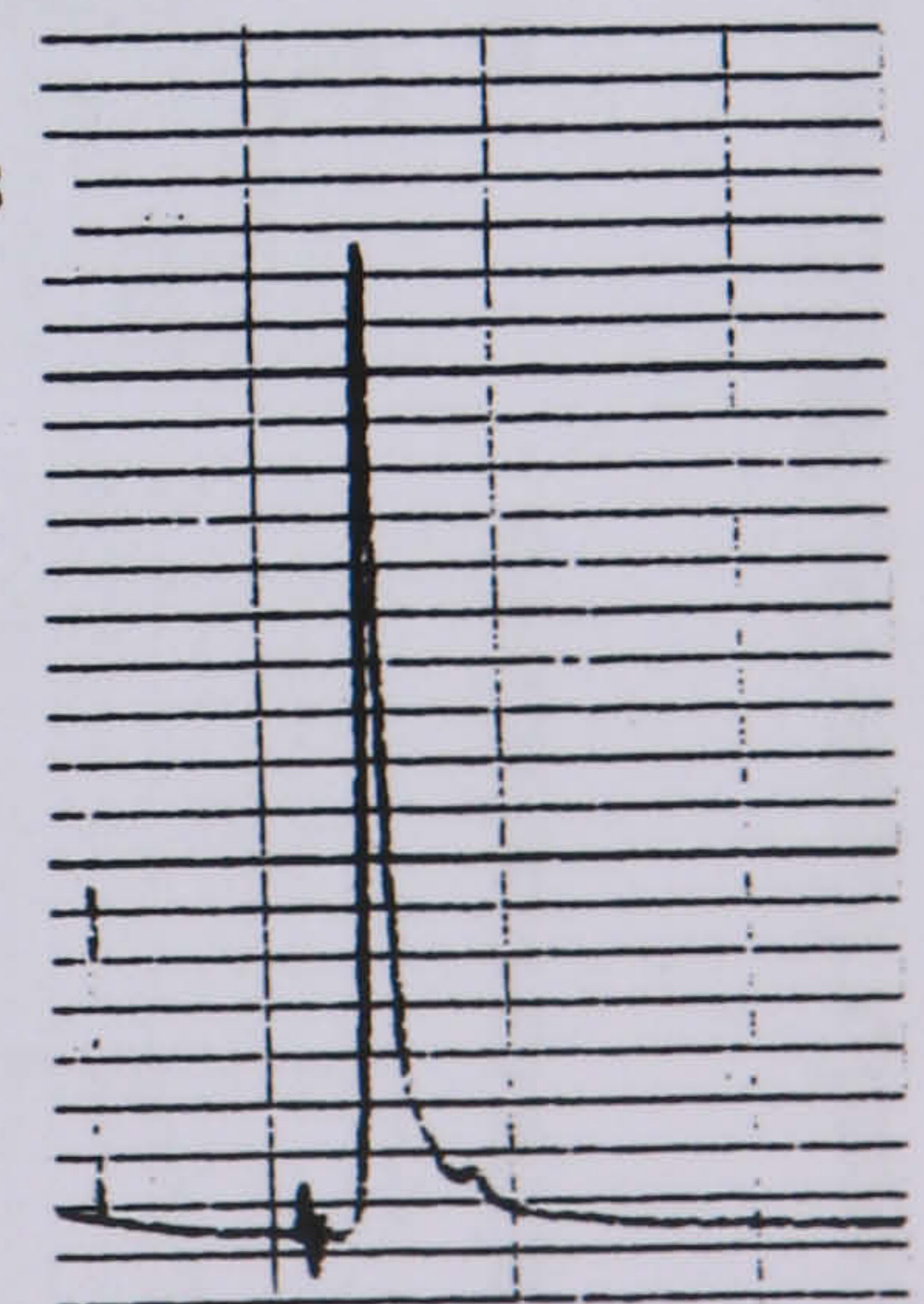
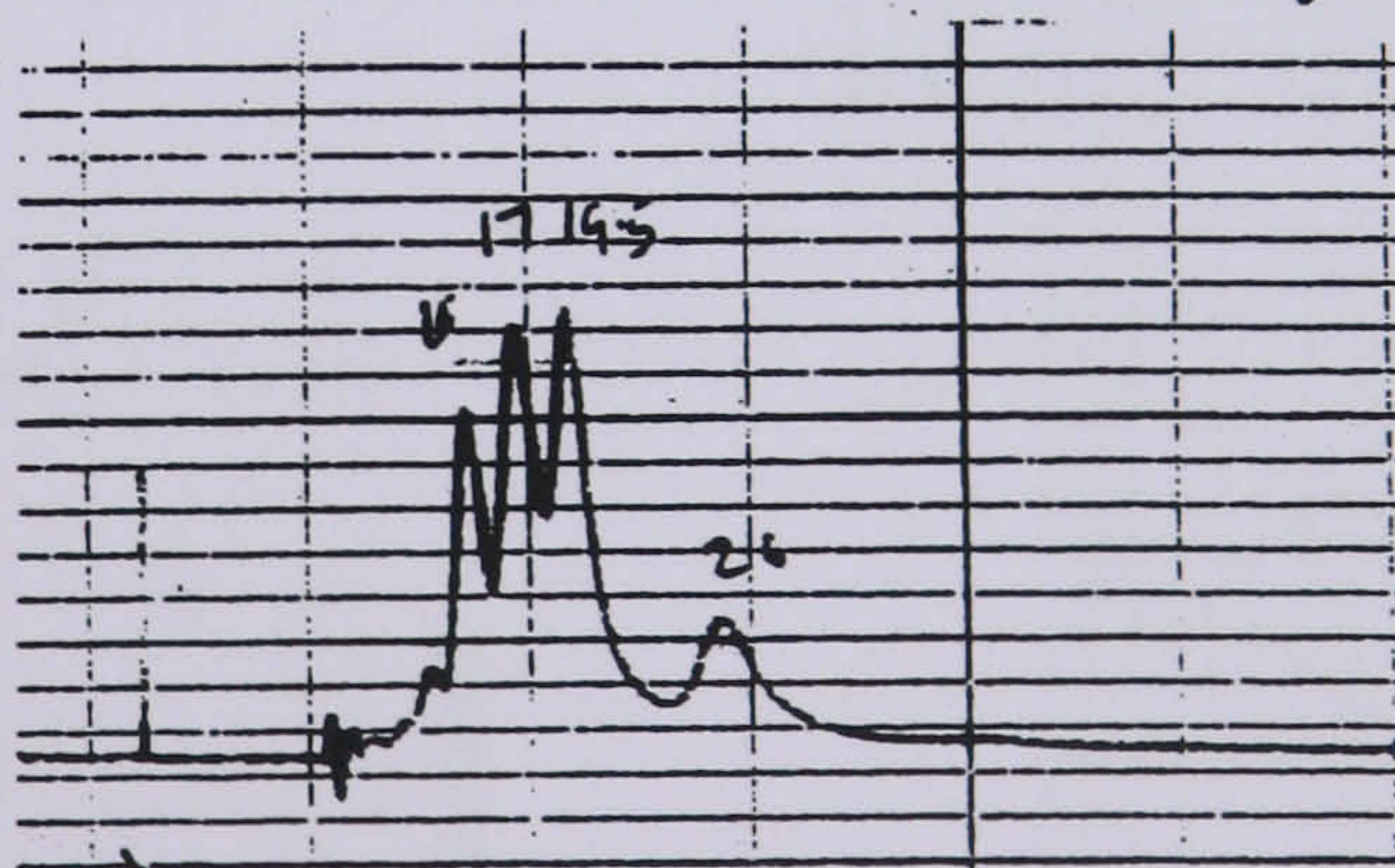


Thionin solution



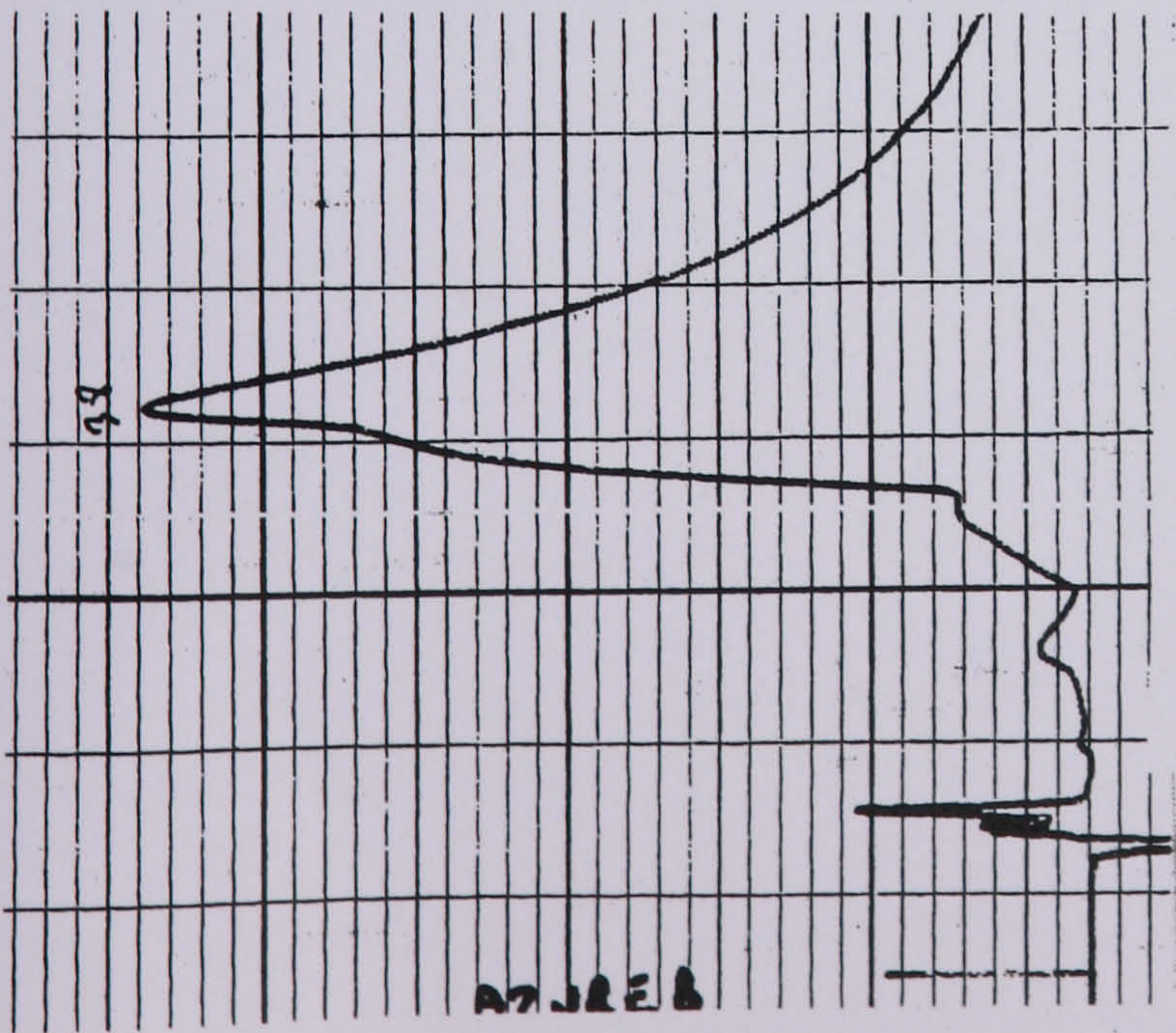
Azure B after 15 minutes electrolysis

Azure A after 15 minutes electrolysis

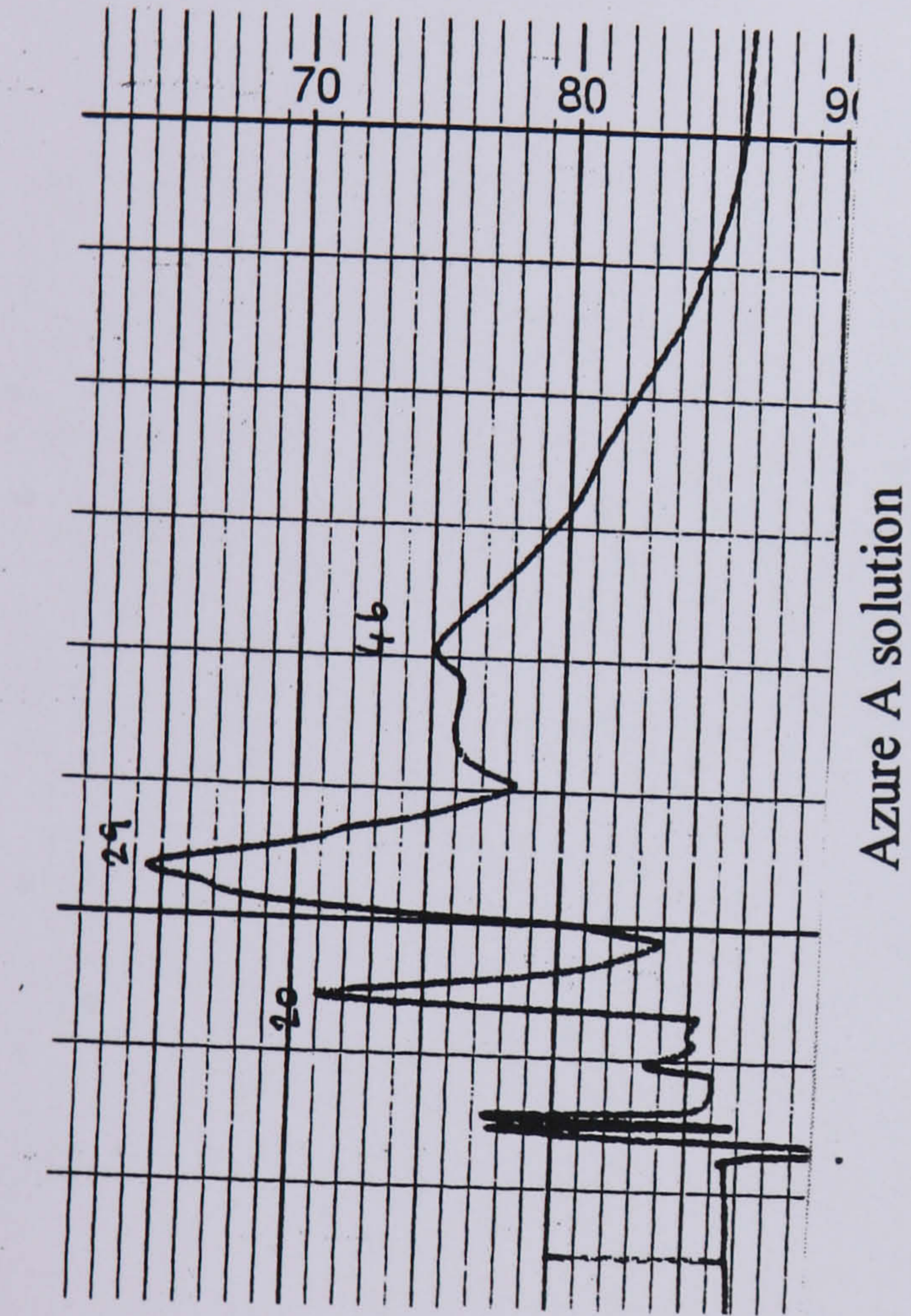


Thionin after 15 minutes electrolysis

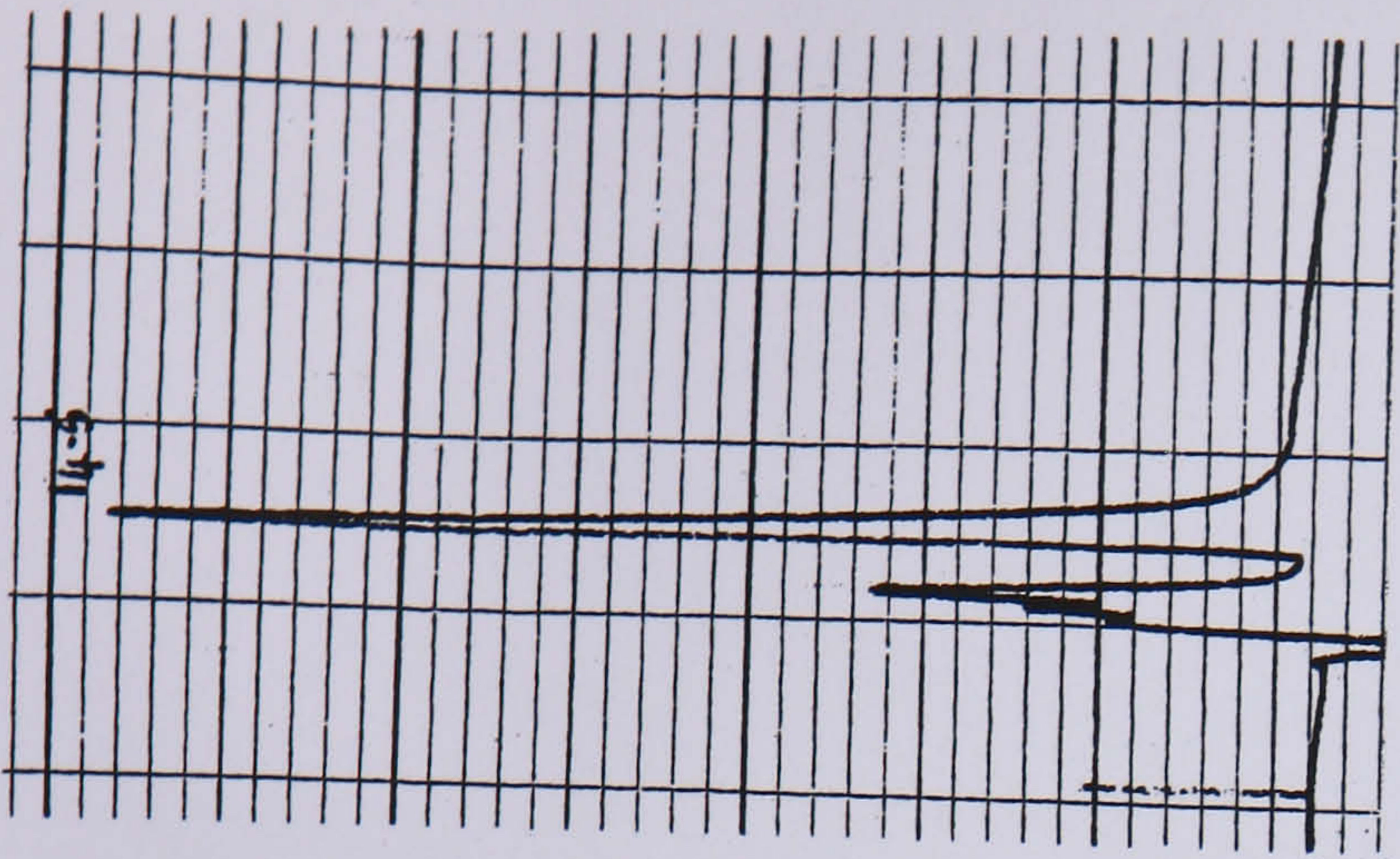
Appendix Figure [8]: HPLC chromatograms of azure B, azure A and thionin solutions and 15 minutes electrolysed solutions using condition (1)



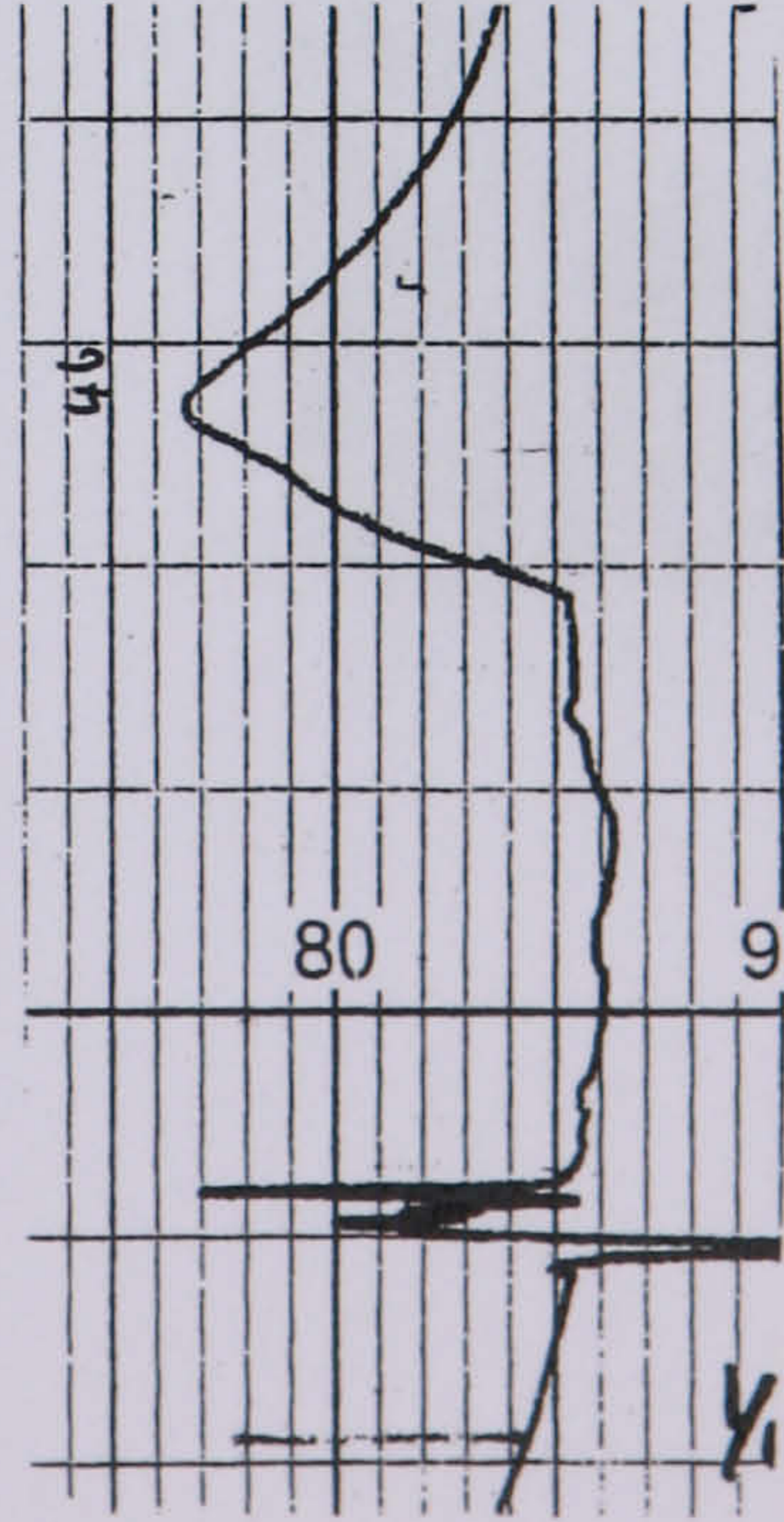
Azure B solution



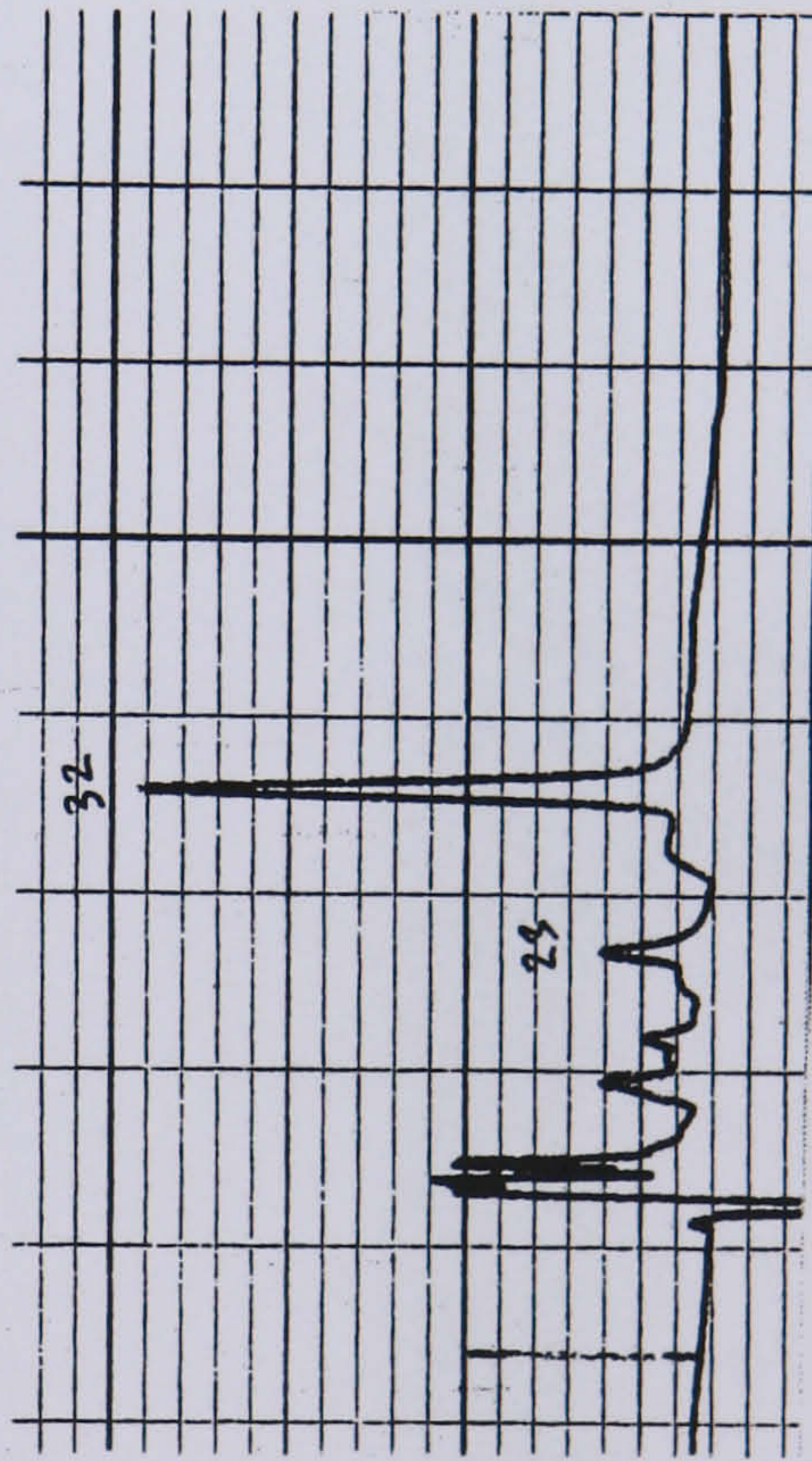
Azure A solution



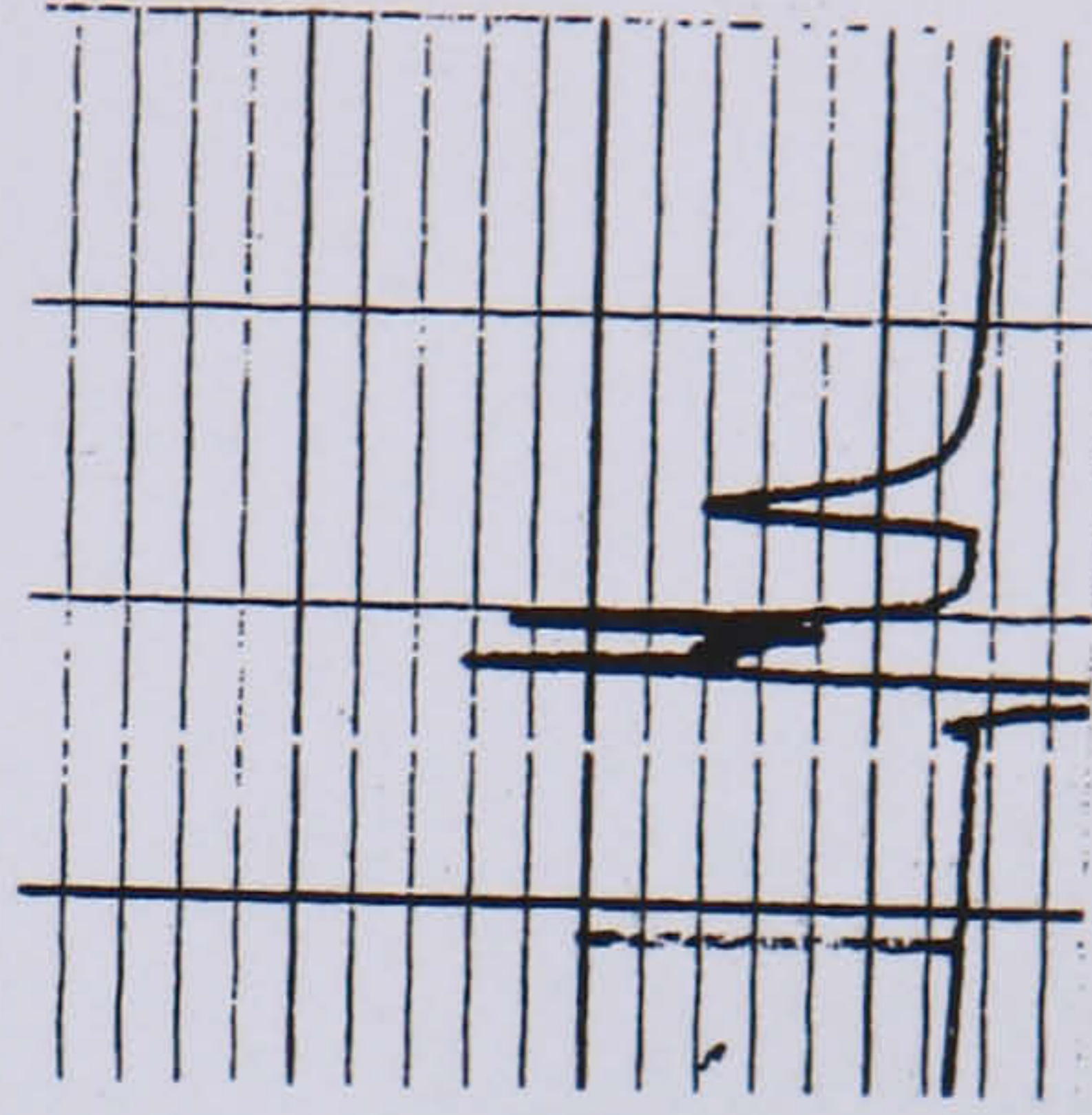
Thionin solution



Azure B after 15 minutes electrolysis



Azure A after 15 minutes electrolysis



Thionin after 15 minutes electrolysis

Appendix Figure [9]: HPLC chromatograms of azure B, azure A and thionin solutions and 15 minutes electrolysed solutions using condition (2)