STUDIES OF LEACHING, RECOVERY AND RECYCLING OF HEAVY METALS

A thesis submitted for the degree of Doctor of Philosophy

By

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ABSTRACT

The leachability of cadmium, cobalt, copper, lead, nickel and zinc metals and their oxides, sulfides and carbonates by water, 0.5 mol dm^{-3} CH_3COOH, 0.1 mol dm^{-3} HCl/NaCl (1:1 mixture) and 2 mol dm^{-3} HNO_3 is reported. The concentrations of the leached heavy metals are compared with the trigger levels set by World Health Organisation (WHO).

Three leaching solutions (nitric, sulfuric and hydrochloric acids) were used to extract copper, zinc, cobalt, nickel, iron and lead from spent catalysts prior to the application of separation technologies. Leaching experiments were conducted using both traditional methods and a microwave-assisted extraction technique. Data are provided on the effects of leaching temperature, leaching time, solid to liquid ratio and acid concentration on the extraction of different metals. The use of 2 mol dm^{-3} sulfuric acid at 50°C for 60 minutes and at a solid/liquid (S/L) ratio of 1:25 achieved more than 90% extraction for all the metals studied. A comparison of the results from traditional and microwave extraction techniques demonstrates that microwave heating reduced the time required to obtain maximum metal extraction.

The kinetics for the traditional extraction procedure showed that diffusion was the rate-controlling process, but it was not possible to conclusively establish the rate controlling process for the microwave leaching.

The feasibility of using an electrodialysis process to separate metal ions, such as copper from zinc, was examined. A laboratory-scale three compartments membrane system was designed, constructed, used and optimised for the separation process. The separation of copper from zinc in the electrodialysis process exploited the greater stability of the Cu-EDTA complex compared with the Zn-EDTA complex. It was observed that Zn^{2+} ions migrated through the cation-exchange membrane from central compartment to catholyte and, simultaneously, the negative Cu-EDTA complex transferred to the analyte compartment crossing the anion exchange membrane. The technique was successfully used to separate mixtures of Cu:Cd and Zn:Ni. The technique could not, however, be used for the separation of Zn from Cd.

An adsorption process was used to prepare copper, iron, nickel and zinc oxides catalysts on γ-Al_2O_3 as support. The materials prepared were used in a fixed bed reactor to assess the catalytic oxidation of volatile organic compounds (methane and ethane) in air. Cu/γ-Al_2O_3 was found to be the most promising catalyst for the complete oxidation of methane and ethane at temperatures of 575°C and 525°C, respectively. Increasing the calcination temperature in the drying and pre-treatment of the catalysts resulted in a decrease in the catalytic activity.

In Loving Memory of My Mother
The Most Precious Person in My Life
Whose Death Prevented Her from Seeing This Work

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List of Abbreviations

AAS	Atomic Absorption Spectroscopy
AEM	Anion Exchange Membrane
ASTM	American Society for Testing and Materials
BMW	Biodegradable Municipal Waste
CEM	Cation Exchange Membrane
COPD	Chronic Obstructive Pulmonary Disease
EEA	European Environment Agency
EDTA	Ethylendiaminetetraacetic Acid
EP	Extraction Procedure
ETEs	Essential Trace Elements
EU	European Union
EWC	European Waste Catalogue
FCC	Fluid Catalytic Cracking
FCCU	Fluid Catalytic Cracking Unit
FID	Flame Ionization Detector
HCl/NaCl	Hydrochloric Acid and Sodium Chloride
HWD	Hazardous Waste Directive
K_{RCD}	Rate Constant Controlled by Diffusion
k_{RPS}	Rate Constant Controlled by Reaction at the Particle Surface
K_{sp}	Solubility Product
MARS	Microwave Accelerated Reaction System
PGM	Platinum Group Metals
PTFE	Polytetrafluoroethylene
RFCC	Residue Fluid Catalytic Cracking
SIC	Standard Industry Code
Tan δ	Dissipation Factor
TCLP	Toxicity Characteristic Leaching Procedure
VOCs	Volatile Organic Compounds
UN	United Nation
UNEP	United Nations Environment Programme
UNFCCC	United Nations Framework Convention on Climate Change
UOP	Universal Oil Product Limited
USEPA	United States Environmental Protection Agency
USRCRA	United States Resource Conservation and Recovery Act
WAC	Waste Acceptance Criteria
WHO	World Health Organization
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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Chapter 1

INTRODUCTION

Chapter 1

INTRODUCTION

"Waste itself is a human concept; everything in nature is eventually used. If human beings carry on in their present ways, they will one day be recycled along with the dinosaurs."(Peter Marshall)

1.1 PROBLEM STATEMENT

Industrial activities generate large amounts of diverse solid wastes that can be hazardous in nature. In order to appropriately dispose such materials, it is important to characterise, quantify and categorise them according to their source, industrial activities, type of waste and their chemical and biological properties [1]. The US in 2005 generated around 245.7 million tons of municipal solid waste and this was less than the amount generated in 2004 by 1.6 million tons [2].

With the increase in global industrial activity, the use of catalysts has also increased significantly. The amount of spent catalyst an industry generates is very much dependent on the amount of fresh catalyst used, deposits formed on them during the reactors and the type of reaction that the catalyst is used for. Overall, the end result has been a growing trend of discarding catalysts as solid wastes.

There is an increasing demand for all types of catalysts, including novel or improved. Many industries such as chemical industry, petroleum/petrochemical refining [3], gas purification and vegetable oil refineries [4] and pharmaceutical manufacturing, are very heavily dependent on catalysts in many different reactions such as fluid catalytic cracking (FCC), residue fluid catalytic cracking (RFCC), dehydrogenation, hydrodesulfurisation (HDS) and many others. Some spent catalysts generated by petroleum refining operations: such as hydrotreating and hydrorefining catalysts have been classified as hazardous solid waste by the United States Environmental Protection Agency (USEPA) [5] as they may release toxic gases and contain components (heavy metals and polyaromatic compounds). These spent catalysts contain valuable metals resource such as Cd, Cr, Cu, Co, Mn, Ni, Pb and Zn, in a matrix that will undoubtedly be classified as hazardous with regard to its disposal.

Spent catalysts contribute a significant amount of the solid wastes generated in the petrochemical industry [6]. Furimsky pointed out that about 400,000 tons of fluid catalytic cracking unit (FCCU) waste catalysts were produced annually [7]. Every year in Kuwait, around 7000 tons of spent catalysts are generated as solid waste from hydrotreating and hydrocracking units [1]. In 1991, in the USA, 190,000 tons of catalysts were used, resulting in catalyst waste of 12,000 tons, with Europe consuming 60,000 tons of spent FCC/RFCC catalyst and Japan consuming 105,000 tons. By 1998, the catalyst demand of FCC and RFCC has been around 570,000 tons [8]. The amount of spent FCC/RFCC catalyst reached about 160,000 tons in 1994 and was estimated to be roughly 370,000 tons in 1998 worldwide [9]. One of the main reasons for this increased usage is the introduction of new or improved catalysts, especially in the USA where in the 1990s, over 130 new/improved catalysts were introduced for catalysing many reactions in biochemical, petroleum, chemical and environmental processes [10]. Based on these figures, catalytic technology is likely to have a major role in industrial processes for many years into the future.

To combat this, and due to the inherently hazardous nature of spent catalysts, many countries have evoked regulations through their relevant environmental authorities to pressurise industries into practising safe handling of spent catalysts. These regulations have become increasingly more stringent. Currently there are several ways in which catalysts are disposed off, they include, disposal in landfills, metal reclamation, regeneration and reuse, or the utilisation of the spent catalyst as raw materials for production of other products or catalysts [11].

The choice taken is dependent on several factors, including economical, legal and technical feasibility [12]. Traditionally, spent catalysts have been incinerated or landfilled, however this is becoming increasing less economical and there are significant air, soil and water pollution issues with such methods.

A large number of metals such as Co, Cu, Ni, Fe, Mo and V are used in the catalyst industry to increase the activity and stability of catalysts [3,13,14]. Heavy metals such as Cu, V, Ni, Mo and Co present in spent catalyst can be leached after disposal and pollute the environment.

In the last decade more attention was paid to the recovery of metals from spent catalysts owing to its environmental and economical benefits [1], furthermore, the treatment of hazardous substances and recovery of the valuable materials reduce the cost and pollution before the final disposal in the landfill [15].

Heavy metal pollution has raised serious environmental concerns worldwide because bioaccumulation of these elements beyond the tolerance thresholds of living organisms poses long term risk to the earth's ecosystem [16]. The main flows of heavy metals to the environment are from industrial and municipal wastes, both of which contain a variety of toxic heavy metals [17]. For example, chemical and electronic industries mainly produce wastes containing Hg; metallic ferrous mining and smelting industries produce wastes containing Pb, Cd, As, Hg, Fe and Ni; metallurgical industries produce wastes containing As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn; the pulp and paper industry generates wastes containing Zn, Cu, Cr, Ni, Al, Fe, and Mn [18]. Other industries, such as electroplating, leather, paint, and dye produce different sets of heavy metal containing wastes [19]. In addition to various industries, many commercial establishments, such as retail stores, restaurants, laundromats, garages, hospitals, schools, laboratories, and photo processors also contribute to the heavy metal load discharged into the environment.

Under growing legislative and economical pressure, industries are attempting to find a more viable yet economical solution that allows the disposing of wastes containing heavy metals such as spent catalysts. Therefore, there is increasing international concern that this type of waste should be properly managed in order to minimise its potential to cause harm to human health and the ecosystem. New methods of regenerating spent catalysts to be reused seem to be a very attractive option to cut costs, adhere to legislation and reduce environmental pollution.

1.2 THE NEEDS FOR RECOVERY AND REMOVAL OF HEAVY METALS

The existing and pending legislations in the European Union (EU) emphasise the promotion of recovering of heavy metals and other valuable materials from industrial wastes. Some member states still have more than 80% dependence on landfill to dispose of the waste generated from various industrial applications. Such a loss of resources is no longer acceptable and this is reflected in the introduction of Directives and Acts such as Waste Framework Directive 75/442/EEC [20], Dangerous Substance Directive 76/464/EEC [21], Hazardous Waste Directive 91/689/EEC [22], Waste Electrical and Electronic Equipment (WEEE) [23], Landfill of Waste 99/31/EC [24] and the Environmental Protection Act 1990 [25] in the UK ensure that regulatory requirements upon companies and organisations are progressively tightened. This increase in environmental legislation has resulted in a rise in treatment and disposal costs, but also much greater interest in alternative remediation and recovery technologies. This clear policy direction has put stress on programmes which actively increase and optimise the recovery of metals from waste. Therefore, the need of efficient treatment of both solid and effluent streams from these industries is in a great importance due to the following three main reasons [26]:

- **Environmental pollution**: Most of the common metals such as copper, zinc, nickel, cadmium are by-products of various industries. The discharge of both solid and liquid waste streams containing these toxic metals can cause harm to human and aquatic environment. In addition, the recovery of these metals can save the depletion of raw materials and it can also promote sustainable development.

- **Environmental regulation**: Most of the metals used in the industrial processes are classified as hazardous substances. Legislative bodies set values which are deemed as acceptable concentrations of hazardous metals, i.e. concentrations that have a negligible impact on humans as well as the surrounding environment.

- **Economic**: The reuse and recycle of metals from both industrial and end-of-life wastes can reduce waste disposal costs and to a lesser extent the use of raw materials.

1.3 CONTRIBUTIONS TO KNOWLEDGE

The three main contributions to knowledge are in the fields of hydrometallurgical leaching process, membrane technology and catalysts. The research work described in the thesis enabled me:

1. To investigate and set optimum leaching conditions for the chosen waste samples using conventional and microwave methods.
2. A three compartment membrane technology was developed and successfully used for the separation of copper from zinc in the presence of ethylendiaminetetraacetic acid (EDTA).
3. Transitional metal oxide supported catalysts have been prepared from leaching solutions obtained from spent catalysts and successfully used them to destroy methane and ethane in air.

1.4 AIMS & OBJECTIVES OF THIS WORK

The principle aim of the work described in this thesis is to develop hydrometallurgical processes appropriate for the extraction, recycling and recovery of heavy metals from industrial wastes. In particular the study deals with the extraction and recovery of toxic and valuable metals from industrial spent catalysts whose disposal to landfill can have a detrimental impact on human health and the environment as well as being economically insensible. Since heavy metals from landfill can be transported through leachate, it is imperative to explore the conditions by which metals can be extracted using different extraction and recovery techniques. Figure 1.1 illustrates an overview of the processes of metal extraction and recovery that needed to be developed and optimised as a part of this research work.

The specific objectives of this research work are:

- To investigate the leachability of heavy metals from their elemental and compounds form in simulated landfill and other environmental conditions.
- To optimise the dissolution process and determine the best leaching conditions for metal extraction from various types of wastes using traditional leaching method and then compare with leaching carried out by the Microwave Accelerated Reaction System (MARS).
- To design, develop and optimise a three compartment membrane technology for the separation of metals from mixed metal solutions.
- To destroy the volatile organic compounds (methane and ethane) using metal oxide supported catalysts prepared by leached transition metal solutions.

1.5 SCOPE OF THIS WORK

This introductory chapter outlines the problems associated with the disposal of wastes containing heavy metals, the need to recover them and the aims and objectives of the research work. The introductory chapter is followed by six chapters. Chapter two provides background information on waste, the classification of waste. hazardous waste and its disposal methods, waste legislations, heavy metals and their toxicological properties and techniques used to recover heavy metals from different types of wastes and wastewater streams. Chapter three investigates the solubility and bioavailability of metals listed as hazardous under different environmental conditions using different leach liquors and pure compounds of metals such as cadmium, cobalt, copper, lead, nickel and zinc. In chapter four, the optimisation of leaching conditions of heavy metals from industrial waste is established. The influences of various parameters on the leaching process of heavy metals from industrial spent catalysts have been investigated. Moreover, a comparative study between conventional leaching and microwave leaching methods is presented. Chapter five focuses on membrane technology for the separation of heavy metals. The separation involves the use of cation and anion exchange membranes in the presence of a chelating agent, EDTA. Chapter six describes the destruction of volatile organic compounds such as methane and ethane in air. The work focused on the preparation of catalysts from solutions attained from leaching of transitional metals from spent catalysts. Chapter seven discusses the conclusions made from this research.

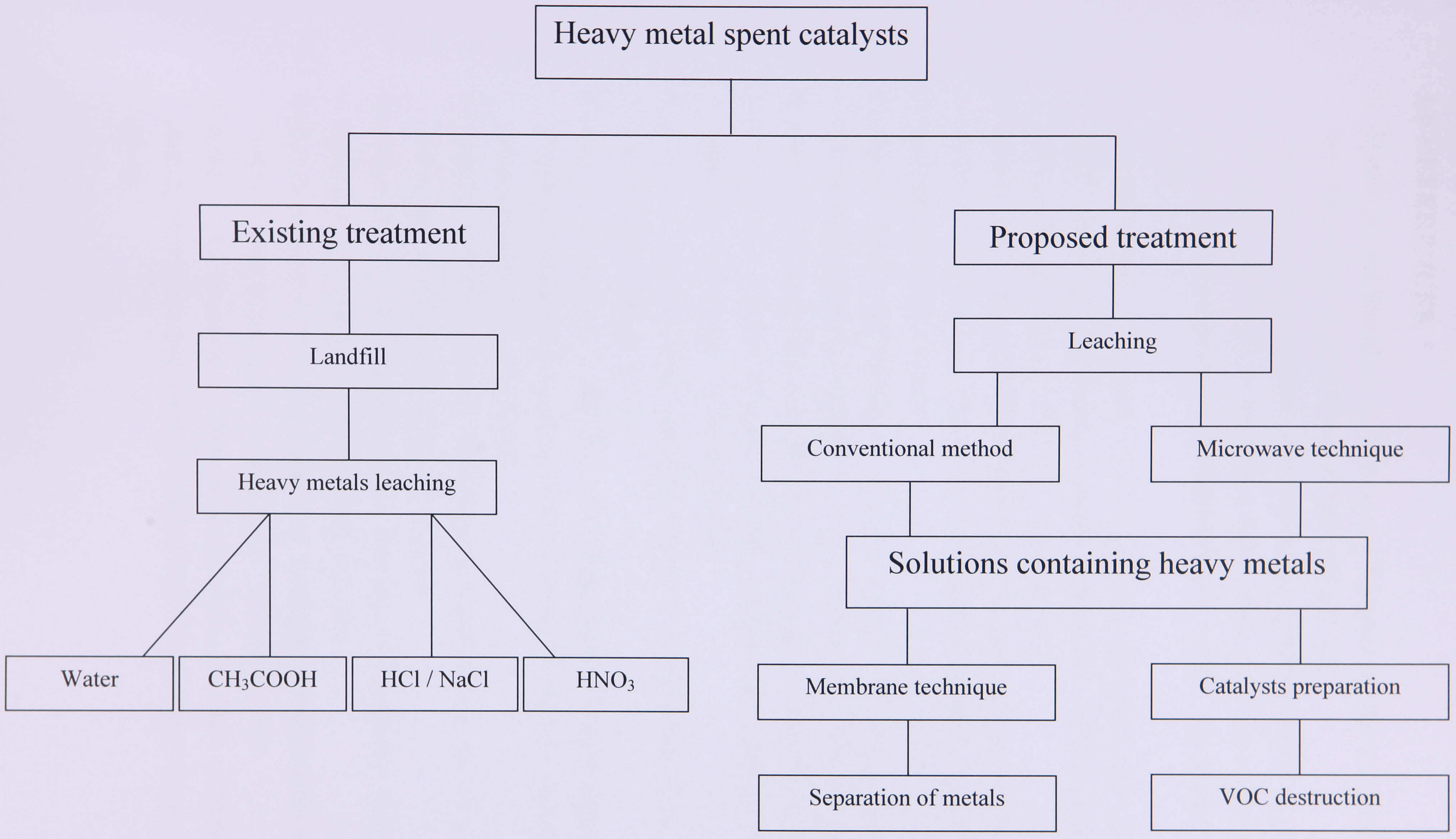

Figure 1.1: A flow chart giving an overview of metal extraction and recovery

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Chapter 2

BACKGROUND TO THE PRESENT WORK

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Recent developments in various industrial and technological sectors have created a situation where huge amounts of raw materials are being extracted, from the finite resources on this planet, to fulfil the needs of human society. With this deemed progress has come a culture of disposing untreated wastes into the different compartments of our environment. In the last few decades millions of tons of industrial waste have been produced worldwide, the overwhelming majority of which has been disposed of in landfills. Such dumping of waste has created many health, social and economic problems, to the extent that governments have had to enforce new regulations to reduce the amount of waste being disposed of in landfills and streams, mainly to protect surface and ground water from heavy metal pollutants, namely cadmium, copper, lead, mercury, chromium and iron.

Waste management by the landfill is not a new approach and in recent years there has been a growing realisation that the planet simply cannot support indefinite extraction of resources for human consumption. Therefore, a new idea was developed based on reusing the metals through actually treating the waste and recovering some of the resources rather than continuously extracting raw materials from the earth and then dumping it in landfills when the produce is no longer required. The extraction of resources from wastes can take place in many ways; the waste can be reused or the energy in the waste can be harnessed to provide electricity. Such methods are referred to as secondary resource recovery or recycling.

Globally, these methods are being employed more commonly, especially in areas where resources are scarce or where the economical benefits of recycling outweigh the extraction of new raw materials from the earth. Terms such as 'sustainable development' are being more commonly used as the key to promoting industry and commerce. Sustainable development is the idea that de-carbonisation, efficiency improvement and reduction of pollutants are not only the best way of reducing harm to future generations but also the best way for economic, industrial and commercial growth in the long run.

However problems arise in extraction of raw materials, especially when dealing with metals, as they are difficult to separate from one another (mainly due to the chemical and physical attributes they commonly share). Hydrometallurgical methods are continuously being improved to optimise extraction and some headway has been made, but there is still a need for novel and better methods of extracting materials from waste, to further improve sustainable growth and development globally.

2.1 WASTE

Waste has been defined in different ways. According to article 2 of the Basel Convention [1], the definition of waste is "substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law".

The Environmental Protection Act 1990 defines waste as [2]:

a) any substance, which constitutes scrap material or any effluent or other unwanted surplus substance arising from the application of a process.
b) any substance or article, which requires to be disposed of as being broken, worn out, contaminated or otherwise spoiled.

In the UK, the word 'waste' is now defined according to the EU Waste Framework Directive 75/442/EEC [3] as amended by 91/156/EEC [4] which describes waste as "any substance or object in the categories set out in Annex I which the holder discards or intends or is required to discard".

Along with the sudden rise in world population and development, waste production has grown to such an extent that annually the globe produces 7000 million tonnes. The European Union is responsible for nearly a third of this, 2200 million tonnes [5]. The UK produces about 430 million tonnes of waste annually. Figure 2.1 shows the annual waste production by weight in the UK in 2005 [6].

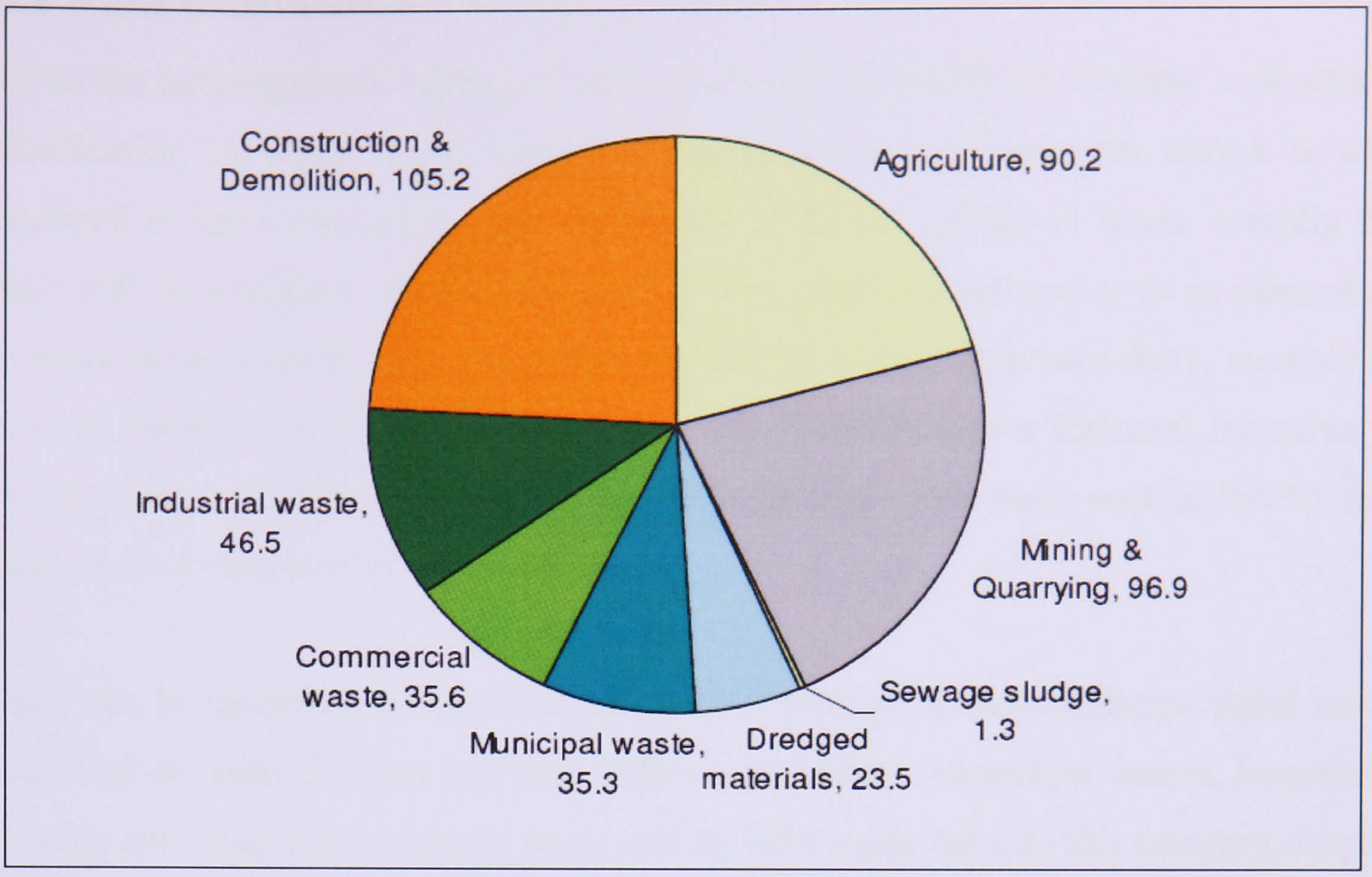


Figure 2.1: UK waste arising by source stream (Million Tonnes, 2005)

For both environmental and economic reasons, it is important that new treatment processes are practised to reduce the quantity of waste and to recover as much of the valuable content as possible. Environmentally sustainable economies require efficient use of resources and an effective management of the subsequent waste. Sustainable management is now a high priority for the United Kingdom government. Government strategy is aimed at the reduction in overall waste volume, more effective management of waste, promotion of recycling, deployment of new management techniques and an increase in the cost of disposing of waste to landfill through the landfill tax. The overall aim of sustainable waste management is to recover as much of the valuable products contained in waste with the use of as little energy as possible [7].

According to information published by the European Environment Agency (EEA), five major waste streams make up the bulk of total waste generation in the European Union, around 2% of this waste total is of a hazardous nature e.g. around 27 million tonnes [8]:

- manufacturing 26%
- mining and quarrying 29%
- construction and demolition 22%
- municipal solid 14%
- agriculture and forestry waste

2.1.1 Waste Classification

Due to the heterogeneous nature of waste, it can be very difficult to apply a structured classification to waste. Such classifications, however, are important and it is also beneficial to have consistency and uniformity in the description of waste. Usually the waste will be a mixture of different types or may even overlap two or three categories. To make matters worse, the same waste can vary in composition on a daily, monthly or seasonal basis, or from one location to another. There is also a financial incentive to classify waste, as some wastes are exempt from environmental taxes such as landfill tax, which is obviously important to companies.

Waste can be classified by chemical, physical or biological characteristics. Solid waste is deemed as waste that has less than 70% water content. Municipal wastes, household garbage, industrial waste, mining waste and oil field waste fall into this category. Liquid waste consists mainly of wastewaters from municipal and industrial sources, that have less than 1% suspended solids. Waste can also be categorised according to whether it is hazardous or non hazardous [9]. Broadly speaking, waste can be also categorised into 'controlled' and 'non-controlled' waste, Figure 2.2.

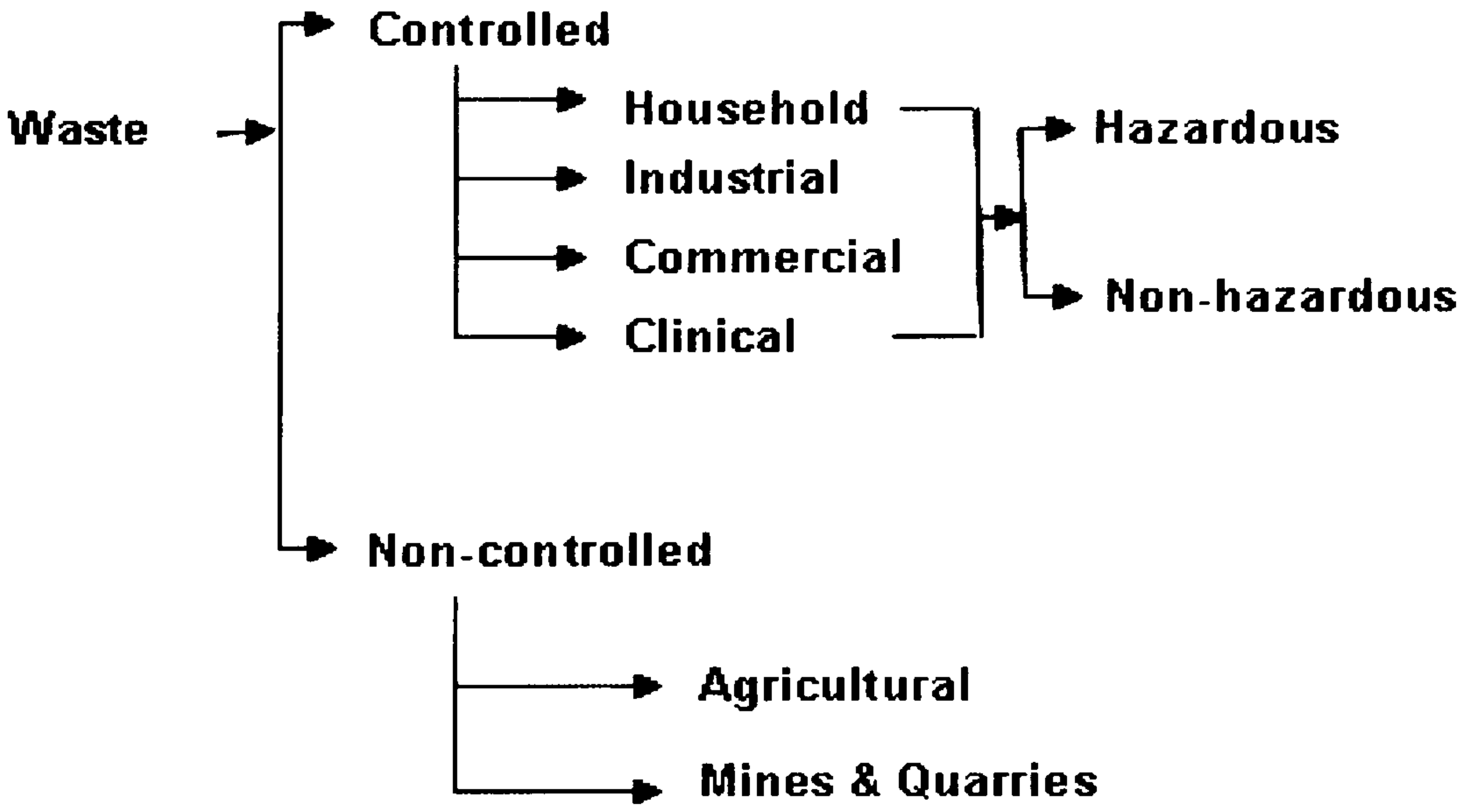


Figure 2.2: Types of wastes in the UK

2.1.1.1 Controlled Waste

The Environmental Agency handles the 'controlled' waste as per article 75(4) of the Environmental Protection Act, 1990. This includes household, industrial, commercial and clinical waste but not quarry, sewage or agricultural waste. This type of waste is governed by Controlled Waste Regulations, 1992 [10]. Controlled wastes can be further divided into hazardous and non-hazardous waste depending on the environmental and health affects they possess. This waste is around 53% of the total annual waste produced in the UK.

2.1.1.2 Non-Controlled Waste

This consists of agriculture, mining and quarry waste. These wastes are subject to separate legislation as are radioactive and explosive wastes. Non-controlled waste is 47% of the total annual waste produced in the UK.

Industrial Waste

The manufacturing industry is responsible for a variety of different wastes arising from many processes such as metal, food, beverage, tobacco, wood and paper production. Industrial waste tends to be very mixed in nature, and it depends largely on the type of industrialisation prevalent in a given country. The Environmental Protection Act of 1990, Section 75(6), classifies industrial waste as waste from "any of the following premises [2]:

- any factory
- any premises used for the purposes of, or in connection with, the provision to the public of transport services by land, water or air.
- any premises used for the purposes of, or in connection with, the supply to the public of gas, water or electricity or the provision of sewerage services.
- any premises used for the purposes of, or in connection with, the provision to the public of postal or telecommunications services."

In a survey conducted by the Environment Agency in 2002/3 which included 4,500 industrial and commercial businesses in England, it was found that the amount of industrial and commercial waste produced was 68 million tonnes. Of this about 38 million tonnes was from industry and 30 million from commerce [11].

Hazardous Waste

Hazardous waste has properties that can be harmful to humans or the environment if not handled properly. A large number of products and goods that human societies have come to rely on generate hazardous waste during production. Industrial and agricultural activities are major contributors to the hazardous waste produced in the UK. Hazardous materials are materials such as: heavy metals, petroleum products, synthetic organic compounds, radioactive materials, asbestos and acids. Hazardous wastes can be solid, liquid or gaseous.

There is not universal consensus on the definition of a hazardous waste although many countries do have similarities in their classification. The United Nations Environment Programme (UNEP) defines hazardous waste as "waste other than radioactive waste which by reason of chemical reactivity, toxic, explosive, corrosive or other characteristics causing danger or likely to cause danger to health or the environment, whether alone or coming into contact with other wastes, are legally defined hazardous in the state in which they are generated or in which they are disposed of or through which they are transported".

The United States Resource Conservation and Recovery Act (USRCRA) of 1976 considers wastes toxic and /or hazardous if they "cause or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible illness; or pose a substantial present or potential hazard to human health or the environment, when improperly treated, stored, transported, disposed of, or otherwise managed" [12].

The Hazard Waste Directive (HWD) 91/689/EEC [13], defines hazardous waste as wastes featuring on a list drawn up by the European Commission, because they possess one or more of the hazardous properties set out in the HWD. Table 2.1 is Annex II of the Directive which gives the constituents of wastes which define them as hazardous when they have the properties described in Annex III. Table 2.2 is Annex III of the Directive that describes the properties of wastes which define them as hazardous.

Table 2.1: Annex II of the Hazardous Waste Directive 91/689/EEC

Waste having as constituents:

C1	beryllium; beryllium compounds
C2	vanadium compounds
C3	chromium (VI) compounds
C4	cobalt compounds
C5	nickel compounds
C6	copper compounds
C7	zinc compounds
C8	arsenic; arsenic compounds
C9	selenium; selenium compounds
C10	silver compounds
C11	cadmium; cadmium compounds
C12	tin compounds
C13	antimony; antimony compounds
C14	tellurium; tellurium compounds
C15	barium compounds; excluding barium sulfate
C16	mercury; mercury compounds
C17	thallium; thallium compounds
C18	lead; lead compounds
C19	inorganic sulfides
C20	inorganic fluorine compounds, excluding calcium fluoride;
C21	inorganic cyanides
C22	the following alkaline or alkaline earth metals: lithium, sodium, potassium, calcium, magnesium in uncombined form
C23	acidic solutions or acids in solid form
C24	basic solutions or bases in solid form
C25	asbestos (dust and fibres)
C26	phosphorus: phosphorus compounds, excluding mineral phosphates
C27	metal carbonyls
C28	peroxides
C29	chlorates
C30	perchlorates
C31	azides
C32	PCBs and/or PCTs
C33	pharmaceutical or veterinary coumpounds
C34	biocides and phyto-pharmaceutical substances (e.g. pesticides, etc.)
C35	infectious substances
C36	creosotes
C37	isocyanates; thiocyanates
C38	organic cyanides (e.g. nitriles, etc.)
C39	phenols; phenol compounds
C40	halogenated solvents
C41	organic solvents, excluding halogenated solvents
C42	organohalogen compounds, excluding inert polymerized materials and other substances referred to in this Annex
C43	aromatic compounds; polycyclic and heterocyclic organic compounds
C44	aliphatic amines
C45	aromatic amines
C46	ethers
C47	substances of an explosive character, excluding those listed elsewhere in this Annex;
C48	sulfur organic compounds
C49	any congener of polychlorinated dibenzo-furan
C50	any congener of polychlorinated dibenzo-p-dioxin
C51	hydrocarbons and their oxygen; nitrogen and/or sulfur compounds not otherwise taken into account in this Annex

Table 2.2: Annex III of the Hazardous Waste Directive 91/689/EEC

H1	'Explosive': substances and preparations which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene.
H2	'Oxidizing': substances and preparations which exhibit highly exothermic reactions when in contact with other substances, particularly flammable substances.
H3-A	'Highly flammable': liquid substances and preparations having a flash point below 21 °C (including extremely flammable liquids), or - substances and preparations which may become hot and finally catch fire in contact with air at ambient temperature without any application of energy, or - solid substances and preparations which may readily catch fire after brief contact with a source of ignition and which continue to burn or to be consumed after removal of the source of ignition, or - gaseous substances and preparations which are flammable in air at normal pressure, or - substances and preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.
H3-B	'Flammable': liquid substances and preparations having a flash point equal to or greater than 21 °C and less than or equal to 55 °C.
H4	'Irritant': non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation.
H5	'harmful': substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risks.
H6	'Toxic': substances and preparations (including very toxic substances and preparations) which, if they are inhaled or ingested or if they penetrate the skin, may involve serious, acute or chronic health risks and even death.
H7	'Carcinogenic': substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence.
	H8 'Corrosive': substances and preparations which may destroy living tissue on contacts.
H9	'Infectious': substances containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms.
H10	'Teratogenic': substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce non-hereditary congenital malformations or increase their incidence.
H11	'Mutagenic': substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce hereditary genetic defects or increase their incidence.
H12	Substances and preparations which release toxic or very toxic gases in contact with water, air or an acid.
H13	Substances and preparations capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above.
H14	'Ecotoxic': substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment.

The classification of a waste as hazardous according to the definition has considerable impact upon industry in determining how such waste is regulated and affects charging, monitoring and inspection regimes. Hazardous waste only consists of around 2% of the total waste produced in Europe. Due to its ability to cause damage to both the environment and human health, however, it is necessary that it should be treated specially [14].

According to figures released by the Environment Agency, hazardous waste production was increased between 1998/99 and 2000 but then gradually fell back in 2003 to about 5% below that produced in 1998/99. Since 2000 the amount of hazardous waste produced has declined further by around 10% [15]. In 2003, England and Wales produced 4.8 million tonnes of hazardous waste, 67% of this amount came from four European Waste Catalogue (EWC) categories construction and demolition wastes, oils and oil-water mixtures, wastes from organic chemical processes and the catch-all category of wastes not otherwise specified [16].

In 1991, the European Commission under an amendment of Hazardous Waste Directive 91/689/EEC [13] to the Waste Framework Directive 75/442/EEC [3] set out the legal framework for the definition of hazardous waste in Europe and identified a number of properties of waste which render it hazardous such as explosive, oxidising, flammable, irritant, harmful, toxic, infectious, carcinogenic, or corrosive. This is called the European Waste Catalogue, which is dealt with later in more details.

Recovery and Disposal Methods of Waste

For industrial nations, the safe disposal of large volumes of waste has always been problematic [17]. In non-industrialised countries, however, lack of public or even government awareness on environmental issues has led to overuse of landfill disposal sites. This in itself constitutes a major problem [18]. Methods of waste disposal vary according to the materials in the waste and include incineration, burial at designated sites (landfill sites), and reclaiming and recycling. Figure 2.3 shows the commonly used methods of waste disposal in United Kingdom [19].

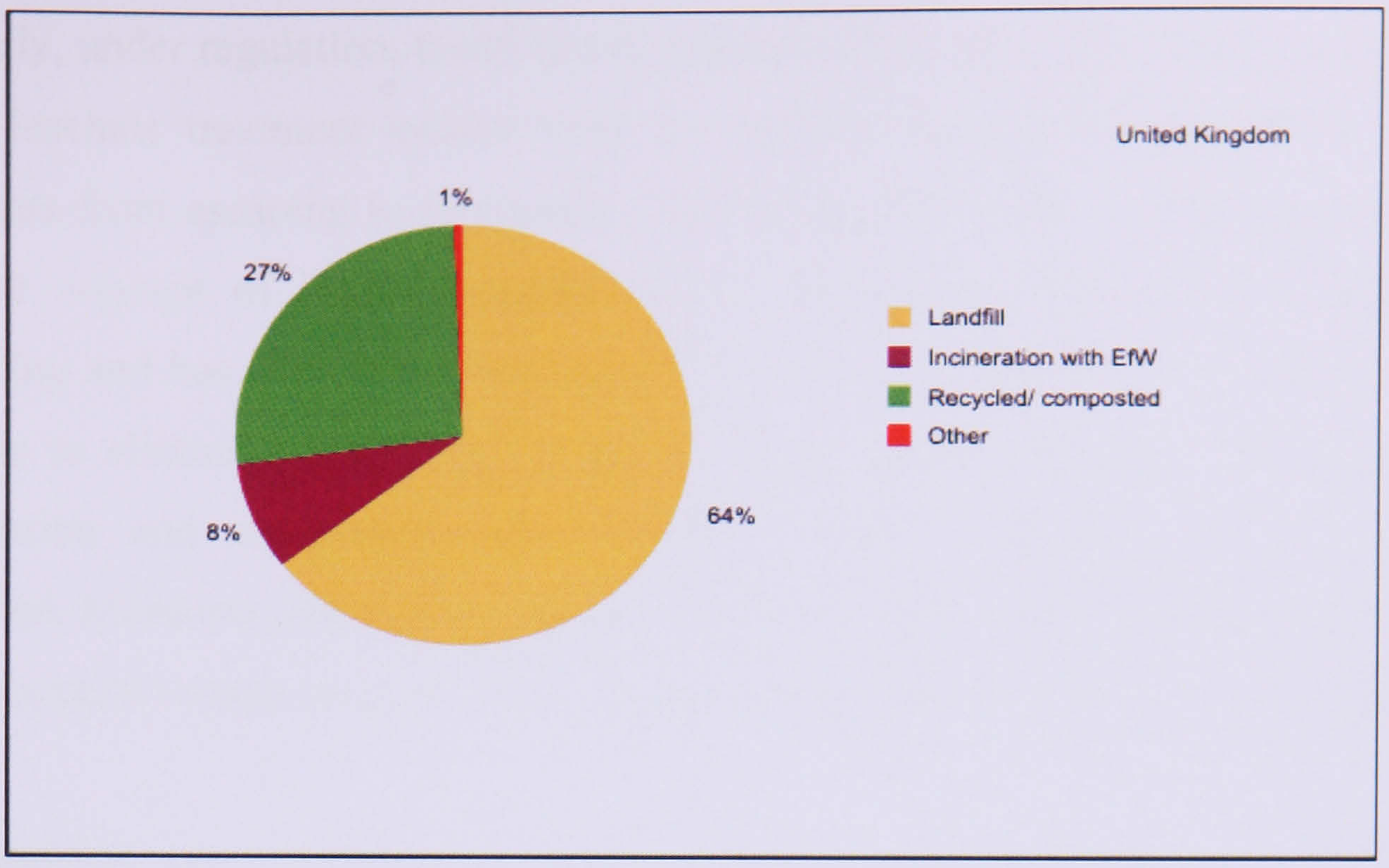


Figure 2.3: Methods of waste disposal in the UK

2.1.2 Landfill

Landfill is the most common method used to dispose of waste in 2005/6 in the UK [19]. Landfilling includes the controlled dumping of waste in specific sites and is in fact the least preferred method of waste treatment according to the waste management hierarchy. The waste management hierarchy is part of the European Directive on waste management, Council Directive 91/156/EEC with the purpose of protecting the environment and ensuring sustainable development. It is an approach to waste management that acts as the basis of government waste strategy, setting out in order the best practical environmental option for dealing with waste disposal. As we descend down the list of the hierarchy, the negative impact on the environment increases:

1. Reduce (most favoured option)
2. Reuse
3. Recycle
4. Recover energy through incineration or from landfills
5. Landfill without energy recovery (least favoured option)

Much of municipal solid waste, construction debris, sewage treatment sludge and waste from other processes is disposed of to landfill. The waste is spread, compacted and then finally covered with soil to reduce the effects on public health and the environment. Landfill disposal can lead to emissions into both air and groundwater. It is inevitable that some emissions will occur, even if the best available techniques to prevent leakage are employed.

Currently, under regulation, landfills are required to be lined with impermeable material and a leachate treatment system must be employed to prevent hazardous waste or pollutants from escaping to surrounding soil or air [20]. Since landfilling does not fit into the concept of closed material cycles, the government does not approve of landfilling and has striven to discourage it as much as possible. It is, however, not yet possible to eliminate landfilling completely as a means of dealing with waste. Both incineration and composting, for example, produce residues, which have to be landfilled. Moreover, the current capacity of incinerators is not large enough to handle all combustible waste, thus part of this waste will also inevitably have to be landfilled.

Classification

Generally speaking, there are three different types of landfill site:

- **Hazardous waste landfills**: only accept hazardous waste, as per the requirements of the European Waste Catalogue.
- **Non-hazardous waste landfills**: only accept non-hazardous waste categories listed in the European Waste Catalogue.
- **Inert landfills**: designed only to receive inert waste.

Landfill and Waste

Humans have been using landfill as a means of disposal of waste for centuries [21]. Due to the complex toxicological factors and complex chemistry of the interactions of the different components in the waste in a landfill, it is difficult to identify all of the potential contaminants. Studies of leachates have shown that organic contaminants leak at active stages of decomposition but then gradually decrease with time as the fill stabilises. Inorganic contaminants however, can leach out for decades. Landfill leachate typically contains heavy metals, organic matter and inorganic ions such as ammonium, phosphate and sulfate [22]. Table 2.3 shows the heavy reliance on landfill for the disposal of waste in the UK [23].

Table 2.3: Proportion of waste landfilled, incinerated, recycled by sector

Waste Type	**Annual Amount (tonnes)**	**% Landfilled**	**% Incinerated**	**% Recycled & Reused**	**% Other**
Household	20	90	5	5	0
Commercial	15	85	7.5	7.5	0
Construction	70	63	0	30	7
Industrial	70	73	1	18	6

Historically, landfills have presented two main types of problem [12]:

- Waste volatility: arising mainly from methane production leading to fires, explosions, and production of toxic fumes arising from problems related to poor management of ignitable, reactive and incompatible wastes.
- Contamination: of soil and both ground and surface waters.

For the leachate to be deemed safe for environmental release, certain criteria have to be met such as:

- Leachate should not contain high concentrations of organic species, ammonium or heavy metal ions.
- Leachate should not be toxic to organisms in the local ecosystem.

Additionally, landfills should not be releasing any gasses that could contaminate ground water supplies, cause explosions or be an odour nuisance.

Advantages & Disadvantages of Landfill

Landfilling has certain advantages such as [24]:

- It is cheap and economically sustainable.
- A wide variety of wastes are suitable for landfill.
- Often it serves as a final disposal route for residues arising from other waste management options such as incineration.
- Landfill gas can be collected and utilized for heat and as a low-polluting fuel for energy generation.
- Restored land can provide valuable space for wildlife habitat or leisure use.

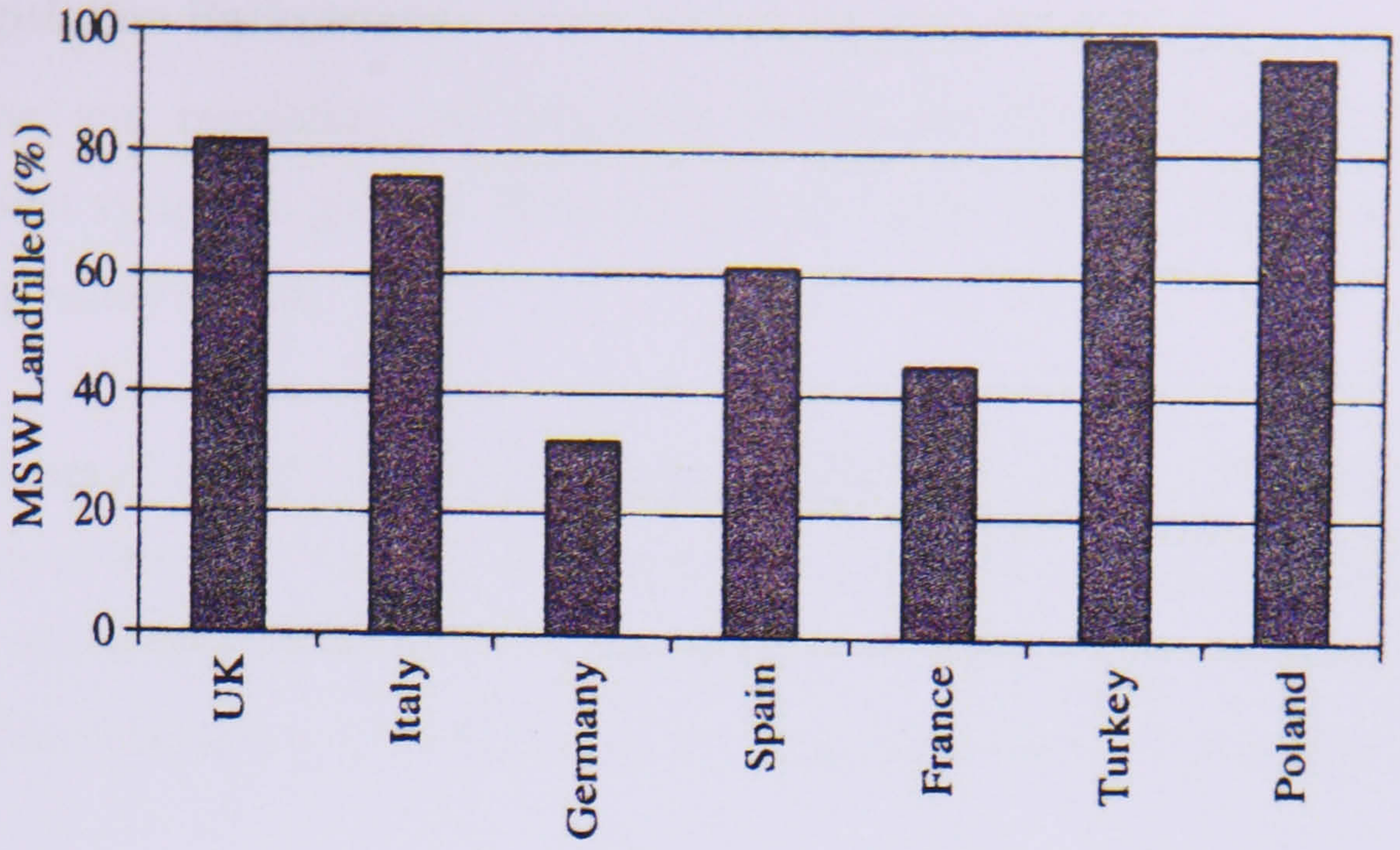
The disadvantages of landfilling include:

- Uncontrollable leakage and pollution from older sites (before the impacts of leachate and landfill gas were realised).
- There is continued risk of contamination from operational landfill sites.
- There are a finite number of landfill sites that can be used, some countries are experiencing shortages of available sites.
- Landfilling achieves a lower conversion of waste into energy than other solid waste management strategies such as incineration and gasification.
- The convenience of landfilling tends to discourage the development of innovative waste management strategies.
- Landfilling may produce contaminated land that is unsuitable for some future uses.
- Landfilling causes noise pollution, odours, unsightliness and, often, heavy vehicle movement adding to air pollution problem.

Landfill in the UK

In the UK (as in most developed nations), the main methods of waste disposal are landfill and incineration [25]. Landfilling is usually considered to be the worst option as it consumes a lot of space and there is a high probability that undesirable waste components will leak into the soil, water or air [26]. On average, nearly 54% of all the commercial and industrial waste and 83% of municipal waste is managed through landfills [27].

Landfill is widely used as a method of waste management because it is highly adaptable, it is the least expensive method and it is a viable option in UK because many areas are geologically suitable for landfill. The use of landfill as a waste management option has been steadily decreasing in the UK, from 131.4 million tonnes in 1995 to 118.5 million tonnes in 2003, a decrease of nearly 10% [28]. It is not just the UK that relies heavily on landfill. Several countries such as Italy, Spain, Finland, Portugal, Ireland, Romania, Poland, Hungary, Bulgaria, Lithuania and Latvia dispose of more than 60% of their municipal solid waste by landfill. Figure 2.4 shows that in many countries across Europe, landfill is the dominant disposal route for municipal solid waste and Figure 2.5 shows the percentage of hazardous waste landfilled by some European countries [29].



Figures 2.4: shows that many countries across Europe are reliant on landfills.

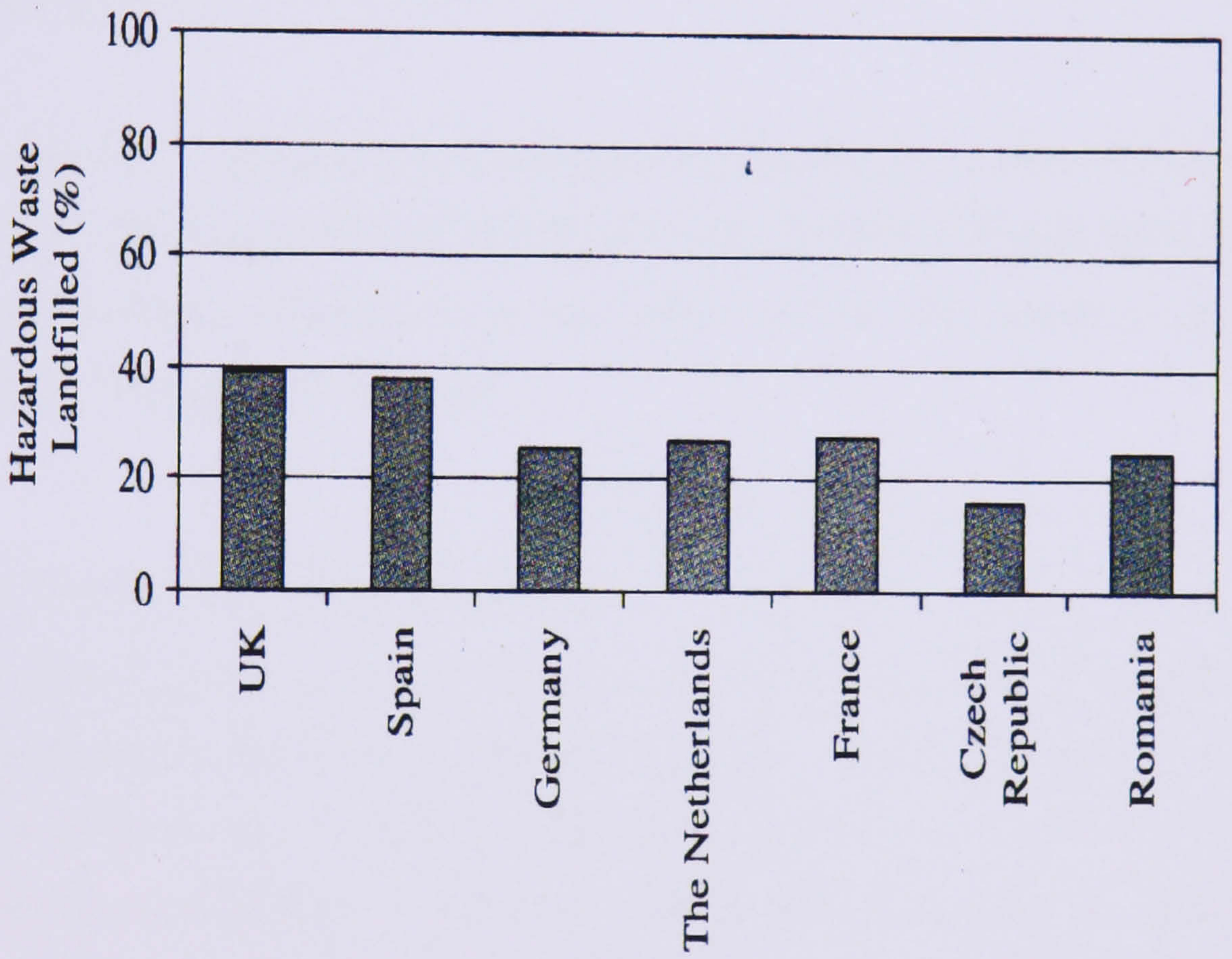


Figure 2.5: Hazardous waste landfilled in selected European countries

It is clear that new waste management options are required to reduce the use of landfill so as to maintain environmental quality. Such new diversion strategies, however, must be economical and technically feasible and there must be a realistic level of social support for the programme [30].

2.1.3 Legislation Background

Legislation and regulation are important drivers for the development of a waste management system in general. This includes the treatment and safe disposal of waste containing heavy metals.

The main aim of the EU waste management strategy is to prevent or at least reduce the generation of harmful waste. If this cannot be achieved, materials should be reused, recycled, recovered or reused as an energy source. Finally, if no further use can be found, waste should be disposed of safely by either incineration or in landfill sites.

According to the Hazardous Waste Directive 91/689/EEC waste materials such as heavy metals are deemed hazardous and therefore their removal and disposal requires strict environmental guidelines and legislation in order to minimise the affect of these metals on the environment.

As a result of EU legislation, the European Community Directives of Waste Framework 75/442/EEC, Hazardous Waste 91/689/EEC and Landfill of Waste 99/31/EC [31] have been implemented, resulting in a big impact on the way waste is sorted, treated, transported, disposed and managed.

2.1.3.1 Directive on the Landfill of Waste

Despite differences in technical standards and operating practises, landfilling remains the single biggest route of waste disposal in the EU. Recently, however, there have been a number of incidents in which there has been gross water and land pollution, forcing the European Commission to introduce certain measures aimed at regulating landfill activity, disposal techniques and establishing a common framework that promotes reuse and recycling in favour of landfills.

Previous reviews of waste management at landfill sites throughout the EU showed that there was considerable variation between member states with regard to landfill setting policies, lining requirements, leachate control and approaches to waste input. Subsequently, the EU decided to standardise waste landfill management across the entire EU in order to achieve a high level of environmental protection [32].

Aim of the Landfill Directive

The Council Directive 99/31/EC of 26th April 1999 on the landfill of waste came into force on 16th July 1999 with the aim of being incorporated in the legislation of member states by 16th July 2001. This Directive aimed to "prevent or reduce as far as possible negative effects on the environment, in particular the pollution of surface water, groundwater, soil and air, and on the global environment, including the greenhouse effect, as well as any resulting risk to human health, from the landfilling of waste, during the whole life-cycle of the landfill" [31].

The Directive requires a substantial reduction in the amount of biodegradable municipal waste (BMW) being landfilled and include the targets:

- by 2010 to reduce BMW landfilled to 75% (by weight) of that produced in 1995
- by 2013 to reduce BMW landfilled to 50% (by weight) of that produced in 1995
- by 2020 to reduce BMW landfilled to 35% (by weight) of that produced in 1995

The Landfill Directive has brought forward progressive measures to further prevent or reduce as far as possible the negative effects of landfilling waste on the environment and on human health. The Directive:

- banned the landfill of liquids and certain solid wastes.
- classified landfill sites as inert, non-hazardous and hazardous.
- defined procedures for waste acceptance to be adopted at landfills.
- classified the types of waste for each class of landfill specified by waste acceptance criteria.
- prevented the co-disposal of hazardous and non-hazardous waste after July 2004.
- required that waste must be pre-treated before being landfilled and that landfill gas must be collected, treated and used to produce energy. This means that if the gas cannot be used it must be flared.
- set out general principles for acceptance of waste at landfills and general procedures for testing and interim guidelines. This was supplemented by Council Decision 2003/33/EC establishing the criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 and Annex II of the Landfill Directive.

Wastes Banned from Landfill

The following wastes may not be accepted in a landfill:

- waste which is corrosive, oxidising, highly flammable, flammable or explosive
- liquid hazardous waste, infectious hospital and other clinical wastes
- whole used tyres (from 2003)
- shredded tyres (from 2006)
- any other type of waste which does not meet the acceptance criteria laid down in Annex II.

Full guidelines for the acceptance of waste at landfill sites were set out by Council Decision 2003/33/EC [33]. The criteria set limits for the concentration of certain contaminants in accordance to EU regulation on such contaminants. The decision put into place a procedure for characterising waste and checking whether the criteria for waste acceptance were being met. Subsequently, domestic legislation across Europe including the UK changed to meet the standards expected by the EU. Moreover, the Council Decision deals with controls on the inputs to landfill such as trying to ensure that leachate produced does not pose a risk to groundwater and surface water. This has a positive impact for the environment as the Council Decision is providing greater protection than would otherwise be the case, with domestic legislation being the only way to set regulations.

Landfill Directive in the UK

Waste management legislation in the UK is developed from European laws. Currently, national controls on waste have their origins in the Control of Pollution Act 1974 which was greatly tightened through the Environmental Protection Act 1990. The legislation originally concentrated on the disposal of waste. Since the EC Framework Directive on waste has been introduced, however, the control has been extended to include storage, treatment, recycling and transport of waste.

The Landfill Directive was transposed in the Landfill (England and Wales) Regulations 2002 [34]. The 2002 Regulations were subsequently amended by the Landfill (England and Wales) (Amendment) Regulations 2004 [35] in order to implement the requirements of the Council Decision. The 2004 Regulations, however, did not make provision in respect of the waste acceptance criteria to be met by monolithic waste (A waste that is deliberately treated to solidify it and strongly bind it).

According to the guidelines of the Council Directive, member states are required to provide the same level of environmental protection afforded by the criteria it lays down in respect to waste that is granular in nature. The 2005 Regulations [36], adapted this criteria for waste that is monolithic in nature. These criteria complete the implementation in England and Wales, of Council Decision 2003/33/EC for monolithic wastes. They also implement Landfill Directive 1999/31/EC by prohibiting the acceptance at existing landfills of whole and shredded used tyres from 16th July 2006 and other specified types of waste from 30th October 2007.

From 16th July 2004 landfills have been classified as inert, non-hazardous and hazardous. Therefore, it is an offence for a waste operator to accept waste which is not covered by their permit. The ban on co-disposal of hazardous and non hazardous wastes in the UK from 16th July 2004 introduced the concept of separate classes of landfill for each waste type. Therefore, the number of landfill sites licensed to accept hazardous waste has fallen from over 250 to a dozen in England with none in Scotland or Wales. Furthermore, the Regulations introduced the concept of pre-treatment of waste prior to final disposal at landfill. Pre-treatment has been partially defined as a process that reduces weight or hazardous nature of a waste or facilitates its handling or enhances its recovery. Effectively, it points towards some recycling being applied to waste from most premises. This requires that, with immediate effect, any landfill that has been granted its license since July 2001 must only take waste that is pre-treated. From July 2004, all hazardous sites must only take waste that is pre-treated.

2.1.3.2 Landfill Tax

Companies, organisations or local authorities that wish to dispose of waste through landfill sites must pay an additional landfill tax as well as the normal landfill rates. It was brought into being by the Finance Act 1996 [37], and it came into force on 1st October 1996 in a strategy by the UK government entitled "Making Waste Work" which set out plans for sustainable waste management and aimed to achieve a 25% recycling rate for household waste. As a part of this strategy, the regulation aims to ensure that the full cost of the environmental implications of disposal are taken into account in the price and that more sustainable approach to waste management in which less waste is produced and more waste is either reused or has value recovered from it is promoted thus providing industries with an incentive to find alternative disposal methods for waste.

The landfill tax is administered by HM Customs & Excise. Originally, landfill tax was charged at a rate of £7 per tonne at the standard rate and £2 per tonne at the reduced rate. The tax for year 2000 was charged at a standard rate of £10 per tonne and a proportionately reduced sum for any additional part of a tonne. A lower rate of £2 per tonne was charged for waste, which is designated as consisting of qualifying materials.

The rates of tax applied from 1st April 2007 were as follows:

- Materials such as rocks, soils, ceramic, concrete, unused minerals, furnace slags, ash, low activity inorganic compounds, water and calcium sulfate/calcium hydroxide and brine (provided that they are disposed of in specific containers) fall into the 'low rate' category, i.e. £2 per tonne of inert waste.
- the standard rate - £24 per tonne for all other landfilled waste including substances that either decay or contaminate land – such as household waste.

The government stated that the standard rate of tax will increase by at least £3 per tonne in subsequent years to a rate of £35 per tonne by 2010. A number of substances are exempted from landfill tax. They include dredgings, disposals from mines and quarries, and waste from reclamation of contaminated land. Landfill Tax is worth between 500 and 600 million pounds per year to the government. Of the amount collected, 6.5% has been available till now for spending on approved projects through the Landfill Tax Credit Scheme.

2.1.3.3 Waste Management Licensing

A waste management licence is a legal document that is issued by the Environment Agency in accordance with the Environmental Protection Act 1990, section 36. Such licenses ensure that industrial and waste disposal activities do not cause pollution of the environment, harm to human health or serious detriment to local amenities. There are two types of waste management licenses: a site licence (authorising the deposit, recovery or disposal of controlled waste in or on land), or a mobile plant licence (authorising the recovery or disposal of controlled waste using certain types of mobile plant).

2.1.3.4 European Waste Catalogue

In 1991, the European Commission under an amendment of Hazardous Waste Directive 91/689/EEC to the Waste Framework Directive 75/442/EEC set out the legal framework for the definition of hazardous waste in Europe and identified a number of properties of waste which render it hazardous such as explosive, oxidising, flammable, irritant, harmful, toxic, infectious, carcinogenic, or corrosive. This was followed by the introduction by the European Commission of a list of over 200 different types of hazardous waste which were listed as part of Council Decision 94/904/EC [38]. The European Commission also introduced a comprehensive list of all wastes, hazardous or otherwise, as part of the Council Decision 94/3/EC [39] in 1994 called the European Waste Catalogue (EWC).

The catalogue is broken down into 20 chapters, containing approximately 900 six digit codes. All waste must now carry a code in accordance with the catalogue on its transfer notes. The EWC replaces the Environment Agency Waste Categories. It was transposed into English & Welsh law by regulation 19 of the Landfill Regulations (England & Wales) 2002.

The Hazardous Waste regulations and List of Wastes regulations (both of which include England and Wales versions) came into force on the 16th July 2005. The Regulations set out procedures to be followed when disposing of, carrying and receiving hazardous waste. They require that waste movements are tracked from cradle to grave using "consignment notes" and specify which materials are to be considered hazardous.

Changes to the European Waste Catalogue have brought many wastes not previously categorised as hazardous within the scope of the wider definitions, including computer monitors, fluorescent tubes, fridges and end-of-life vehicles that have not been drained of liquid or other hazardous components. Typical hazardous waste according to the List of Wastes (England) Regulations are [40]: Acids, alkaline solutions, batteries, industrial solvents, oil sludges, pesticides, pharmaceutical compounds, photographic chemicals, waste oil, wood preservatives, TVs, computer monitors, paint and fluorescent tubes.

2.1.3.5 Waste Acceptance Criteria

The Landfill Directive 99/31/EC sets more stringent standards on wastes that can be accepted at landfills through the publication of the Waste Acceptance Criteria (WAC). Only waste that is in accordance with Annex II of the Directive can be sent to a landfill. In Article 16 of the Directive, there are procedures for introducing certain criteria or test methods and associated limit values for each class of landfill (hazardous, non-hazardous and inert).

England and Wales transposed the Directive into legislation in 2002. In Schedule 1 of the regulations [34], the WAC for different types of wastes is outlined. The regulations clearly state that only certain wastes may be accepted at a landfill. These are wastes that would not pollute the environment, endanger human health, jeopardise environmental protection systems, and prevent the stabilisation of the landfill within its projected lifetime. On 19th December 2002, the Council Decision (2003/33/EC) was adopted and in January 2003, it was published. This Decision was amalgamated into the landfill Regulations 2004 in England and Wales which itself was based on the Pollution, Prevention and Control Act of 1999.

The final WAC was put into force on 16th July 2005. The new acceptance criteria apply to all hazardous wastes going to a landfill, including stable, non-reactive hazardous waste. Procedures for hazardous waste acceptance at landfills are given and these procedures are divided into three levels [41]:

- Level 1: Basic characterisation

  For each new waste that is to be landfilled, certain information is required; such as;
    - Source and origin
    - Standard Industry Code (SIC) and process that has produced the waste
    - Treatment applied or reason for not treating the waste
    - Composition of waste
    - Appearance
    - European Waste Catalogue code
    - Hazardous properties
    - Confirmation that the waste is not prohibited from a landfill (i.e. corrosive or flammable etc)
    - The class of landfill suitable for the waste i.e. hazardous

- Likely behaviour of waste once it is in a landfill
- Possibility of recycling the waste

This comprises a methodical establishment of the short and long-term leaching behaviour and/or characteristic properties of the waste. Level 1 is almost entirely the responsibility of the waste producer, although the waste contractor may be involved in characterisation of the waste (using WAC analysis). Ultimately it is still the responsibility of the waste producer to make sure that the waste is characterised correctly and that the information about the waste is correct.

- Level 2: Compliance testing
  This level is mainly the responsibility of the landfill site operator. It must be done at least once a year, more frequently if the waste is variable. Tests should be carried out periodically to establish that the waste complies with the available permit conditions and meet the set criteria. The testing is based on the variables identified in Level 1.

- Level 3: On-site verification
  The landfill operator is required to carry out visual inspections of each waste delivery to the site (before unloading if waste is accessible) and to check that all the required documentation is in order. Appearance, odour, colour and other relevant information regarding the waste being delivered is to be checked and recorded.

In the UK non-hazardous waste does not require criteria to be disposed of in a non-hazardous landfill, though this may change in the future following pressure from the EU.

2.1.3.6 Hazardous Waste Regulations

The Special Waste Regulations 1996 (as amended) was replaced by the Hazardous Waste (England and Wales) Regulations 2005 on 16th July 2005 [42]. There are many changes from the Special Waste Regulations, the two main ones being that the producers of hazardous waste will be required to pre-register before any hazardous waste can be collected from their premises and secondly, that the regulations apply the EWC codes of hazardous wastes, which will affect a much wider range of producers.

The European Commission has also revised its list of hazardous wastes and has incorporated it into the EWC. The new, revised list considers certain materials such as television sets, computer monitors, refrigerators, fluorescent tubes and end-of-life vehicles that will now require collection under the new hazardous waste notification and documentation procedures. This list was transposed into national legislation by the List of Wastes Regulations at the same time as the new Hazardous Waste Regulations.

The main reason that these regulations were introduced was to simplify the documentation involved with the collection and disposal of hazardous waste and create an approach that would follow the waste from the 'cradle to the grave'.

The term "Hazardous Waste" has now replaced what was previously called 'Special Waste'. The new regulations for hazardous wastes now contain all the previous 'special wastes' as well as an additional 200 types of waste. Since July 16th 2005, it has been an offence to collect hazardous waste from a site that has not been registered or deemed exempt. Hazardous wastes banned by the Landfill Directive were stopped from being landfilled immediately. Instead, they had to be managed by treatment or incineration. Furthermore, the current 2005 regulations ban the mixing of different categories of hazardous waste, or the mixing of hazardous and non hazardous waste with other substances or materials, unless this is specifically permitted by a licence.

After these new regulations, it is increasingly difficult to landfill wastes mainly because hazardous wastes are now tested, and since many do not meet any of the waste acceptance criteria, they cannot be landfilled. In these cases, the waste is to be treated so that it meets the criteria or alternatively another disposal route must be taken.

New Regulations and Waste Producer

The new regulations that have come into force in 2005 have a significant impact on many waste producers and businesses. Under the Hazardous Waste Regulations 2005, some commonly used items such as televisions, lead-acid batteries and fluorescent light tubes, have joined the existing list of toxic, corrosive and irritant substances. This will undoubtedly result in an increased number of businesses being defined as producing 'hazardous waste' and they will have to conform to the new WAC. Failure to comply with these criteria will result in heavy fines and even possible prison sentences.

Certain sites that will produce less than 200 kg of hazardous waste a year, such as offices, shops and schools are exempt from registration, although they would have to register if they are expecting to go above this amount per year.

According to the new regulations of 2005, new consignment notes will have to be issued. Each consignment will require a fee to be paid to the Environmental Agency by the consignee and each consignment may require more than one fee. Producers and consignors must keep a register of the consignment note for three years and carriers are required to keep copies of the consignment note for 12 months.

The responsibility of ensuring correct classification, transportation and disposal is allocated to the producer of the waste. Fixed penalties of up to £300 will be issued to those producers that provide false information or fail to notify their premises. Additionally, heavier penalties of up to £5,000 and/or two years jail can result from conviction in a Magistrate's court. More serious offences may be tried in the Crown Court where there is no limit on the level of fines or prison sentence that can be imposed.

All non-exempt sites that produce hazardous waste must be registered even if they are unlikely to have that waste collected for some time. Recent Environment Agency guidance has clarified that it is an offence to produce hazardous waste on site and not be registered. Each site that produces hazardous waste must by law have a separate registration although it is possible to register multiple sites on the same notification. This makes it easier for businesses to register their sites, as a head office or central site can register many branches or sites of the company in one notification, although each site would have a unique registration number and would require a separate fee.

The hazardous waste producer:

- has a duty of care to ensure hazardous waste is disposed/recovered properly.
- if transporting hazardous waste, must be a registered carrier, to whom the duty of care also applies.

- is responsible for disposal/recovery of hazardous waste within permit (licence) conditions, to minimise risk to human and environmental health.

The Environment Agency:

- regulates producers, through integrated pollution prevention and control legislation, to minimise hazardous waste generation
- regulates the cradle to grave system of tracking hazardous waste movements
- licenses and checks sites, to ensure their ability to receive specified hazardous waste and operate to a high standard, to minimise harm to the environment
- provides information to local authorities, to support production of strategic waste management plans.

Influence of Legislation on Waste Producer in UK

The new legislation that came into force in 2005 will have substantial economic effects on businesses. The Landfill Directive and Landfill Regulations of 2002 had already put waste producers and landfill operators under great pressure, because the landfill option of waste disposal will become less cost effective.

Since the Landfill Regulations affect all producers of waste, producers will find it difficult to find landfill sites that would be suitable for waste disposal. There has also been the introduction of a wide range of controls to limit what can and cannot be landfilled, resulting in fewer landfill options being available. Controlled checks are carried out at all sites to ensure that the site is operating in accordance to the WAC.

As a result of these increased pressures, producers are increasingly looking at ways to cut costs and help manage their waste in accordance to the new regulations. Extra investment is likely to be required to manage the waste produced in accordance with the new regulations and this will include pre-treatment of or recovery from certain wastes.

As the cost of waste disposal rises, there will be incentives to recover or recycle waste that is deemed hazardous, thereby minimising the total hazardous waste sent to landfill sites. Previously, landfills provided producers with a cheap, easy and convenient disposal route.

This new European and national waste legislation has challenged traditional waste management practises, and the reliance on landfills will be diminished. The new regulations will undoubtedly force more producers to opt for more sustainable waste management, recycling and recovery of waste. A significant step change will be required, and businesses need to consider whether this change represents a significant threat to their activities, or if, in fact, it presents opportunities that can be exploited to their advantage.

2.1.4 The Basel Convention

The sharp rise in waste production in the second half of the 20th century, along with the transboundary movement of waste, led to urgent protocols being put in place under the United Nation auspices to manage waste transportation and disposal.

2.1.4.1 Origin of Basel Convention

One of the main factors that led to the creation of the Basel Convention was the Khian Sea waste disposal incident in which a ship carrying incinerated toxic waste from America was unable to unload its cargo at any port, so it dumped much of it illegally.

On 22nd March 1989, the Basel Convention was adopted by 116 states of the UN at the Conference of Plenipotentiaires of the Global Convention on the Control of Transboundary Movements and Disposal of Hazardous Wastes, held in Basel, Switzerland. Three years later, the convention came into force after it was ratified by 20 countries. By March 2000, 134 nations had ratified it, and by 2005, only three of the 166 nations had not ratified it (Afghanistan, Haiti and USA).

2.1.4.2 Objectives of Basel Convention

The convention was designed to control transboundary movement of hazardous waste and prevent dumping of waste from developed countries to less developed ones. The convention has strict guidelines on the storage, transportation and final management of waste so as to minimise the threat to the environment and public health. The main objectives of the Basel Convention [1] are to:

- reduce the transboundary movements of hazardous wastes
- ensure that disposal of wastes is carried out in environmentally sound manner and as close to the possible source as possible.
- minimise the generation of hazardous wastes in terms of quantity and hazardousness.
- control over the movement of hazardous wastes across borders as well as the prevention of illegal traffic.
- prohibit shipments of hazardous wastes to countries lacking the legal, administrative and technical capacity to manage and dispose of them in an environmentally sound manner.
- assist developing countries in the environmentally sound management of hazardous and other wastes they generate.

The EU previous Directives were replaced by Council Regulation 259/93/EEC in 1993 on the supervision and control of transfrontier shipments of waste. The regulations of 1993 encompass the main framework for the movement of both hazardous and non hazardous waste in and out of the EU. The regulations have set out complex procedures such as a compulsory pre-notification scheme waste description, authorisation and consignment note system. The EU Regulations draw the distinction between wastes for disposal, for example, via landfill or incineration, and recycling.

According to the Waste Shipments Regulation (Annexes II, III and IV) waste can be classified into three categories [43]:

- The red list (Annex IV) containing the most hazardous wastes. It is the most hazardous including, for example, toxic wastes such as asbestos, dioxins and polychlorinated biphenyls (PCBs).
- The amber list (Annex III) containing hazardous waste includes waste oils and gasoline sludges.
- The green list (Annex II) containing non-hazardous waste such as paper, plastics and glass

Under the Basel Convention, the prime determinant for classifying a waste as hazardous is its intrinsic properties (i.e. it exhibits or possesses one or more hazardous characteristics of Annex III of the convention). Annex I of the Convention lists the categories of wastes that are characterized as hazardous under the Convention, and provides a list of 45 categories of wastes which are themselves divided into:

- waste stream (for example clinical wastes, waste mineral oil, PCBs, etc).
- wastes having as constituents of certain substances, for example, copper compounds, cadmium compounds, lead compounds, zinc compounds, hexavalent chromium compounds and organic phosphorous compounds.

According to the work carried out by a group of technical experts from countries who are parties to the Convention (Technical Working Group), two lists A and B were produced [44]:

List A: Wastes contained in this list are characterized as hazardous under Article 1, paragraph 1 (a), of the Convention.

List B: Wastes contained in this list will not be wastes covered by Article 1, paragraph 1 (a), of this Convention unless they contain Annex I material to an extent causing them to exhibit an Annex III characteristic.

The Conference of the parties decided to add the two lists of wastes referred to above as two new annexes to the Convention, namely, Annex VIII (List A) and Annex IX (List B). The Conference of the parties also instructed the Technical Working Group to keep List A and List B of wastes under review.

In June 1996, the United Kingdom policy plan for exports and imports of waste for disposal and recovery came into force and aimed [45]:

- to protect the environment and human health
- to reduce tranfrontier of movements of waste for disposal
- to give priority for recovery of materials from wastes and disposal of wastes as close as possible to their source of generation
- to make sure that the UK's engagement in the movement of waste is environmentally friendly
- to reduce the amount of waste generated and endorse the idea of waste being handled according to the waste hierarchy

The plan contains a number of policies aimed at achieving the above objectives together with detailed guidance to enforcement authorities and those involved in the international waste trade.

As a result of the above legislations, legal pressures, as well as environmental and economical factors, there have been a pressing need to extract the maximum amount of metals from wastes. Consequently, more emphasis has been put on optimising leaching conditions in order to achieve greater extraction from wastes. Such optimisation methods are an important part of industrial economics as well being a key factor in legislation and legality of waste disposal. For the recovery of metals from wastes to be cost effective, less time intensive and the concentration of certain metals in disposed wastes to be in keeping with legislation, it is important to investigate the best conditions in which this extraction can take place as to maximise productivity of extraction in the least amount of time, with the least cost.

2.2 HEAVY METALS

Metals are an important aspect of industrial development and play a significant role in modern economy and society. In the last century there has been a rapid and dramatic use of heavy metals in many industrial applications, such as: car manufacture, electrical equipment and machinery, mining and extractive industries, chemical production, dyeing, electroplating and heat treatment, and the production of batteries. Wastes generated from these industries contain several potentially hazardous metals such as Pb, Zn, Ni, Cu, Cd, Cr Hg and Co. The release of these metals can alter the environment both physically and chemically with serious consequences and threats to both human and non-human life [9]. Inefficient recovery of metals after use puts more pressure on primary sources and can affect the environment negatively. The recovery of metals is a practice that dates back to ancient civilisations [46]. With today's growing population and, therefore, demand on such resources, the incentive to recover and reuse metals is higher than ever.

Metals are found naturally in animals, plants, soil, rocks and the general natural environment in many forms, including dissolved ions, vapours, salts, minerals, granules or rocks. They can be either in organometallic or inorganic compounds. Additionally, metals can exist in many different chemical forms (species). For example, mercury can exist as a liquid, a vapour in the form of, e.g., monomethyl-mercury. dimethyl-mercury or a solid, e.g., mercury chloride. The exact species of a heavy metal in any system is dictated by the solubility of a compound, the environmental conditions and available complexing agents.

Heavy metals are present naturally in the earth's crust, in varying concentrations. Industry and agriculture have greatly contributed to the introduction of more heavy metals into the environment, through waste disposal, smelter stacks, atmospheric deposition, fertilizer and pesticide use and the application of sewage sludge. Heavy metals are usually stable and persistent in the environment, since they cannot be degraded nor destroyed. This robustness allows them to accumulate in the environment and in biological tissues. Being non-biodegradable makes the problem of natural elimination much more difficult, and levels of heavy metals are now a major problem especially in developed countries as this bioaccumulation allows dangerous levels of heavy metals to enter the human food chain [9]. This is also a problem in developing countries due to bad practice and dumping. Excessive accumulation can have severe adverse effects on humans and the environment [47- 49].

2.2.1 Sources of Heavy Metals

There are two sources of heavy metal emissions into the environment, natural and anthropogenic:

- The natural sources of heavy metal emission are the erosion and alteration of rocks, making the heavy metals available to plants, animals, soil and water. The concentration can vary, depending on the rock. The heavy metals in these rocks are usually dissolved by rain or surface water (especially if it is acidic) and the metal ions can then enter underground and surface water reservoirs.

- Anthropogenic sources are sources of pollution from industrial processes such as metal processing, mining, plating, rubber, plastic, electrical and metal casting industries. All of the above industries release heavy metals into the environment in some form. at varying concentrations. The metals released include, lead, chromium, copper. zinc, arsenic and cadmium.

2.2.2 Metal Production from Primary and Secondary Resources

Metal production starts with either a primary or secondary source material. Primary sources usually contain relatively high concentrations of metals and are generally found at depths of 1 Km beneath the earth's surface. Secondary sources encompass those metals that have entered the economy but are no longer useful in their current forms. The choice of metal production from either primary or secondary sources is dependent on the type and capacity of the existing equipment, metal prices, quality of the feed, supply and cost benefit ratio of each source. Naturally, metals usually exist in combination with oxygen (oxides) or sulfur (sulfides). Ore deposits are of three types:

1. High grade 'alluvial' or 'massive' deposits: can usually be subjected to pyrometallurgical (smelting) or hydrometallurgical (leaching) processes.
2. Metal compounds with impurities: consists of metal ores in combination with valueless 'gangue' minerals. Usually treated by crushing and/or grinding followed by physical separation techniques (e.g., gravity or magnetic separation, flotation) to produce high grade concentrates.
3. Dispersed minerals: cannot usually be separated physically from the 'gangue' minerals and must be leached or smelted. The metal concentrations in this class are usually quite low.

2.2.3 Environmental Impacts of Metal Production

The production of metal, regardless of the process carries with it environmental consequences such as land contamination, noise pollution, disfigures a landscape and waste disposal as a direct or indirect result of the mining process, purification, treatment and finalisation of the end product. Undesirable liquids, solids and gases are released during these processes and some of the steps within such manufacturing are very heavily energy dependent. Furthermore, certain metals are themselves toxic in even small quantities, but are useful materials to society nonetheless, such as cadmium, mercury and lead. Some metals which are biologically beneficial in low concentrations such as zinc and copper, can be quite toxic in higher levels, as mining processes would undoubtedly produce. As a result of what can be quite profound environmental consequences, it is prudent to recycle and reuse as much of the already mined and processed metals as possible.

2.2.4 Metal Uses

Metals have certain characteristics and properties that make them useful. They form hard and robust materials that can be used in the construction of automobiles, buildings, trains, barriers and containers. They are ductile and can be stretched into long strips and are also excellent conductors of electricity, making them ideal for transferring electricity. Human society is very much dependent on the chemical and physical properties of metals and a significant sector of the world economy will undoubtedly be affected by metal production and demand, so much so that certain economic theories are predicting that the growth in demand for metal production will actually determine the pace of the global economy. Other opinions, however, predict that the rate of future growth in the metal sector will actually decrease owing to a rise in information or knowledge based industries, as well as competition from other non metal materials.

2.2.5 Exposure Routes

Humans can be exposed to heavy metals from a variety of sources, such as air, consumption of contaminated water or food and exposure to contaminated soil or industrial waste. The most common exposure route is through ingestion of either contaminated water or food although heavy metals can also enter the body through skin contact or by inhalation. For metals in solution, the ability to cause harm depends on their solubility; their ability to leach through soils and the potential toxic effects on humans and other ecosystems.

2.2.6 Toxicity and Health Effects

Metals are directly and/or indirectly involved in all aspects of microbial growth, metabolism and differentiation. They can be harmful to animals, plants and general living tissue because of their ability to interact with microbial cells and be accumulated as a result of physico-chemical mechanisms and transport systems of varying specificity, independent of, or directly or indirectly dependent on metabolism. Ions of heavy metals tend to bond or interfere with enzymatic activity of cells, therefore disrupting many key biochemical reactions at the cellular level.

In small concentrations, however, some of the heavy metals or Essential Trace Elements (ETEs) are necessary for growth and the maintenance of health. Chromium, cobalt, iron, copper, manganese, selenium and zinc are all involved in essential cellular reactions as either part of enzymes or as controllers of chemical reactions. These metals, although essential at low levels, become toxic with increasing concentration at a point known as the 'threshold of toxicity'.

This threshold is dependent on the organism, the type of metallic element and environmental factors. Adverse human health effects can occur from inadequate (deficiency) and high (toxicity) intake of these metals. Figure 2.6 shows the acceptable range of oral intake from the typical U-shaped dose response curve for these metals. In humans homeostasis is a mechanism that attempts to counteract any change in the body to maintain concentrations of ETE's at an acceptable level. Adverse effects occur when these homeostatic mechanisms are overcome and homeostasis is unable to maintain acceptable levels in the body. This can be due to either to low concentrations i.e. a deficiency or excessively high concentrations, i.e. toxicity [50].

There are two types of intoxication:

- Acute intoxication, which is caused by a short-time exposure to a large amount of toxic material and causes rapid and intense effects.
- Chronic intoxication occurs when a person is exposed to a smaller amount of toxic material over a longer period.

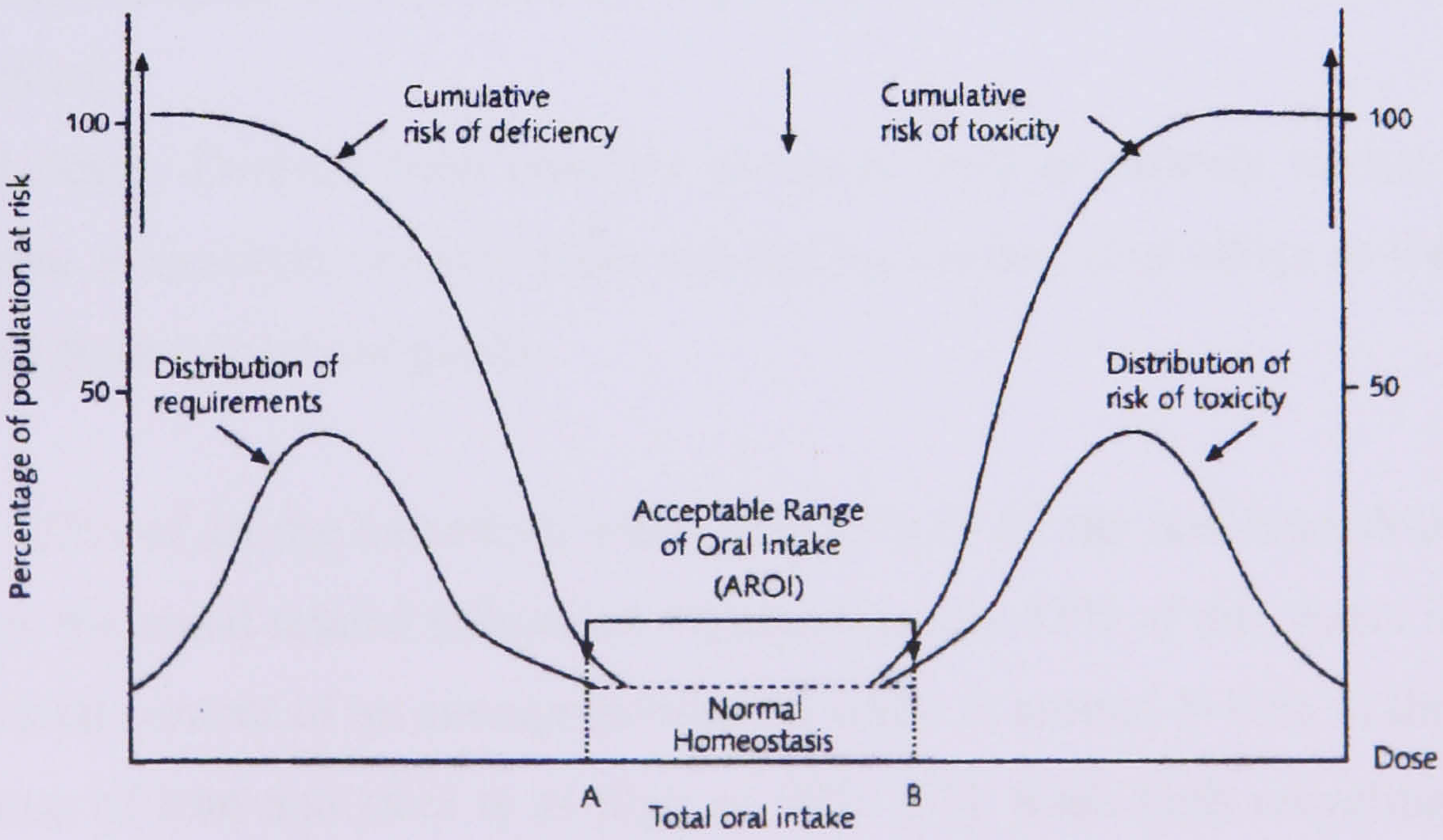


Figure 2.6: Percentage of population at risk of deficiency and toxicity effects according to oral intake.

The amount of damage to biological tissue is dependent on several factors, such as the toxicity of the metal, the concentration, duration of exposure and the susceptibility of that organism to the metal. In humans, heavy metals tend to reduce growth, cause tissue damage and even death. They affect all major bodily functions and areas including, kidney, liver, heart, nervous system, immune system and joints. Children exposed to heavy metals at a young age can develop memory impairment, learning difficulties, behavioural problems such as aggression and hyperactivity as well as general reduction in growth rate. They also have a habit of eating rubbish like paint. Children are also more likely to suffer from toxic compounds as the amount of food they eat for their body weight is far greater than in adults, and they tend to absorb metals more readily in their intestines than adults.

2.2.7 Metal Recycling

Scrap metal accounts for the largest single industrial material that is routinely recycled. Recycling remains the most economical and environmentally sound practise for the management of metal waste. The processing of metal waste is usually a cheap, energy saving and simple method of providing high-grade metal product with far less environmental issues than mining natural ores. Scrap metal is derived from two main sources [51].

- New scrap: Derived from metal processing such as off-cuts, stampings, turnings and grindings from industrial metal processes. This waste metal is almost 100% recycled.
- Old Scrap: Derived from obsolete products, such as railway tracks, industrial plants, automobiles, copper sheet and piping, die cast zinc alloys as well as light scrap from household goods.

In the UK, 27% of all the hazardous waste and 13% of all the non-hazardous waste is produced by the metal related industries. At present, only 53% of this waste is recycled [52]. The metal content of an average household waste is around 5-10% in the UK. The recycling rate of iron and steel is as high as 60% [53]. Such high recycling rates are present in the UK owing to the high economic value of the metals, e.g. 42% of the 5.3 billion aluminium cans used in the UK are recycled. The data in Figure 2.7 show that recycling rates vary with scrap metal type [54]. Recycling the cans saves up to 95% of the energy required to make aluminium from virgin materials, recycling steel saves up to 75% [55].

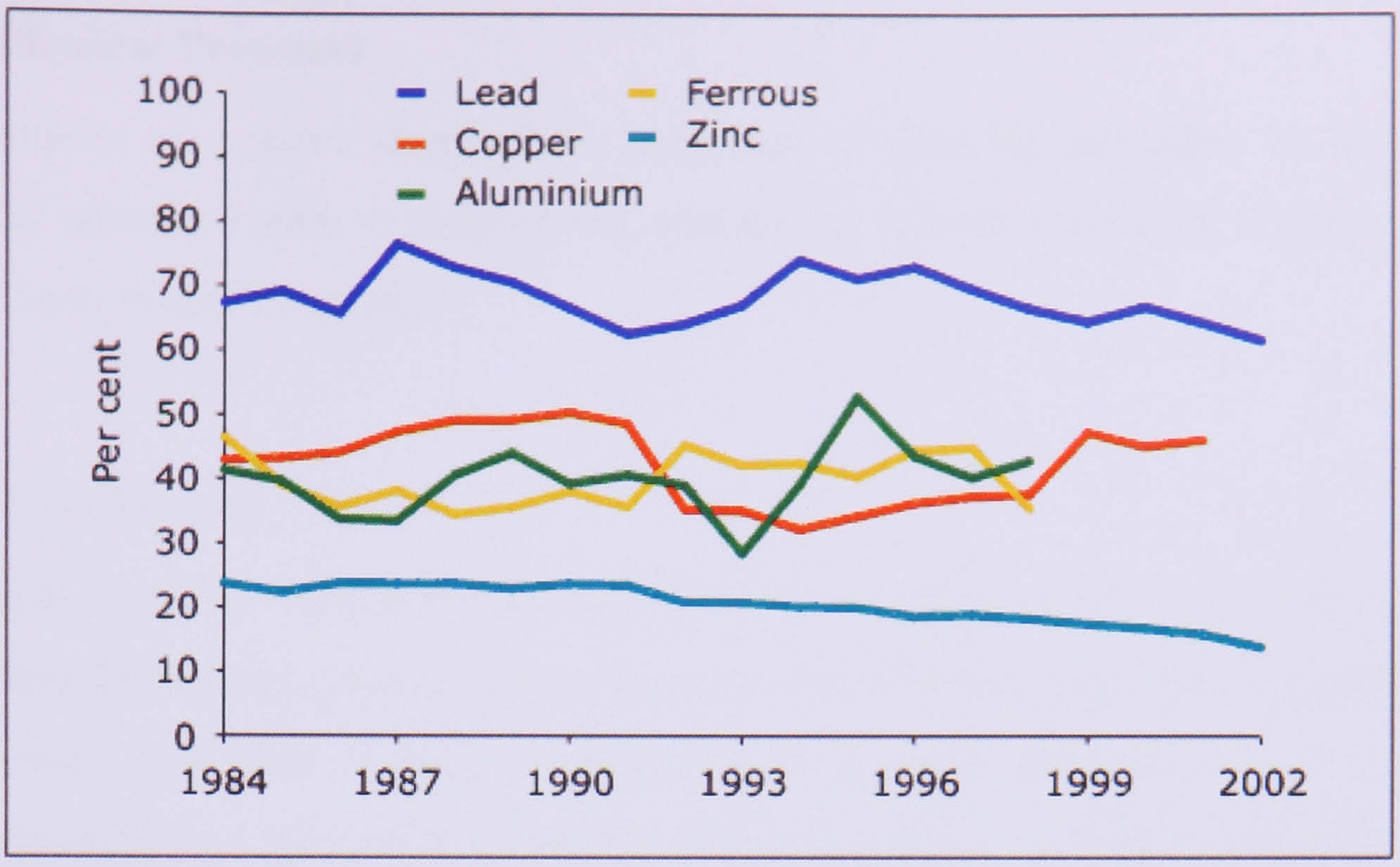


Figure 2.7: Trends in recycling rates vary with scrap metal type.

It is not always easy to recycle heavy metals. For example, there is a limited market for recycled cadmium, as cadmium is a by-product of zinc manufacture. The use of cadmium in products such as paints, pigments and batteries is declining as other more environmentally acceptable technologies are developed. Recycling of cadmium-bearing wastes is, therefore, uneconomical unless they contain other valuable raw materials.

Around 40% of commercial waste and 14% of household waste were recycled or composted in England and Wales in 2003. Approximately 75% of UK's municipal waste is sent to landfill, 9% is incinerated and only 16% is recycled. This compared with many other EU countries that recycle 30-60%. In 2001 the UK recycled [56]:

- 64% of lead, 46% of copper and 16% of zinc
- 39% of paper and 33% of glass
- 6.3% of plastic

2.3 RECOVERY TECHNIQUES

Heavy metal removal and recovery is an important industry with much research and innovation. The innovation is being driven by the need for effective and economical techniques that can treat and remove or recover metals. Many physical, chemical and biological treatment processes have been used for a long time to remove and recover metals from wastes.

2.3.1 Physical Processes

The volume of a waste destined for treatment or disposal can often be reduced by physical processes such as evaporation, adsorption, solvent extraction, reverse osmosis, centrifugation and stripping.

2.3.1.1 Evaporation

Evaporation can be used as a metal salt recovery technique. In the evaporation process, water and the volatile constituents are removed from the aqueous waste to concentrate it by heating a thin layer of liquid or sludge waste spread on a heated surface [57]. There are essentially two types of evaporators: those that operate at atmospheric pressure and those that operate under vacuum. This technique has advantages such as recovered chemicals can be reused, reduced volume to waste treatment facility, self-operating, low maintenance, widely applicable and atmospheric evaporators are inexpensive. On the other hand, the disadvantages are evaporators increase the concentration of impurities which usually require further treatment, the process is energy intensive, vacuum evaporators are capital intensive.

2.3.1.2 Adsorption

Adsorption is the process in which substances adhere to the surface or interface of a solid or liquid phase. A substance is said to be adsorbed if the concentration in a boundary region is higher than in the interior of a contiguous phase. There are different absorption equilibria, such as adsorption between a gas and a solid or a liquid and a solid. The extent to which this process proceeds is dependent on several factors such as the physical or chemical characteristics of the adsorbent (adsorbing surface) and the surface area available for interaction. The adsorbate (molecule or ion adsorbed) is removed from solution overcoming the forces that would retain it in solution [58]. Commonly used sorption materials include activated carbon, starch xanthate, discarded automotive tyres and serpentine material (a group of common rock-forming hydrous magnesium iron phyllosilicate ($(Mg, Fe)_3Si_2O_5(OH)_4$) minerals) as well as discarded agricultural products such as peat moss and straw [59].

2.3.1.3 Solvent Extraction

The metallurgical industry has used solvent extraction for many years for a broad range of separations. It is used for the hydrometallurgical processing of copper, nickel, cobalt, zinc, uranium, molybdenum, tungsten, vanadium, rare earths, zirconium, hafnium, niobium, tantalum, indium, gallium, germanium, the platinum group metals, boron, reprocessing nuclear fuels, purification of wet process phosphoric acid, nitric acid recovery, etc [60]. It is also used in the treatment of wastewaters to remove soluble metals [61].

The separation occurs when an organic phase containing an extractant comes in contact with an aqueous phase containing the metal of interest. The extractant chemically reacts with the metal to form complex that is soluble in the organic phase. Many impurities do not react with the extractant and remain in the aqueous phase. The organic phase, containing the metal complex, is separated from the aqueous phase. The metal is then recovered by different recovery methods such as precipitation, crystallisation and electrolysis. Various types of reagents can be used for the extraction: carboxylic acids, aliphatic or aromatic amines, amino acids, alkyl phosphates, phenolic compounds etc. The non-selective removal of metal contaminants in aqueous solutions can be obtained with a wide range of organic reagents. The technique can easily be fouled by suspended solids. The metal ion working range is from 1 to 300g dm^{-3} [62].

2.3.1.4 Reverse Osmosis

Reverse osmosis is a process that is used to remove species as small as ions from a solution. The theory behind this process is the use of a semi-permeable membrane that allows the fluid that is being purified to pass through it, while rejecting the contaminants that remain. It is used to purify water and remove salts and other impurities in order to improve the colour, taste or properties of the fluid. The most common use is in water purification and desalination, waste material treatment and wastewater treatment. Many other chemical and biochemical processes such as pharmaceutical solutions and chemical streams depend on reverse osmosis. The process requires a driving force (the most common force is pressure) to push the fluid through the membrane, producing a concentrate containing high levels of dissolved salts. The higher the pressure, the larger the driving forces. As the concentration of the fluid being rejected increases, the driving force required to continue concentrating the fluid increases. The advantages of this process are:

- ability to recover process chemicals
- ability to recycle process water
- the achievement of high separation rates
- no chemicals are used
- the floor space requirement is small

The disadvantages are membrane durability problems, sensitivity to hard water salts and fouling of membranes due to feeds high in suspended solids where feed filtration is essential. The particle size range for applications of reverse osmosis is approximately 0.0001-0.001μm [63].

2.3.1.5 Centrifugation

Centrifugation is the process in which solid or liquid particles of different densities are separated by rotating them in a tube in a horizontal circle. The denser particles tend to move along the length of the tube to a greater radius of rotation, displacing the lighter particles to the other end.

2.3.1.6 Stripping (air or steam stripping)

In this technique a 'stripping tower' is used to partition the volatile materials in a gas phase (air or steam). The tower is laden with trays to allow the greatest amount of contact or turbulence between the liquid and the gas phase. This provides a useful method of separating volatile elements from less volatile ones in a liquid mixture [64-66]

2.3.2 Chemical Processes

Chemical treatment processes may be used to alter the chemical properties of wastes in order to facilitate or enable further treatment. Examples of chemical treatment are acid/base neutralisation, reduction/oxidation, chemical precipitation. cementation and chemical extraction and leaching.

2.3.2.1 Acid/Base Neutralisation

Neutralization is the process in which chemical waste in solution is neutralised rendering in nearly harmless. The most common neutralization situation occurs when acidic waste is filtered through a neutralizing media, most often a specific size and composition of limestone. The active ingredient in the limestone is calcium carbonate, which reacts with acidic waste and helps raise effluent pH to acceptable levels for discharge into the water system.

2.3.2.2 Reduction/Oxidation

Reduction/oxidation (Redox) reactions chemically convert hazardous contaminants to non-hazardous or less toxic compounds that are more stable, less mobile, and/or inert. Redox reactions involve the transfer of electrons from one compound to another. Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons). The oxidizing agents most commonly used for treatment of hazardous contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Factors that may limit the applicability and effectiveness of the process include:

- Incomplete oxidation or formation of intermediate contaminants may occur depending upon the contaminants and oxidizing agents used.
- The process is not cost-effective for high contaminant concentrations because of the large amounts of oxidizing agent required.

2.3.2.3 Chemical Precipitation

Precipitation has long been the primary method of treating and removing metals in industrial wastewaters. In this process, the metal is transferred from the soluble ionic state into an insoluble precipitate. Advantage is taken of the fact that many heavy metal hydroxides are insoluble in aqueous solution, particularly at moderately high pH. By adjusting the pH to an appropriate value that varies with the metal, the metal can be precipitated [25,67].

The method of precipitation used most often to remove metals from wastewater consists of precipitating them in the form of hydroxides. Each dissolved metal has a distinct pH at which the optimum hydroxide precipitation will occur. The usual procedure involves the addition of chemicals such as lime, sodium hydroxide, hydrogen sulfide, sodium sulfide, sodium hydroxide and phosphoric acid. The main disadvantage of precipitation by hydroxides is that different metals have different pH levels for minimum solubility and the reactions are of an equilibrium type, i.e., some of the metal hydroxide will disassociate with the resulting metal ions going back into solution. The precipitation of metals by carbonates or sulfides is an effective alternative to hydroxide precipitation. The use of carbonates allows the precipitation of metals to occur at pH values lower than those necessary with the hydroxides. Moreover, the precipitates thus formed are denser and have better characteristics of solid-liquid separation. Precipitation by sulfides is normally carried out with reagents such as Na_2S, NaHS, H_2S or FeS. In acidic media, the lower solubility of metal sulfides (Cd, Co, Cu, Cr, Ni, Mn, Zn, etc.), makes it possible to reach concentrations lower than those obtained by precipitation as hydroxides. Figure 2.8 shows relationships between pH value and solubility for six common heavy metals [67].

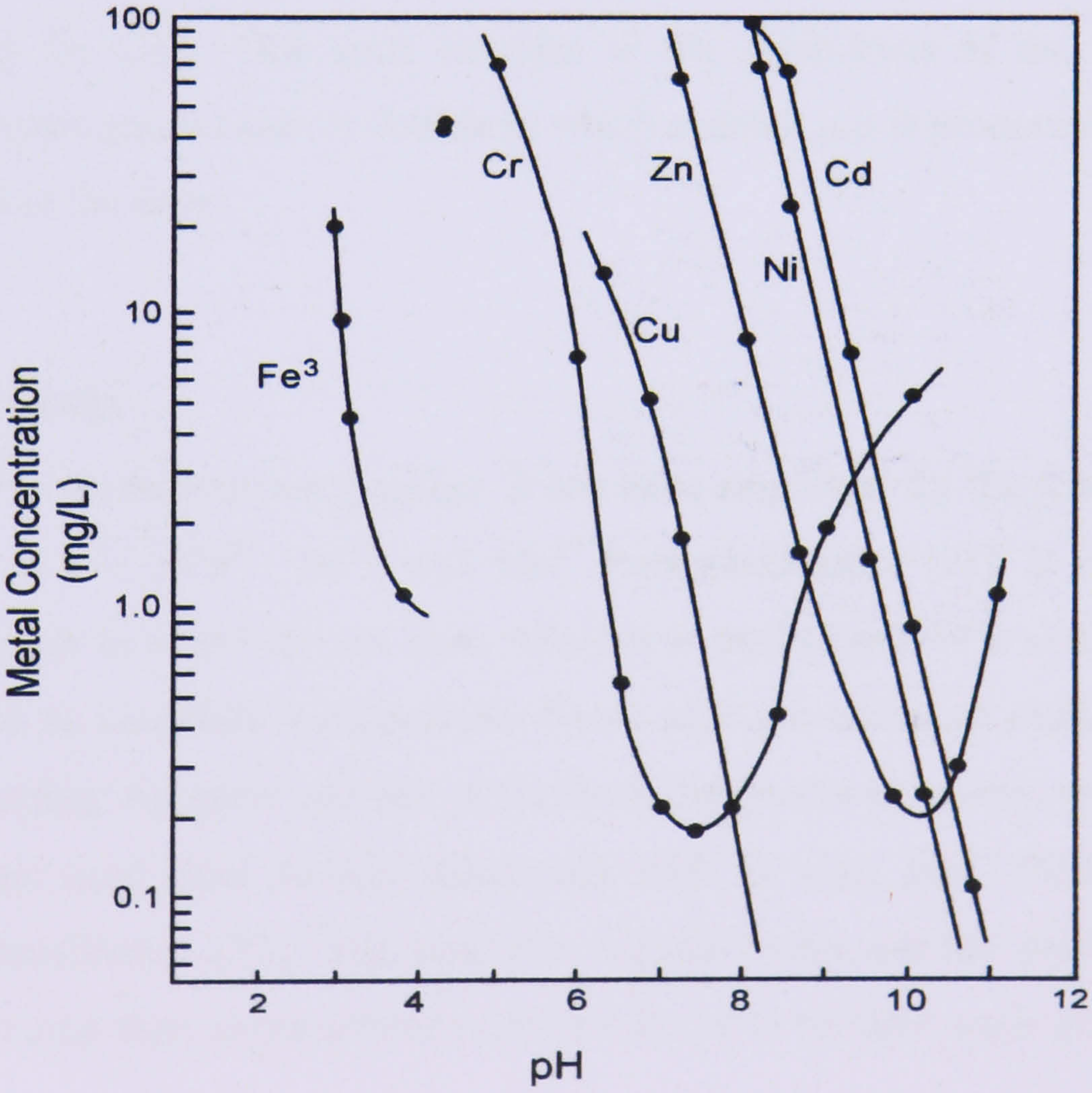


Figure 2.8: Precipitation of heavy metals as hydroxides

The major disadvantage of chemical precipitation is that it is seldom single metal specific and the reacting precipitates have to be further treated to separate the metals into single components.

2.3.2.4 Cementation

Cementation is one of the oldest and simplest hydrometallurgical processes, which has been used as a means of extracting metals from solution [68]. It is a type of precipitation method with an electrochemical mechanism. In this process, a metal having a higher oxidation potential passes into solution to replace a metal having a lower oxidation potential. Copper is the metal most frequently separated by cementation [69,70]. The noble metals Ag, Au and Pd, however, as well as Cd, Ni and Co can also be recovered in this manner. The use of scrap aluminium and zinc metals as the cementing agent is common.

2.3.2.5 Chemical Extraction and Leaching

Through chemical extraction, materials that are insoluble or poorly soluble (such as heavy metals or their salts) can be extracted into a solution [57]. Electrolysis or other methods of separation is then applied to allow further extraction. In some instances such as those where acid leaching is chosen, caution must be applied, as some of the vapours produced may be toxic. One such example is the application of the acid leaching technique to hydrogen cyanide or sulfide in which cyanide gas is produced in the former and sulfur gas in the latter.

2.3.3 Ion Exchange

Ion exchange is another recovery option. It has been employed for the removal of metal cations such as Co^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} from wastewater [71]. It is a reversible chemical reaction in which an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The first ion exchangers used were natural substances such as clay, peat, charred bone and natural aluminosilicates [72]. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications.

Ion exchangers are insoluble substances having in their molecular structure acidic or basic groups able to exchange with ions in solution, without modification of their physical structure. For the extraction of metals, the removal of cations in solution is usually carried out with the sulfonic acid group ($-SO_3^-H^+$) on a polystyrene resin, or, with a chelating resin containing iminodiacetate functional groups [67]. The sulfonic acid groups -$SO_3^-H^+$ are the active sites used for ion exchange. The -$SO_3^-H^+$ group is chemically bound to the resin but the counter ion (H^+) may be exchanged for another cation. If, for example, a solution of sodium chloride is passed through an ion exchange column in the hydrogen form reaction in equation 1 occurs;

$$R - SO_3^- H^+ + Na^+ \longrightarrow R - SO_3^- Na^+ + H^+ Cl^- \qquad (1)$$

An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin.

Ion exchange resins are classified as cation or anion exchangers, cation exchange have positively charged mobile ions available for exchange, while anion exchangers have exchangeable negatively charged species. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionisable group attached to the hydrocarbon network. It is this functional group that determines the chemical behaviour of the resin. Resins can be broadly classified as strong or weak acid or base exchangers.

The main advantages of the ion exchange method are low energy requirement, efficient removal of ions from dilute solutions and resins can be selected to remove specific ions. Like most other techniques, this process has disadvantages. These include the production of a concentrated solution that needs further treatment, difficulties in finding a suitable resin for treatment of a waste solution containing mixed metal ions, sensitivity to temperature, solids and organic materials, limited concentration ability, time consuming regeneration required and feed concentrations that must be closely monitored. This method is useful in the recycling of process water and in the recovery of process chemicals.

2.3.4 Electrochemical Methods

2.3.4.1 Electrowinning

Electrowinning is a well-established technology that is widely employed in the mining and metallurgical, metal transformation (wastes from plating and metal finishing), electronics and electrical industries for the removal and/or the recovery of metals in solution. It is a process in which an electric current is passed through a liquid, causing a chemical reaction to take place. The metal ions are removed from wastewaters by plating the metal onto the cathode by means of an electrochemical cell. Many metals (Ag, Au, Cd, Co, Cr, Cu, Ni, Pb, Sn and Zn) present in effluents can be recovered by this method. The electrolysis of metallic solutions is useful in putting metal coatings on objects, and in refining, or purifying, metals.

Electrowinning is different from other recovery technologies (e.g., evaporation, ion exchange) in that an elemental metal is recovered rather than a metal bearing solution. The main advantages of this method; metals are recycled, no generation of waste, very few chemicals used, recover only metals, generally non-hazardous products, energy efficient and low maintenance. The disadvantage is energy inefficiency at very low concentrations.

2.3.4.2 Electrodialysis

Electrodialysis is an electromembrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of a potential gradient such as a direct current. The electrical charges on the ions allow them to be driven through the membranes fabricated from ion exchange polymers. These membranes are either anionic which are only permeable to anions and impermeable to cations, or cationic that are only permeable to cations but impermeable to anions. Applying a current through the electrolyte generates the potential field required for this. Since the membranes used in electrodialysis have the ability to selectively transport ions having positive or negative charge and reject ions of the opposite charge, useful concentration, removal, or separation of electrolytes can be achieved by electrodialysis [73]. Electrodialysis is discussed in more detail in chapter six. Figure 2.9 shows the relative energy consumption by various separation technologies.

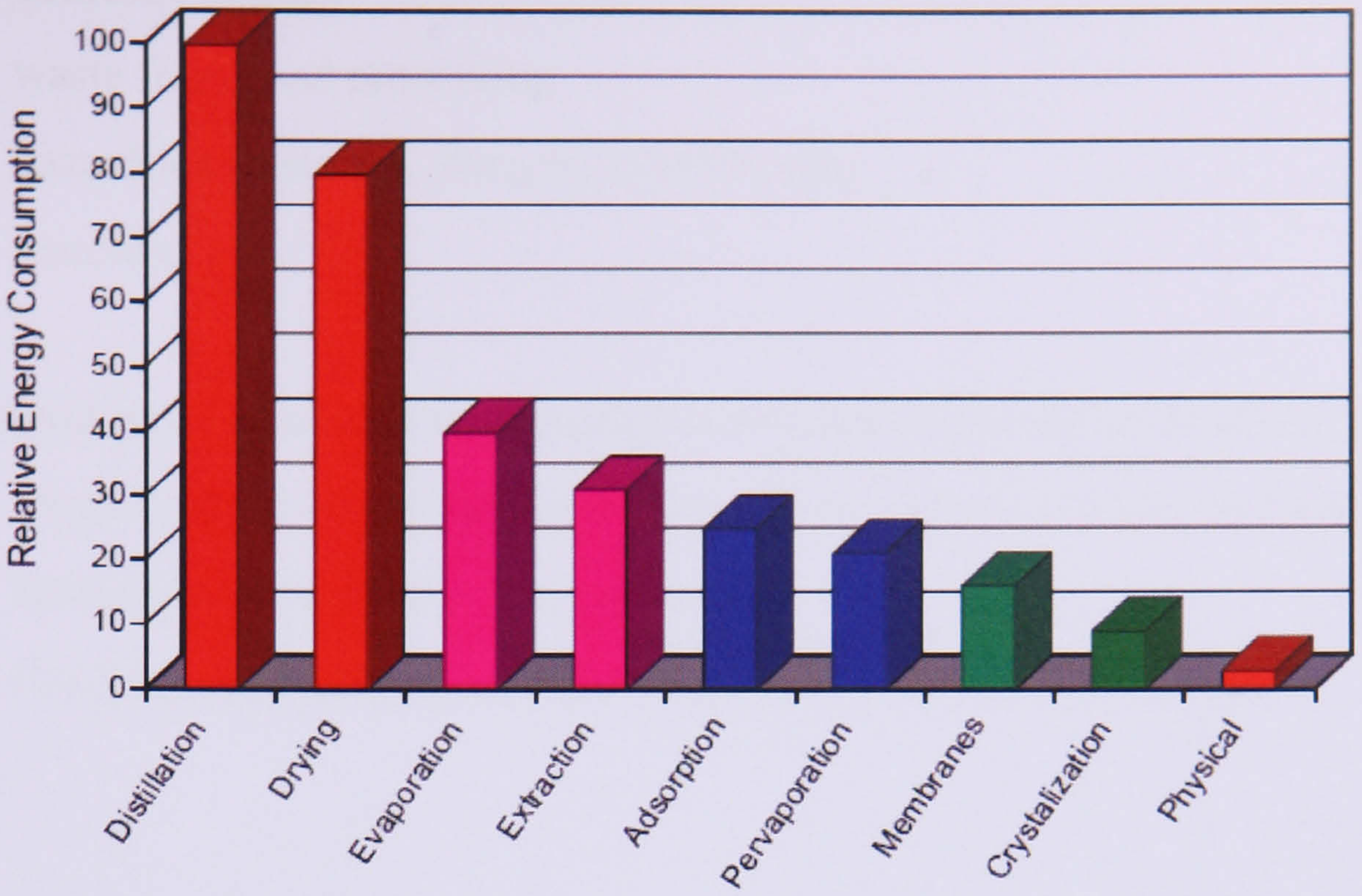


Figure 2.9: Relative energy use by various separation technologies

2.3.5 Biological Treatment

Biological treatment methods are processes whereby microorganisms are used to destroy or at least reduce the toxicity of a waste stream. Biological methods such as biosorption/ bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods [74]. Microorganisms can take up metal either actively (bioaccumulation) and/or passively (biosorption).

The use of adsorbents of biological origin has emerged in the last few decades as one of the most promising alternatives to conventional heavy metal management strategies [75]. Biosorption of heavy metals by microbial cells has been recognized as a potential alternative to existing technologies for recovery of heavy metals from industrial waste streams. Many aquatic microorganisms, such as bacteria, yeast and algae can take up dissolved metals from their surroundings onto their bodies and can be used for removing heavy metal ions successfully [76].

Normally biological treatment of predominantly aqueous wastes such as leachate is accomplished in specially designed bioreactors. A suitable culture of the microorganisms or microbial association, either aerobic or anaerobic, is chosen. Biological treatment is now firmly established as the standard method of waste treatment for wastes with low concentrations of metal contaminates such as:

- domestic sewage
- waste from food processing
- hazardous waste e.g. phenols, cyanide, oils
- leachates

The general types of transformations that can be accomplished biologically include:

- Degradation of organics to products such as carbon dioxide, methane and water
- Reduction of inorganic ions e.g. nitrate
- Complexation of heavy metals e.g. nickel

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Chapter 3

Investigation of the Solubility and Bioavailability of Different Metals under Different Environmental Conditions

Chapter 3

Investigation of the Solubility and Bioavailability of Different Metals under Different Environmental Conditions

3.1 INTRODUCTION

Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems. However, because of certain useful physical and chemical properties, some heavy metals such as Pb, Zn, Ni, Cu, Cd, Cr, Hg and Co and their compounds are used in various consumer and industrial products. Some of the general applications or uses of each of the metals and their compounds used in this work are shown in Table 3.1.

Waste containing metals generated from these industries have been traditionally disposed of into landfills. These metals can leach into the surrounding soil and groundwater under various environmental conditions. Their bioavailability is of great importance because of the potential toxicities of some of these metals to humans [1,2]. They can also adversely affect soil ecology, agricultural production [3], animals and plants, or product quality, water quality and the environment in general [4].

Waste in landfills immediately becomes incorporated into the complex hydrological system of the environment. Fluid derived from snowmelt, rainfall or groundwater as well as the fluids from the waste interacts with the waste through complex bio-chemical processes, resulting in the creation of leachate. The free flowing and newly formed leachate, can then act as a medium for the transportation of heavy metals and their distribution into the groundwater either through direct infiltration on site or by infiltration of leachate-laden runoff offsite [5]. Waste disposed in landfill will lead to a potential risk of contamination of groundwater depending upon; waste composition, leachate production and migration. In any particular leachate, the concentration of heavy metals varies greatly, depending on landfill age, moisture availability, water content, temperature, waste characteristics as well as concentration of the said metals in the landfill itself. The introduction of leachates into groundwater could lead to the contamination of drinking water and through oral intake and ingestion of water or foodstuffs contaminated with heavy metals, humans can become exposed to such heavy metals.

The two main aims of this work are:

- to evaluate the predictive abilities of certain extraction liquors (such as water, acetic acid, hydrochloric acid/sodium chloride and nitric acid) to extract regulated elements from their elemental form and compounds, under standard conditions of atmospheric pressure and temperature.
- to evaluate the predictive leaching abilities of water and nitric acid under more aggressive conditions (higher pressure and temperature) using microwave technique.

Table 3.1: Some of the general uses of the metals used in this study

Metal / Compound	Uses
Cu / Cu compounds	plumbing & heating, catalysts, electrical and electronics industry, dyeing industry, structural engineering, household products, chemical and biochemical applications, automobile industry, air conditioning & commercial refrigeration, coinage, telecommunications, food stuffs industry, medicines, medicine, insecticides, fungicides, electroplating, electrolysis, textiles, glass, ceramics, nylon, paper products, flame proofing, fuel additives, pigments.
Co / Co compounds	batteries, magnets, medicine, catalysts, alloys, dyeing industry, ceramics, binder materials, pigments, electroplating, medicine, agriculture, drying agents, radiography.
Zn / Zn compounds	batteries, hot dip galvanising, castings, brass, paints, wood preservatives, automobile industry, building and construction industries, coinage, organic synthesis, lubricants and grease, rubber industry, pigments, agriculture. glass and ceramics.

Cd / Cd compounds	batteries, alloys, pigments, solder, electroplating, catalysts, PVC, pesticides, plastics, fertilisers, semiconductors, rubber industry, photographic chemicals,
Ni / Ni compounds	batteries, alloys, catalysts, consumer products, coinage, stainless steel industry, magnets, glass, ceramics.
Pb / Pb compounds	building construction, batteries, alloys, heat transferring agents, paints, lubricants and additives, plumbing, constructional materials, pigments, as a detonator for explosives, insecticides.

3.2 LEACHATE

Landfill leachate is a potentially polluting fluid formed when water is percolated through the waste and reacts with the products of decomposition and other materials. It may cause harmful effects on the groundwater and surface water that surround a landfill site if it is not treated and managed properly. Leachate can contain dissolved and suspended materials and have elevated concentrations of contaminants such as organic compounds, heavy metals and ammoniacal nitrogen.

Leachate generated from common landfills that contain waste from various sources such as industries, commercial and municipals are characterised as water based solutions of four groups of pollutants; dissolved organic matter, inorganic, heavy metals and xenobiotic organic compounds [6]. Leaching of metals from soil into groundwater by variation in environmental conditions such as pH, redox potential, temperature, CO_2 content, organic matter, etc is important [7]. Heavy metals may be retained by soil due to chemical interactions with the solid phase. This retention is a major factor that controls heavy metal bioavailability as well as mobility.

In recent landfill sites, liners that have low permeability are used, however even such controlled or engineered landfills still have the potential to contaminate surface groundwater, aquifers and subsurface water tables through the movements of leachates. If leachate does escape to the environment, then it is difficult and expensive to tackle and can also have effects that will remain for many years or decades. Therefore, it is very imperative that a good monitoring system is put in place during the different stages of the landfill from the development, operation to the pre-closure stage of the site.

The majority of metals that are used in this work are examples of Annex I metals of the Basel Convention [8]. A number of trigger guide levels and limit values have been set up with the aim of confining these metals to permissible levels and thus minimising their effects. Trigger values in Table 3.2 from the World Health Organization (WHO) represent the acceptable level of concentration of a metal in drinking water at which it presents no harm to humans and the environment [9].

Table 3.2: Trigger Guide Levels

ELEMENT	TRIGGER LEVEL (MG/L)
Cadmium	0.003
Cobalt	0.002
Copper	2
Lead	0.01
Nickel	0.07
Zinc	3

There has been much research investigating the leaching process of heavy metals from waste into soil and groundwater. Chang et al. [10] reported a comparison of metal leachability for various wastes by using the toxicity characteristic leaching procedure (TCLP), extraction procedure (EP) and American Society for Testing and Materials (ASTM) methods. Various types of waste including chemical sludges (electroplating and dye-stuff sludges), municipal solid waste incineration bottom ash, leather debris, and steel-mill bottom residue containing cadmium, chromium, copper, lead and zinc were used in their study. The results showed that the metal concentration leached from the various waste samples using the three different techniques followed the order: TCLP $\approx$ EP > ASTM. The three techniques displayed approximately the same efficiency in the extraction of metals from wastes with low metal content (e.g. copper and zinc) in the incineration bottom ash, bottom residue, dye-stuff sludge and leather debris. The addition of acetic acid can influence the concentration of the metal leached in the high metal content wastes, such as copper and zinc in electroplating sludge and chromium in leather debris.

Li et al. [11] reported the leachability of municipal solid waste ashes in simulated landfill conditions using batch and column leaching tests. The leachability of different anions and cations in the waste ashes at different pH were examined. The obtained results reveal that using water or acid solution with pH 3-6 as a leaching media led to a slow dissolution of the metals. Whereas, at pH 2 the dissolution process accelerated and more metals leached out from the waste into the solution. The concentration of the metals leached out was higher than the environmental standards even for the leaching carried out with deionised water.

In this chapter, work was carried out to show that if wastes containing heavy metals are disposed in landfill under different environmental conditions representing worse case scenarios, the heavy metals might leach from the waste to the surrounded land and water. The leachability of cadmium, cobalt, copper, lead, nickel and zinc metals, as well as their compounds was investigated in this work.

3.3 PRINCIPLE OF SOLUBILITY

The solubility of a solute is the maximum quantity that can dissolve in a certain quantity of solvent at a specified temperature when equilibrium is reached. It is a characteristic physical property of both the solute and the solvent. It is usually expressed in units of grams of solute per 100 cm^3 of solvent. The equilibrium constant for the equilibrium between a solid and its dissolved form is called the solubility product, K_{sp}, of the solute [12].

Factors that affect solubility:

- temperature
- presence of other solutes, i.e. other dissolved ions or compounds, can influence the solubility - although they do not alter K_{sp}
- nature of solute or solvent
- particle size
- stirring
- pH

3.3.1 Effect of Temperature on Solubility

When a solid dissolves into a liquid, heat is required to break the bonds in the solid, at the same time heat is released when the new solute is formed. Therefore, the solubility of a solute is very much dependent on the temperature. The solubility of solids is usually increased with a rise in temperature, as the increased temperature causes an increase in the energy of the motion of the particles (increases their kinetic energy) in the liquid. This increased kinetic activity also helps overcome the lack of attraction between polar and non-polar molecules. The amount of solid that can be dissolved is variable and can either increase or decrease with temperature. Pressure usually does not affect the solubility of materials as the volume of materials changes only slightly when dissolved. As solids dissolve in water, their structure becomes more chaotic and as a result they give a positive ΔS_{soln}. The entropy of a solution, i.e. the temperature difference between two systems in contact with one another, dictates the effect temperature has on the solution [13].

$$\Delta G = \Delta H - T\Delta S$$

Where,

ΔG = Change in free energy

ΔH = Change in the enthalpy

T = Temperature

ΔS = Change in entropy

The above denotes that with rising temperature, the solubility of the compound increases. Such compounds can be said to have positive entropy.

Lower solubility at higher temperature will not always be obvious, because rates of reactions are increased by temperature. Therefore, solids will dissolve faster in hot water than in cold water, even if they do not dissolve as much.

3.3.2 Solubility and Bioavailability of Metals

The fate of various metals, including chromium, nickel, copper, manganese, mercury and lead, and metalloids, including arsenic, antimony and selenium in the natural environment is of great concern [14,15]. Metals of major interest in bioavailability studies, as listed by the USEPA are Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se and Sb [16].

Some of these metals were selected in this study because of their potential for human exposure and increased health risks.

The solubility and bioavailability of heavy metals in soil are of environmental significance due to their potential toxicity to humans and the environment. Some of these metals, such as copper and zinc, are necessary for human life and others are not, for example cadmium and lead [17]. Since most metals are not soluble in water by themselves, they must react with other compounds and form water soluble metal compounds. The other compound that converts the metal into a water soluble compound is usually acid. Metals tend to be more soluble at low rather than high pH. Therefore acids and acid conditions normally contribute to high heavy metal concentrations. Partitioning of these metals in soils is affected strongly by variations in pH, redox state, organic content and other environmental factors [7].

Solubilities of such toxic metals are dependant on the pH and temperature of the water that dissolves them. pH is probably the most important factor governing metal speciation, solubility from mineral surfaces, transport and eventual bioavailability in aqueous solution. pH affects both solubility of metal hydroxide minerals and adsorption-desorption processes. Most metal hydroxide minerals have very low solubilities under the pH conditions in natural water. Because hydroxide ion activity is directly related to pH, the solubility of metal hydroxide minerals increases with decreasing pH. Thus more dissolved metals become potentially available for incorporation into biological processes as pH decreases. Ionic metal species also are commonly the most toxic form to aquatic organisms [7].

Heavy metals in leachate can be present in the form of free and exchangeable ions, organic and inorganic complexes and can also be bound within the crystalline lattice structure of primary minerals. Among the different forms, the water-soluble metal salts are the most mobile. The most stable heavy metal forms are those incorporated into a crystal lattice structure by isomorphic substitution. The most unstable heavy metals are those exchangeable between the soil solution and the zone affected by the charged colloidal surfaces or the diffuse layer. Temperature exerts an important effect on metal speciation because most chemical reaction rates are highly sensitive to temperature changes. Once dissolved, their most immediate impact is on plant life and fauna and later on humans and other animals that feed upon the plants.

The solubility of heavy metals in rain water is extremely low. They are still deemed a threat to human health, however, because of their capability to disrupt bodily functions at even minuscule levels. For this reason the leaching of toxic materials into ground water is a major health concern.

The extent to which pollutant molecules or ions transfer from their pure forms into water is the aqueous solubility. Owing to their electric charge, inorganic ions interact strongly with the oxygen atom of the water molecule (H_2O), thus, ions that are readily solvated by water exhibit high potential solubility. There are competing interactions, however, that limit the solubility of many inorganic compounds. The fate of heavy metals in soil-water systems is primarily controlled by the congruent-incongruent solubility of the carbonates, oxides, sulfates and sulfides of metals and by the adsorptions of free and complexed metals at solid-solution interface. Although many toxic materials have low solubility in water, the concentrations that are deemed hazardous are also very low. Furthermore, many toxic compounds are accumulated by living cells and can be more concentrated inside than outside a cell. This is why long-term exposure is a serious problem; encountering a low concentration of a toxic material a few times may not be dangerous, but having it in your drinking water day after day and year after year can be deadly. Different sources of each of the metals used in this work were selected for the leaching studies and these are summarised in Table 3.3 along with a comment on their respective solubilities [18].

Table 3.3: Samples and their solubilities

Sample	**Solubility in water 100/cm^3**	**Sample**	**Solubility in water 100/cm^3**	**Sample**	**Solubility in water 100/cm^3**
Cu	insoluble	Co	insoluble	Cd	insoluble
Cu_2O	insoluble	-	-	-	-
CuO	insoluble	CoO	insoluble	CdO	insoluble
CuS	0.000033	-	-	CdS	0.00013
$CuCO_3$	insoluble	$CoCO_3$	insoluble	$CdCO_3$	insoluble
Ni	insoluble	Pb	insoluble	Zn	insoluble
NiO	insoluble	PbO	0.0017	ZnO	0.00016
-	-	-	-	ZnS	insoluble
$NiCO_3$	0.0093	$PbCO_3$	0.00011	$ZnCO_3$	0.001

3.4 LEACHING

Leaching is the removal of materials by dissolving them away from solids. It is a chemical process used by various industries and the process is usually called extraction, when organic solvents are often used [19]. The overall recovery of the metal and the difficulty of separating it from impurity metals are generally governed by the efficiency and selectivity of the leaching process. Leaching tests have become a key regulatory tool for classification of wastes and determination of safe reuse and disposal routes. In order to evaluate potential risks to human health and contamination of groundwater, several leaching test protocols have been developed which mimic leaching processes of waste in landfill and disposal sites. Leaching test aims [20]:

- to regulate waste and classify it as either a hazardous or non-hazardous material.
- to replicate conditions that occur in waste sites to evaluate the extent of leaching at such sites.
- to evaluate the amount of leaching that would occur from waste under certain environmental conditions.
- to provide a clear and true representative of the actual amount of leaching produced from waste in the field.
- to determine the appropriate waste management scenario or the environment in which waste is to be disposed.
- to measure how effective treatments are in waste management.
- to establish partition and kinetic parameters for the modelling of contaminant transport.

Chemical and physical factors influence leaching from waste material. The chemical factors include pH, redox conditions, precipitation, complexation with organic or inorganic chemicals, organic carbon content and the common ion effect. The physical factors consist of particle size, homogeneity, liquid-to-solid ratio, leaching time, porosity, sorption, partitioning, leaching temperature, type of flow, kinetics and chemical speciation of pollutants of interest [20].

Extraction of substance(s) using conventional techniques for sample preparation such as shakers, separating funnels, manual and automated Soxhlet etc have been in use for many years and are well developed. Desired substances have been removed from other materials using many of these techniques but generate large volumes of waste solvents and are slow to process as well as having the potential of exposing laboratory workers to toxic solvents [21].

A mechanical shaker is used in this work. This gives very mild leaching conditions, as the leaching takes place at room temperature and atmospheric pressure for a certain period of time which simulates the environmental conditions in a landfill.

3.5 MICROWAVE EXTRACTION TECHNIQUE

Unlike the conventional method, extraction using the microwave technique produces very harsh conditions in the form of elevated temperature and pressure. In a system which uses a closed vessel, the extraction efficiency is enhanced and the extraction time reduced by elevating the temperature well above the atmospheric boiling point of the solvent used. This leads to separation of the analyte from the matrix, allowing greater efficiency of extraction. At high temperatures, the targeted analytes are more readily soluble in the solvents. Furthermore, surface tension and solvent viscosity are reduced with temperature, allowing improvement in sample wetting and the penetration of the matrix [22].

Like many modern technologies, microwaves have been continuously developed and improved in terms of their power, capacity and ability to heat objects. Microwaves are now used for many purposes. The principle is to convert electrical energy to microwave energy to heat objects. This is achieved by the high voltage system provided in the microwave [22]. Microwave technology is becoming widely used in analytical laboratories due to the advantages provided i.e. reduced solvent consumption, reduced reaction/extraction time, improved efficiency and better working environment [23].

Microwave radiation has been demonstrated to be a very effective heating source in chemical reactions. Microwaves can accelerate the reaction rate, provide uniform and selective heating, produce greater reproducibility of reactions, provide better yields and help in developing cleaner and greener synthetic routes. There are some limitations of microwave chemistry such as scalability, limited application, and the hazards involved in its use.

There are two types of microwave extraction systems that are commercially available: a closed-system and an open-vessel system. The closed-vessel system operates under controlled pressure and temperature; therefore, it allows the temperature of the solvent to be raised above its boiling point. The main advantage of this technique is that losses due to volatilization are minimized because the samples are allowed to cool before the vessels are opened. Whereas major disadvantages of this technique are (i) the time associated with the mechanics of the closed vessel technique, (ii) sample size seems to play a more critical role in extraction efficiency and (iii) the significant amounts of time for the samples to cool and depressurize. Extractions using the open-system are performed at atmospheric pressures. When the temperature of the solvent approaches the boiling point, the solvent vaporizes, rises to a reflux condenser where it is condensed and returned to the extraction vessel. This method will allow the target analytes to first be isolated and then reacted. The main advantages of the open-system are the ease of making reagent additions, large sample capacity, efficient solvent/matrix heating and speed. The disadvantages are losses due to volatilization, single sample per run and energy put into the sample can not be accurately controlled in this method [24].

3.5.1 Theory of Microwave Energy

Microwave energy is based on the direct effect of microwaves on molecules by ionic conduction and dipole rotation. Heat energy is dissipated throughout solutions when exposed to microwave energy. This heating works on the basis that ions within the solution have dipoles that change position once exposed to such energy. This movement of ions is resisted by the solution, causing friction and therefore release of thermal energy.

Dipole rotation means that these molecules have positive and negative ends, so they tend to behave like microscopic magnets. In many applications, these two mechanisms take place simultaneously at 2450 MHz (which is the frequency used in commercial systems).

Microwaves interact with polar molecules in such a way that the polar molecules align themselves and oscillate in time with the oscillation of the electric field of the microwave Figure 3.1 [25]. Since dipoles have a positive and negative aspect, the affect of microwaves on the dipoles can be thought of as in two cycles. In the positive half of the cycle the microwave penetrates the object, the negative particles of the molecules are attracted and attempt to align themselves with the positive field of energy. The subsequent collision and friction between these moving molecules and the rapid return of dipoles to their original position at a rate of 4.9×10^9 times per second, results in the generation of thermal energy and therefore rapid heating. The more polar a molecule, the greater the influence that microwave energy will have on it, therefore the greater the heat generated. Then, when the microwave energy alternates to the negative half cycle, the opposite occurs, causing a flipping motion [22].

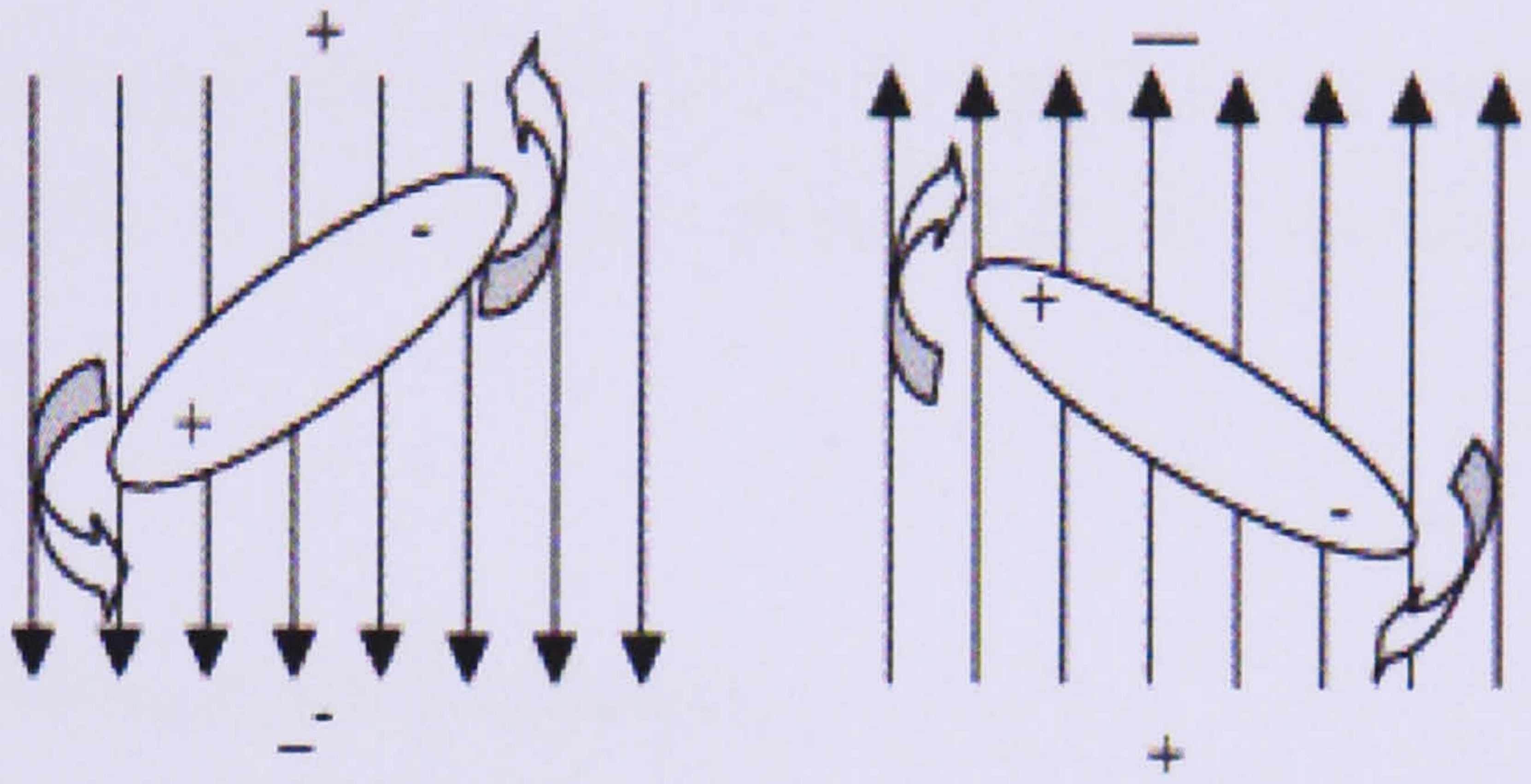

Figure 3.1: Realignment of a dipole in an electromagnetic field

The dissipation factor (Tan δ) reflects the potential of a solvent to absorb and convert microwave energy into heat at a particular frequency and temperature. This dissipation factor is a ratio of the sample's dielectric loss to its dielectric constant and is expressed in the following equation [26]:

$$Tan\,\delta = e'' / e'$$

Where,

(e'') is the dielectric loss which measures the efficiency with which the energy of the electromagnetic radiation can be converted into heat.

(e') is the dielectric constant and describes the ability of the molecule to be polarised by the electric field.

Generally, the greater the dielectric constant the greater the degree of microwave absorption and the more rapid is the heating for a given frequency. Water is a good example of a polar solvent with the highest dielectric constant of common solvents. The dissipation factor, however, is significantly lower than other solvents. So, the rate at which water absorbs microwave energy is higher than the rate at which the system can dissipate the heat. The ability of material to convert microwave energy into thermal energy is dependent upon its polarizibility and absorption (loss factor) characteristic. It is imperative to select the right solvent that has the ability to absorb microwave energy (high dielectric constant) and as well as a high dissipation factor.

The physical parameters that must be considered when choosing parameters for microwave extraction include: solubility, dielectric constant, and the dissipation factor (δ). Factors that govern the extraction of an analyte from a matrix by microwave technique are the solubility of the analyte in the solvent, the mass transfer kinetics of the analyte from the matrix to the solution phase, and the strength of analyte/matrix interactions.

3.5.2 Advantages of Microwave Technique

Microwave technique has many advantages such as [21]:

1. It is able to carry out extraction of samples in 15-20 minutes and up to 14 samples can be heated per cycle.
2. Solvent mixtures in the sealed vessels are heated to temperatures above atmospheric boiling point of the extracting solvent, through the use of microwave technology.
3. Environmental pollutants can be extracted from solid matrices such as sludge, sediment or soil.
4. The technology extraction efficiency is comparable to Soxhlet extraction with an 80-90% reduction in solvent consumption and a 95% reduction in extraction time on a per-sample basis.
5. The maximum operating conditions for the system are 200°C and 200 psi for GreenChem™ Extraction vessels. Typical operating conditions for the extraction process are 110°C to 135°C and 100 psi.
6. Samples are limited to a maximum size of 20 g with a typical sample size of 5 to 10 g. Solvent volumes are limited to 65 cm^3 with a typical volume of 25 to 30 cm^3.

3.5.3 Applications of Microwave Technique

In recent years, there has been widespread use of microwaves in analytical chemistry. with recent advances in several fields such as [27]:

- sample digestion for elemental analysis
- solvent extraction
- sample drying
- measurement of moisture
- analyte desorption and adsorption
- sample clean-up

3.6 EXPERIMENTAL

Four different leaching media were used in the experiments described in this work, Table 3.4. Each mimic a specific set of environmental conditions.

- Leaching with deionised water has been used by many members of the European Community, including France and Germany, as well as Japan utilize deionised water leaching tests. The reason for using deionised water was to demonstrate the contamination potential to drinking water and groundwater from a waste that comes into contact with drinkable water.

- A combination of hydrochloric acid and sodium chloride (HCl/NaCl) in the ratio 1:1 mimics the gastric conditions in humans under which metals can dissolve.

- The Toxicity Characteristic Leaching Procedure (TCLP) was developed by USEPA for determining whether a waste was hazardous by virtue of its toxicity. TCLP fluid contains dilute (pH 5.0) acetic acid, which mimics the organic acids typically found in landfill leachate where decomposition of organic materials in the "anaerobic phase" in a landfill take place after waste is disposed in the landfill.

- The total measurement of metal content is carried out using digestion with a strong acid such as nitric acid. This is used to break down the matrix of the sample and so release the metals into solution.

Table 3.4: Leach liquors used in this work

Leach liquor	**Simulated environmental condition**
Deionised water	Water
HCl/NaCl (1:1 mixture, 0.1 mol dm^{-3})	Gastric Conditions
CH_3COOH (0.5 mol dm^{-3})	Toxic Characteristic Leaching Procedure Test
HNO_3 (2 mol dm^{-3})	Pesudo total heavy metal fraction analysis for soils

3.6.1 Mechanical Shaker Extraction Method

A mechanical Flask Shaker SF1, Figure 3.2, was used to investigate the leachability of different metallic ions in conventional extraction. The shaker is designed to hold eight flasks at one time and has two switches to control the shaking time and the shaking speed. All conventional extractions were carried out at a constant shaking speed of 10 revs/min and at room temperature for a period of one hour except in extractions where acetic acid was used when the time period was 24 hours. The procedures for metal extraction using the four leaching liquors are described below.

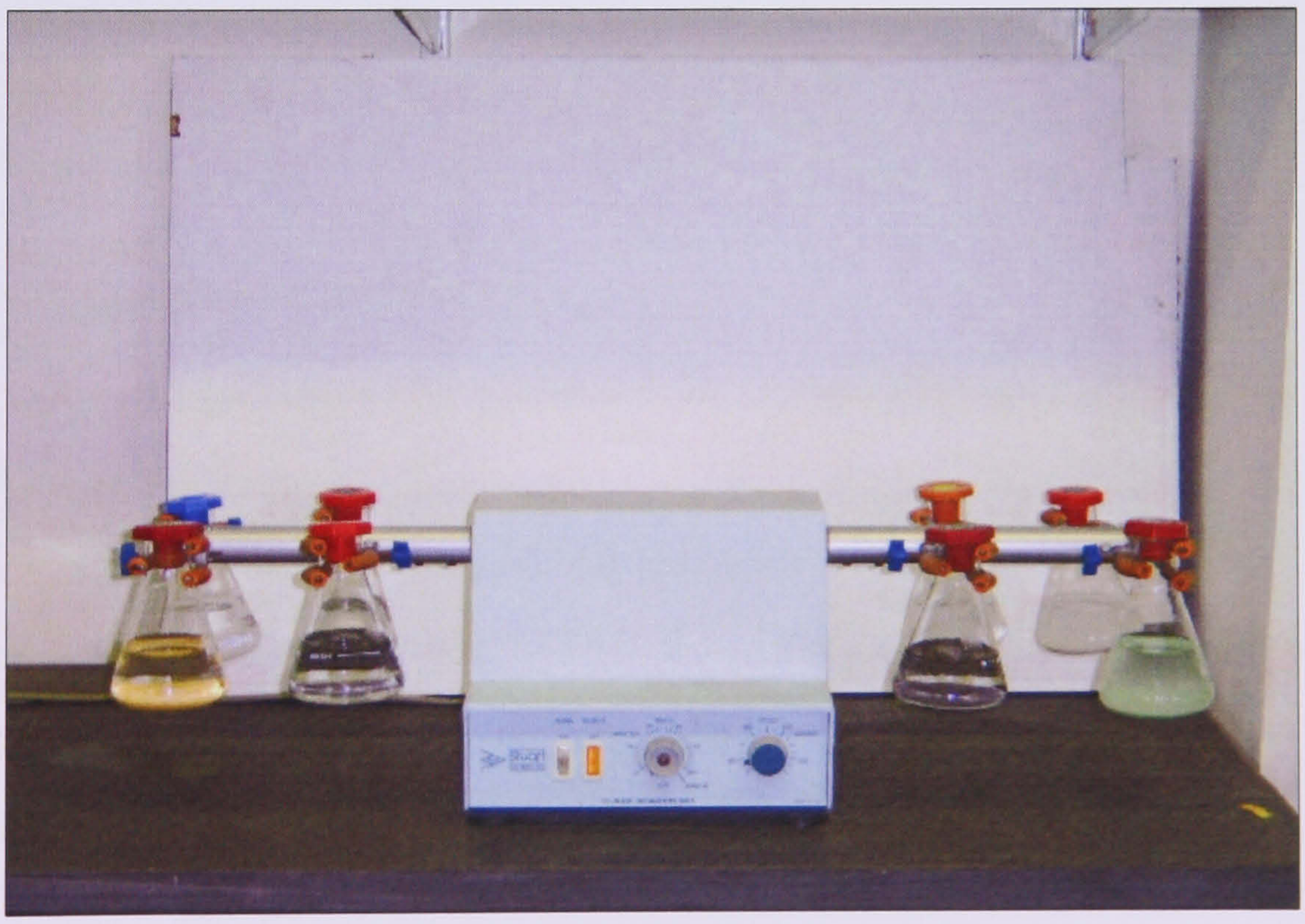

Figure 3.2: Show the mechanical shaker used in this work

3.6.1.1 Deionised Water Extraction

10 g of each sample was placed in a separate conical flask of 250 cm^3 capacity. To this, 100 cm^3 of deionised water was added, the flask stoppered and shaken for 1 hour at a constant shaking speed of 10 revs/min. Each solution was filtered using an ashless Whatman filter paper and the residue washed with deionised water. The resultant filtrate was transferred to a volumetric flask of 200 cm^3 capacity and the final volume was made up to the mark with deionised water.

3.6.1.2 Acetic Acid Extraction

During this leach procedure which is a variation of the Toxic Characteristic Leaching Procedure – EPTOX 1310. A sample of 10 g was placed in a 250 cm^3 stoppered conical flask. After the addition of deionised water (160 cm^3), the flask with its content was shaken on a mechanical shaker for 15 minutes. The shaker was stopped and then a pH meter (Delta 320) was used to measure the pH of the solution. The pH of the solution was maintained at 5.0 ± 0.2 with the addition of a required volume of 0.5 mol dm^{-3} acetic acid, unless it dropped below 4.8 in which case 40 cm^3 of deionised water was also added to restore the pH to 5.0 ± 0.2. The sample was then shaken to for 24 hours and after 1, 3 and 6 hours, the pH was monitored, with the last monitoring at 24 hours. The experiment was terminated after 24 hours, the solution was filtered and the filtrate was transferred to a volumetric flask of 250 cm^3 capacity. The final volume was made up to the mark with deionised water.

3.6.1.3 Hydrochloric Acid Extraction

This leach test was carried out by placing 0.5 g of sample into a 250 cm^3 conical flask. 100 cm^3 of leach solution, a 1:1 mixture of 0.1 mol dm^{-3} hydrochloric acid and 0.1 mol dm^{-3} sodium chloride, was added and the stoppered flask was shaken for 1 hour. The solution was filtered using an ashless Whatman filter paper and the residue washed with deionised water. The resultant filtrate was transferred to a volumetric flask of 200 cm^3 capacity and the final volume was made up to the mark with deionised water.

3.6.1.4 Nitric Acid Extraction

10 g of each sample was added to a separate conical flask of 250 cm^3 capacity, followed by 100 cm^3 of 2 mol dm^{-3} nitric acid, the flask stoppered and shaken for 1 hour. The

sample then filtered using an ashless Whatman filter paper and the residue washed with deionised water. The resultant filtrate was transferred to a 200 cm^3 standard flask and made up to volume with deionised water.

3.6.2 Microwave Accelerated Reaction System

The second extraction technique used was Microwave Accelerated Reaction System (MARS), Figure 3.3 [28], which is designed for laboratory use in extracting, dissolving, hydrolyzing or drying a wide range of inorganic and organic materials. The MARS utilises microwave energy to rapidly heat samples in either polar or ionic solutions at elevated pressures.

Figure 3.3: Microwave Accelerated Reaction System

3.6.2.1 Deionised Water Extraction

1 g of sample was placed in a microwave vessel. To this, 10 cm^3 of deionised water were added. The vessel was placed in the microwave, which was set to reach 150°C in the first 10 minutes, then held at 150°C for the next 15 minutes. Finally, the system was allowed to cool for 30 minutes. The solution was later filtered using an ashless Whatman filter paper and the resultant filtrate was transferred to a 20 cm^3 standard flask.

3.6.2.2 Nitric Acid Extraction

The same experimental procedure in section 3.6.2.1 was applied in the microwave extraction using 2 mol dm^{-3} nitric acid as a leaching medium

All experiments were conducted in triplicate as a minimum to achieve reproducibility and the results presented as averages of the measurements. In all cases, samples were analysed using Perkin–Elmer 2380 Atomic Absorption Spectrometer (AAS).

3.7 RESULTS

3.7.1 Mechanical Shaker Extraction Method

Due to the similarity in the experimental data obtained during the extraction of the metals, the data in this section of the thesis are presented in table and figure form. The data obtained from cadmium is used in the following text as an example of the species type and result and applies to all of the other metals investigated.

Cadmium

1. Cadmium powder

Since cadmium is insoluble in water at room temperature and atmospheric pressure, the deionised water extracted a minute amount, around 0.005% of the total cadmium present in the sample. The results in Table 3.5 show that acetic acid which is a weak acid extracted 1.2% of the total cadmium present in the sample. Using a mixture of hydrochloric acid and sodium chloride, which mimics the gastric condition in the human stomach, 57.3% of cadmium present in the sample was extracted. In the case of using HNO_3 as leach liquor 47.0% of cadmium present in the sample was extracted due to the solubility of cadmium in HNO_3, Figure 3.4.

2. Cadmium oxide

Deionised water was shown to extract the least amount 0.002% of cadmium present in the sample. This is due to the insolubility of cadmium oxide in water. Acetic acid was able to extract 2.7% of cadmium. It was found that using HCl/NaCl as leaching medium, more cadmium was extracted than with other solvents 69.1%, this would indicate that a person ingesting one gram of cadmium oxide would have absorbed 691.2 mg of cadmium into their bloodstream and biologically would be exposed to this amount of cadmium. Nearly 52.1% of cadmium was extracted using 2 mol dm^{-3} nitric acid.

3. Cadmium sulfide

The results show that deionised water extracted 0.22% of the cadmium present in the sample. Acetic acid was able to extract a small amount of cadmium 2.7% and the HCl/NaCl mixture extracted 70.5%. The results in Table 3.5 and Figure 3.4 illustrate that because cadmium sulfide is soluble in acids, therefore, 54.4% of the total cadmium in the sample, was extracted using 2 mol dm^{-3} nitric acid.

Cadmium was selected as an example for the rest of the experimental studies carried out on the other metals as they have all acted approximately the same in relation of their extraction from the elemental and compound forms.

4. Cadmium carbonate

Deionised water extracted the least amount of cadmium 0.0004% because of the insolubility of cadmium carbonate in water. Under the landfill condition around 2.1% of cadmium is extracted. The amount of cadmium extracted using HCl/NaCl was high at 55.4% of the total cadmium present in the sample. This is an indication of the amount ingested by a person exposed. Nitric acid (2 mol dm^{-3}) extracted 63.0% of the cadmium present.

The results in red in Table 3.5 confirm that the obtained values for each leaching tests were exceeded the trigger levels mentioned in Table 3.2 which is set by the World Health Organisation (WHO) for drinking water.

Tables 3.6 - 3.10 and Figures 3.5 – 3.9 show the extracted values of Co, Cu, Pb, Ni and Zn and their compounds using the same leach medium that was used in the leaching of cadmium.

Table 3.5: Leaching of cadmium compounds – conventional method

Leach liquor	Conc. of cadmium leached (mg/l)	Amount of cadmium leached per gram of sample (mg/g)	% of Cd leached
Cadmium Powder			
Deionised water	2.4	0.05 ± 0.02	0.005 ± 0.001
CH_3COOH	490	12.2 ± 1.8	1.2 ± 0.15
HCl/NaCl	1433	573.2 ± 15.6	57.3 ± 1.8
HNO_3	23500	470.0 ± 11.0	47.0 ± 1.2
Cadmium Oxide			
Deionised water	0.89	0.02 ± 0.02	0.002 ± 3×10^{-4}
CH_3COOH	960	27.4 ± 1.4	2.7 ± 0.2
HCl/NaCl	1512	691.2 ± 16.3	69.1 ± 1.5
HNO_3	22800	521.1 ± 17.6	52.1 ± 1.8
Cadmium Sulfide			
Deionised water	86	2.2 ± 0.5	0.22 ± 0.05
CH_3COOH	860	27.6 ± 0.7	2.7 ± 0.6
HCl/NaCl	370	704.3 ± 19.2	70.5 ± 1.8
HNO_3	21150	544.0 ± 16.4	54.4 ± 1.6
Cadmium Carbonate			
Deionised water	0.14	0.004 ± 0.002	0.0004 ± 2×10^{-4}
CH_3COOH	1560	21.0 ± 1.2	2.1 ± 0.1
HCl/NaCl	900	554.0 ± 10.2	55.4 ± 1.1
HNO_3	20500	630.0 ± 18.6	63.0 ± 1.7

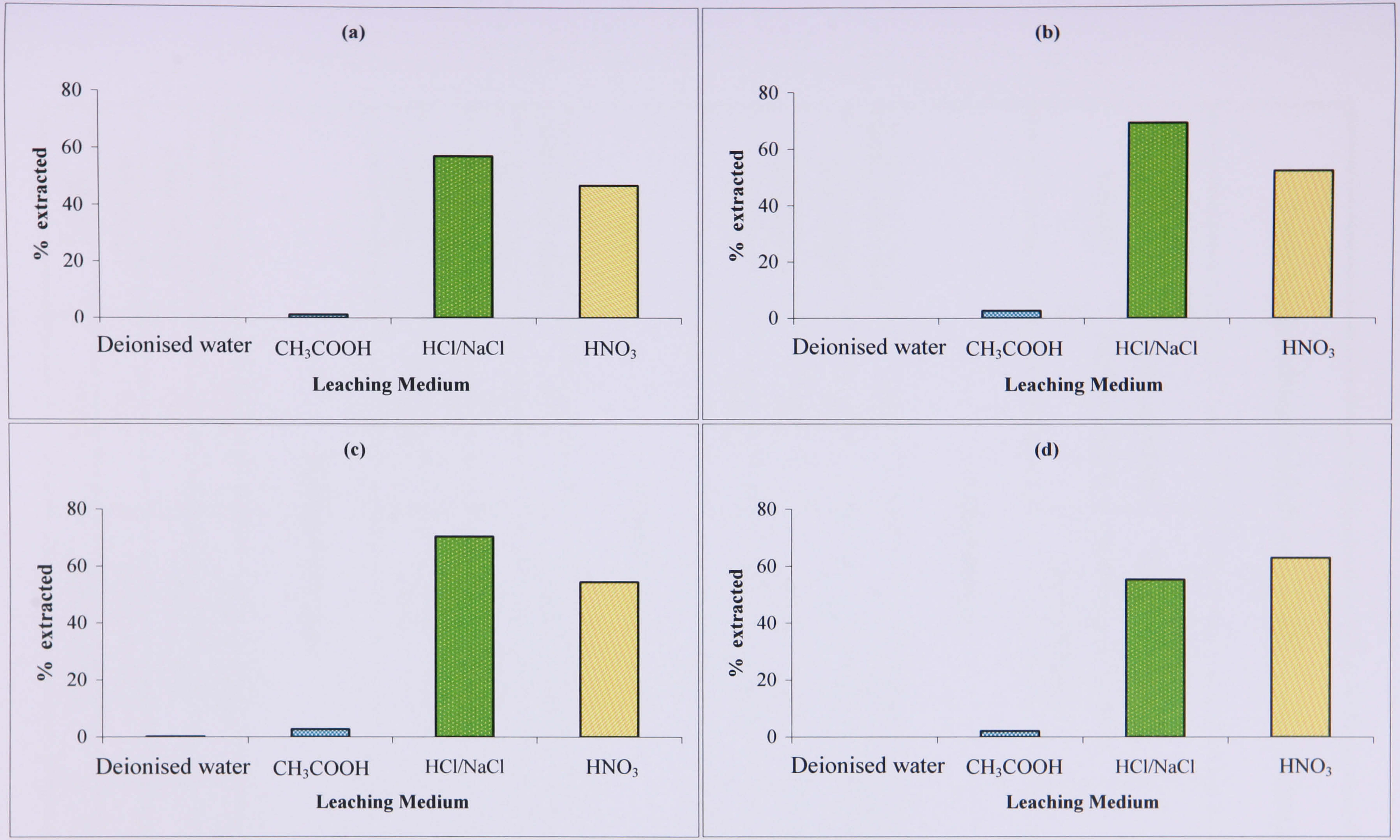

Figure 3.4: Leaching of cadmium from (a) cadmium powder, (b) cadmium oxide, (c) sulfide cadmium and (d) cadmium carbonate using different leach liquors in conventional method.

Table 3.6: Leaching of cobalt compounds – conventional method

Leach Liquor	Conc. of cobalt leached (mg/l)	Amount of cobalt leached per gram of sample (mg/g)	% of Co leached
Cobalt Powder			
Deionised water	2.3	0.05 ± 0.02	0.005 ± 0.0018
CH_3COOH	730	18.3 ± 1.0	1.8 ± 0.086
HCl/NaCl	755	302.0 ± 10.4	30.2 ± 1.11
HNO_3	22500	450.0 ± 11.0	45.0 ± 1.2
Cobalt Oxide			
Deionised water	0.13	0.003 ± 0.001	0.0003 ± 1.0×10^{-4}
CH_3COOH	1030	32.7 ± 1.6	3.2 ± 0.2
HCl/NaCl	850	432.2 ± 9.2	43.2 ± 1.0
HNO_3	15620	397.2 ± 12.2	39.7 ± 1.3
Cobalt Carbonate			
Deionised water	0.87	0.03 ± 0.008	0.003 ± 0.0007
CH_3COOH	590	29.7 ± 1.2	2.9 ± 0.1
HCl/NaCl	815	652.0 ± 17.5	65.2 ± 1.8
HNO_3	13800	556.4 ± 15.2	55.6 ± 1.6

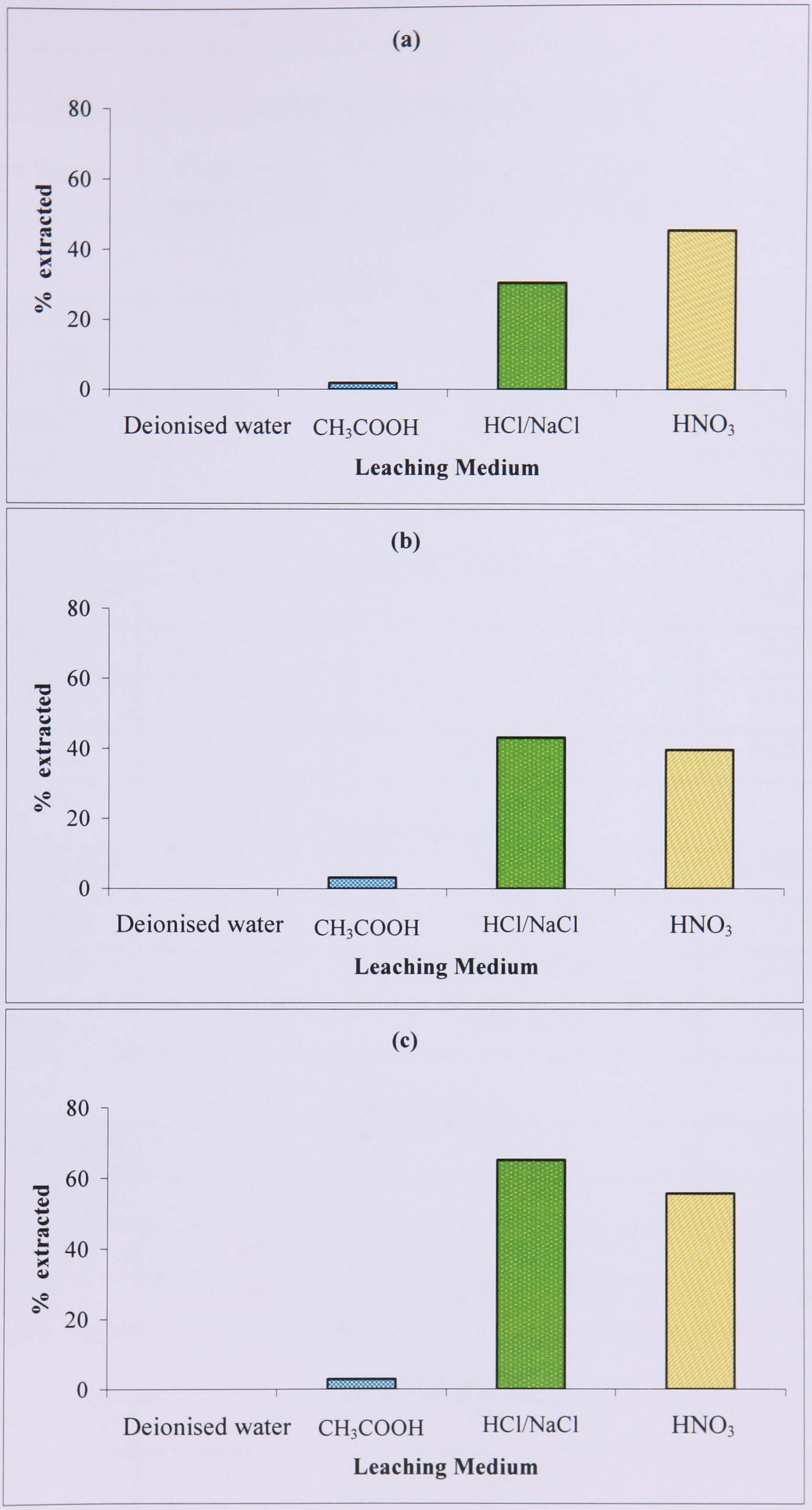

Figure 3.5: Leaching of cobalt from (a) cobalt powder, (b) cobalt oxide, and (c) cobalt carbonate using different leaching media in conventional method.

Table 3.7: Leaching of copper compounds – conventional method

Leach liquor	**Conc. of Cu leached (mg/l)**	**Amount of copper leached per gram of sample (mg/g)**	**% of Cu leached**
Copper Powder			
Deionised water	2.1	0.04 ± 0.001	0.004 ± 0.001
CH_3COOH	440	11.0 ± 1.2	1.1 ± 0.1
HCl/NaCl	700	280.0 ± 6.1	28.0 ± 0.56
HNO_3	26700	534.0 ± 10.4	53.4 ± 1.1
Copper (I) Oxide			
Deionised water	1.4	0.06 ± 0.02	0.006 ± 0.002
CH_3COOH	396	22.2 ± 1.1	2.2 ± 0.1
HCl/NaCl	492	443.2 ± 13.6	44.3 ± 1.4
HNO_3	12100	545.0 ± 14.5	54.5 ± 1.5
Copper (II) Oxide			
Deionised water	2.4	0.06 ± 0.02	0.006 ± 0.001
CH_3COOH	355	11.1 ± 0.4	1.1 ± 0.03
HCl/NaCl	530	365.6 ± 10.3	26.6 ± 1.1
HNO_3	23040	577.0 ± 17.0	57.7 ± 1.6
Copper Sulfide			
Deionised water	120	3.6 ± 0.3	0.4 ± 0.03
CH_3COOH	950	35.7 ± 1.6	3.5 ± 0.2
HCl/NaCl	850	512.0 ± 22.3	51.2 ± 2.1
HNO_3	15750	474.2 ± 14.4	47.4 ± 1.5
Copper Carbonate			
Deionised water	0.8	0.06 ± 0.02	0.006 ± 0.001
CH_3COOH	130	12.2 ± 1.0	1.2 ± 0.1
HCl/NaCl	312	472.7 ± 18.5	47.2 ± 1.8
HNO_3	4620	347.8 ± 14.8	34.7 ± 1.5

Figure 3.6: Leaching of copper from (a) copper powder, (b) copper (I) oxide, (c) copper (II) oxide, (d) copper sulfide and (e) copper carbonate using different leach liquors in conventional method

Table 3.8: Leaching of lead compounds – conventional method

Leach liquor	Conc. of lead leached (mg/l)	Amount of lead leached per gram of sample (mg/g)	% of Pb leached
Lead Powder			
Deionised water	0.4	0.008 ± 0.002	0.0008 ± 2.1×10^{-4}
CH_3COOH	790	19.7 ± 1.1	2.0 ± 0.12
HCl/NaCl	613	245.2 ± 6.2	24.5 ± 0.7
HNO_3	14500	290.0 ± 5.2	29.0 ± 0.6
Lead Oxide			
Deionised water	4.4	0.05 ± 0.01	0.005 ± 0.001
CH_3COOH	1560	42.0 ± 1.3	4.2 ± 0.1
HCl/NaCl	810	349.0 ± 9.2	34.9 ± 0.9
HNO_3	27150	585.0 ± 18.2	58.5 ± 1.7
Lead Carbonate			
Deionised water	1.6	0.04 ± 0.01	0.004 ± 0.001
CH_3COOH	359	11.6 ± 1.0	1.2 ± 0.1
HCl/NaCl	1057	545.4 ± 16.8	54.4 ± 1.6
HNO_3	24500	374.1 ± 12.2	37.4 ± 1.2

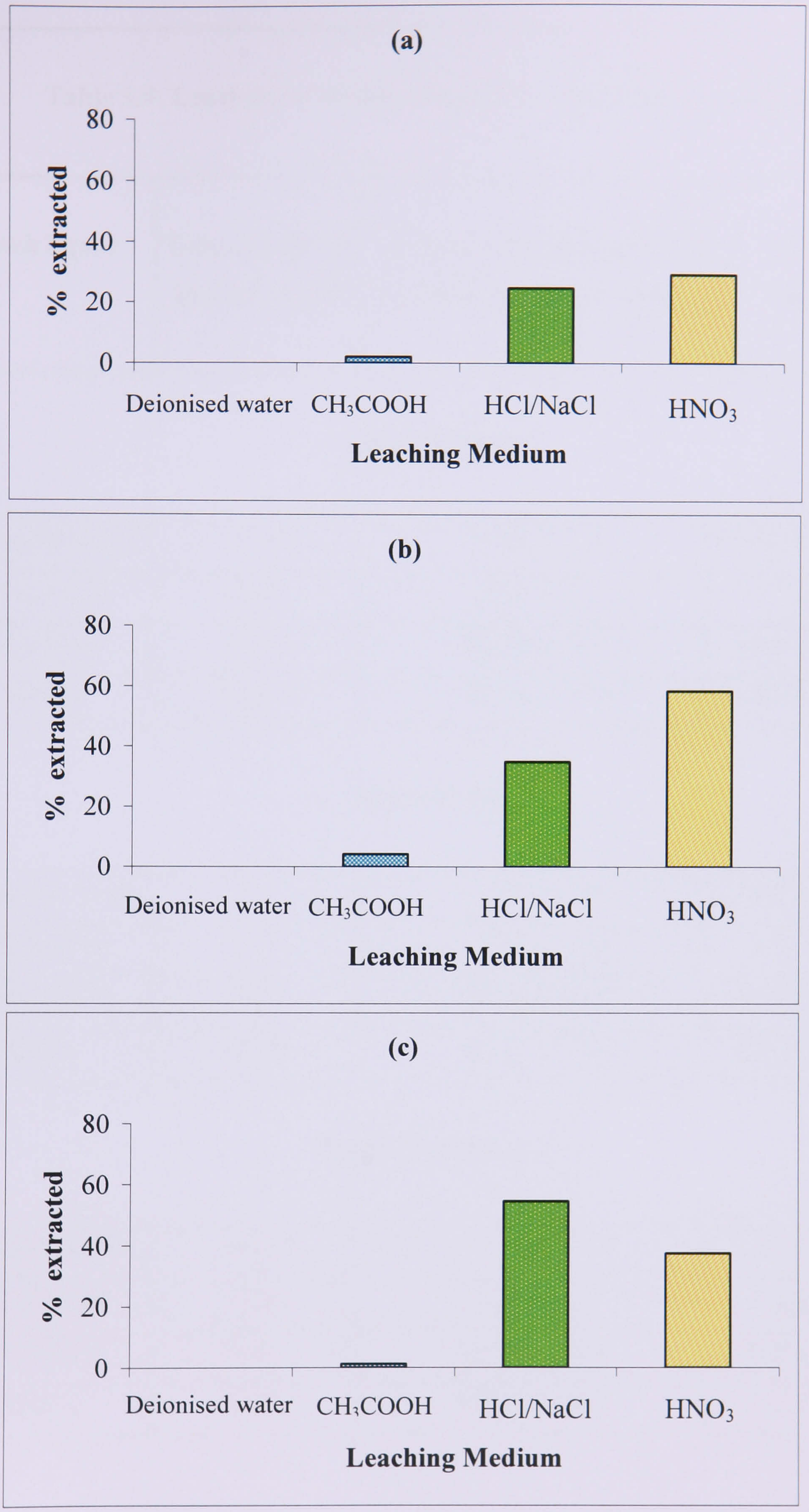

Figure 3.7: Leaching of lead from (a) lead powder, (b) lead oxide and (c) lead carbonate using different leach liquors in conventional method

Table 3.9: Leaching of nickel compounds – conventional method

Leach liquor	Conc. of nickel leached (mg/l)	Amount of nickel leached per gram of sample (mg/g)	% of Ni leached
Nickel Powder			
Deionised water	1.68	0.03 ± 0.01	$0.003 \pm 1 \times 10^{-3}$
CH_3COOH	580	14.5 ± 1.1	1.5 ± 0.1
HCl/NaCl	1120	448.0 ± 8.2	44.8 ± 1.0
HNO_3	24000	480.0 ± 11.2	48.0 ± 1.1
Nickel Oxide			
Deionised water	1.4	0.03 ± 0.01	$0.003 \pm 61 \times 10^{-3}$
CH_3COOH	870	27.6 ± 1.8	2.7 ± 0.2
HCl/NaCl	940	477.5 ± 15.2	47.7 ± 1.6
HNO_3	19870	505.2 ± 16.6	50.5 ± 1.6
Nickel Carbonate			
Deionised water	1.2	0.2 ± 0.07	0.02 ± 0.007
CH_3COOH	118	18.8 ± 1.1	1.8 ± 0.1
HCl/NaCl	240	615.4 ± 18.5	61.5 ± 2.0
HNO_3	3150	402.5 ± 14.3	40.2 ± 1.5

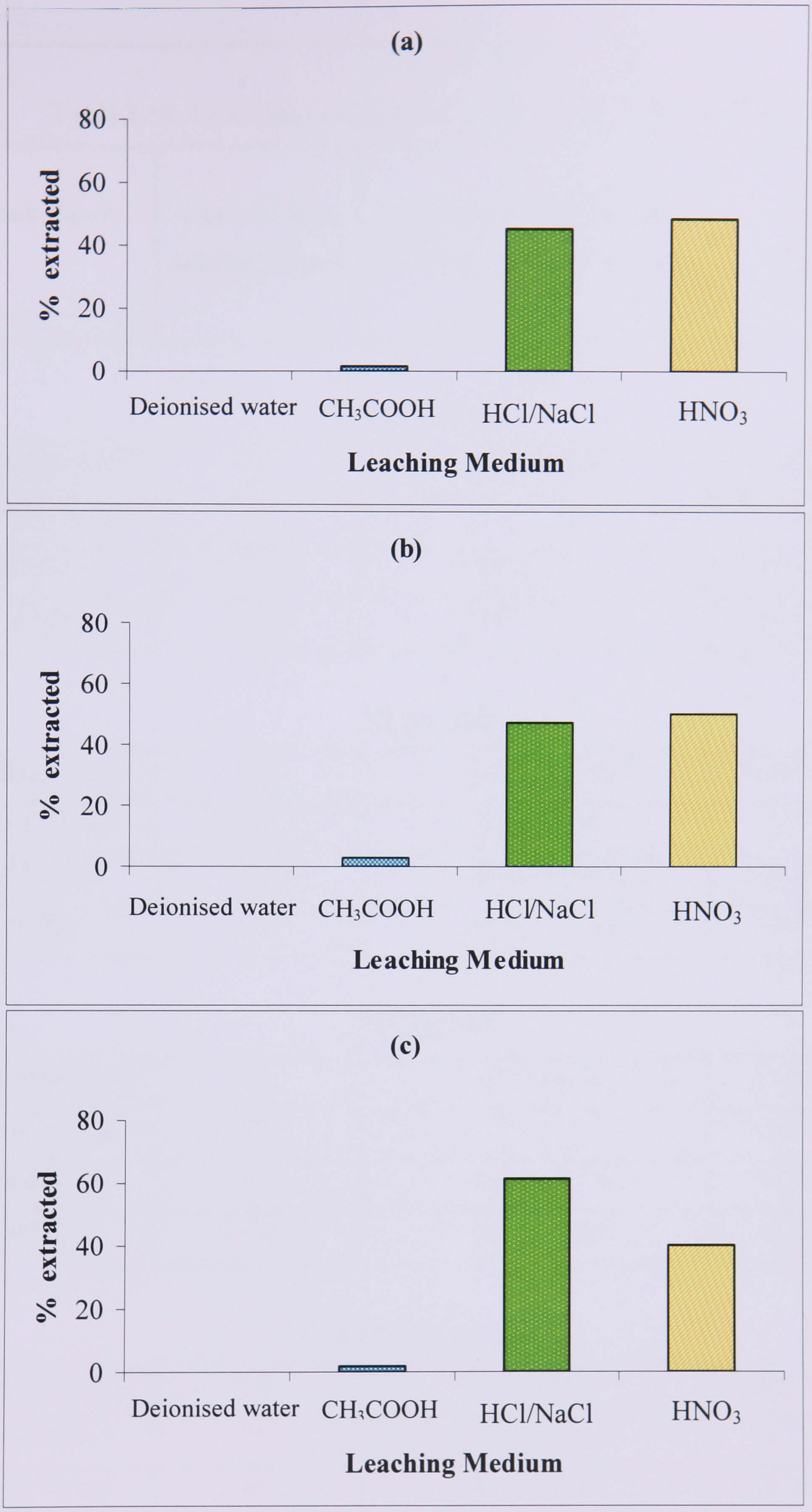

Figure 3.8: Leaching of nickel from (a) nickel powder, (b) nickel oxide and (c) nickel carbonate using different leach liquors in conventional method.

Table 3.10: Leaching of zinc compounds – conventional method

Leach liquor	Conc. of zinc leached (mg/l)	Amount of zinc leached per gram of sample (mg/g)	% of Zn leached
Zinc Powder			
Deionised water	0.8	0.02 ± 0.002	0.002 ± 0.001
CH_3COOH	510	12.7 ± 1.2	1.3 ± 0.13
HCl/NaCl	1390	556.0 ± 12.4	55.6 ± 1.3
HNO_3	18156	363.1 ± 9.3	36.3 ± 1.0
Zinc Oxide			
Deionised water	3.6	0.07 ± 0.02	0.007 ± 0.002
CH_3COOH	510	15.8 ± 1.4	1.5 ± 0.1
HCl/NaCl	1250	622.2 ± 16.0	62.2 ± 1.7
HNO_3	21580	537.0 ± 15.1	53.7 ± 1.5
Zinc Sulfide			
Deionised water	86	2.56 ± 0.4	0.26 ± 0.04
CH_3COOH	175	6.5 ± 0.4	0.60 ± 0.03
HCl/NaCl	690	412.0 ± 15.5	41.2 ± 1.6
HNO_3	14560	433.4 ± 16.8	43.3 ± 1.7
Zinc Carbonate			
Deionised water	1.2	0.2 ± 0.08	0.02 ± 0.008
DI-water	190	39.6 ± 1.1	3.9 ± 0.1
CH_3COOH	85	283.3 ± 8.9	28.3 ± 0.8
HCl/NaCl	1860	310.0 ± 6.5	31.0 ± 0.6

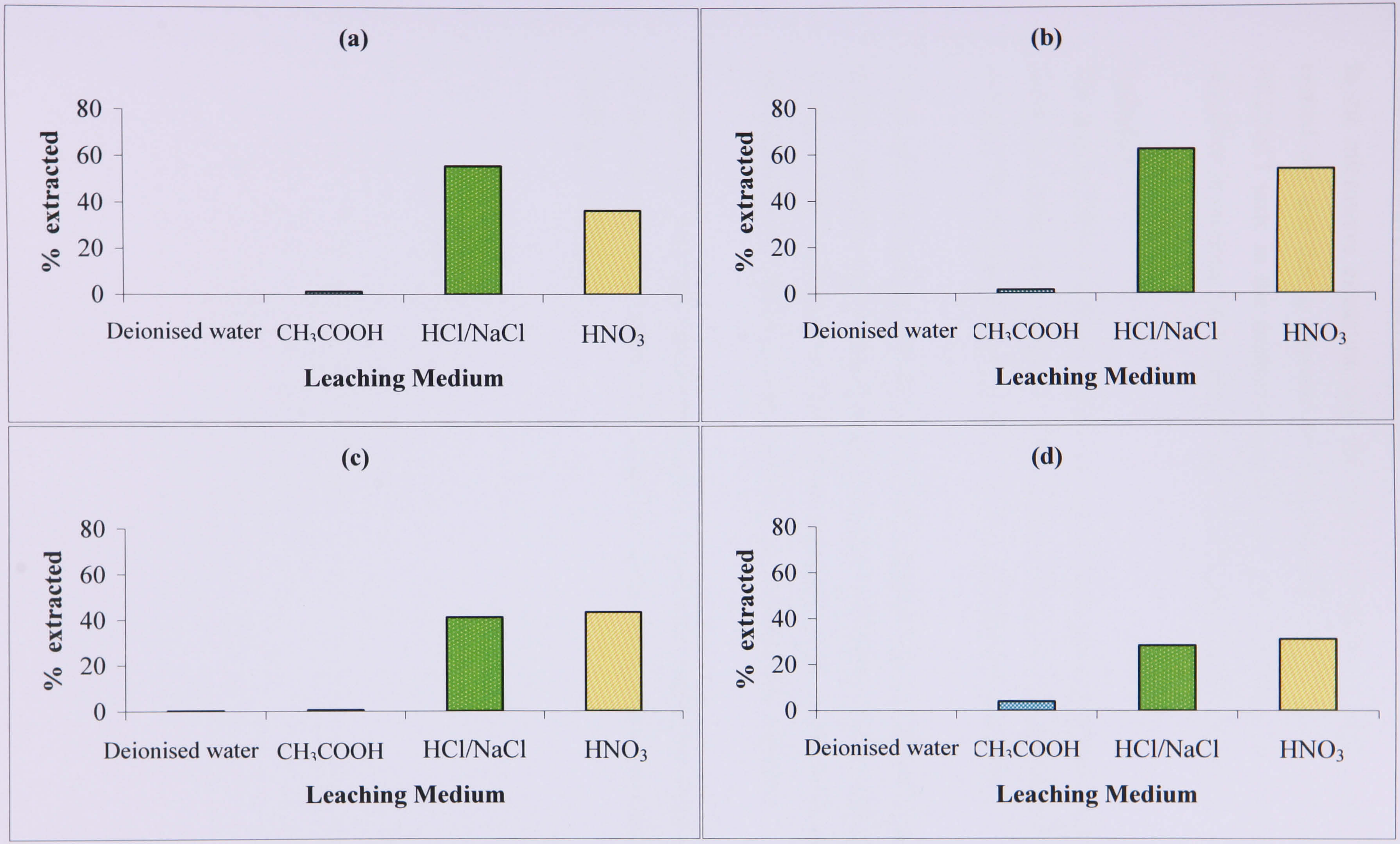

Figure 3.9: Leaching of zinc from (a) zinc powder, (b) zinc oxide, (c) zinc sulfide and (d) zinc carbonate using different leach liquors in conventional method.

3.7.2 Microwave Extraction Results

In the microwave extraction only the deionised water and nitric acid extraction was carried out and this is because the impracticality of the use of acetic acid and the HCl/NaCl tests in the microwave extraction. All experiments followed the method described in sections 3.6.2.1 and 3.6.2.2 in the experimental methodology.

Cadmium

The data in Table 3.11 show that the amount of cadmium extracted with deionised water using the microwave technique. The highest amount was extracted from cadmium sulfide 1.7% and the minimum extracted from cadmium powder 0.02%.

Nitric acid was found to extract considerably high amount of Cd from the samples. The highest amount was extracted from cadmium carbonate 79.2% and then from Cd powder 74.8% compared to 58.8% from cadmium oxide. However, it can be noticed that the amount of cadmium extracted was over 50% from the samples.

Tables 3.12 - 3.16 and Figures 3.10 and 3.11 show the extracted values of Co, Cu, Pb, Ni and Zn and their compounds using the same leach media that was used in the leaching of cadmium.

Table 3.11: Leaching of cadmium using microwave technique

Sample Metal/ Compound	Leaching medium	Conc. of Cd leached (mg/L)	Amount of Cd leached per gram of sample (mg/g)	% of Cd leached
Cadmium Powder	Deionised water	10	0.2 ± 0.04	0.02 ± 0.005
	HNO_3	37420	748.4 ± 19.8	74.8 ± 2.0
Cadmium Oxide	Deionised water	70	1.6 ± 0.2	0.16 ± 0.02
	HNO_3	25750	588.6 ± 18.6	58.8 ± 1.9
Cadmium Sulfide	Deionised water	685	17.7 ± 2.4	1.7 ± 0.2
	HNO_3	25235	654.6 ± 18.5	65.4 ± 1.8
Cadmium Carbonate	Deionised water	302	9.3 ± 0.7	0.9 ± 0.1
	HNO_3	25800	792.5 ± 21.4	79.2 ± 2.0

Table 3.12: Leaching of cobalt using microwave technique

Sample Metal/ Compound	Leaching medium	Conc. of Co leached (mg/L)	Amount of Co leached per gram of sample (mg/g)	% of Co leached
Cobalt Powder	Deionised water	5.13	0.1 ± 0.01	0.01 ± 0.001
	HNO_3	24850	497.0 ± 9.0	49.7 ± 0.88
Cobalt Oxide	Deionised water	147.5	3.7 ± 0.2	0.40 ± 0.02
	HNO_3	20600	23.7 ± 18.4	52.4 ± 1.8
Cobalt Carbonate	Deionised water	855.8	34.5 ± 0.8	3.50 ± 0.09
	HNO_3	17986	725.5 ± 19.5	72.5 ± 2.0

Table 3.13: Leaching of copper using microwave technique

Sample Metal/ Compound	Leaching medium	Conc. of Cu leached (mg/L)	Amount of Cu leached per gram of sample (mg/g)	% of Cu leached
Copper Powder	Deionised water	27.5	0.55 ± 0.02	0.06 ± 0.002
	HNO_3	35062	701.2 ± 12.9	70.1 ± 1.3
Copper Oxide (I)	Deionised water	237.5	10.7 ± 1.1	1.0 ± 0.1
	HNO_3	17020	766.6 ± 15.0	76.6 ± 1.6
Copper Oxide (II)	Deionised water	512.5	12.8 ± 1.1	1.2 ± 0.1
	HNO_3	24750	620.3 ± 17.0	62.0 ± 1.7
Copper Sulfide	Deionised water	1313.5	40.8 ± 2.0	4.0 ± 0.2
	HNO_3	24800	764.9 ± 21.0	76.4 ± 2.1
Copper Carbonate	Deionised water	428.3	32.3 ± 1.2	3.2 ± 0.1
	HNO_3	7750	584.9 ± 19.1	58.4 ± 1.8

Table 3.14: Leaching of lead using microwave technique

Sample Metal/ Compound	Leaching medium	Conc. of Pb leached (mg/L)	Amount of Pb leached per gram of sample (mg/g)	% of Pb leached
Lead Powder	Deionised water	21	0.42 ± 0.1	0.04 ± 0.01
	HNO_3	17166	343.2 ± 6.2	34.3 ± 0.6
Lead Oxide	Deionised water	770	16.6 ± 0.7	1.60 ± 0.07
	HNO_3	28150	606.8 ± 19.0	60.6 ± 2.0
Lead Carbonate	Deionised water	600	15.8 ± 1.1	1.6 ± 0.1
	HNO_3	28152	743.7 ± 18.4	74.3 ± 1.9

Table 3.15: Leaching of nickel using microwave technique

Sample Metal/ Compound	Leaching medium	Conc. of Ni leached (mg/L)	Amount of Ni leached per gram of sample (mg/g)	% of Ni leached
Nickel Powder	Deionised water	327.5	0.6 ± 0.2	0.06 ± 0.02
	HNO_3	28120	562.4 ± 19.8	56.2 ± 2.0
Nickel Oxide	Deionised water	387.5	9.8 ± 0.4	1.00 ± 0.04
	HNO_3	22335	568.3 ± 20.7	56.8 ± 2.0
Nickel Carbonate	Deionised water	210	26.9 ± 1.2	2.6 ± 0.1
	HNO_3	5250	673.0 ± 19.6	67.3 ± 2.0

Table 3.16: Leaching of zinc using microwave technique

Sample Metal/ Compound	Leaching medium	Conc. of Zn leached (mg/L)	Amount of Zn leached per gram of sample (mg/g)	% of Zn leached
Zinc Powder	Deionised water	0.85	0.02 ± 0.004	$0.002 \pm 4 \times 10^{-4}$
	HNO_3	25460	509.2 ± 13.2	51.0 ± 1.3
Zinc Oxide	Deionised water	650	16.1 ± 1.1	1.6 ± 0.1
	HNO_3	25740	641.0 ± 15.2	64.1 ± 1.6
Zinc Sulfide	Deionised water	217	6.5 ± 0.2	0.60 ± 0.02
	HNO_3	18468	550.4 ± 16.4	55.0 ± 2.0
Zinc Carbonate	Deionised water	151	25.2 ± 1.1	2.5 ± 0.1
	HNO_3	4445	740.8 ± 20.0	74.0 ± 2.1

Figure 3.10: Leaching of (**a**) Cd, (**b**) Co, (**c**) Cu, (**d**) Pb, (**e**) Ni and (**f**) Zn from their elemental/compounds with deionised water using microwave extraction technique.

Figure 3.11: Leaching of (**a**) Cd, (**b**) Co, (**c**) Cu, (**d**) Pb, (**e**) Ni and (**f**) Zn from their elemental/compounds with nitric acid using microwave extraction technique.

3.8 DISCUSSION

The results obtained in this work, revealed what would be likely to occur in a reception system of municipal solid waste when its composition contains a significant percentile of metallic materials that might leach under different simulated landfill and environmental conditions.

A leaching test by deionised water was used to evaluate the potential environmental risk associated with the metals and their compounds. As shown in the results, the leaching percentage of heavy metals released from their elemental and compound form is less than 1% of the total heavy metal content. This is due to the fact that most of the metals and their compounds used in this study were insoluble in water and their tendency to leach under standard environmental conditions was probably very low. These results are in agreement with the studies carried out by other researchers [29].

It can be noticed from the results that two factors have influenced the leaching process. First the pH, the extraction carried out with deionised water is taking place in a pH around 5-6 compared to the leaching experiments carried out in more acidic condition represented in this study by the acetic acid and nitric acid. The experiments that were carried out with the 2 mol dm^{-3} nitric acid show that higher amounts of metals were leached than in the other two leaching media (deionised water and acetic acid) and a variation was noticed in the amount of metals leached from different sources. A general trend can discerned that more heavy metal was leached at low pH value. Bruder-Hubscher et al. [30] described the use of sequential extraction to study the release of metals from bottom ash, and reported that Pb and Zn can be released under acidic conditions and Cr leached under strong acidic conditions.

With the decrease of pH, metal in the form of their oxides, sulfides and carbonates can be dissolved and released. The same portion of metal could not be released during the leaching by deionised water because of the medium pH. The result of pH-dependent leaching can help explain the exact mechanism involved in heavy metals releasing from the chemical compounds. For instance, the percentage of Cd, Cu and Pb leached with the deionised water was 0.005%, 0.004% and 0.0008%, and these values increased with the use of acetic acid to 1.2%, 1.1% and 2.0%, and even higher percentage were leached with the use of nitric acid 47.0%, 53.4% and 29.0%, respectively.

It was noticed that the amount of metals leached from their elemental and compounds form was higher when leaching was carried out with the modified Toxic Characteristic Leaching Procedure Test using acetic acid than the leaching with deionised water. Landfill sites are typically acidic due to the production of organic acids as a result of fermentation organic matters present in municipal solid waste which begins as the oxygen available in the initial waste begins to deplete. Thus, the metallic material content of the waste undergoes redox process and reacts with the acetic acid and it releases the metallic species to the medium, a part of that is retained in the waste mass and the other part is carried by the leached. Acidic conditions i.e. an environment of low pH tends to favour higher metallic solubility. This is partly due to the displacement of cations on the soil adsorption sites by protons. Xiaoli et al. [29] investigated the characteristics and migration of heavy metals in Shanghai Laogang Landfill. The study reported that, under standard environmental conditions, the amount of heavy metals released was low and increased when conditions became more acidic.

It can be noticed from the results that the amount of metals leached was high in all the experiments carried out with the use of the solution that mimic or represent the gastric condition in human beings and this show that the high leachability and mobility of the metals from the landfill to the soil and the groundwater and their uptake by plants and consumption of contaminated food and water with these metals and their compounds could lead to the uptake of high percentage by the stomach. The human stomach has an environment that favours release of these heavy metals from their compounds and water or foodstuffs contaminated with such heavy metals are likely to cause significant health problems.

Studies of possible health effects show that exposure to heavy metals leached from waste which are dumped into the landfill and are not properly controlled could leak out as leachate. Exposure to nickel could cause skin irritation and dermatitis, ingestion-stomatitis, gingivitis and possible diarrhoea and exposure to lead could cause severe anorexia, abdominal pain and constipation, toxic megacolon, headaches, fatigue, depression, dropped wrist, proximal renal tubular dysfunction, chronic nephropathy and hypertension. Tao et al. [31] show that changes in the major soil properties including redox potential, dissolved organic carbon and microbial activities all favour a transformation of copper from less available to more available fractions, leading to variations in the various copper species of the maize Rhizosphere. Some of the metals and their compounds studied are considered to be carcinogenic such as cadmium and can therefore have significant detrimental effects.

Another key factor within the landfill that affects the behaviour and solubility of heavy metals is temperature. With a rise in temperature comes a higher state of atomic excitability and therefore more vigorous ionic movement resulting in a faster rate of reaction. An increase in the temperature causes an increase in the rate of dissolution of the metal ions and this has been demonstrated by the experiments carried out using the microwave technique. It can be seen that all the metals were leached more with increasing the leaching temperature and pressure even in the case of using deionised water as a leaching medium. The results of the microwave extraction showed a significant impact on the dissolution process of the heavy metals within the samples. The resultant could be attributed to the high temperature and pressure combined with the effect of electromagnetic radiation which may facilitate a strong interaction and binding between the free metal ions and dipolar molecules in the leaching solutions.

3.9 CONCLUSIONS

The main aim of this study was to investigate the possibility of heavy metals migration under different environmental and landfill conditions. Four leaching experiments were conducted in order to investigate the mobility of heavy metals in the studied chemical compounds.

For the studied conditions, heavy metal concentrations obtained from all the leaching experiments except for a few, have exceeded the trigger levels shown in Table 3.2 even in the case of using deionised water as a leaching medium. Therefore, waste giving such leaching data could be classified as hazardous. Hence the eventual leaching of metals in a landfill should be a major concern in terms of affecting bioactivity in the landfill and accumulating high metal concentrations in leachate.

The results suggest that the production of acetic acid due to the decomposition of organic materials under landfill condition was able to dissolve high concentration of Cd, Co, Cu, Pb, Ni and Zn from their elemental and compound forms and these results have exceeded the trigger levels set by WHO. Therefore, under no circumstances waste containing these metals should be mixed with biodegradable waste in landfill. One way of achieving this is by taking into account the impact of household waste. Households should be knowledgeable on this matter. Specifically, they should be educated of what hazardous and non- hazardous waste are and encouraged to separate them before the waste is collected from their premises and taken to landfills. This in turn would separate sources of metals such as cans, metal containers, batteries, paint, dyes, DIY tools and materials...etc that are currently mixed with biodegradable waste.

The results of this kind of work could assist the environmental authorities in the decision making process to determine the type of waste objects or substances that can go to hazardous or non-hazardous landfill on the basis of the hazardous nature shown by them. In addition, the values of the metal concentrations under different environmental conditions can be used to further changes in reviewing the trigger guide levels for the metals studied in this work.

It may be concluded that industrial waste containing heavy metals dumped in landfills may cause health hazards. so treatment of wastes is essential prior to disposal.

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Chapter 4

OPTIMISATION OF LEACHING CONDITIONS FOR METAL RECOVERY

OPTIMISATION OF LEACHING CONDITIONS FOR METAL RECOVERY

4.1 INTRODUCTION

Separation and recovery of heavy metals and valuable compounds from industrial wastes is of a great importance not only as a method of recycle but also to reduce the detrimental effects of these metals on the environment and to save raw materials [1].

By its very definition spent catalysts are waste. They are no longer an asset to various industrial processes and therefore areas regulating the disposal of these catalysts have experienced many changes. This can be seen with many of the rules and legislative measures that have been introduced by sovereign states and organisations. The surge of international awareness has not made it easy or cheap for generators to dispose of spent catalysts as they require safe disposal in environmentally friendly ways. The rapid growth in industrial activities as well as the increased demand for high purity metals has raised concerns over potential adverse environmental effects. Factors such as the need for lower operating costs in a competitive market, the depletion of high grade ores and changes in many mining practises have resulted in the reusing or retreatment of ores that are of lesser quality. Many ores that were previously considered uneconomical are now treated for this exact purpose. There is also an environmental factor during the treating waste from metal winning processes because these wastes may contain materials hazardous to human health.

Leaching remains an important concept in hydrometallurgical processes as the total recovery of the metal and its ease of separation from impurity is dictated by the selectivity and the efficiency of the leaching process.

The work described in this chapter is a study of the optimisation of the dissolution process of heavy metals such as cobalt, copper, zinc, nickel, lead and iron from industrial spent catalysts using conventional methods to determine the best leaching conditions. The results obtained from the conventional method were then compared to the results obtained with the use of a Microwave Accelerated Reaction System (MARS). The parameters for both methods were determined in order to establish the best conditions to be used in leaching. This study focused on the leaching operation aiming to find an efficient, eco-friendly and economical hydrometallurgical route to recover valuable/hazardous metals and reduce the hazardous character of the waste stream before final disposal.

4.2 METALLURGICAL PROCESSES

Metallurgy is the art and science of extracting metals from their ores. Two main extraction processes are used to extract metals from their ores; pyrometallurgy and hydrometallurgy.

4.2.1 Pyrometallurgical Processes

High temperatures are used in pyrometallurgical processes to recover metals from their ores. These recoveries produce pure metals or intermediate minerals and alloys that are of a quality that is suitable for further refining or commercial applications. During this process, an ore, after being concentrated by beneficiation (crushing, concentrating, washing and drying) is sintered or heated with other materials such as coke or a flux. The concentrate is then smelted in a blast furnace so that the ore chemicals are reduced and the desired metals produced are fused into an impure molten mass. The metal mass then undergoes a further treatment to refine the metal to the required level of purity. In each step of the pyrometallurgical processes, waste materials are produced. Many of the pyrometallurgical processes are autogenous, requiring little energy to continue the reaction as the exothermic nature of the reaction provides sufficient energy to maintain the process. Pyrometallurgical processes capitalise on the differences between constituent oxidation potential, melting point, vapour pressure, density and/or miscibility when melted.

4.2.2 Hydrometallurgical Processes

With the depletion of high grade ores/concentrates, the hydrometallurgical processing of secondary metal sources/wastes is gaining importance for the recovery of valuable metals. In a hydrometallurgical process, an aqueous solution is used to extract and recover desired metals from their primary and secondary sources. Two distinct processes are involved in hydrometallurgy. The most important step of a hydrometallurgical process is generally the first, which is leaching, in which the metal content in the source is taken into solution. The second step is recovery of valuable metals from solution, usually involves purification or concentration step or both, using an appropriate method.

Hydrometallurgy is a broad process extending beyond ore processing to treatment of metal concentrates, metal scrap and revert materials, and intermediate products from metallurgical processes. While in aqueous solutions, constituents have differences in solubilities and hydrometallurgical processes are dependent on these differences to recover and separate the metals. Leaching, chemical precipitation, electrolytic recovery, membrane separation, ion exchange and solvent extraction are all used for this purpose. Nowadays, hydrometallurgical processes are competitive with, and often more economical than pyrometallurgical processes. The advantages of hydrometallurgical processes can be summarized as follows [2]:

1. Metals may be obtained directly in a pure form from the leach solution e.g. by electrolysis.
2. High-purity metals may be recovered from impure leach solutions.
3. The siliceous gangue in the ore is unaffected by most leaching agents, whereas in pyrometallurgical smelting processes this gangue ends up as waste slag.
4. Corrosion problems are relatively mild in hydrometallurgical processes compared with the deterioration of refractory linings in furnaces and the necessity for periodic shutdown and replacement.
5. Many hydrometallurgical processes are carried out at room temperature, and therefore there is no consumption of large amounts of fuel as in pyrometallurgical processes.
6. Handling of leached metal-containing solutions is much cheaper and easier than handling molten mattes, slags and metals.
7. Hydrometallurgical processing is especially suitable for the treatment of low-grade ores.
8. A hydrometallurgical process may start on a small scale and expand as required. A pyrometallurgical process, on the other hand, must be designed as a large-scale operation, since it is more economical to build one big furnace than multiple small ones to achieve the same capacity.

9. Hydrometallurgical plants usually do not pollute the atmospheric environment as do smelters. This factor is playing an important role at present due to the strict anti-air-pollution laws.
10. Low cost requirements

Metals such as copper and zinc can be recovered hydrometallurgically and pyrometallurgically [3,4]. There has, however, been a growing interest in the use of hydrometallurgical processes to recover these metals from industrial wastes as they provide an efficient method for processing low-grade complex ores in an eco-friendly way.

4.3 LEACHING AND LANDFILL

The disposal of hazardous wastes in landfills is a major environmental issue worldwide [5]. Within a landfill, a complex sequence of physically, chemically, and biologically mediated events occur. As water percolates through the landfill, contaminants are leached from the solid waste. A variety of heavy metals can be found in landfill leachate including zinc, copper, cadmium, lead, nickel, chromium and mercury [6].

The quantity, characteristics and chemical composition of industrial wastes at landfill sites are considered to be very important factors in predicting leachate generation and in determining a design approach for leachate collection systems in landfills to reduce the possible risk posed by the continuous discharge of these wastes into the land and water systems. Leaching tests are frequently used to characterize the potential of a solid waste to leach when disposed in a landfill.

Two fundamental issues in the leaching processes are important, equilibrium and kinetics. When the flow of fluid through the waste is low, there is time for many of the contaminants in the waste to reach equilibrium. Conversely, when the fluid high, the concentration of the contaminants in the leachant is controlled by the rate at which they can dissolve or otherwise be transformed. There are always situations between these two extremes in which the concentration of a contamination is a function of both the equilibrium process and kinetics. pH controls the leaching of many inorganic contaminants as well as affecting the speciation of many metals.

Heavy metals in leachate from landfills have been extensively studied and monitored. Compared to the total amount of heavy metals disposed into landfills the content of heavy metals in leachate is relatively low. The major part of the metal is retained in the landfill. As a consequence, it must be expected that leaching of heavy metals from the landfills will continue for a long time. Heavy metal release in the landfill is a function of characteristics of physical and chemical factors.

4.3.1 Physical Factors

The physical access of the leachant to the waste as well as the chemical solubility of the substance concerned determines the leaching characteristics of waste. The physical access of the leachant to the waste surface is controlled by:

- Flow characteristics of the leachate around particles e.g. static saturation such as underwater application and percolation.
- Average surface area of the waste, which is determined by particle size distribution, internal pore structure and size.

These factors will affect the amount of leachant that comes into contact with the waste surface as well as the time of contact and the ability to approach equilibrium concentration.

Overall these physical factors will cause the leaching potential to increase as the amount and ease of access of the leachant increases. This is particularly so where solubility is the controlling factor in the release of the element from the waste surface. In larger impermeable particles or monolithic structures the access of the leachant is limited to the outside of the waste and diffusion to the surface becomes the more important controlling factor in the determination of the rate of dissolution.

4.3.2 Chemical Factors

The chemical factors that control the inherent solubility of elements in waste are pH, equilibrium conditions that depend on the chemical form of the metal salt, complexation with chemicals present in the leachant. and the oxidation-reduction potential of the microenvironment and sorption.

The leaching of waste is strongly dependent on the pH of the system. The pH of the system is governed by the solid phase at low liquid solid ratios and by the leachant. Natural leachants, such as rainwater or landfill leachate which are slightly acid, will progressively lower the pH of the system as time and the quantity of leachant increase. Most of the toxic metals tend to increase their solubility under acidic conditions (low pH) and reach a minimum solubility at higher pH. Some elements, however, exhibit higher solubility under alkaline conditions e.g. molybdenum. Other metals exhibit high solubilities at both low and high pH and these are termed amphoteric (e.g. zinc, lead). pH has a dominant effect on leaching test results and is considered as the most significant factor in waste leaching. This is due not only to its direct role in affecting solubility but also to influences on secondary factors, such as redox potential and complexation.

Leaching agents that have been used include sulfuric acid, ammonia solution, hydrochloric acid, sulfur dioxide solution, nitric acid and sodium hydroxide. Selection of a suitable solvent depends on the chemical state and physical environment of the metals [7]. Leaching test methods can be divided into two general categories: static extraction tests and dynamic extraction tests. Static extraction protocols make use of a single specified volume of leaching fluid with no replacement or addition of the fluid, while in the dynamic extraction protocols, leaching fluid is continuously renewed throughout the process. In the static extraction protocols, leachate is removed at specific times (usually at the end of the test) for analysis. In this process, it is generally assumed that a steady and unchanging environment is maintained from the beginning to the end of the test. Types of static extraction tests include: agitated and non-agitated extraction test and sequential chemical extraction tests.

Leaching studies have been carried out on the leachability of metals from industrial wastes. Chaudhary et al. [8] reported hydrochloric acid leaching process for the recovery of nickel as nickel oxide from a spent catalyst containing 17.7% nickel. The obtained results show that a maximum of nickel extraction of 73% could be achieved by carrying out the leaching process with 28.8% HCl at 80°C. Arslan et al. [9] described the recovery of copper, cobalt and zinc from copper smelter and converter slag. In their leaching experiments, the effects of roasting time, acid/slag ratio, roasting temperature and application of thermal decomposition prior to leaching on the metals dissolution extents have been investigated. For example the results obtained from roasting the slag with sulfuric acid and leaching the product with hot water revealed that the highest metal recoveries observed at 150°C for 2 hours with a 3:1 acid/slag ratio were 88% for copper, 87% for cobalt, 93% for zinc and 83% for iron. Increasing the roasting time to 4 hours increased copper extraction to 95% and 100% copper dissolution was observed as a result of roasting at 250°C with a 3:1 acid/slag ratio for 3 hours. Whereas, increasing acid roasting temperature and time had no effects on the cobalt and zinc dissolution process.

Abdel-Aal et al. [10] studied the effect of various parameters such as particle size, temperature, extraction time, solid/liquid ratio and acid concentration on leaching of a spent nickel oxide catalyst. They reported that extraction of 94% was achieved when extraction conditions were optimised to the following: particle size −200+270 mesh, temperature 85°C, reaction time 150 min, solid/liquid ratio 1:20 g/ml and sulfuric acid concentration 50%. Altundogan et al. [11] have described the sulfuric acid leaching of copper converter slag in the presence of dichromate. The study concluded that an increased copper recovery is achieved by leaching with a leachant containing potassium dichromate and sulfuric acid rather than with sulfuric acid alone. Although copper extraction increases with the use of sulfuric acid with potassium dichromate, other metal extractions are decreased due to the formation of insoluble chromates. In addition, the authors reported that extraction yields of all metals increase with increasing H_2SO_4 concentration and generally copper extraction yields are low for leaching media without potassium dichromate. Al-Mansi et al. [12] reported on the possibility of extraction of nickel from an Egyptian spent catalyst. The optimum conditions for 99% nickel extraction were < 500 micron particle size, 100°C temperature, 5 hours leaching time, solid/liquid ratio of 1:12, 50% sulfuric acid concentration and 800 rev/min stirring rate.

Abdel Basir et al. [13] described the hydrometallurgical recovery of metal values from brass melting slag. Parameters affecting the recovery efficiency such as stoichiometric ratio, solid dross, leachant ratio, temperature, time and pH of the system were investigated. The study showed that the successful recovery of copper, zinc and lead by hydrometallurgical treatment could be achieved using acid and alkali leachants. The results showed that more than 98% by weight of copper, zinc and lead originally present in the slag dissolves in mineral acids and the percentage extraction obtained with acid leaching increases in the order nitric > hydrochloric > sulfuric acid. It was also found that the alkali leachant, ammonium hydroxide/hydrogen peroxide, was an effective leaching agent to selectively leach copper.

In a study carried out by T. Kinoshita et al. [14] the hydrometallurgical recovery of zinc from ashes of automobile tyre wastes was investigated. The study concluded that there was no significant effect of temperature on the leaching process, whereas the concentration of metal in leach liquor increased proportionally with increasing solid/liquid ratio. It was also found that leaching of metals (Zn, Co, Fe, Cu, Al, Mg, Ti and Mn) was suppressed for all the metals as the acid concentration decreases.

Chao-Yin Kuo et al. [15] reported on the removal of copper from industrial sludge by traditional and microwave acid extraction. Several parameters such as the effects of acid concentration, extraction time, sludge particle size and solid/liquid (S/L) ratio on copper removal efficiency were studied. The copper extraction efficiency of microwave acid extraction increased sharply in the first 10 minutes, reaching equilibrium after approximately 20 minutes. The addition of a microwave absorber such as activated carbon promoted extraction and shortened extraction time required to achieve 80% copper extraction efficiency from 20 to 10 minutes. The percentage extraction of copper increased with the acid concentration. The dependence of the efficiency of traditional acid extraction on the acid concentration was noticeable at acid concentrations below 1N.

4.4 EXTRACTION METHODS

Due to the increasing number of analytical samples in modern day applications, such as environmental, pharmaceutical and agricultural, there is a need for developing fast dissolution techniques and clean up procedures in order to increase sample throughput. This is even more important when carrying out trace analysis. For any clean-up procedure to be deemed acceptable, it must pass certain criteria such as being applicable to a wide range of sample types and must be non-matrix dependent. Hawthorne and Majors [16,17] have regarded these techniques as the most tedious, time consuming, and error prone step of an analytical procedure. Therefore, from the economical and environmental point of view, it was necessary to find alternative techniques that can minimise these disadvantages. It was out of this need that the use of microwaves was studied in this work.

Recently, there has been an increasing demand for new extraction techniques, with shortened extraction times and reduced solvent consumption, reducing sample preparation cost. The microwave extraction technique is becoming popular because of its rapidity, simplicity and low cost of operation. Furthermore, it requires a very short time and uses less solvent than other conventional techniques. Microwave heating techniques have been used in analytical chemistry, [18,19] and have found widespread use in very different areas including clinical, food and environmental analysis [20-23]. Microwave technology possesses the capability of partitioning an analyte of interest from the sample matrix to the extractant solvent through the application of microwave energy to heat solvents in contact with a sample to elevated temperatures and pressures, consequently accelerating the mass transfer of target analytes from the sample matrix.

The process of dissolving a solute in a solvent using the microwave technique takes place in several steps. Once the solvent contacts with the solute, a strong intermolecular interaction is formed as the result of an interaction between the solute and solvent molecules; consequently, the solute dissolves. Increasing the temperature of the solvent leads to an increase in its solvating power. When a dynamic equilibrium process is reached between the solute and solvent molecules, the extraction becomes efficient [24].

Microwave heating offers a number of advantages over conventional heating [25]:

- non-contact heating
- energy transfer not heat transfer
- rapid heating
- heats selective materials
- volumetric heating
- quick start-up and stopping
- heating starts from interior of the material body
- higher level of safety and automation, less floor space, higher production rates
- environmentally cleaner.

On the other hand, there are some limitations to microwave techniques

- lack of scalability
- limited applicability
- health and safety hazards relating to the use of microwave heating apparatus.

The application of microwave energy to the samples may be performed using two technologies; closed vessels and open vessels. In closed vessels, the solvent can be heated to a point above the natural boiling point of the solvent at atmospheric pressure thus enhancing both extraction speed and efficiency. While in the open system, extraction proceeds at atmospheric pressure and consequently, the maximum possible temperature is determined by the boiling point of the solvent at that pressure.

4.5 TRANSFER OF THERMAL ENERGY

Transfer of thermal energy in conventional methods occurs in three ways, conduction convection, and radiation from the surface of the material. Energy transfer in solids occurs mainly through conduction while in liquids and gases free movement of particles allows convection of thermal energy to achieve thermal equalisation throughout the material.

During heat transfer, energy is transferred in accordance with thermal gradients, i.e. energy is transferred from areas of high thermal energy to areas of lower thermal energy. In hot plates, there is a considerable temperature difference between the hot plate and the temperature of the solid being treated. As the hotplate is activated, thermal energy is transferred to the material, through conduction and the temperature gradient decreases. Firstly, heat is transferred from the hot plate to the vessel walls through conduction, and then this heat is transferred to the contents of the vessel through the generation of convection currents, Figure 4.1 [26]. In liquids and mobile solids such as fine powders, transfer of thermal energy can be assisted by stirring or circulation.

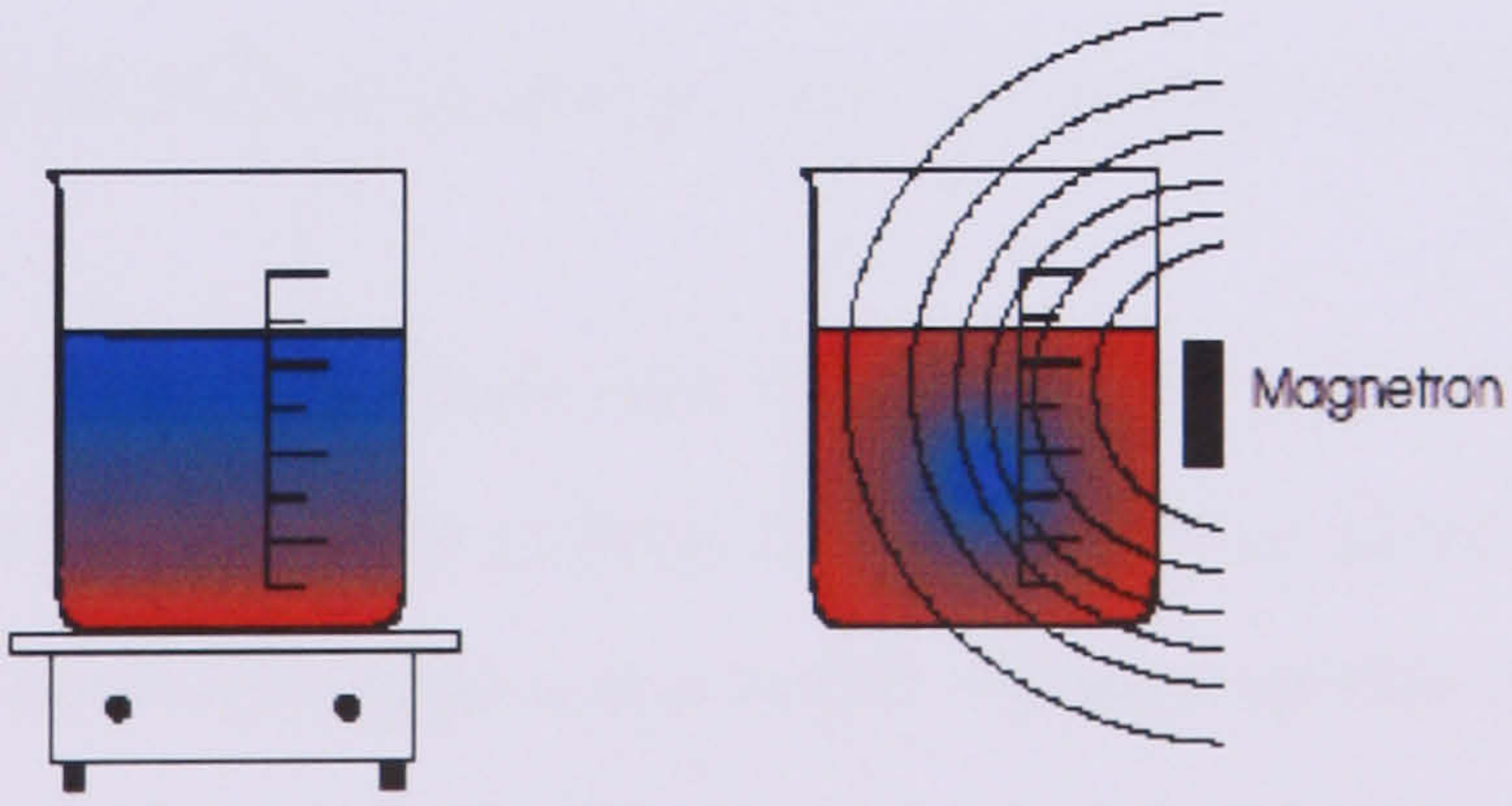


Figure 4.1: Temperature gradient in a liquid heated on a hotplate (left) and in a microwave oven (right). (Colour key: the temperature increases from blue to red)

In such systems, extraction is governed by the average bulk temperature. In microwave energy, the energy is transferred to materials through interaction with the electromagnetic field produced by microwave energy at very high rates of 10^{-9} seconds with each cycle of electromagnetic energy. The kinetic molecular relaxation of this energy is far less than the rate of microwave energy (10^{-5} seconds). This means that the molecules are in a constant state of non equilibrium and are prevented from relaxing. Thus, at high temperature, a greater fraction of the molecules have energy above the activation energy (EA), which is the energy that must be overcome in order for a chemical reaction to start, giving a state of constant energy generation, Figure 4.2. According to the Arrhenius equation, a high fraction of molecules will increase the rate constant making the transfer of heat faster. Therefore, in microwaves, energy can be said to be converted rather than transferred. This difference in the way energy changes occur, gives microwave technology many advantages for the processing of materials over conventional methods [27].

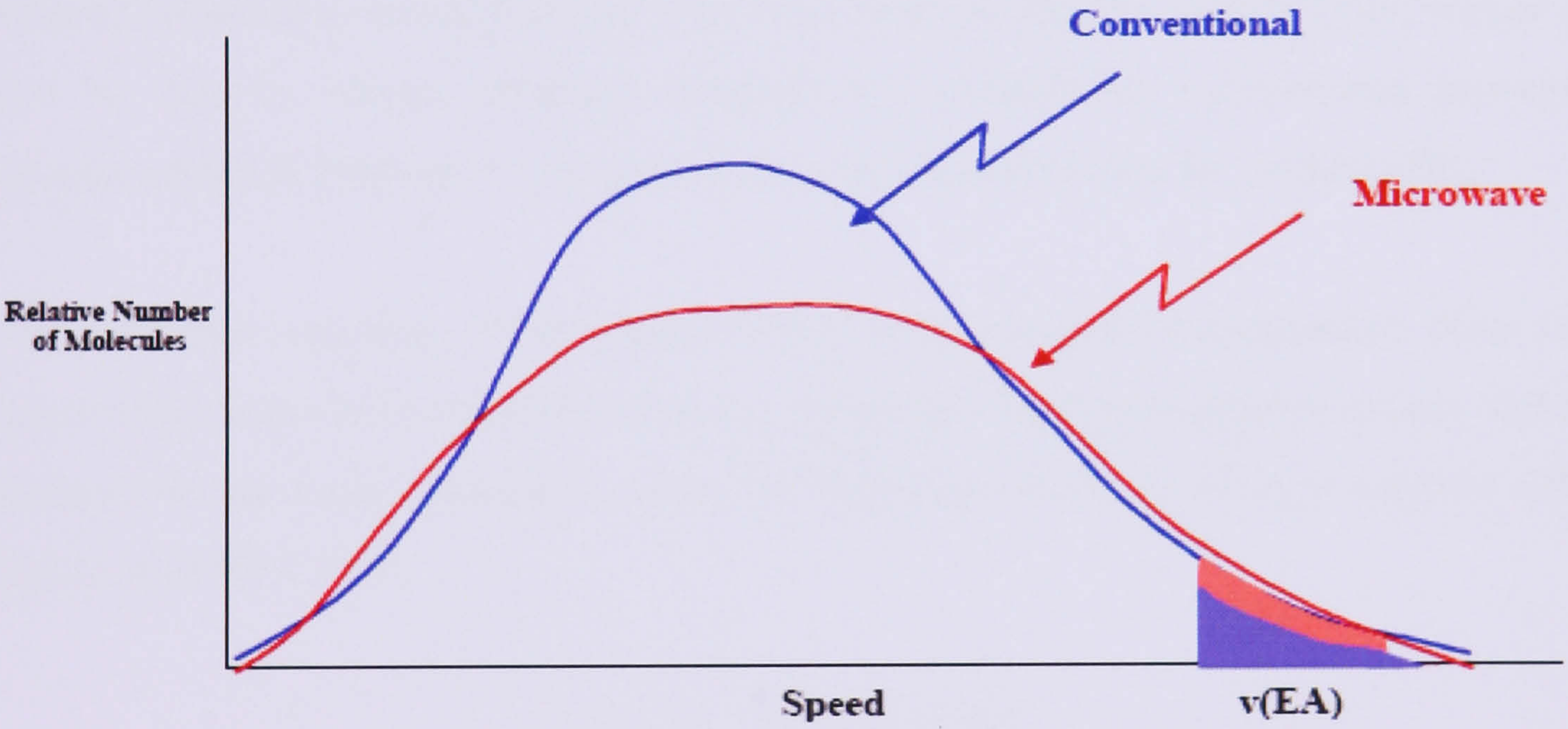


Figure 4.2: Conventional heating versus microwave heating

Since microwaves can penetrate materials and cause energy conversion throughout a material (i.e. microwave allows thermal energy to be converted more homogeneously) rapid heat generation can occur throughout the entire volume of the material. This is a distinct advantage over conventional methods as it is not dependent on energy diffusion from the surfaces and it is therefore possible to achieve rapid, uniform heating of even thick materials. Additionally, traditional heating methods have a cycle time that is controlled by the slow heating rates that are chosen in order to minimise radical and steep thermal gradients that would result in process-induced stresses. In materials such as polymers and ceramics, which have very low thermal conductivity, this can result in drastically reduced processing times. Thus, there is often a balance between processing time and product quality in conventional processing. Since microwaves are able to transfer energy throughout the entire volume of the material, processing time is greatly reduced and the overall quality of the heating is greatly enhanced.

Since microwaves affect molecules with different dipoles differently and will always affect molecules with stronger dipoles, microwaves can be utilised for selective heating of materials. This selective heating allows a more efficient use of energy in processes. For example, in conventional methods of joining ceramics or polymers, energy is wasted in heating up the interface by conduction through the substrates. However microwaves, allow the joint to be heated *in situ*, by incorporating a higher loss material at the interface. In multi phase materials, some phases couple more readily with microwaves, thereby it is possible to process materials with new or unique microstructures by controlling and selectively heating distinct phases. Microwaves may also be able to initiate chemical reactions not possible in conventional processing through selective heating of reactants. Thus, new materials may be created [28].

The Arrhenius equation which explains that with increasing temperature, there is an exponential increase in reaction rate to the extent that there is an approximately 100 fold decrease in the time required to carry out digestion at 175°C when compared with a digestion at 95°C [29].

$$k = Ae^{-Ea/RT}$$

K: rate constant for the reaction of interest

A: is the pre-exponential factor

T: temperature

E_a: activation energy

R: the ideal gas constant.

4.6 PRESSURE AND EXTRACTION

Microwave technique and conventional oven systems are both used to heat samples but they have different effects on the internal pressure of the system. Closed system microwave digestion has a distinct advantage over the hot plate digestion method, in that the microwave system allows higher temperatures to be reached without increasing the internal pressure significantly.

In any closed system, the internal gas pressure is very much dependent on the gas-phase temperature, vessel volume and vessel composition. When water is heated in a steel-jacketed Teflon bomb in a conventional oven, the liquid molecules gain more kinetic energy and evaporate, thereby the rate of evaporation increases and condensation conversely decreases. This results in more of the water being present in the gaseous phase and, therefore, there is an increase in pressure on the vessel walls which ultimately increase the internal pressure of the system. Furthermore, conventional ovens also tend to heat the vessel wall, and thereby maintain water in a gaseous phase i.e. heat the gas, further reducing the condensation rate and increasing the internal temperature.

However, in a microwave-closed vessel, things work differently. For a start the vessel materials are microwave transparent and have a minor insulating capacity, therefore, they remain cold in comparison to the solution during heating, resulting in an increased condensation rate. An increased condensation rate means that there is less gaseous vapour circulating and therefore there is less pressure on the vessels walls (and by extension less internal pressure). Then end result is the achievement of lower internal pressures at high temperatures.

4.7 EXPERIMENTAL DATA VALIDATION

In any analytical process, inevitably, mean values are generated that are different from the true value. This error in generation of an incorrect mean value is due to shortcomings of the analytical method employed, malfunctioning equipment or an error on behalf of the analyst. Due to the high chance of such an error occurring, it is imperative that these uncertainties are kept to an average level by making quantitative estimates of the error in a given measurement. The degree to which a given value varies or 'deviates' from the mean can be measured by a statistical method called standard deviation. Standard deviation measurements permit calculation of the level of uncertainty in a process and since this provides a result that is of the same units as the mean value, a comparison of how far a value is from the mean can be easily undertaken. Standard deviation can be calculated by using the following equation [30].

$$\boxed{S = \sqrt{\frac{\Sigma (x - \bar{x})^2}{n}}}$$

where:

s = Standard Deviation
x = represents the individual measurements
$\bar{x}$ = the mean from a number of measurements
$\sum$ = the Greek capital letter Sigma that means total of or sum of
n = the number of measurements

In a normal distribution, a standard deviation (s) of ±1 encompasses 68.2% of the measurements, S = ±2 encompasses 95.5% of the measurements and S = ±3 account for 99.7% of the measurements, Figure 4.3, [31].

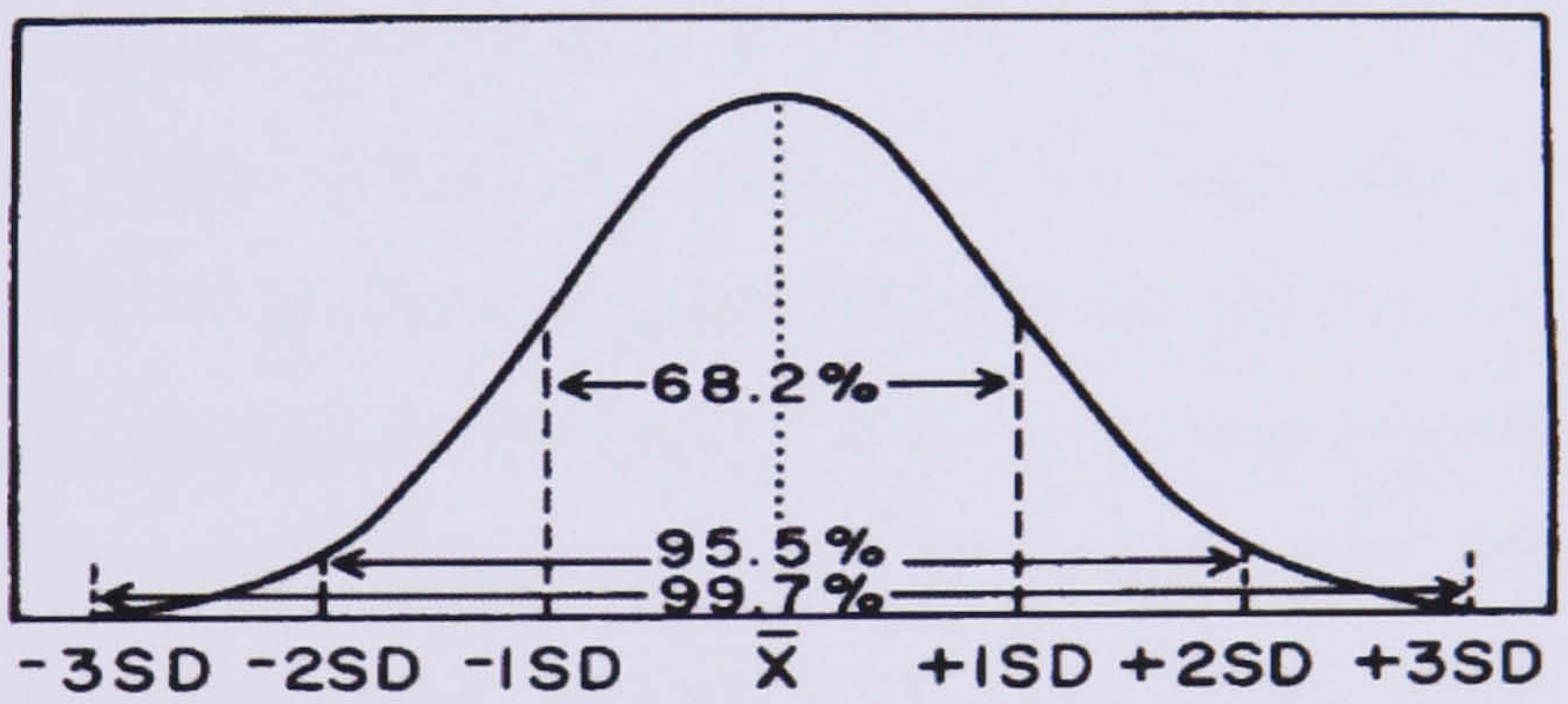


Figure 4.3: Shows normal distribution of the measurements

4.8 EXPERIMENTAL

The experimental part of this work includes the characterisation of the spent catalyst samples, determination of sample composition and optimisation of leaching parameters using the conventional method. The main parameters affecting the leaching process, namely, choice of reagent, sample size, temperature, time, solvent volume and solvent concentration were systematically examined with the conventional method. The obtained results were compared with results from the microwave extraction technique.

4.8.1 Sample Characterisation

Four spent catalyst samples HA01, HA02, HA03 and HA04 were supplied by Amlon Metals limited, United Kingdom. Prior to the extraction process, samples were homogenised to a physical state that provides the extracting medium with a greater surface area per unit mass. Solid samples that are of fine particle size can be extracted more rapidly than samples with larger surface area. There are several methods to reduce sample particle size, namely, chopping, cutting, blending, grinding, homogenizing, macerating, pulverizing and sieving. The samples in this work were homogenised by grinding them to a very fine powder using a Fritsch ball mill (Planetary Mono Mill, Pulverisette 6) and later dried at 80°C for 24 hours and stored for the subsequent tests. The samples were characterised by means of X-ray fluorescence (XRF) to identify the elemental composition of each sample and X-ray diffraction (XRD) to determine the crystalline phases present. Both XRF and XRD techniques are used for qualitative, not quantitative analysis.

4.8.2 Determination of Sample Composition

In order to find out the percentage composition of metal present in each spent catalyst sample, 2 g of each sample was mixed with 100 cm^3 of *aqua regia* (1 HNO_3: 3 HCl) in four separate flange flasks of 0.5 dm^3 capacity. Each flask was later placed on a hot plate and stirred for four hours at a constant temperature of 75°C. The leachate obtained was filtered through an ashless Whatman filter paper and transferred to a 200 cm^3 volumetric flask and made up to the mark with deionised water. Further dilutions were made to make the sample solution suitable for measuring the concentration of each of the metals present using AAS.

4.8.3 Conventional Acid Extraction Procedure

Conventional acid extraction has been one of the most employed methods for the extraction of interested analytes from different matrixes [32]. The experimental set up for the extraction of the analytes of interest is given in Figure 4.4. It comprises of a closed flange glass vessel fitted with a thermometer, water condenser and a hot plate fitted with a magnetic stirrer. A magnetic follower was used for continuous stirring of the sample over the entire extraction period.

The development and optimization of parameters of extraction that influence recoveries namely, reagent type, sample size, temperature, time, acid volume and acid concentration were studied, with the objective of choosing the best extraction conditions.

Reagent of Choice

The main aim of these experiments was to determine the best leaching solution that would give optimal extraction efficiency for the given analytes. Samples were leached using different kinds of leach solutions such as HNO_3 69% (w/w), HCl 32% (w/w) and H_2SO_4 98% (w/w) at fixed concentration 3 mol dm^{-3}. 2 g of sample was mixed with 100 cm^3 of the leach solution in a 0.5 dm^3 flange flask. Then the flask was placed on a hot plate for four hours at 75°C. The mixture was stirred using a magnetic stirrer. The leachate obtained was filtered through an ashless Whatman filter paper and transferred to a 200 cm^3 volumetric flask and made up to the mark with deionised water. In these experiments, the leaching solution acted as the variable and all of the other parameters were kept constant.

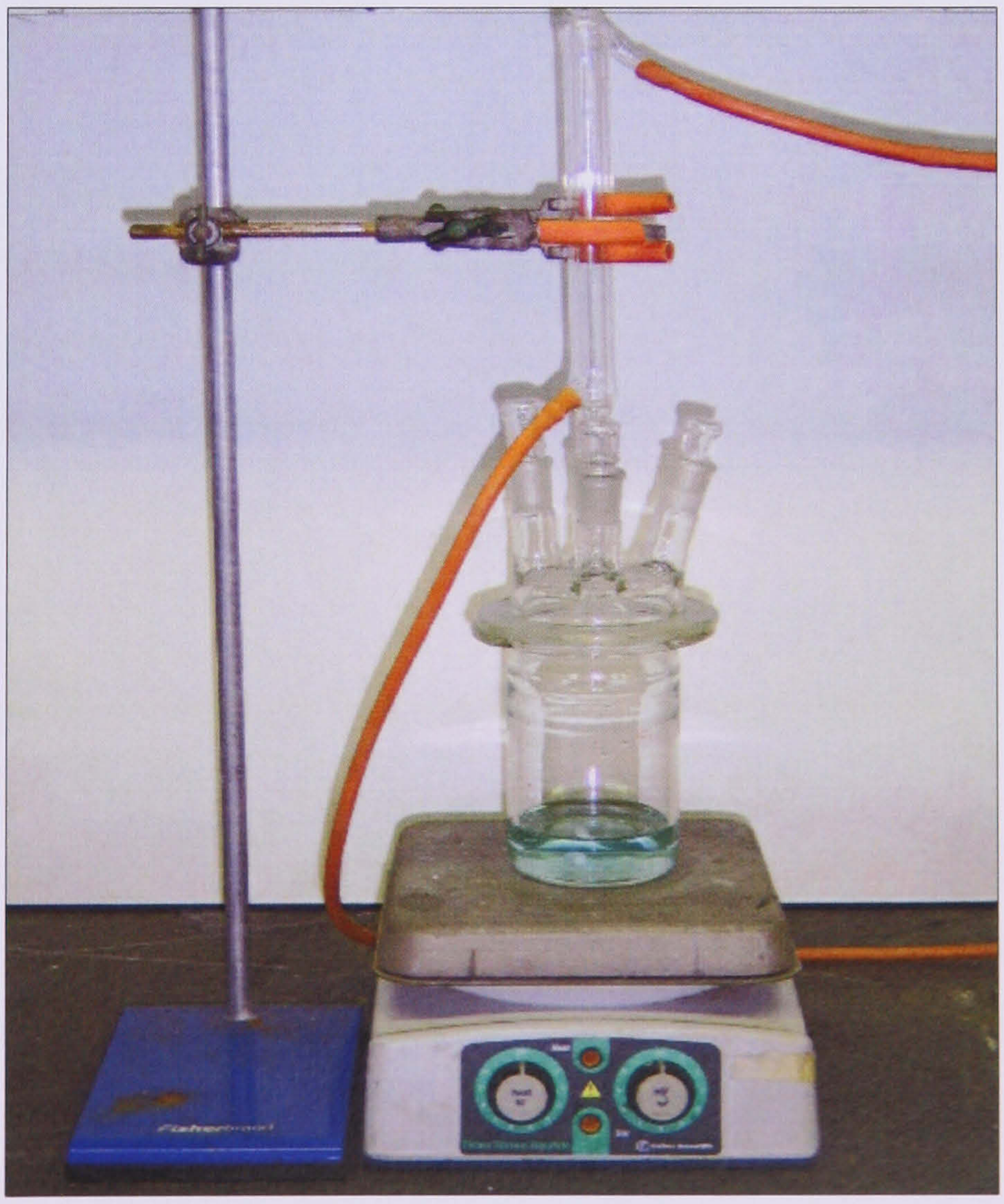


Figure 4.4: A photo of the apparatus setup for metal leaching

Sample Mass

Set of experiments were carried out to investigate the effect of sample weight in the extraction process. In these experiments the mass was varied to determine the appropriate sample weight. Four different amounts, 0.5, 1, 1.5 and 2 g, were used. Only mass was varied, all other parameters were constant.

Extraction Temperature

The effect of temperature on metal extraction was performed at four different temperatures 25, 50, 75 and 100°C, while all other parameters were kept constant.

Extraction Time

The fourth set of experiments was carried out to identify the most suitable extraction time. The times used were 1, 2, 3 and 4 hours. The other parameters were kept constant.

Extraction Solution Volume

The effects of changing the solid:liquid (S/L) phase ratio were studied for the extraction of the metals. In these experiments the volume of the leaching solution was varied 25, 50, 75 and 100 cm^3. All other variables were kept constants.

Leach Solution Strength

The effect of acid concentration on the extraction of the metals was studied. The final experiments were aimed at varying the strength of the leach liquor while maintaining all other parameters constant. Four different concentrations were selected 1, 2, 3 and 4 mol dm^{-3}.

4.8.4 Extraction in the Microwave Accelerated Reaction System

Effect of Temperature and Acid Concentration

1 g of sample was weighed accurately directly into the microwave reaction vessel and 25 cm^3 of sulfuric acid diluted to three different molarities, 0.5, 1 and 2 mol dm^{-3}, were added to the sample (in separate experiments). The top of the reaction vessel was screwed on and hand-tightened. The extraction vessel was later housed in the support module which in turn was placed on the carousel and the safety door shut. A built-in control computer was used to specify the extraction programme to control the

microwave and hold a library of samples and methods. The microwave was set to reach the selected temperature 50, 100, 125, 150 and 175°C in 10 minutes, and hold at that temperature for 10 minutes.

Effect of Extraction Time

1 g of sample was weighed directly into the microwave reaction vessel and 25 cm^3 of sulfuric acid diluted to different molarities, 0.5, 1 and 2 mol dm^{-3}, were added to the sample (in separate experiment). The microwave was set to reach 150°C in 10 minutes and hold at that temperature for selected times 5, 10 and 15 minutes.

There was a cooling down period of 30 minutes in all the extractions carried out using microwave extraction technique.

All extractions were conducted in triplicate as a minimum to achieve reproducibility and the results presented are averages of the measurements. Metal determination in the extracts was carried out by means of a Perkin-Elmer AAS model 2380. Hollow cathode lamps were used as radiation sources. The resonance lines employed were 324.8, 240.7, 232.0, 248.3, 217.0, and 213.9 nm for Cu, Co, Ni, Fe, Pb and Zn, respectively. Lamp intensity and band pass width were used according to the manufacturer's recommendations.

Ready made stock metal solutions (1000 mg dm^{-3}) for AAS were used. Standard calibration solutions were prepared daily by appropriate dilution of the stock solutions. The mean value and the standard deviation of replicates are indicated in all the tables. The results are expressed as the amount of metal extracted as a percentage of the amount used in each experiment.

4.9 RESULTS

4.9.1 Sample Characterisation

The resulting spectra of the analysis by X-ray fluorescence (XRF) and X-ray diffraction (XRD) of the four industrial spent catalyst samples are shown in Figures 4.5 – 4.6 (a. b, c, d and e). The X-ray fluorescence data show the presence of copper and zinc in samples HA01 and HA02, nickel, iron, copper and zinc in sample HA03 and cobalt, copper, zinc, nickel, iron and lead in sample HA04. The XRD spectra of the as supplied samples have confirmed the presence of metal oxides mainly.

4.9.2 Determination of Sample Composition

The elemental composition of the solid samples used in this study was determined (See section 4.8.2 for procedure) and the results are summarised in Table 4.1. It is noted that the amounts of copper and zinc are significant in sample HA01, HA02 and HA04 but they are below 1% in sample HA03. Nickel and iron are the major metallic ions present in sample HA03 and their percentage composition are 19.1% and 1.5% respectively. Sample HA04 contains, in addition to copper and zinc, other metal and the percentage composition of cobalt, nickel, iron and lead are 9.7%, 3.5%, 4.9% and 35% respectively.

Table 4.1: Elemental composition of the spent catalyst samples with standard deviation

Sample	**Cu%**	**Zn%**	**Co%**	**Ni%**	**Fe%**	**Pb%**
HA01	41.2 ± 1.3	12.8 ± 1.4				
HA02	23.6 ± 1.8	50.7 ± 1.4				
HA03	0.60 ± 0.1	0.60 ± 0.1		19.1 ± 1.1	1.5 ± 0.4	
HA04	11.3 ± 1.5	9.3 ± 1.2	9.7 ± 1.6	3.5 ± 0.5	4.9 ± 1.0	35.0 ± 1.8

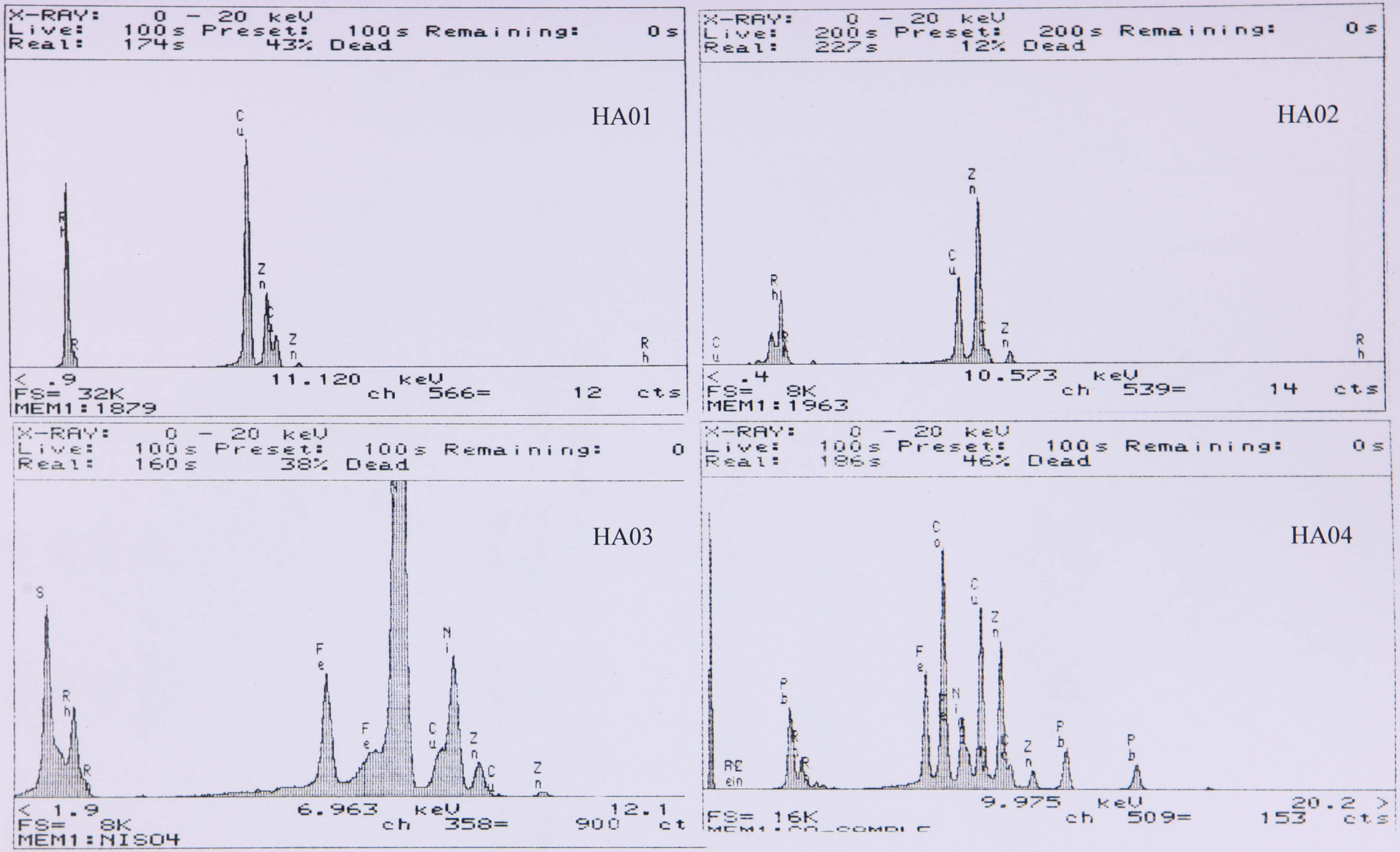


Figure 4.5: X-ray fluorescence spectra of sample HA01, HA02, HA03 and HA04

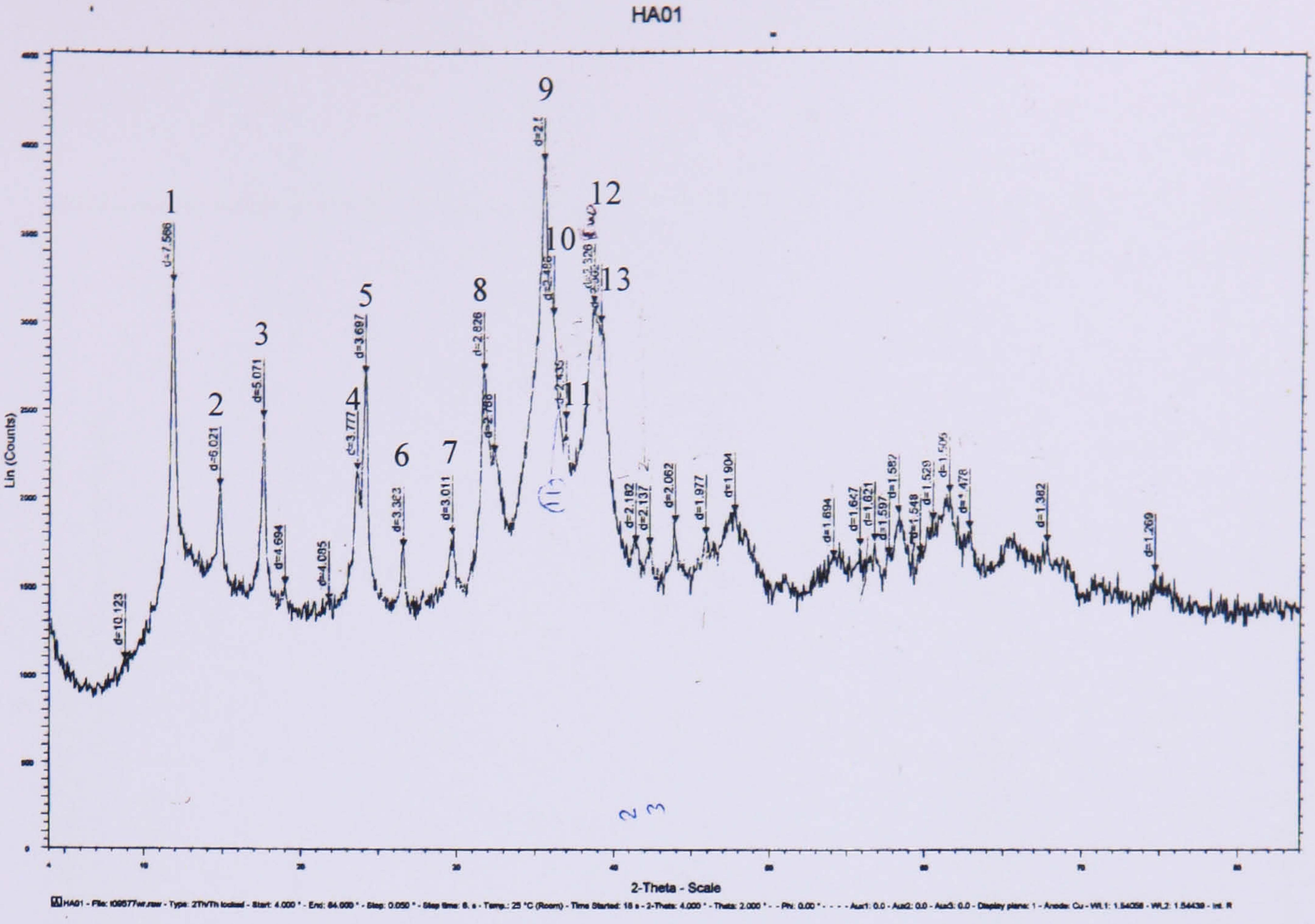


Figure 4.6a: X-ray diffraction spectrum of sample HA01

X-ray diffraction data for sample HA01

No	Angle	D space	Relative intensity	Peak Identity	Identity D space
1	11.9	7.566			
2	14.9	6.021			
3	17.5	5.071			
4	23.6	3.777			
5	24.2	3.697			
6	26.5	3.363			
7	29.4	3.011			
8	31.5	2.826	40	$CuAlO_2$	2.820
9	35.8	2.529	100	CuO	2.520
10	36.2	2.486	100	ZnO	2.480
11	36.8	2.435	100	Cu_2O	2.430
12	38.7	2.326			
13	39.2	2.302	20	ZnO	2.300

Figure 4.6b: X-ray fluorescence spectrum of sample HA01

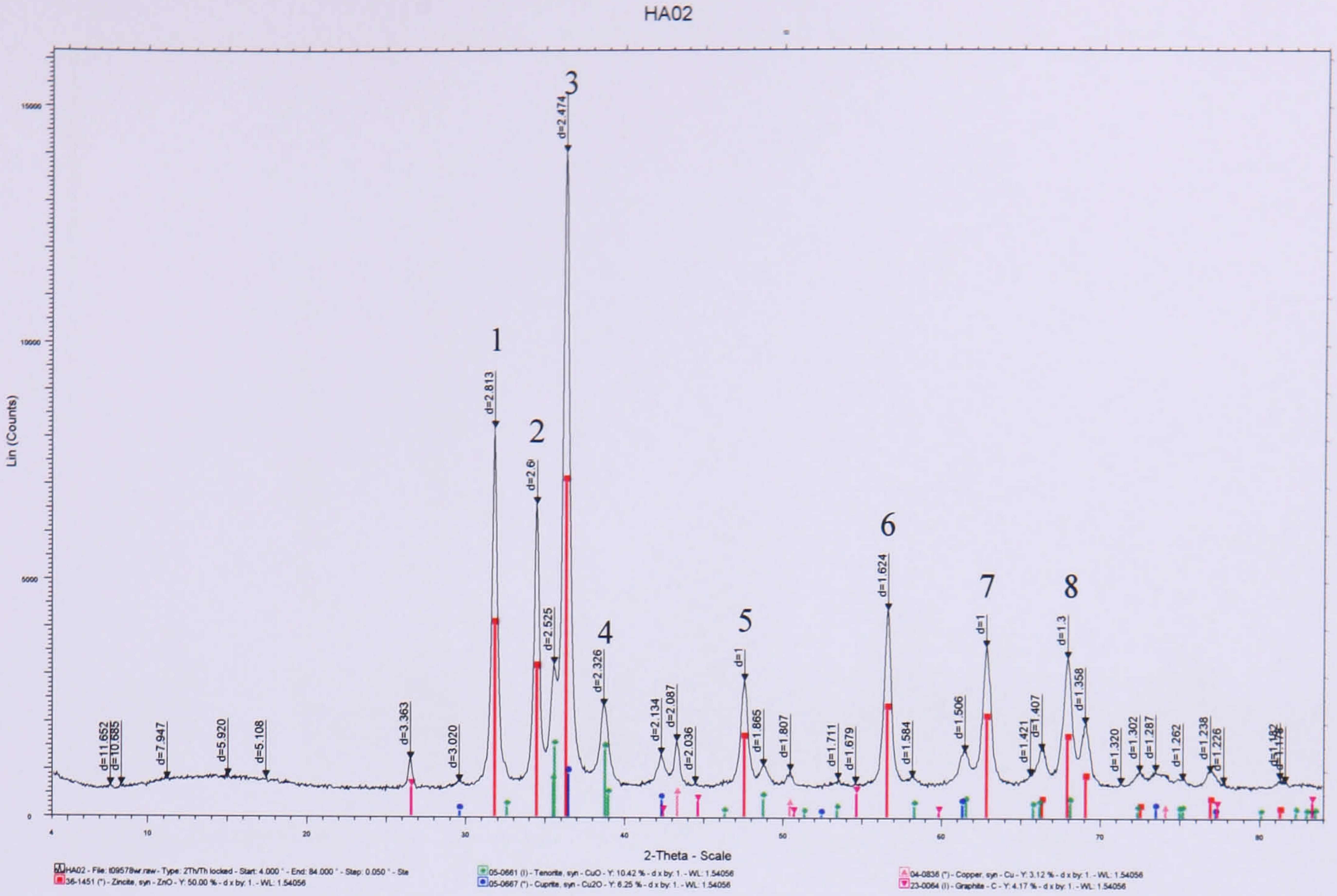


Figure 4.6c: X-ray diffraction spectrum of sample HA02

X-ray diffraction data for sample HA02

No	Angle	D space	Relative intensity	Peak Identity	Identity D space
1	31.8	2.813	57	ZnO	2.814
2	34.5	2.602	44	ZnO	2.603
3	36.3	2.474	100	ZnO	2.475
4	38.8	2.326			
5	47.5	1.910	23	ZnO	1.911
6	56.6	1.624	32	ZnO	1.624
7	63.9	1.477	75	Cu_2O	1.486
8	67.9	1.378	23	ZnO	1.378

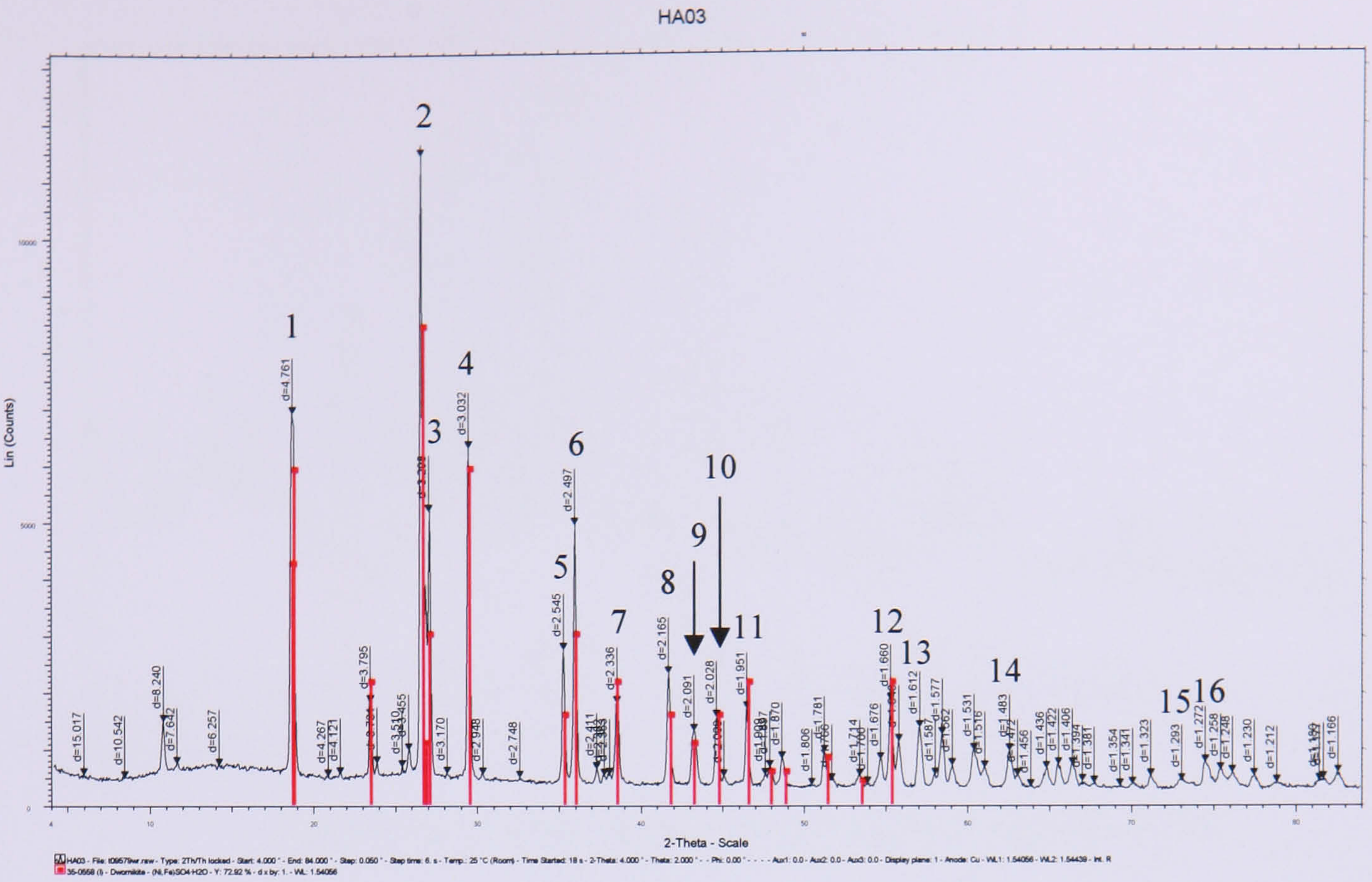


Figure 4.6d: X-ray diffraction spectrum of sample HA03

X-ray diffraction data for sample HA03

No	Angle	D space	Relative intensity	Peak Identity	Identity D space
1	18.8	4.761			
2	26.8	3.358	80	$NiSO_4$	3.560
3	27.2	3.298			
4	29.4	3.032			
5	35.3	2.545	20	Fe_2O_3	2.548
6	36.1	2.497	80	FeO	2.490
7	38.7	2.336	100	$Ni(OH)_2$	2.330
8	41.8	2.165			
9	43.2	2.091	100	NiO	2.090
10	44.8	2.028	100	NiO	
11	46.6	1.951			
12	55.4	1.660	40	Fe_2O_3	1.660
13	58.2	1.577	90	ZnO	1.570
14	62.5	1.483	75	Cu_2O	1.486
15	74.5	1.272	50	Cu_2O	1.274
16	75.3	1.258	80	Cu_4O_3	1.250

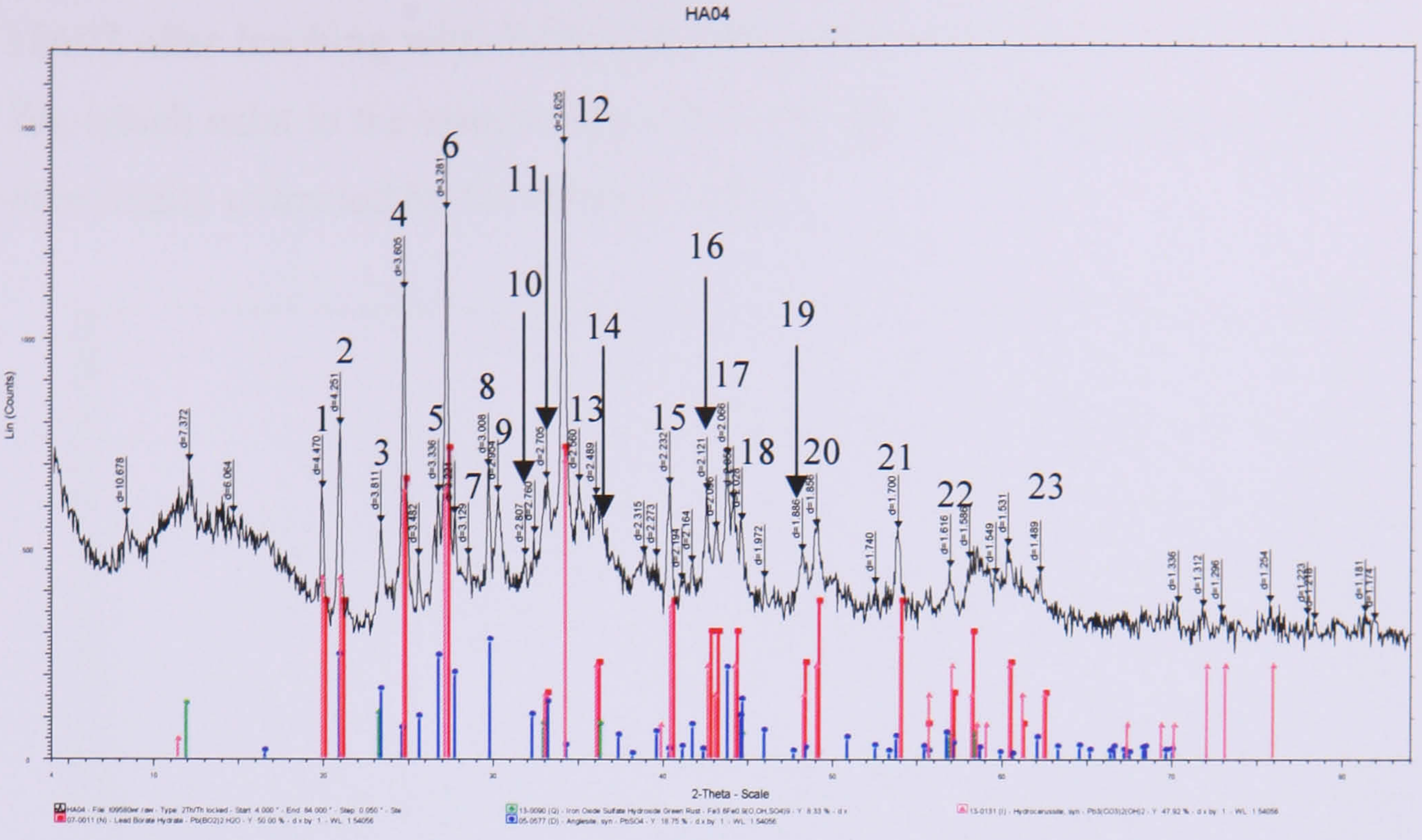


Figure 4.6e: X-ray diffraction spectrum of sample HA04

X-ray diffraction data for sample HA04

No	Angle	D space	Relative intensity	Peak Identity	Identity D space
1	20.2	4.470			
2	21.0	4.251	80	$Zn(OH)_2$	4.25
3	23.3	3.811	20	pbO	3.819
4	24.8	3.605	100	Fe_2O_3	3.60
5	26.8	3.336			
6	27.5	3.281	100	$Zn(OH)_2$	3.28
7	28.3	3.129	100	pbO	3.13
8	29.8	3.008	60	Fe_2O_3	3.00
9	30.7	2.954	92	pb_2O_3	2.956
10	31.8	2.807	100	pbO_2	2.80
11	33.1	2.705	80	$pb(OH)_2$	2.70
12	34.2	2.625	70	pbO_2	2.630
13	35.5	2.560			
14	36.2	2.489	80	FeO	2.486
15	40.7	2.232			
16	42.8	2.121	100	CoO	2.121
17	43.9	2.066			
18	44.0	2.028	50	Cu_2O	2.02
19	48.4	1.886			
20	49.2	1.856	50	pbO_2	1.86
21	54.2	1.700	50	$ZnCO_3$	1.70
22	57.0	1.616	25	Cu_2O	1.617
23	62.1	1.489	75	Cu_2O	1.486

Figure 4.7 shows the X-ray fluorescence spectrum carried out on the residue left from sample HA02 after leaching with H_2SO_4. It can be seen from the spectrum that neither Cu nor Zn, which exist in the sample, are left in the residue and this means that the two metals were totally extracted by the method used.

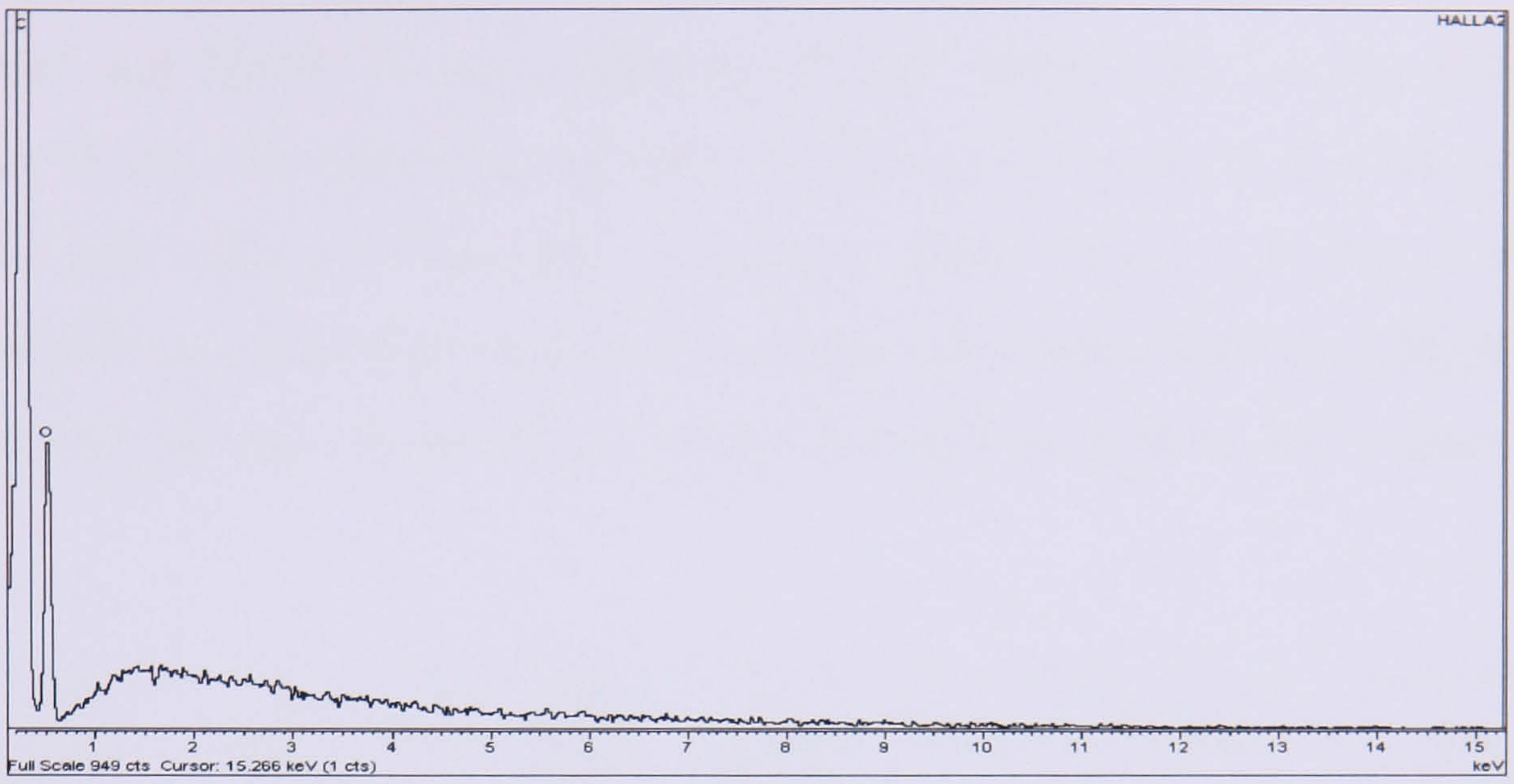


Figure 4.7: X-ray fluorescence spectrum of sample HA02 after leaching with H_2SO_4

4.9.3 Conventional Acid Extraction Procedure

4.9.3.1 Extraction Reagent

Experiments were carried out using 3 mg dm^{-3} of HNO_3, HCl and H_2SO_4 to investigate the effects of leaching media suitable to extract maximum metals. The variable parameter in this experiment was the extraction reagent. The fixed parameters in this set of experiments were 2 g of sample, 75°C temperature, 4 hours extraction time and 100 cm^3 of extraction liquor.

The results in Table 4.2 show that the three acids extracted nearly the same amount of copper from sample HA01, HA02 and HA04. While in sample HA03 nitric acid extracted 98.1% of copper present in the sample compared to 95.5% and 96.9% by HCl and H_2SO_4 respectively.

In sample HA01 the amounts of zinc extracted by nitric acid was equal to the amount extracted by sulfuric acid 96.5% and 95.9% respectively and both were less than the amount extracted by hydrochloric acid 98.9%. Hydrochloric acid was able to extract 98.5% of zinc from sample HA02 and this is slightly higher than the amount extracted by nitric and sulfuric acids 97.0% and 96.1% respectively. The extraction of zinc from sample HA03 was in the order of HCl > $HNO_3 \geq H_2SO_4$ as 98.3%, 95.5% and 94.8% respectively. It was noticed that the highest amount of zinc extracted in sample HA04 was by hydrochloric acid 98.6%.

The three leach liquors were able to extract nearly the same amount of nickel from sample HA03 and HA04. In the extraction of lead, HNO_3 was considerably better extractant as 98.0% was extracted, and HCl 73.7% and H_2SO_4 0.1% and this is due to the fact that lead sulfate is insoluble in sulfuric acids. Figure 4.8 shows the XRF spectrum carried out on the residue left from sample HA04 after leaching with H_2SO_4, it can be seen that the only metal shown in the spectrum is lead which is insoluble in H_2SO_4.

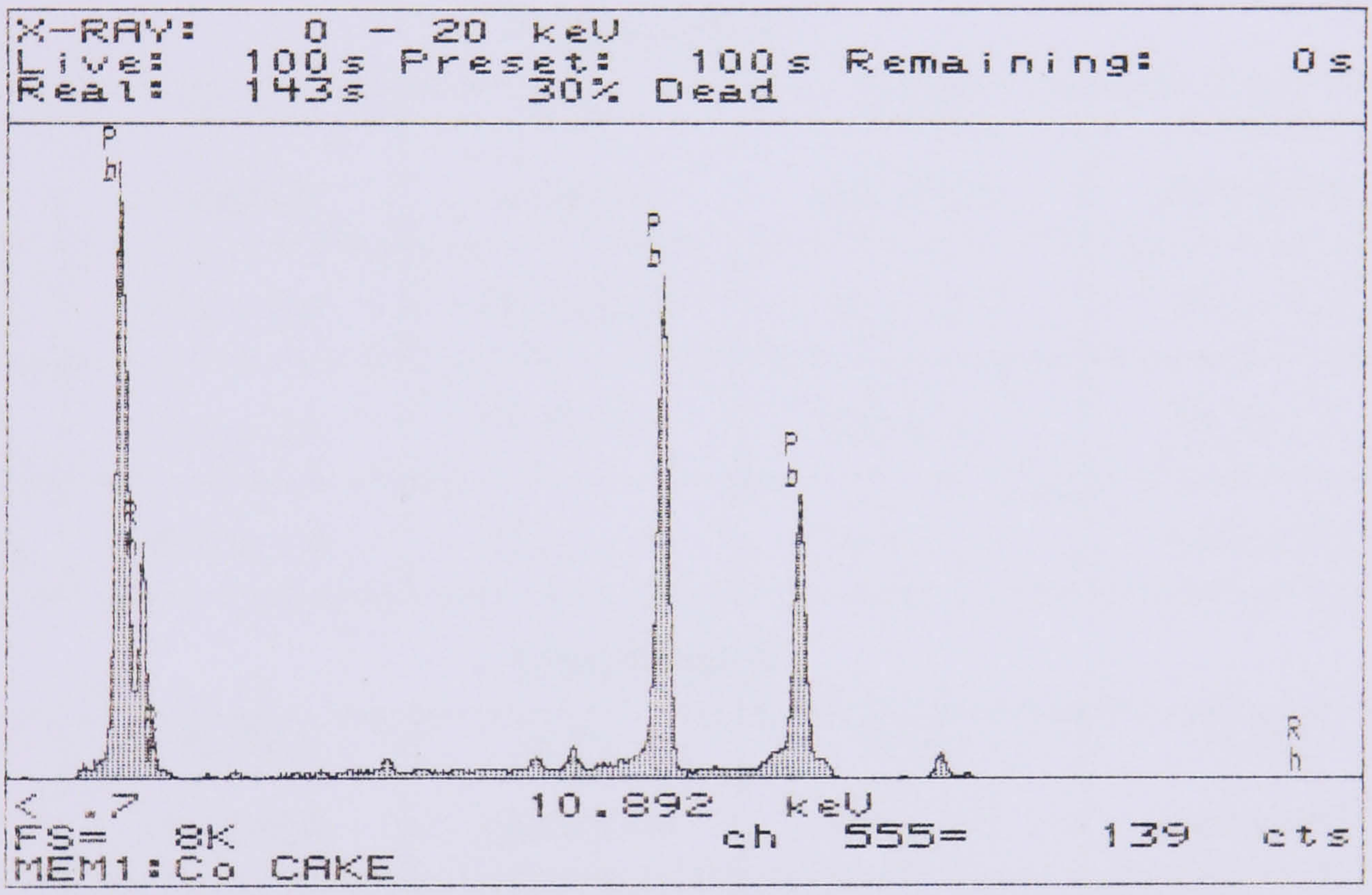


Figure 4.8: X-ray fluorescence spectrum of residue for sample HA04 after leaching with H_2SO_4

Changing the acid solution had no effect on the extraction of iron from sample HA03 and HA04. The order of extracting cobalt from sample HA04 was $HCl \geq HNO_3 > H_2SO_4$ 97.7%, 97.1% and 95.7% respectively. Despite of the fact that sometimes sulfuric acid extracted slightly less amount of metal of interest than the other two leach media, it was selected as an extraction medium due to its environmental and economical advantages. In many hydrometallurgical processes, sulfuric acid has been selected as the cheapest and the most effective leachant [27,33]. The use of HNO_3 and HCl leach solutions were ruled out, mainly to avoid the production of nitrogen oxides and chlorine.

Table 4.2: Extraction of metals using different extraction solutions by conventional method

Solvent	Sample HA01		Sample HA02	
	% Cu extracted	% Zn extracted	% Cu extracted	% Zn extracted
HNO_3	97.1 ± 1.5	96.5 ± 2.0	97.8 ± 1.0	97.0 ± 1.1
HCl	96.0 ± 0.7	98.9 ± 1.0	96.6 ± 1.2	98.5 ± 1.4
H_2SO_4	96.1 ± 1.1	95.9 ± 1.6	96.7 ± 0.6	96.1 ± 0.8
Sample HA03				
	% Ni extracted	% Fe extracted	% Cu extracted	% Zn extracted
HNO_3	97.8 ± 1.6	98.5 ± 0.5	98.1 ± 0.9	95.5 ± 0.7
HCl	96.4 ± 2.1	97.0 ± 0.6	95.5 ± 1.1	98.3± 1.1
H_2SO_4	96.6 ± 1.0	97.3 ± 1.1	96.9 ± 1.5	94.8 ± 1.2
Sample HA04				
	% Co extracted	% Cu extracted	% Zn extracted	% Ni extracted
HNO_3	97.1 ± 0.8	98.5 ± 0.7	95.1 ± 2.3	97.8 ± 1.8
HCl	97.7 ± 1.1	96.1 ± 1.9	98.6 ± 0.8	97.0 ± 2.9
H_2SO_4	95.7 ± 1.6	97.3 ± 0.9	95.9 ± 0.5	97.0 ± 1.5
	% Fe extracted		% Pb extracted	
HNO_3	98.4 ± 1.3		98.0 ± 1.0	
HCl	96.8 ± 0.9		73.7 ± 1.8	
H_2SO_4	97.1 ± 2.1		0.1 ± 0.0	

2 g of sample, 75°C, 4 hours, 100 cm^3 of 3 mol dm^{-3} solution concentration

4.9.3.2 Sample Size

The effect of sample weight (ranging 0.5 – 2.0 g) on the extraction process for all metals was investigated. The data in Table 4.3 show that changing the sample size for all four samples had no effect on the extraction of different metal ions. Consequently, it was decided to use 1 g of sample in each extraction process during all the extractions.

4.9.3.3 Extraction Temperature

The effect of temperature on the extraction of metals was studied by performing experiments at 25, 50, 75 and 100°C.

The extraction of almost all of the metals was relatively low at ambient temperature. This could be due to the fact that, at low temperatures, not many of the reactant molecules have enough kinetic energy to break the bonds in the solid matrix. When temperature of the reaction is increased to 50°C and 75°C, the rate of the extraction is also increased and the necessary energy would be provided to accomplish the extraction completely.

It can be seen from the results in Table 4.4 that higher temperatures than ambient resulted in faster rates of leaching and in larger amounts being extracted for all metals studied. High solution temperatures increase extraction efficiency and thus reduce extraction time. Therefore, the selection of an appropriate temperature is crucial for the migration of compounds from the sample matrix into the solution. Copper and zinc extraction were similar as their extraction increased with increase the temperature of the reaction till reaches 50°C and no further extraction was obtained in HA01, HA02 and HA03 samples. While in sample HA04 both metals copper and zinc extraction increases with increase the temperature till reaches 75°C.

Increasing temperature played a considerable role in nickel extraction from sample HA03 as the percentage extracted was increased from 81.1% to 93.9% and to 95.9% when temperature was increased from 25 °C to 50°C and to 75°C. Further increase had no more effect on the extraction process. This is in agreement with the results obtained by Ivascanu and Roman [34] in which 99% of nickel was recovered from a spent nickel catalyst by leaching with 80% sulfuric acid at a reaction temperature of 70°C in 55 minutes.

Table 4.3: Extraction of metals using different sample size by conventional method

Weight (g)	Sample HA01		Sample HA02	
	% Cu extracted	% Zn extracted	% Cu extracted	% Zn extracted
0.5	95.8 ± 1.7	95.6 ± 1.8	95.3 ± 1.7	95.5 ± 1.2
1.0	96.9 ± 0.7	95.8 ± 1.3	96.2 ± 1.2	96.8 ± 1.3
1.5	96.5 ± 1.7	96.2 ± 2.6	96.7 ± 1.2	96.9 ± 0.9
2.0	95.7 ± 1.1	95.9 ± 1.6	96.7 ± 0.6	96.1 ± 0.8
Sample HA03				
	% Ni extracted	% Fe extracted	% Cu extracted	% Zn extracted
0.5	95.9 ± 1.5	96.1 ± 1.8	95.3 ± 1.6	93.1 ± 1.5
1.0	95.9 ± 1.8	97.2 ± 1.6	95.7 ± 1.8	94.3 ± 2.9
1.5	96.1 ± 1.4	97.0 ± 1.3	96.0 ± 1.0	94.5 ± 1.7
2.0	96.6 ± 1.0	97.3 ± 1.1	96.9 ± 1.5	94.8 ± 1.2
Sample HA04				
	% Co extracted	% Cu extracted	% Zn extracted	% Ni extracted
0.5	95.0 ± 1.6	97.0 ± 1.9	95.6 ± 1.6	97.8 ± 1.2
1.0	94.9 ± 0.8	97.5 ± 0.6	96.9 ± 0.9	97.8 ± 1.4
1.5	95.4 ± 1.8	97.4 ± 1.6	95.9 ± 1.2	97.6 ± 1.6
2.0	95.7 ± 1.6	97.3 ± 0.9	95.9 ± 0.5	97.0 ± 1.5
	% Fe extracted			
0.5	96.5 ± 1.4			
1.0	97.2 ± 1.4			
1.5	96.1 ± 1.3			
2.0	97.1 ± 2.1			

75°C, 4 hours, 100 cm^{3} of 3 mol dm^{-3} solution concentration

Table 4.4: Extraction of metals using different temperatures by conventional method

Temperature (°C)	Sample HA01		Sample HA02	
	% Cu extracted	% Zn extracted	% Cu extracted	% Zn extracted
25	83.6 ± 0.7	86.5 ± 2.3	87.9 ± 1.2	90.5 ± 1.7
50	96.1 ± 1.6	95.1 ± 1.7	95.5 ± 1.8	96.1 ± 1.3
75	96.9 ± 0.7	95.8 ± 1.3	96.2 ± 1.2	96.8 ± 1.3
100	97.0 ± 1.5	96.3 ± 2.4	96.6 ± 2.3	96.4 ± 2.3
Sample HA03				
	% Ni extracted	% Fe extracted	% Cu extracted	% Zn extracted
25	81.1 ± 1.7	95.6 ± 1.9	88.5 ± 2.8	75.0 ± 2.5
50	93.9 ± 1.8	96.6 ± 1.3	94.3 ± 1.4	94.0 ± 1.8
75	95.9 ± 1.8	97.2 ± 1.6	95.7 ± 1.8	94.3 ± 2.9
100	96.9 ± 1.4	97.1 ± 1.3	96.5 ± 1.2	94.0 ± 2.5
Sample HA04				
	% Co extracted	% Cu extracted	% Zn extracted	% Ni extracted
25	85.5 ± 2.1	77.8 ± 3.1	88.6 ± 1.7	79.4 ± 2.0
50	91.1 ± 1.0	91.4 ± 1.1	93.7 ± 0.5	97.1 ± 1.2
75	94.9 ± 0.8	97.5 ± 0.6	96.9 ± 0.9	97.8 ± 1.4
100	95.9 ± 1.1	96.4 ± 1.3	97.4 ± 1.6	97.1 ± 1.2
	% Fe extracted			
25	88.1 ± 2.3			
50	96.2 ± 1.0			
75	97.2 ± 1.4			
100	97.7 ± 1.7			

1 g of sample, 4 hours, 100 cm^3 of 3 mol dm^{-3} H_2SO_4

The percentage extraction of nickel from sample HA04 was increased from 79.4% to 97.1% when the extraction temperature was raised from 25°C to 50°C. Further increase in the extraction temperature had no significant influence on the percentage of nickel extracted.

Iron was the only metal in sample HA03 which was not affected by the increase in extraction temperature as 95.6% was extracted at 25°C and no advantage was achieved by increasing the temperature to 50°C. While iron in sample HA04 behaved differently as the extraction at 25°C yielded 88.1% and this value increased to 96.2% as the temperature was increased to 50°C. Further increase had no influence in the extraction process.

The extraction of cobalt was influenced by the reaction temperature. Increasing the extraction temperature had a profound effect on the extraction of cobalt as the percentage extracted was increased from 85.5% to 91.1% and to 94.9% when temperature was increased from 25°C to 50°C and to 75°C.

4.9.3.4 Extraction Time

It is possible to say from the results in Table 4.5 that the reaction time between the solid and liquid phase seems to be a relevant parameter in leaching copper and zinc, 1 hour seeming to be enough for the systems to achieve equilibrium. Indeed, for both metals, their dissolution by sulfuric acid solutions is completed within about 1 hour.

The results in Tables 4.6 - 4.8 indicate that some of the metals behaved similarly as they were extracted less in the first hour and gradually increased in the second hour. During the first two hours of the extraction the leaching rate increases, since the concentration of the product increases with time as the concentration of the reactant decreases. It, therefore, appeared that extraction time has a profound effect on the release of metals from the solid samples within the first two hours. Prolonging the contact time to more than two hours led to no further enhancement in the extraction of majority of the metals. The result is in agreement with those results obtained by other researchers [19].

Table 4.5: Effect of leaching time on the extraction of metals from sample HA01 using a conventional method

Time (hour)	% Cu extracted	% Zn extracted
1	96.7 ± 1.8	94.3 ± 1.3
2	96.6 ± 1.0	94.7 ± 1.9
3	96.9 ± 1.2	95.4 ± 1.8
4	96.1 ± 1.6	95.1 ± 1.7

1 g of sample, 50°C, 100 cm^3 of 3 mol dm^{-3} H_2SO_4

Nickel was extracted more from sample HA03 and HA04 when the extraction time was extended as 90.5% and 91.5% were extracted in the first hour and increased to 94.7% and 97.1% in the second hour, respectively. Prolonging the extraction time is accompanied by a noticeable increase in the nickel extraction which means that nickel extraction is a rate process depending on the time of the reaction.

Table 4.6: Extraction of metals from sample HA02 using different times by conventional method

Time (hour)	% Cu extracted	% Zn extracted
1	95.8 ± 1.3	95.8 ± 0.6
2	95.8 ± 1.5	95.7 ± 1.3
3	95.5 ± 1.7	95.8 ± 1.7
4	95.5 ± 1.8	96.1 ± 1.3

1 g of sample, 50°C. 100 cm^3 of 3 mol dm^{-3} H_2SO_4

Table 4.7: Extraction of metals from sample HA03 using different times by conventional method

Time (hour)	% Ni extracted	% Fe extracted
1	90.5 ± 1.5	96.6 ± 1.1
2	94.7 ± 1.3	97.6 ± 1.4
3	94.6 ± 1.6	97.6 ± 1.1
4	93.9 ± 1.8	97.2 ± 1.6
	% Cu extracted	% Zn extracted
1	93.5 ± 1.8	94.3 ± 1.6
2	95.4 ± 1.5	94.3 ± 1.3
3	96.2 ± 2.9	94.6 ± 1.8
4	93.9 ± 1.8	94.0 ± 1.8

1 g of sample, 50°C, 100 cm^3 of 3 mol dm^{-3} H_2SO_4

Prolonging the extraction time played no role in the extraction of iron as 96.6% was extracted in the first hour and 97.6% in the third hour from sample HA03 and 96.2% in the first hour and 96.7% in the third hour from sample HA04.The percentage extraction of cobalt from sample HA04 increased with the increase in the extraction time as 90.8% was extracted in the first hour and increased to 95.4% in the third hour.

Table 4.8: Extraction of metals from sample HA04 using different times by conventional method

Time (hour)	% Co extracted	% Cu extracted
1	90.8 ± 0.8	93.6 ± 1.0
2	94.4 ± 1.1	94.9 ± 1.4
3	95.4 ± 2.4	96.6 ± 0.6
4	94.9 ± 0.8	97.5 ± 0.6
	% Zn extracted	**% Ni extracted**
1	92.3 ± 1.6	91.5 ± 2.3
2	97.9 ± 1.4	97.1 ± 1.2
3	97.1 ± 2.4	97.9 ± 1.4
4	96.9 ± 0.9	97.8 ± 1.4
	% Fe extracted	
1	96.2 ± 2.3	
2	96.2 ± 1.0	
3	96.7 ± 0.9	
4	97.2 ± 1.4	

1 g of sample, 75°C, 100 cm^3 of 3 mol dm^{-3} H_2SO_4

4.9.3.5 Solvent Volume

The only variable in this set of experiments was the sulfuric acid volume, different volumes 25, 50, 75 and 100 cm^3 were used, Tables 4.9 – 4.12. An increase in the volume of sulfuric acid led to no increase in the extraction of all the metals. Attempts were made to use less than 25 cm^3 of H_2SO_4, but due to the thickening of the mixture stirring became difficult. It was, therefore, decided to select 1:25 g/cm^3 as solid/liquid ratio. Abdul-Aal et al. used a solid/liquid ratio of 1:20 g/cm^3 during the extraction of nickel from a nickel oxide catalyst leached with sulfuric acid [10].

Table 4.9: Extraction of metals from sample HA01 using different H_2SO_4 volumes by conventional method

Volume (cm^3)	% Cu extracted	% Zn extracted
25	97.5 ± 1.1	94.7 ± 1.9
50	97.5 ± 1.2	94.6 ± 1.6
75	97.0 ± 1.2	93.9 ± 1.7
100	96.7 ± 1.8	94.3 ± 1.3

1 g of sample, 50°C, 1 hour and 3 mol dm^{-3} H_2SO_4

Table 4.10: Extraction of metals from sample HA02 using different H_2SO_4 volumes by conventional method

Volume (cm^3)	% Cu extracted	% Zn extracted
25	95.5 ± 1.7	95.8 ± 1.1
50	95.8 ± 1.8	95.9 ± 1.8
75	95.5 ± 1.1	95.9 ± 2.2
100	95.8 ± 1.3	95.8 ± 0.6

1 g of sample, 50°C, 1 hour and 3 mol dm^{-3} H_2SO_4

Table 4.11: Extraction of metals from sample HA03 using different H_2SO_4 volumes by conventional method

Volume (cm^3)	**% Ni extracted**	**% Fe extracted**
25	94.6 ± 1.8	96.3 ± 1.0
50	94.7 ± 1.9	97.4 ± 1.4
75	94.8 ± 1.5	97.3 ± 0.9
100	94.7 ± 1.3	97.6 ± 1.4
	% Cu extracted	**% Zn extracted**
25	94.9 ± 1.6	95.1 ± 1.6
50	94.8 ± 1.6	94.0 ± 2.6
75	95.1 ± 2.1	94.3 ± 2.3
100	95.4 ± 1.5	94.3 ± 1.3

1 g of sample, 50°C, 1 hour and 3 mol dm^{-3} H_2SO_4

Table 4.12: Extraction of metals from sample HA04 using different H_2SO_4 volumes by conventional method

Volume (cm^3)	% Co extracted	% Cu extracted
25	94.4 ± 0.8	94.4 ± 1.3
50	94.1 ± 1.9	94.4 ± 1.0
75	94.7 ± 0.5	94.7 ± 0.7
100	94.4 ± 1.1	94.9 ± 1.4
	% Zn extracted	**% Ni extracted**
25	97.1 ± 2.0	97.1 ± 1.2
50	97.4 ± 1.2	96.4 ± 2.0
75	97.1 ± 1.3	97.2 ± 2.3
100	97.9 ± 1.4	97.1 ± 1.2
	% Fe extracted	
25	95.7 ± 1.7	
50	95.6 ± 1.6	
75	95.7 ± 1.7	
100	96.2 ± 1.0	

1 g of sample, 75°C, 2 hours and 3 mol dm^{-3} H_2SO_4

4.9.3.6 Sulfuric Acid Concentration

The effect of sulfuric acid concentration, ranging from 1 – 4 mol dm^{-3}, on all the metal extraction was investigated. The data in Tables 4.13 – 4.16 show that increasing the sulfuric acid concentration led to increase the percentage of copper extracted from sample HA01, HA02, HA03 and HA04 from 91.2%, 90.2%, 89.3% and 91.1% at 1 mol dm^{-3} H_2SO_4 to 98.0%, 96.8%, 95.4% and 95.7% at 4 mol dm^{-3} H_2SO_4, respectively.

Zinc extraction was similar to copper as the sulfuric acid concentration increased the percentage of zinc extracted from each sample was also increased.

Nickel was extracted more with the increase in the sulfuric acid concentration from sample HA03 and HA04 as 89.1% and 92.2% was extracted at 1 mol dm^{-3} H_2SO_4 and increased to 96.7% and 97.8% at 4 mol dm^{-3} H_2SO_4, respectively.

Increasing the H_2SO_4 concentration led to an increase in the percentage of iron extracted in samples HA03 and HA04 as 92.8% and 93.7% were extracted at 1 mol dm^{-3} H_2SO_4 and increased to 97.6% and 96.2% when the acid concentration was increased to 4 mol dm^{-3}. The percentage of cobalt extracted from sample HA04 was considerably affected by the increase in the H_2SO_4 concentration as 88.0% was extracted at 1 mol dm^{-3} H_2SO_4 and improved to 95.9% at 4 mol dm^{-3} H_2SO_4.

Based on the above experimental results, the final economical and optimum leaching conditions for the four samples used in this work were as follow:

- **Sample HA01**: 1 g of sample, 50°C, 1 hour, 25 cm^3 of 2 mol dm^{-3} of H_2SO_4.
- **Sample HA02**: 1 g of sample, 50°C, 1 hour, 25 cm^3 of 2 mol dm^{-3} of H_2SO_4.
- **Sample HA03**: 1 g of sample, 50°C, 1 hour, 25 cm^3 of 2 mol dm^{-3} of H_2SO_4.
- **Sample HA04**: 1 g of sample, 75°C, 2 hours, 25 cm^3 of 3 mol dm^{-3} of H_2SO_4.

Table 4.13: Extraction of metals from sample HA01 using different H_2SO_4 concentration by conventional method

H_2SO_4 mol dm^{-3}	% Cu extracted	% Zn extracted
1	91.2 ± 1.9	90.4 ± 1.3
2	97.6 ± 1.5	95.1 ± 1.3
3	97.5 ± 1.1	94.7 ± 1.9
4	98.0 ± 1.2	95.5 ± 1.7

1 g of sample, 50°C, 1 hours and 25 cm^3 H_2SO_4

Table 4.14: Extraction of metals from sample HA02 using different H_2SO_4 concentration by conventional method

H_2SO_4 mol dm^{-3}	% Cu extracted	% Zn extracted
1	90.2 ± 1.4	91.6 ± 0.9
2	96.0 ± 1.9	95.5 ± 1.0
3	95.5 ± 1.7	95.8 ± 1.1
4	96.8 ± 1.3	96.4 ± 1.7

1g of sample, 50°C, 1 hours and 25 cm^3 H_2SO_4

Table 4.15: Extraction of metals from sample HA03 using different H_2SO_4 concentration by conventional method

H_2SO_4 mol dm^{-3}	**% Ni extracted**	**% Fe extracted**
1	89.1 ± 1.1	92.8 ± 1.0
2	94.7 ± 1.1	95.1 ± 1.1
3	94.6 ± 1.8	96.3 ± 1.0
4	96.7 ± 1.7	97.6 ± 1.5
	% Cu extracted	**% Zn extracted**
1	89.3 ± 1.4	88.5 ± 1.9
2	94.6 ± 1.4	95.4 ± 1.4
3	94.9 ± 1.6	95.1 ± 1.6
4	95.4 ± 0.8	96.5 ± 1.6

1 g of sample, 50°C, 1 hours and 25 cm^3 H_2SO_4

Table 4.16: Extraction of metals from sample HA04 using different H_2SO_4 concentration by conventional method

H_2SO_4 mol dm^{-3}	% Co extracted	% Cu extracted
1	88.0 ± 1.5	91.1 ± 1.5
2	90.8 ± 1.3	92.9 ± 0.7
3	94.4 ± 0.8	94.4 ± 1.3
4	95.9 ± 1.5	95.7 ± 0.9
	% Zn extracted	**% Ni extracted**
1	89.9 ± 1.9	92.2 ± 1.4
2	92.6 ± 0.9	96.4 ± 2.0
3	93.1 ± 2.0	97.1 ± 1.2
4	94.4 ± 1.4	97.8 ± 1.4
	% Fe extracted	
1	93.7 ± 1.7	
2	95.2 ± 1.4	
3	95.7 ± 1.7	
4	96.2 ± 2.3	

1 g of sample, 75°C, 2 hours and 25 cm^3 H_2SO_4

4.9.4 Extraction in the Microwave Technique

In this section, the effect of high temperature, time and sulfuric acid concentration in the extraction of copper and zinc from sample HA01 and HA02 were studied using a Microwave Accelerated Reaction System.

4.9.4.1 Effect of Temperature

Tables 4.17 and 4.18, show that an increase in the temperature accompanied by an increase in pressure played a significant role in the extraction of copper and zinc from samples HA01 and HA02.

Table 4.17: Extraction of Cu and Zn using microwave technique on sample HA01

Temperature (°C)	Concentration of H_2SO_4		
	0.5 mol dm^{-3}	1 mol dm^{-3}	2 mol dm^{-3}
Percentage of Copper Extracted			
50	31.4 ± 1.3	45.3 ± 2.3	59.8 ± 2.0
100	58.0 ± 1.0	68.6 ± 2.0	75.0 ± 1.8
125	68.5 ± 2.7	75.2 ± 2.6	92.1 ± 2.5
150	79.2 ± 1.5	89.5 ± 1.5	97.8 ± 1.1
175	83.6 ± 1.2	93.0 ± 1.0	98.9 ± 1.0
Percentage of Zinc Extracted			
50	37.1 ± 2.7	50.5 ± 1.3	65.4 ± 2.7
100	63.1 ± 1.9	77.5 ± 1.0	90.8 ± 0.8
125	74.4 ± 1.3	84.3 ± 0.7	93.1 ± 1.0
150	80.7 ± 1.0	90.0 ± 1.0	96.8 ± 1.3
175	82.3 ± 1.5	94.5 ± 0.8	98.2 ± 1.2

1 g of sample, 10 minutes and 25 cm^3 of H_2SO_4

It can be seen that the extraction of copper increases with increasing temperature as the recovery improves substantially from 31.4% to 83.6% when the extraction temperature was increased from 50°C to 175°C at 0.5 mol dm^{-3} H_2SO_4 concentration.

The percentage extraction of copper from sample HA02 was increased from 22.0% to 83.7% when the temperature was raised from 150°C to 175°C at 0.5 mol dm^{-3} H_2SO_4 concentration.

Increasing the temperature from 50°C to 175°C led to a considerable increase in the percentage of zinc extracted as 37.1% and 82.3% extracted from sample HA01, respectively using 0.5 mol dm^{-3} sulfuric acid. Maximum percentage was extracted when temperature was increased to 175°C as 98.2% was extracted from the sample using 2 mol dm^{-3}. Zinc percentage extracted also increased with increasing temperature and sulfuric acid together in sample HA02.

Generally speaking, copper and zinc extraction was lower at low temperatures than at higher temperatures. Increasing the temperature of the extraction process, however, had a significant role in their extraction as it led to increase the percentage of extraction from the samples.

Table 4.18: Extraction of Cu and Zn using microwave technique on sample HA02

Percentage of Copper Extracted

Temperature (°C)	Concentration of H_2SO_4		
	0.5 mol dm^{-3}	1 mol dm^{-3}	2 mol dm^{-3}
50	22.0 ± 2.2	30.6 ± 2.3	42.3 ± 2.1
100	47.8 ± 1.8	59.6 ± 2.9	78.2 ± 1.6
125	62.1 ± 1.6	74.4 ± 1.3	90.7 ± 1.2
150	77.2 ± 1.9	86.5 ± 1.8	97.1 ± 1.3
175	83.7 ± 1.2	92.2 ± 2.2	98.3 ± 0.8
Percentage of Zinc Extracted			
50	32.6 ± 3.2	46.3 ± 2.3	54.6 ± 2.1
100	61.2 ± 2.1	71.6 ± 1.2	83.8 ± 1.6
125	70.2 ± 1.7	84.2 ± 2.4	91.4 ± 1.4
150	80.1 ± 1.5	89.6 ± 1.2	96.6 ± 1.2
175	82.5 ± 1.3	92.5 ± 1.3	98.7 ± 0.8

1 g of sample, 10 minutes and 25 cm^3 of H_2SO_4

4.9.4.2 Effect of Extraction Time

The data in Tables 4.19 and 4.20 show that copper extraction from samples HA01 and HA02 were similar as both indicate that at extraction period of 5 minutes and sulfuric acid concentration of 0.5 mol dm^{-3}, the amount of copper extracted is lower than the amount extracted when the extraction time was prolonged to 10 and 15 minutes. Prolonging the extraction time from 10 to15 minutes had very slight influence on the amount of copper extracted from sample HA01. The effect of increasing the sulfuric acid concentration was more noticeable when it was increased from 0.5 mol dm^{-3} to 1 mol dm^{-3} than the increase from 1 mol dm^{-3} to 2 mol dm^{-3}. Maximum copper was extracted at sulfuric acid concentration of 2 mol dm^{-3} as 98.8% was extracted within the 15 minutes of the extraction from sample HA01. In sample HA02, 98.1% of copper was extracted in 15 minutes when the sulfuric acid concentration was 2 mol dm^{-3}.

Table 4.19: Extraction of Cu and Zn using microwave technique on sample HA01

Time (minute)	**Concentration of H_2SO_4**		
	0.5mol dm^{-3}	**1mol dm^{-3}**	**2mol dm^{-3}**
Percentage of Copper Extracted			
5	53.5 ± 2.3	74.6 ± 1.8	85.5 ± 1.5
10	79.2 ± 1.5	89.5 ± 1.5	97.8 ± 1.1
15	80.2 ± 2.5	92.2 ± 2.5	98.8 ± 1.1
Percentage of Zinc Extracted			
5	68.9 ± 1.8	83.1 ± 2.1	91.3 ± 1.5
10	80.7 ± 1.0	90.0 ± 1.0	96.8 ± 1.3
15	84.7 ± 1.2	95.0 ± 1.4	98.1 ± 1.0

1 g of sample, 150°C and 25 cm^3 of H_2SO_4

Prolonging the extraction time from 5 to 10 minutes improved the amount of zinc extracted from sample HA01; further increase in the extraction time to 15 minutes had no significant effect on the extraction process. Maximum zinc 98.1% was extracted when 2 mol dm^{-3} of sulfuric acid for 15 minutes was used in sample HA01 and 97.5% when 2 mol dm^{-3} of sulfuric acid for 15 minutes in sample HA02.

Generally speaking, prolonging the extraction time played a significant roll in the extraction of copper and zinc from samples HA01 and HA02. Increasing the extraction temperature with increasing the sulfuric acid concentration led to an increase in the amount of copper and zinc extracted from both samples.

Table 4.20: Extraction of Cu and Zn using microwave technique on sample HA02

Percentage of Copper Extracted			
Time (minute)	**Concentration of H_2SO_4**		
	0.5mol dm^{-3}	**1mol dm^{-3}**	**2mol dm^{-3}**
5	64.8 ± 1.9	78.8 ± 1.8	89.1 ± 0.8
10	77.2 ± 1.9	86.5 ± 1.8	97.1 ± 1.3
15	82.2 ± 1.9	92.5 ± 1.8	98.1 ± 1.5
Percentage of Zinc Extracted			
5	70.1 ± 1.6	80.4 ± 2.0	87.0 ± 0.9
10	80.1 ± 1.5	89.6 ± 1.2	96.6 ± 1.2
15	89.3 ± 1.4	93.6 ± 1.2	97.5 ± 1.0

1 g 1g of sample, 150°C and 25 cm^3 of H_2SO_4

4.9.5 Microwave Technique and Conventional Method

The data in Table 4.21 show a comparison between conventional and microwave extraction techniques for sample HA01. It was found that the conventional method was able to extract 97.6% of copper at 50°C in 60 minutes compared to 59.8% obtained by the microwave method at the same temperature in 10 minutes. However, the obtained results also show that increasing the reaction temperature to 150°C in the microwave extraction technique to extraction time of 10 minutes led to an enhancement in the amount of copper extracted 97.8%.

In the extraction of zinc using conventional method 95.1% was extracted at 50°C in 60 minutes and this was more than what extracted by the microwave extraction technique 65.4% at 50°C in 10 minutes. Nevertheless, the percentage of zinc enhanced to 96.8% when the extraction was carried out at higher temperature 150°C in extraction time of 10 minutes.

The results obtained from the conventional extraction were compared with the microwave results from sample HA02 and are presented in Table 4.22.

The advantage of the microwave extraction technique in comparison with traditional hot plate method lies in the significantly higher working temperatures which can only be achieved in the microwave extraction system. While in hot plate method these temperatures are limited by the acid solution's boiling point, temperatures up 250°C can be typically achieved in sealed extraction vessels. This results in a dramatic acceleration of the reaction kinetics, allowing extraction reactions to be carried out in a very short time. However, these methods also make it clear that the temperature itself actually represents the most significant reaction parameter. Therefore, the microwave extraction technique is considered to be a viable alternative to the conventional extraction methods because of its more intensive reaction conditions.

Table 4.21: Comparison between conventional and microwave techniques sample HA01

Extraction technique	Sample weight (g)	H_2SO_4 (mol dm^{-3})	Temperature (°C)	Volume (cm^3)	Time (min)	Percentage Extracted
Copper						
Conventional	1	2	50	25	60	97.6 ± 1.5
Microwave	1	2	50	25	10	59.8 ± 2.0
Microwave	1	2	150	25	10	97.8 ± 1.1
Zinc						
Conventional	1	2	50	25	60	95.1 ± 1.3
Microwave	1	2	50	25	10	65.4 ± 2.7
Microwave	1	2	150	25	10	96.8 ± 1.3

Table 4.22: Comparison between conventional and microwave techniques sample HA02

Extraction technique	Sample weight (g)	H_2SO_4 (mol dm^{-3})	Temperature (°C)	Volume (cm^3)	Time (min)	Percentage Extracted
Copper						
Conventional	1	2	50	25	60	96.0 ± 1.9
Microwave	1	2	50	25	10	42.3 ± 2.1
Microwave	1	2	150	25	10	97.1 ± 1.3
Zinc						
Conventional	1	2	50	25	60	95.5 ± 1.0
Microwave	1	2	50	25	10	54.6 ± 2.1
Microwave	1	2	150	25	10	96.6 ± 1.2

4.10 DISCUSSION

4.10.1 Conventional Metal Extraction

It can be seen from the results that nearly all the metal extraction took place during the first 60 minutes of the extractions and within temperature of 50-60°C. Therefore, it was decided to carry out several sets of experiments to investigate the type of reaction that take place during the first 60 minutes of the extraction. For this purpose sample HA04 was selected as a model for the rest of the other samples. The following parameters were investigated:

4.10.1.1 Effect of Sulfuric Acid Concentration

The influence of H_2SO_4 concentration on the extraction of the metals from sample HA04 was determined by varying the concentration of H_2SO_4. Figure 4.9a illustrates the effect of varying H_2SO_4 concentration from 1 to 3 mol dm^{-3} on the dissolution of iron. The extraction process was carried out at temperatures of 25°C and solid/liquid ratio was 1:25 g cm^{-3}. The percentage recovery of iron increased with increasing sulfuric acid concentration up to a certain range and then further increase had no effect on the extraction process. This means that at up to acid concentrations of 2 mol dm^{-3} more than 80% of the metal present in the sample was extracted and at higher concentration no significant increase was noticed. Figure 4.9b-d reveals that similar effect has been observed for Ni, Cu, Zn and Co at different H_2SO_4 concentration.

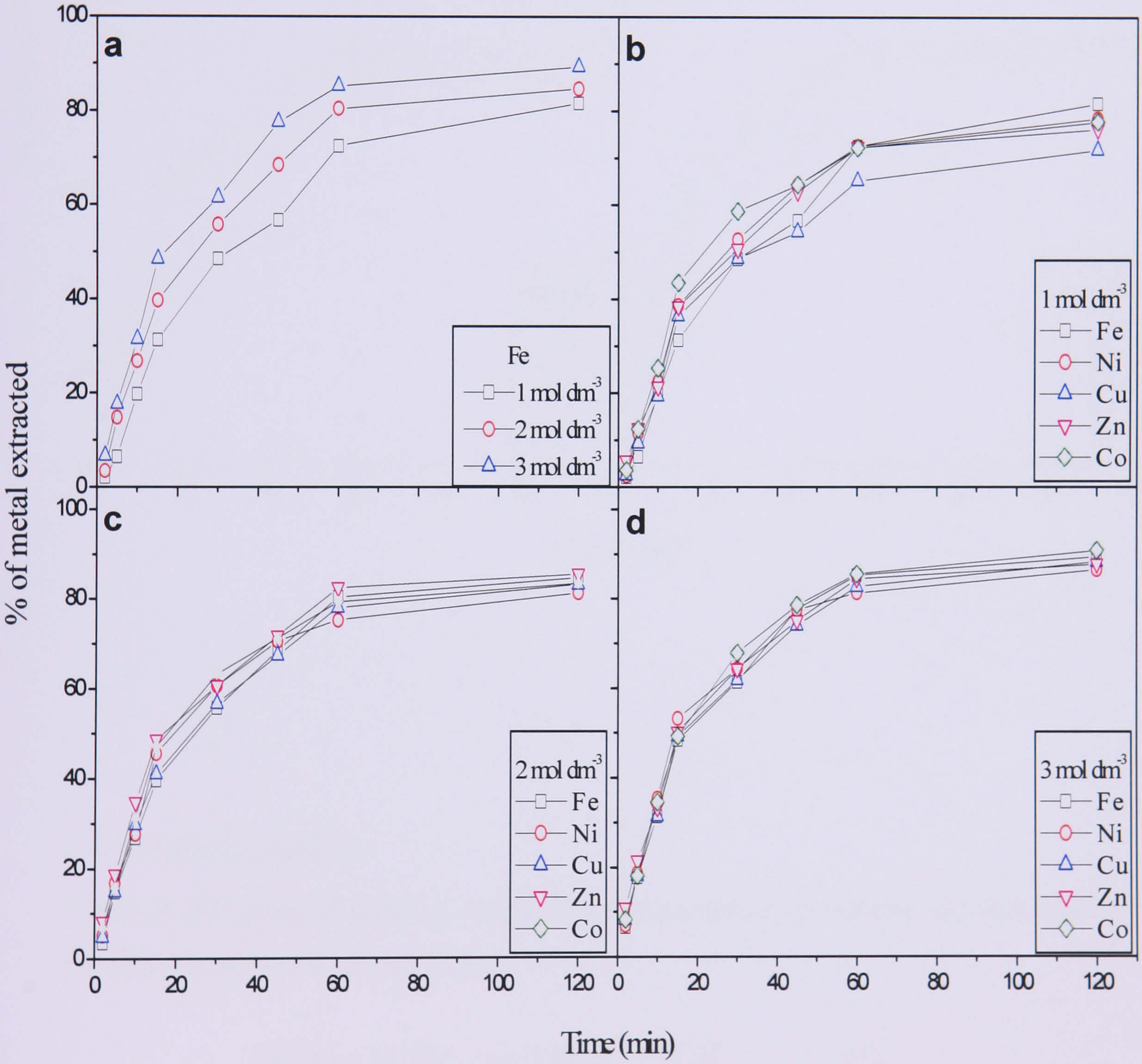
4.10.1.2 Effect of Reaction Temperature

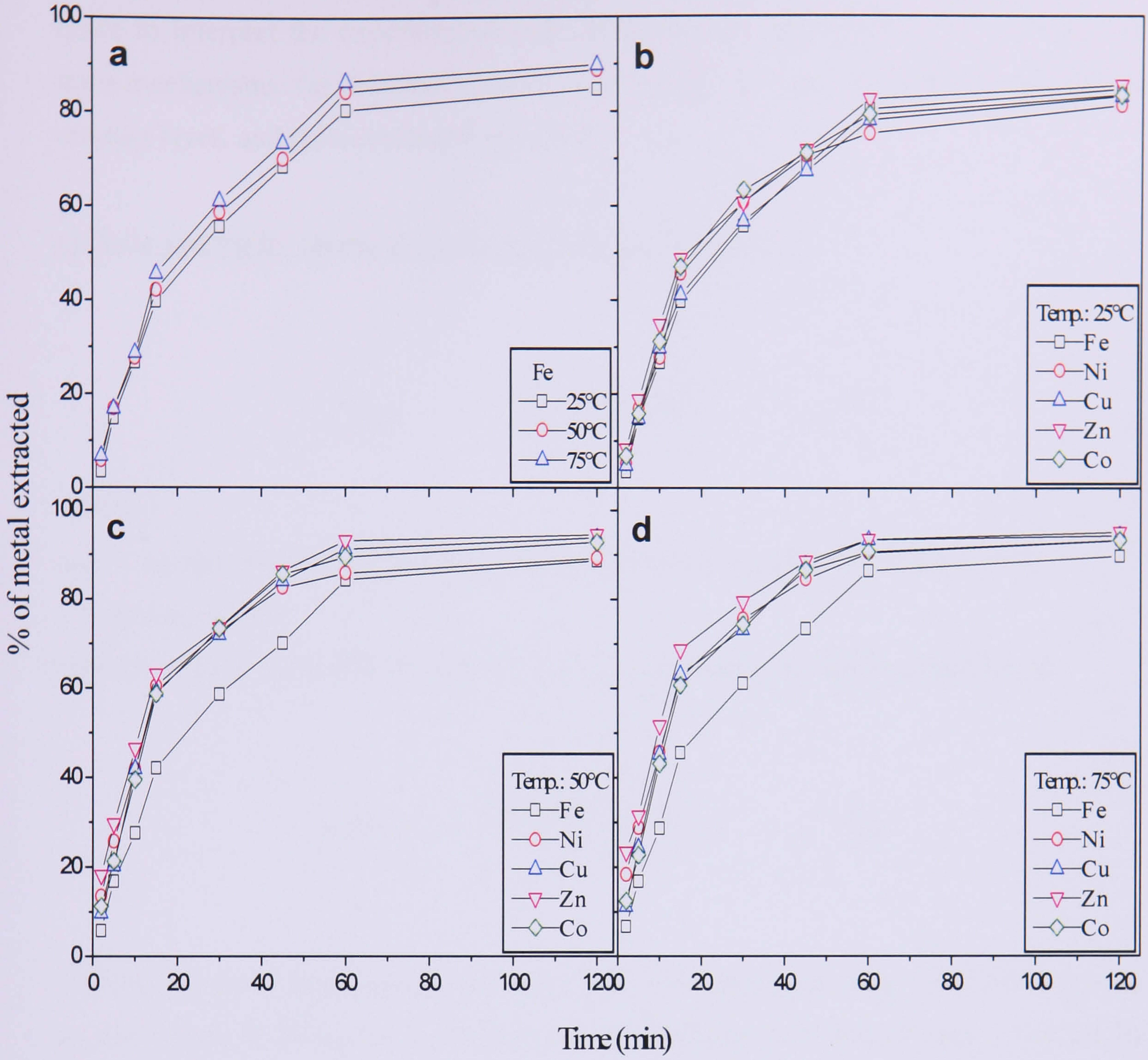
The effect of reaction temperature on metals extraction was studied by performing experiments at 25, 50 and 75°C. Figure 4.10 show the influence of the reaction temperature on the extraction of different metals. For example, the extraction of iron, Figure 4.10a, increased by increasing the reaction temperature. The percentage extraction increased to more than 80% at reaction temperature of 50-60°C, with acid concentration of 2 mol dm^{-3} and when the solid/liquid ratio was 1: 25 g cm^{-3}.

The obtained results indicate that the studied reaction temperatures have a noticeable effect on the dissolution of the metals ranging from room temperature to 50°C. A further increase in reaction temperature to 75°C has no significant effect on the percentage extraction of different metals.

4.10.1.3 Effect of Extraction Time

The data in Figures 4.9 and 4.10 show that prolonging the extraction time to 60 minutes is led to an increase in the metal extraction. This means that the extraction conversion is a rate process depending on the time of the reaction.





4.10.1.4 Kinetic Aspects

Metals in the assumed form of oxides dissolve according to reaction (1) and remain in the aqueous phase as sulfates [35]:

$$MO(s) + H_2SO_4 \longrightarrow MSO_4 + H_2O \qquad (1)$$

In order to determine the mechanism controlling the leaching process, an attempt was made to interpret the experimental data obtained from the leaching experiments with three mechanisms: (a) chemical reaction at the particle surface; (b) diffusion through the product layer; and (c) a combination of both.

(a) Rate control by chemical reaction at the particle surface:

$$k_{RPS}t = 1-(1-[Metal])^{\frac{1}{3}} \qquad (2)$$

Where,

k_{RPS} = reaction rate constant controlled by reaction at the particle surface (min^{-1})

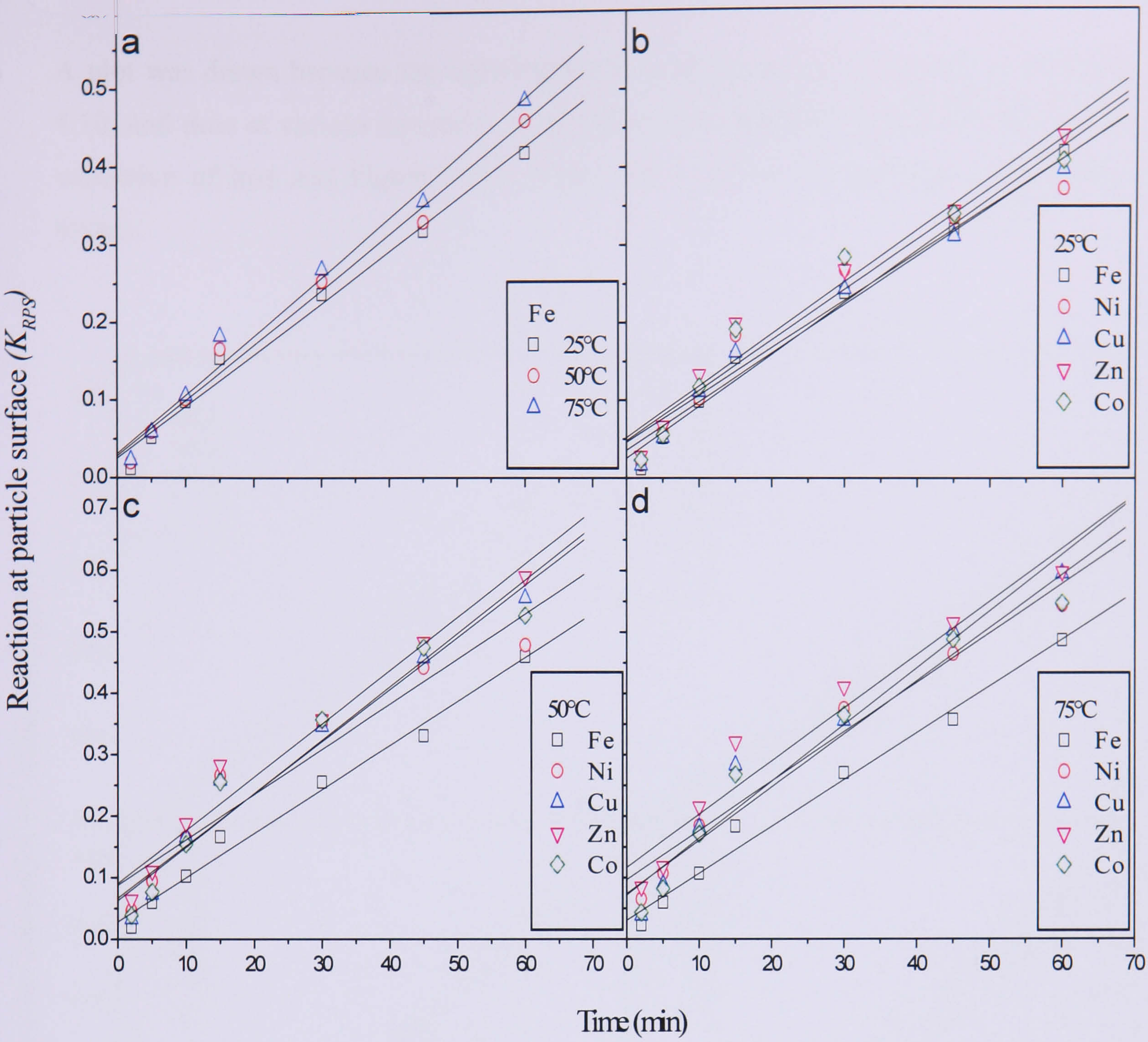
t = time in minutes

[Metal] = fraction reacted of metal ion and is calculated from the % extraction as:

$$[Metal] = \frac{\%[Metal]_{extracted}}{100} \qquad (3)$$

The experimental data obtained in Figure 4.10 for temperature range 25-75°C was used to plot Figure 4.11a for the extraction of iron and Figure 4.11b, 4.11c and 4.11d for the extraction of Fe, Ni, Cu, Zn and Co employing the right-hand side of equation (2). It can be noticed from Table 4.23 and Figure 4.11 that the data are almost linear and are not giving zero point intercepts.

Temperature (°C)	**Intercept value**	**Correlation coefficient (R^2)**
25	0.0251	0.9926
50	0.0280	0.9932
75	0.0304	0.9926



(b) Rate controlled by diffusion through the product layer:

The Ginstling and Brounshtein's model [36] for the diffusion controlled reaction is given in equation (4):

$$= 1 - \frac{2}{3}[Metal] - (1 - [Metal])^{2/3} \qquad (4)$$

Where, k_{RCD} = rate constant controlled by diffusion.

A plot was drawn between the right-hand side of equation (4), using data from Figure 4.10, and time at various extraction temperatures and depicted in Figure 4.12a for the extraction of iron and Figure 4.12b, 4.12c and 4.12d for the extraction of the other metals.

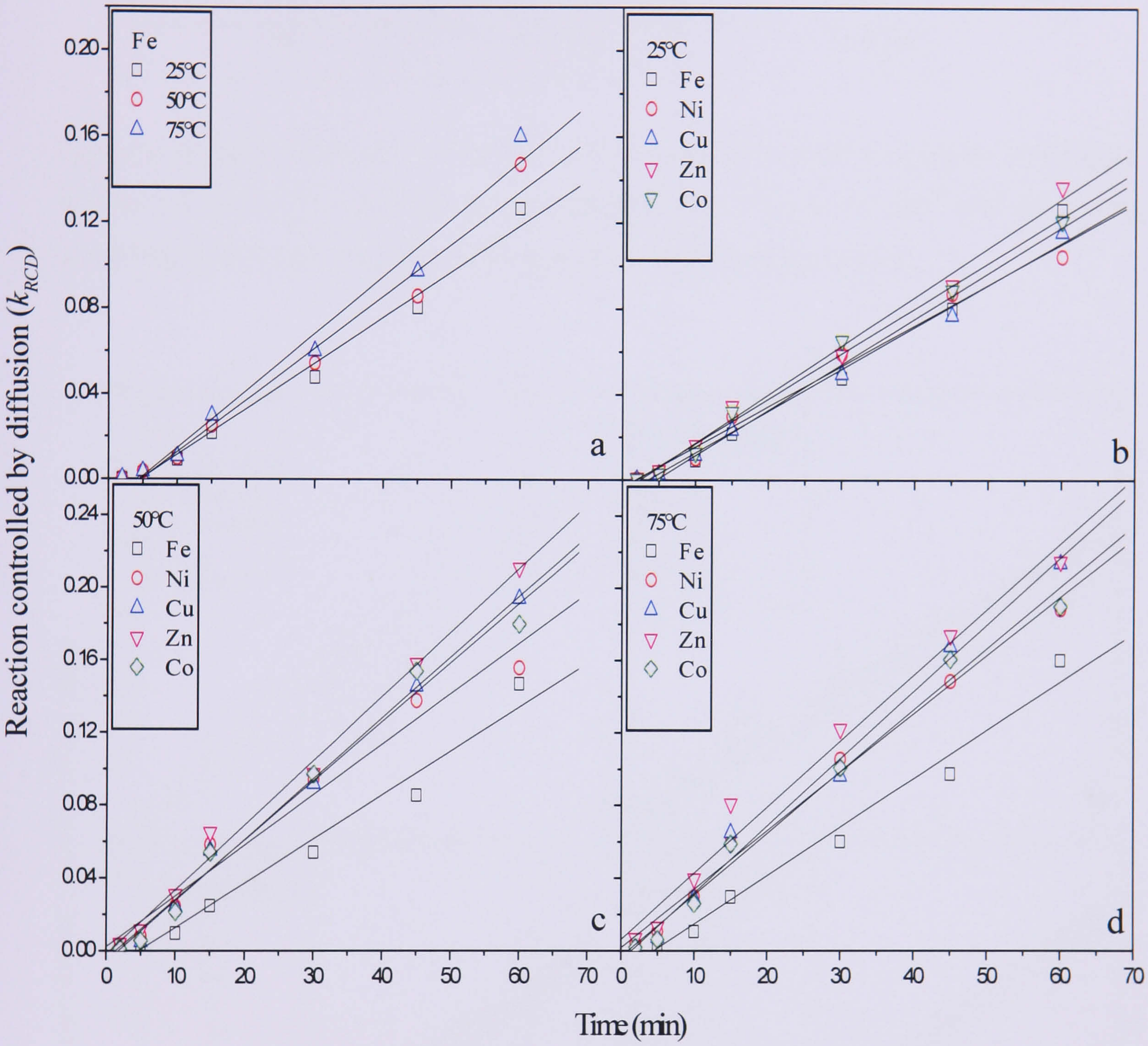


Figure 4.12 illustrate that the reaction took place was different to the previous reaction (chemical reaction at the surface). The experimental data in Table 4.24 show that the intercept values at different temperatures are close to zero. From the slopes of the straight lines in Figure 4.12 the apparent rate constant, k, was utilised to determine the activation energy for each metal within the sample.

Table 4.24: show the values of the intercept and correlation coefficient for iron in the diffusion controlled reaction

Temperature (°C)	**Intercept value**	**Correlation coefficient (R^2)**
25	- 0.0099	0.9930
50	- 0.0115	0.9875
75	- 0.0120	0.9904

Figure 4.13 and 4.14 show two plots of data obtained for metals extraction from Figure 4.9 for the sulfuric acid concentration ranging from 1 to 3 mol dm^{-3} and are drawn according to the right-hand side of equations (2) and (4), respectively.

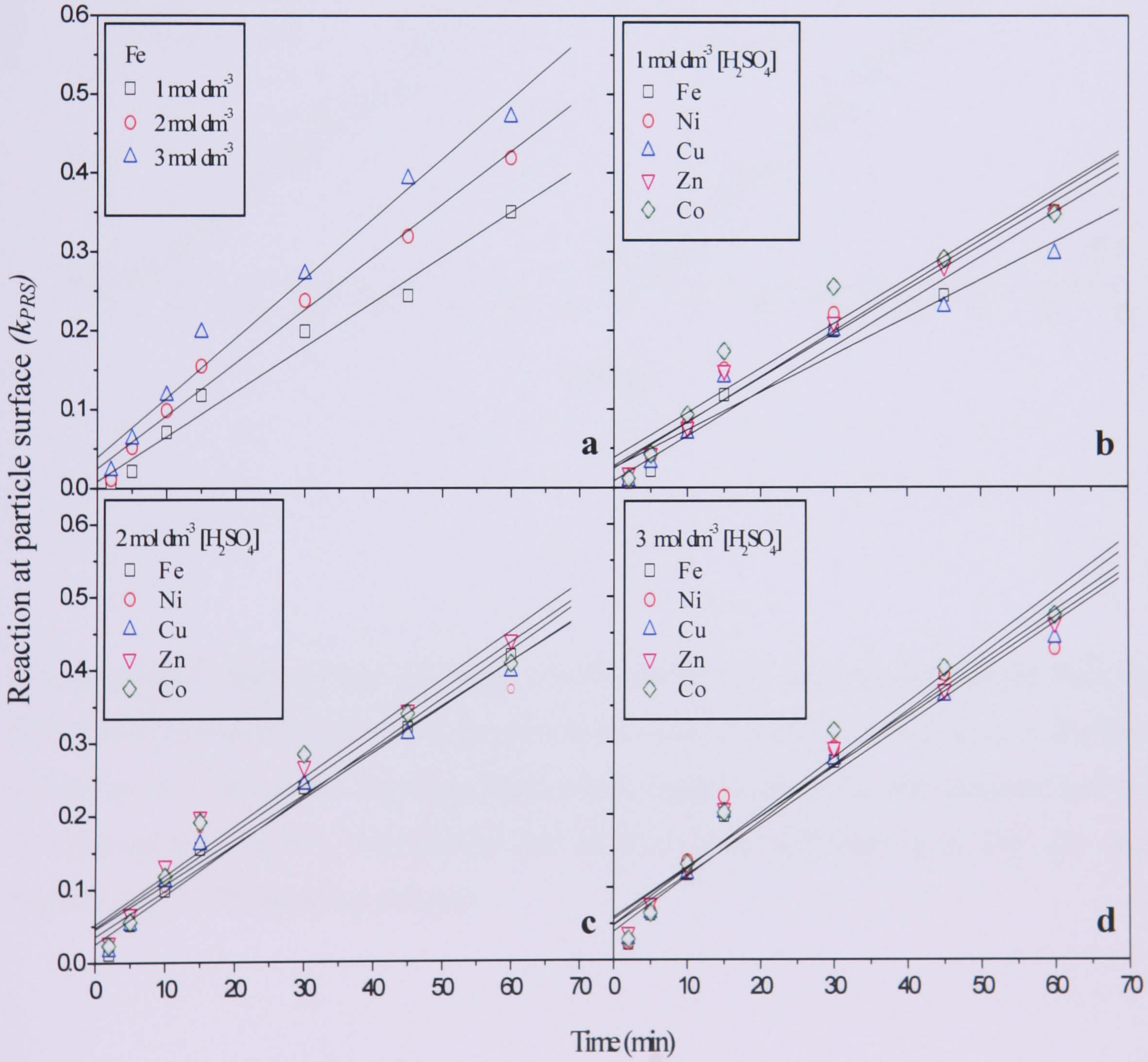
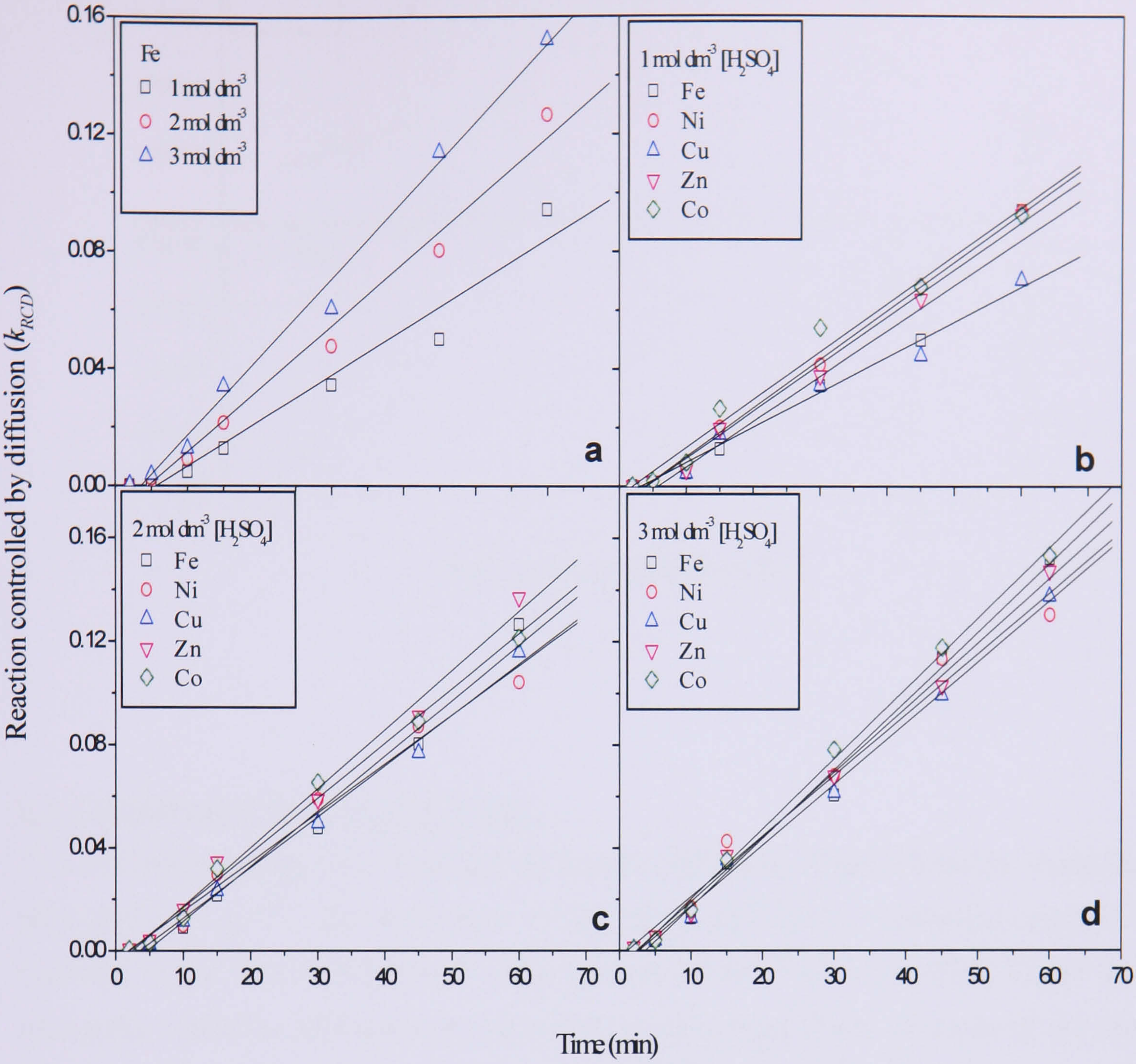
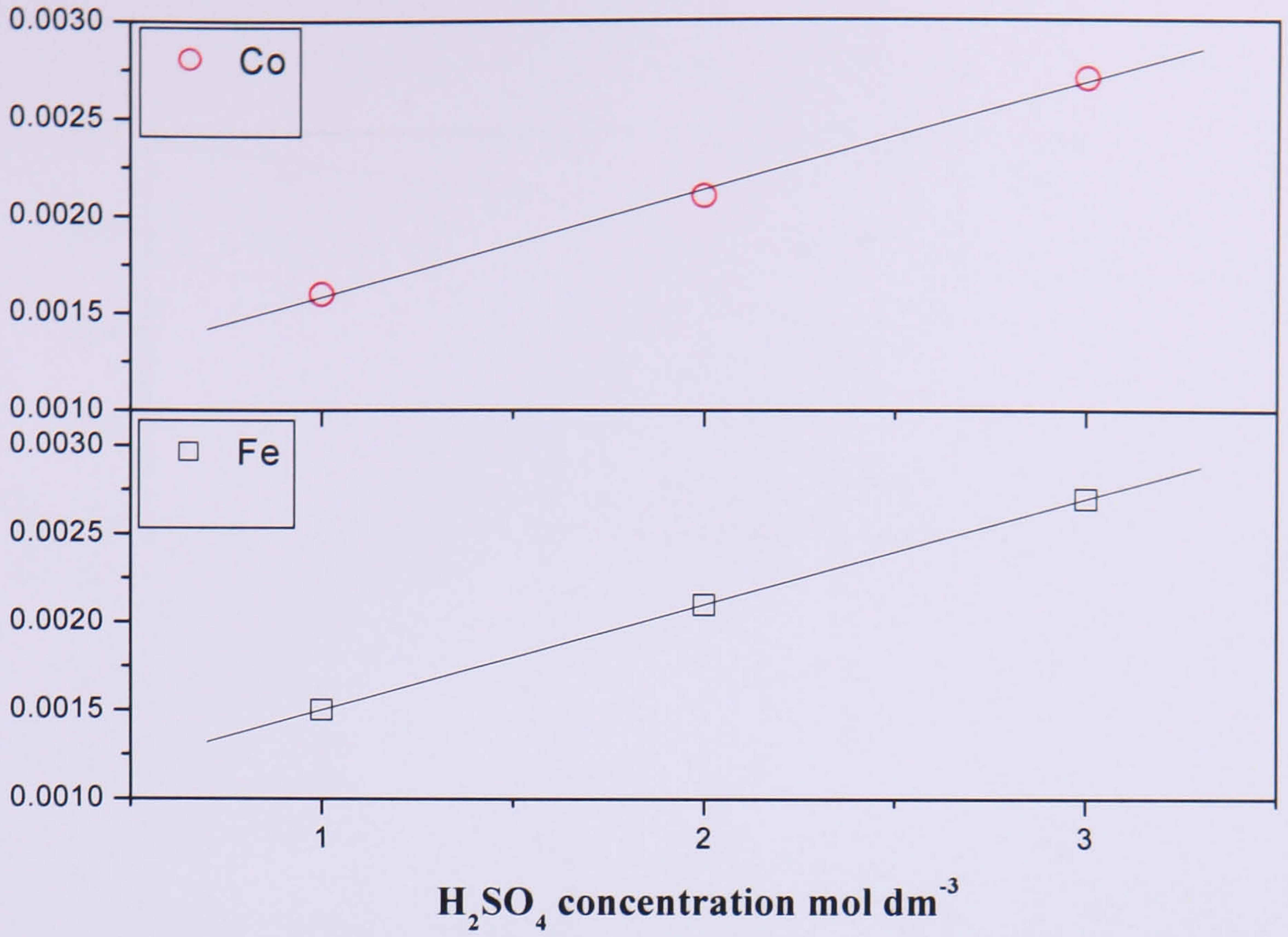


Figure 4.13: Plots of reaction at the particle surface versus time at various concentration of H_2SO **a**) Fe at 1, 2 and 3 mol dm^{-3}, **b**) Various metals at 1 mol dm^{-3}, **c**) Various metals at 2 mol dm^{-3} and **d**) Various metals at 3 mol dm^{-3}.



The calculated apparent rate constants obtained from the slops of the straight lines in Figure 4.14 is plotted versus sulfuric acid concentration as shown in Figure 4.15 for iron and cobalt as an example. The clear linear relationship between the rate constant and the concentration of H_2SO_4 reveals that the product layer diffusion is in fact the rate limiting step of the leaching process.



(c) Calculation of the activation energy.

The activation energy of a diffusion-controlled process is characterized as being less than 40.0 KJ mol^{-1}. The activation energy for a chemically controlled process is typically larger than 40.0 KJ mol^{-1} (falls between 40 to 80 KJ mol^{-1}) [10]. Figure 4.16 shows the Arrhenius plot for iron and nickel in the sample. From the slope of the plot, the activation energy was calculated for iron and nickel, 8.5 KJ mol^{-1} (~ 2.0 kcal mol^{-1}) with the correlation coefficient R^2 =0.995 and 20.8 KJ mol^{-1} (~ 5.0 kcal mol^{-1}) with the correlation coefficient R^2 =0.988, respectively. This activation energy is close to the values of the activation energy of 13.4 KJ mol^{-1} calculated for the diffusion controlled reactions of low-grade zinc silicate ore with sulfuric acid [37] and 16.6 kJ mol^{-1} calculated for nickel in spent catalyst leached with sulfuric acid solution [38].

The lower activation energies for the metals extraction suggests that the extraction rates might be controlled by a diffusion process, and this is in agreement with the results obtained by other studies [38]. Table 4.25 shows the rate constants and corresponding activation energy calculated for Fe, Ni, Cu, Zn and Co in sample HA04.

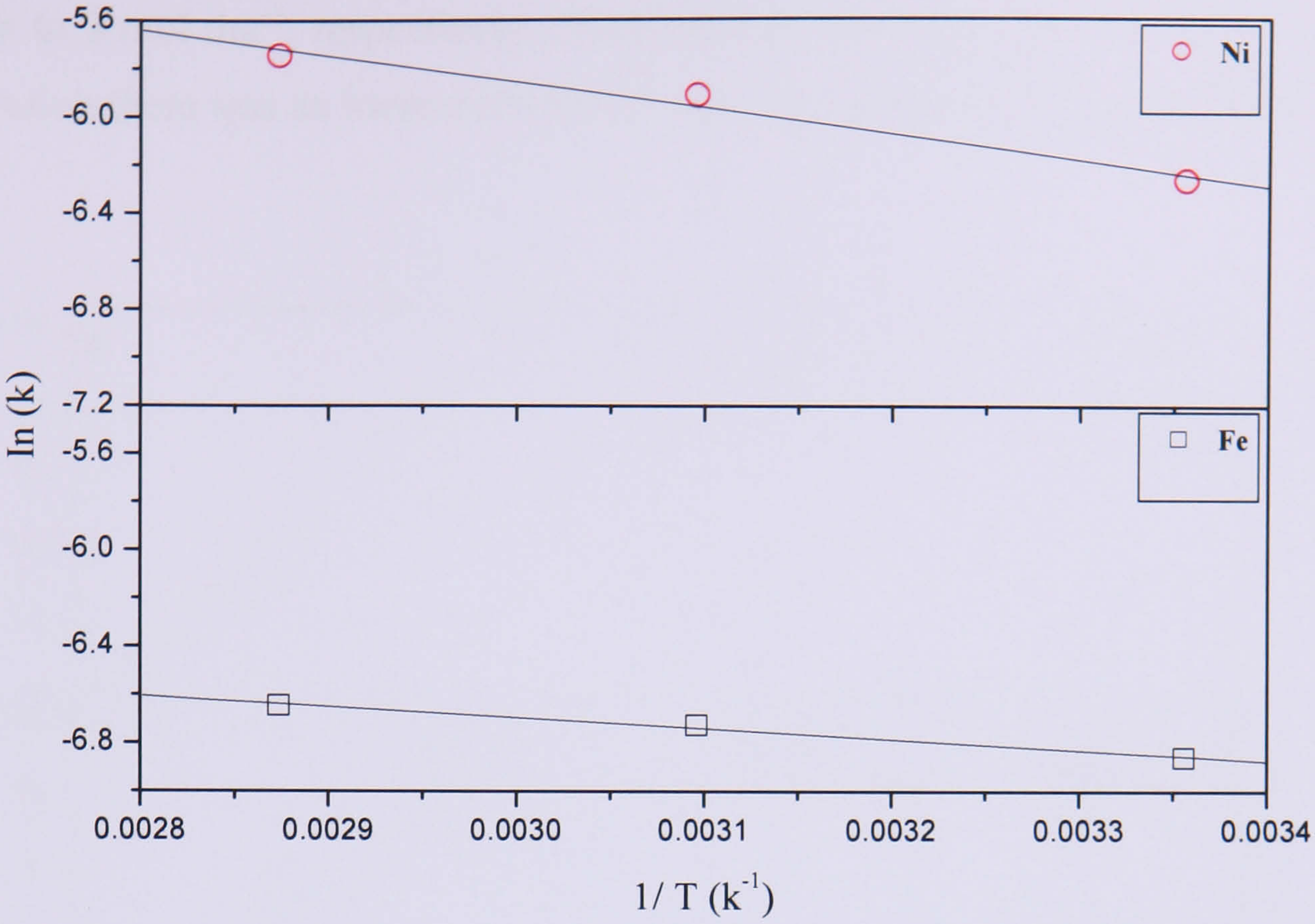


Table 4.25: Activation Energy and diffusion controlled rate of reaction for extracted metals.

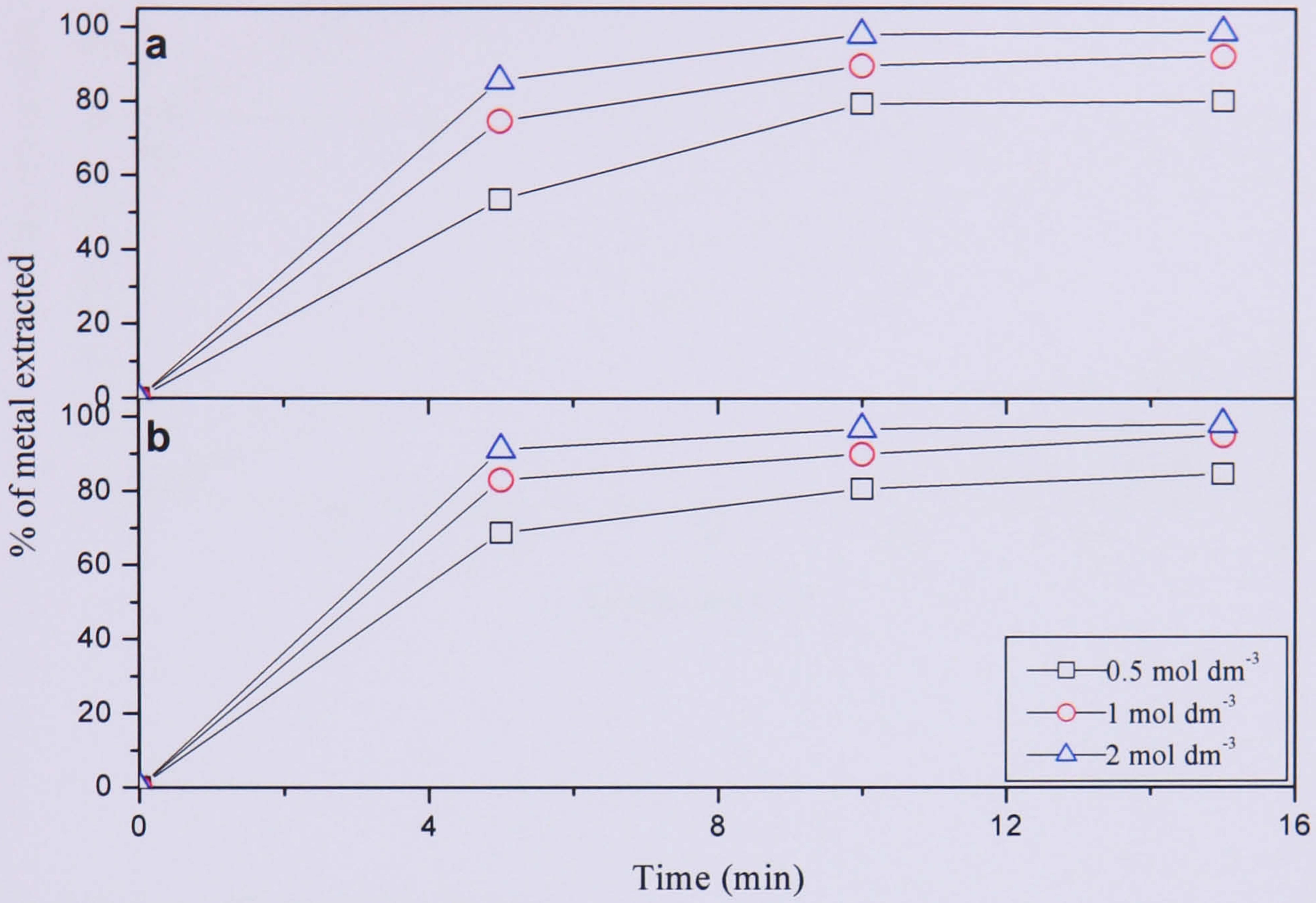
Metal	Activation energy / 10^3 J mol^{-1}	k / 10^{-4} min^{-1}
Fe	8.5 ± 0.85	6.0 ± 0.80
Ni	20.8 ± 3.23	3.0 ± 1.11
Cu	26.9 ± 7.21	6.0 ± 0.63
Zn	20.0 ± 7.44	5.0 ± 1.12
Co	19.5 ± 6.04	6.0 ± 1.06

4.10.2 Microwave Metal Extraction

4.10.2.1 Effect of Sulfuric Acid Concentration

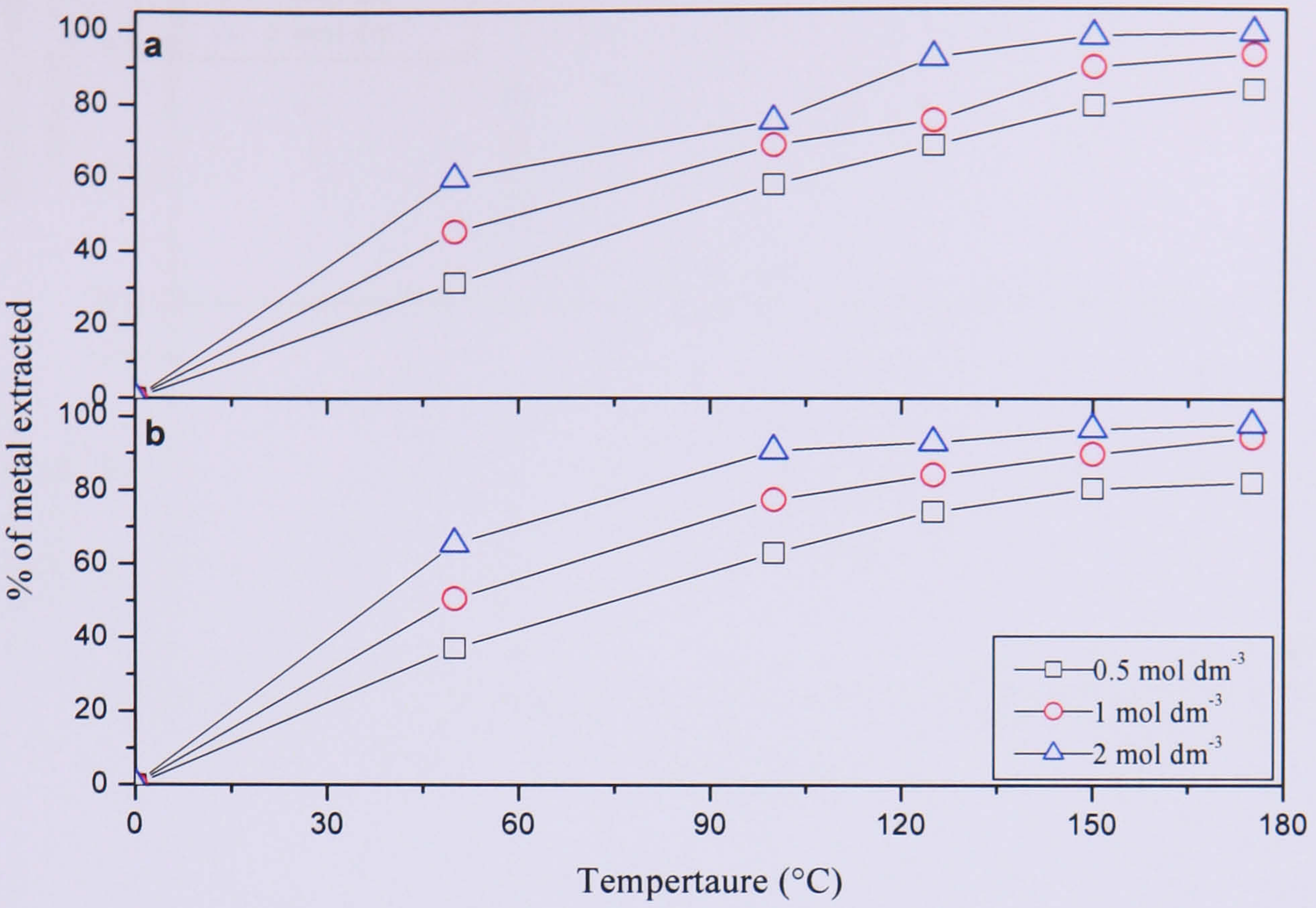
The effect of sulfuric acid concentration ranging from 0.5 to 2 mol dm^{-3} on the extraction conversion of copper and zinc in samples HA01 was studied using microwave extraction technology. The extraction process was set at 150°C for 10 minutes and solid/liquid ratio was 1: 25 g cm^{-3}. Figures 4.17a and 4.17b show that the extraction percentage for copper and zinc in sample HA01 was ranged from 79.2% at

0.5 mol dm^{-3} H_2SO_4 to 97.8% and from 80.7% to 96.8% when the acid concentration increases to 2 mol dm^{-3}, respectively,. This indicates that with the increase of the acid concentration there was an increase in the extraction percentage of copper and zinc.



4.10.2.2 *Effect of Reaction Temperature*

The effect of reaction temperature on metals extraction was investigated using the microwave extraction technology. The extraction was performed at different temperatures ranging from 50 to 175°C, keeping the solid/liquid ratio as 1: 25 g cm^{-3} for a period of 10 minutes. It was noticed that increasing the extraction temperature had a considerable effect on the extraction process and led to an increase in the extraction of copper and zinc in sample HA01. At the temperature of 50°C approximately 59.8% of Cu and 65.4% of zinc was extracted, and this was increased when temperature was increased to 150°C reaching 97.8% and 96.8%, respectively. The temperature effects on the extraction of Cu and Zn are shown in Figures 4.18a and 4.18b, respectively.



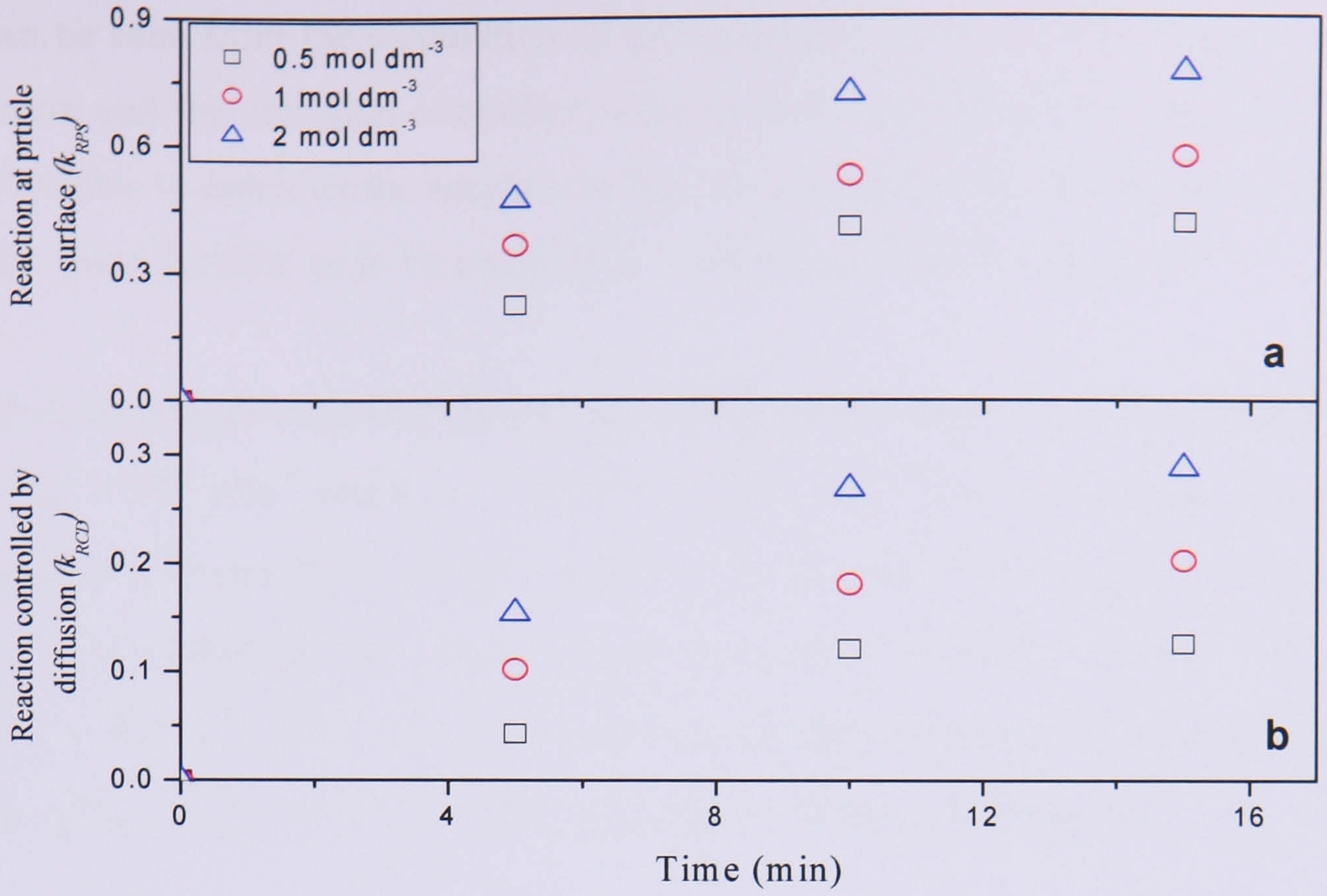
4.10.2.3 Effect of Extraction Time

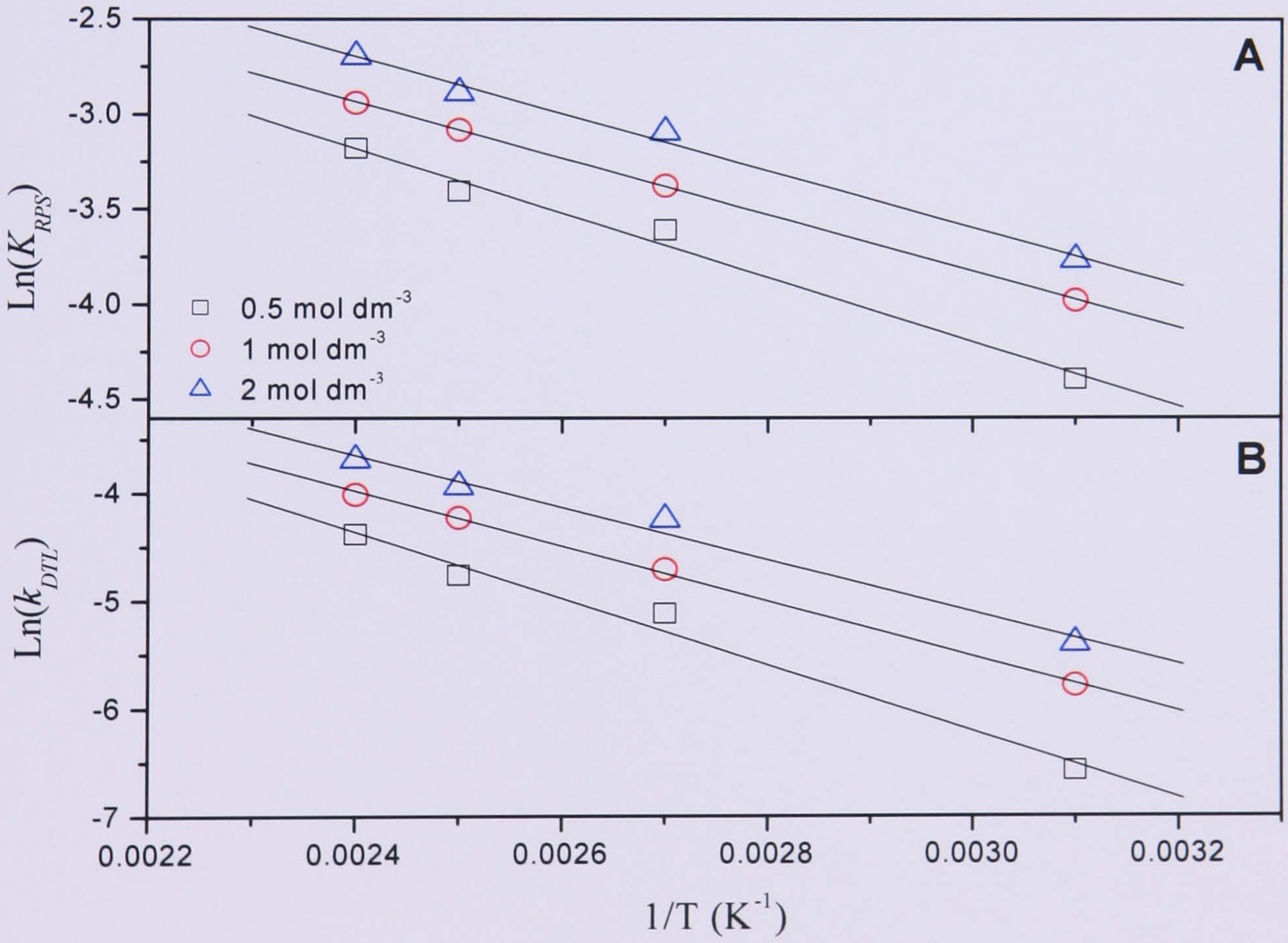
The obtained results in section *4.9.3.4* show that extending the extraction time from 5 minutes to 10 and 15 minutes increased the percentage of copper and zinc extracted from the sample.

4.10.2.4 Kinetic Aspects

A plot of reaction at the particle surface, the right-hand side of equation (2) versus time (*t*) for copper is given in Figure 4.19a. While, the plot of reaction controlled by diffusion, the right-hand side of equation (4), versus *t* time is given in Figure 4.19b.

The data in this figure are fairly correlated to linearity; the plot couldn't answer for the type of the reaction that could take place. In other words, it can't tell whether the reaction is chemically controlled by the reaction at the particle surface or a diffusion-controlled process. On the other hand, the value of the activation energy for the reaction using chemical reaction controlled by reaction at the particle surface, Figure 4.20a, was found as 29.94 ± 1.79 KJ mol^{-1} and the corresponding value found using diffusion controlled was 51.48 ± 1.41 KJ mol^{-1}, Figure 4.20b.


0.9
0.6
0.3
0.0
Reaction at prticle surface (k_{RPS})
0.5 mol dm^{-3}
1 mol dm^{-3}
2 mol dm^{-3}
a
0.3
0.2
0.1
0.0
Reaction controlled by diffusion (k_{RCD})
b
0
4
8
12
16
Time (min)


-2.5
-3.0
-3.5
-4.0
-4.5
Ln(K_{RPS})
A
0.5 mol dm^{-3}
1 mol dm^{-3}
2 mol dm^{-3}
-4
-5
-6
-7
Ln(k_{DTL})
B
0.0022
0.0024
0.0026
0.0028
0.0030
0.0032
1/T (K^{-1})

It can be seen from the calculation of the activation energy for the chemical controlled reaction and the diffusion controlled reaction under the microwave leaching that it was implausible to consider the reaction to be a rate controlled by the reaction on the surface of the spent particle, or to be consider as a diffusion controlled process.

Both models were used and showed fair fitting and revealed rate constants $k_{RPS} = (16.05 \pm 1.02) \times 10^{-3}\ \mathrm{min}^{-1}$ and $k_{RCD} = (49.01 \pm 5.82) \times 10^{-3}\ \mathrm{min}^{-1}$ for copper. The activation energy were found to be $\Delta E_{RPS} = 29.94 \pm 1.02$ KJ mol^{-1} and $\Delta E_{RCD} = 51.48 \pm 1.41$ KJ mol^{-1}. The corresponding values for zinc were: $k_{RPS} = (20.44 \pm 2.88) \times 10^{-3}\ \mathrm{min}^{-1}$ and $k_{RCD} = (10.00 \pm 1.27) \times 10^{-3}\ \mathrm{min}^{-1}$ and the corresponding activation energy were found to be $\Delta E_{RPS} = 27.25 \pm 1.65$ KJ mol^{-1} and $\Delta E_{RCD} = 45.84 \pm 5.58$ KJ mol^{-1}.

4.11 CONCLUSIONS

In this work, traditional and microwave acid extractions were adopted to evaluate the efficiency of metal removal from industrial spent catalysts. The results confirm the importance of an optimised choice of conditions for each step during the extraction process. Four spent catalysts were used to study the extractability of heavy metals (Cu, Zn, Co, Ni and Fe). The experimental results for the traditional acid extraction procedure reveal, that better results were obtained in most of the extractions with nitric and hydrochloric acid rather than with sulfuric acid. However, it was decided to select sulfuric acid for studies due to economic and environmental reasons. The results show that the extraction temperature and acid concentration played significant roles in the extraction process. Extraction at ambient temperature was low for almost all the metals, while an increase in temperature to 50°C and 75°C had a great influence on the recovery of all the metals. Increasing the sulfuric acid concentration led to an increase in the percentage of all the metals extracted when concentration above 1 mol dm^{-3} were used

In the extractions carried out using the microwave technique, parameters of temperature, time and sulfuric acid concentration had a significant role in the extraction process of copper and zinc. The extraction efficiency of copper and zinc in the microwave acid extraction increased sharply with increasing the temperature to 150°C and sulfuric acid concentration to 2 mol dm^{-3}. The percentage of copper and zinc enhanced with the increase in the extraction time from 5 minutes to 10 in sample HA01 and HA02.

Comparison of the microwave process to the traditional extraction procedure for the two metals studied (Cu and Zn), showed that both methods led to similar results. The traditional method extracted 97.6% and 95.1% of copper and zinc respectively compared to 97.8% and 96.8% by the microwave techniques from sample HA01. For sample HA02, 96.0% and 95.5% of Cu and Zn respectively were extracted in the traditional method and 97.1% and 96.6% in the microwave technique.

The efficiency achieved for the extraction of Fe, Ni, Cu, Zn and Co from sample HA04 was above 80% at 50°C with 2 mol dm^{-3} H_2SO_4 and solid to liquid ratio of 1 to 25 g/ cm^3. The heavy metal conventional extraction kinetics of the spent catalysts was studied. Despite of the fact that the experimental data showed no significant differences for the intercept and correlation coefficient values between the chemical controlled reaction and the diffusion controlled reaction. The kinetic study indicates that the leaching process is a diffusion controlled reaction as the conventional method revealed that the calculated activation energies were 8.5, 20.8, 26.9, 20.0 and 19.5 KJ mol^{-1} for Fe, Ni, Cu, Zn and Co respectively; and these values are consistent with the values of activation energies reported for reaction whose rate is controlled by diffusion through the product layer less than 40 KJ mol^{-1}.

The efficiency achieved for the extraction of Cu and Zn using microwave heating technique showed an extraction percentage of copper ranged from 79.2% at 10 min, 0.5 mol dm^{-3} H_2SO_4 and 150°C to 97.8% when the acid concentration increased to 2 mol dm^{-3} for sample HA01. The kinetic study for the leaching under microwave heating showed it was unlikely to deem the reactions to be consistent with a rate controlled reaction on the surface of the spent particle, or with the diffusion controlled process.

According to the results obtained in this work, the microwave technique offers a good choice for extraction as it is relatively faster than the traditional method and therefore will be probably a cost effective method compared to the traditional method. However, since current technology limits the large scalability of microwave applications, the use of industrial instruments is restricted to laboratories. Therefore, users of products related to microwave technology are restricted to corporate laboratories and various educational and research institutions involved in microwave chemistry research.

According to the extraction activation energies obtained in this study, both physical diffusion and chemical reaction play important roles in the overall extraction process. The detailed extraction mechanism, involving both physical and chemical processes, needs to be future investigated.

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Chapter 5

PROCESS OPTIMISATION FOR THE SEPARATION OF DISSOLVED METALS USING ELECTRODIALYSIS SYSTEMS IN THE PRESENCE OF EDTA AS A CHELATING AGENT

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5.1 INTRODUCTION

The recovery of dissolved metals from industrial effluents and their separation as pure metals or added value chemicals is important for both effluent cleanup and metal recycle. In this work, the potential of electrodialysis in the presence of the chelating agent ethylendiaminetetraacetic acid (EDTA) is studied as a means of achieving metal recovery and separation.

Copper and zinc are essential elements in various biological and enzymatic reactions [1] and are also major constituents of important alloys and industrial products. Copper is used in electrical and electronic products, building construction, industrial machinery and equipment, consumer and general products and transportation equipment [2]. Zinc and its compounds are used in production of alloys (brass, bronze, dye and cast alloys) as anticorrosion coatings (galvanization) on steel and iron products, in electrical apparatus, especially dry cell batteries, in the rubber and textile industry, glass ceramic manufacture, and chemical manufacture [3]. The major metal components of effluents from many metallurgical and plating industry processes are copper and zinc. In high concentration in the environment copper and zinc can severely affect aquatic as well as human life. Cu and to lesser extent Zn also affects plants and animals. Therefore, the separation of copper and zinc has been considered to have relatively high priority based upon the environmental risk and reserve depletion.

Many separation methods such as precipitation [4], electrowinning [5], solvent extraction [6,7], liquid membrane technology [8] and ion-exchange [9] have been used in the past to recover and separate Cu and Zn. In this chapter, electrodialysis in the presence of EDTA is studied as a means of copper and zinc separation.

The previous research carried out in the Centre for Environment Research, Brunel University [10], focussed on the separation of nickel and cobalt by electrodialysis in the presence of EDTA using a three-compartment cell. The study proved that the separation of Co and Ni could be achieved in the presence of a complexing agent such as EDTA. Santarosa et al. [11] described the efficiency of two different ion-selective membranes in the separation of zinc and nickel. They reported 90% recovery of zinc and nickel in the first 2 hours of the electrodialysis. Cifuentes et al. [12] studied the effectiveness of various ion exchange membranes for the separation of anolyte and catholyte components in the separation of copper and iron. Qdais and Moussa [13] investigated the removal of copper and cadmium from wastewater by reverse osmosis (RO) and nanofiltration (NF) technologies. The results showed that high removal efficiency of 98% copper and 99% cadmium was achieved using reverse osmosis. The nanofiltration process removed 90% copper but this value increased to 98% with the application of reverse osmosis. Furthermore, the removal efficiency of both systems were compared and the results showed that reverse osmosis was more effective in the removal of the metals attaining 99.4% compared to 97% by the nanofiltration. Cherif et al. [14] have described a method of separation of Ag^+ from Zn^{2+} and Cu^{2+} ions using a monovalent cation specific membrane.

The main aim of the present study was to exploit the difference in the stability constants of the two metals in the presence of chelating agent such as ethylendiaminetetraacetic acid. The stability constant of the Cu-$EDTA^{2-}$ ($10^{-18.8}$) complex is greater than the Zn-$EDTA^{2-}$ ($10^{-16.7}$) complex [15] therefore, the Cu ions form a stronger complex with the EDTA which should migrate towards the anolyte compartment. In contrast, uncomplexed hydrated Zn^{2+} ions should migrate from the middle compartment in a three compartment system to the catholyte compartment. The results of this study were extended to consider zinc-nickel, zinc-cadmium and copper-cadmium separation.

5.2 MEMBRANE TECHNOLOGY

5.2.1 Definition of Membrane

A membrane is a barrier between two phases, some of which are semi-permeable which prevents intimate contact. This barrier can be in any state, solid, liquid or gas but must be permselective, i.e. specific in its restriction of molecular movement. Molecules or particles are transported across the membrane, under the action of a force on the molecule or particle [16].

The extent of this force is determined by the gradient potential, or approximately by the difference in potential, across the membrane (ΔX) divided by the membrane thickness (L) as in equation (1):

$$Driving\ force = \Delta X / L \left[N / mol \right] \qquad (1)$$

Two main potential differences are important in membrane processes, the chemical potential difference (Δμ) and the electrical potential difference (ΔF) (the electrochemical potential is the sum of the chemical potential and the electrical potential) [17].

Permselectivity can be obtained by many mechanisms [16]:

- Size exclusion or molecular sieving
- Differences in diffusion coefficients (bulk as well as surface)
- Differences in electrical charge
- Differences in solubility
- Differences in adsorption and/or reactivity on (internal) surfaces

The effectiveness of the membrane in a certain application depends on the detailed morphology, microstructure of the membrane system and the physicochemical mechanisms. A schematic representation of membrane separation is given in Figure 5.1 [18]. Side 1 is the feed or upstream while side 2 is the downstream or permeate.

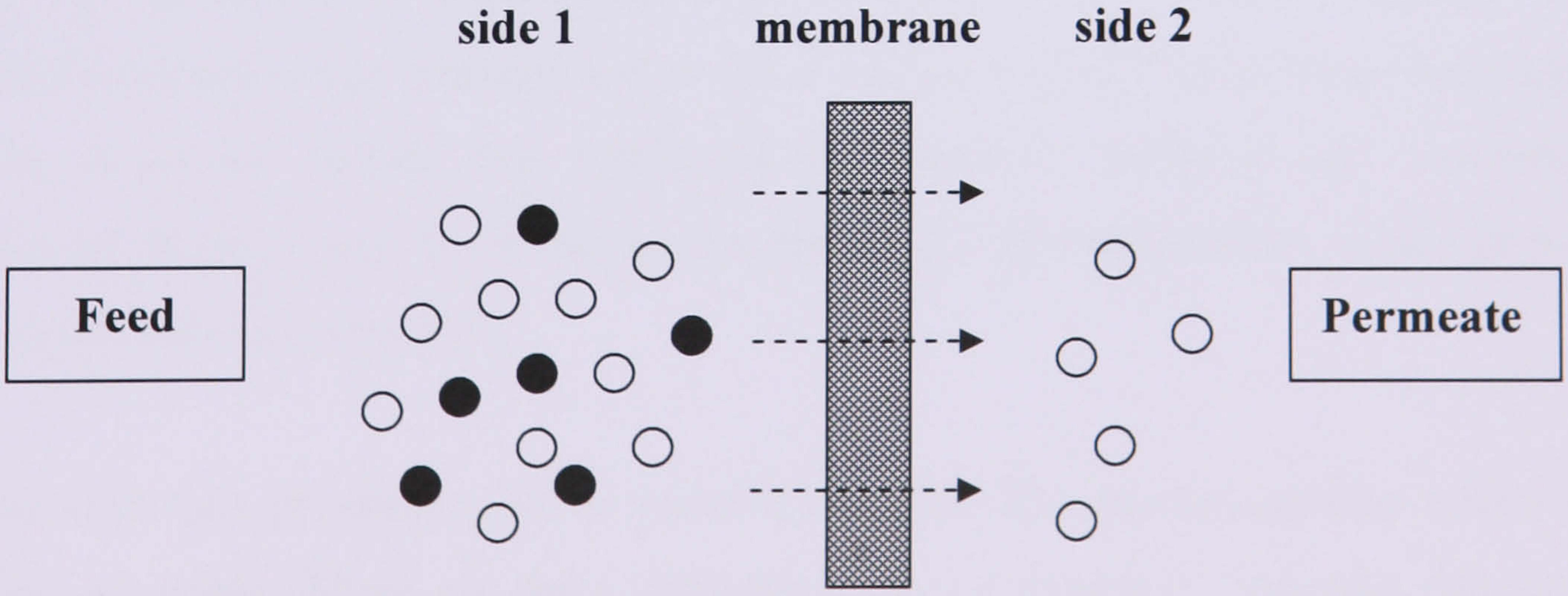


Figure 5.1: Schematic representation of a system separated by a membrane

Separation can be caused since the membrane has the ability to transport a component from the feed mixture with more ease than the other components. The performance and efficiency of a membrane is characterised by two factors; its selectivity and flow through the membrane. The flow through the membrane is usually indicated by the flux or permeation rate, defined as the volume flowing through the membrane per unit area and time. To be effective for separation, membrane materials should ideally possess the following properties [19]:

- Chemical resistance (to both feed and cleaning fluids)
- Mechanical stability
- Thermal stability
- High permeability
- High selectivity
- Stable operation

5.2.2 Classification of Membranes

Membranes are varied, they can be thick or thin, homogeneous or heterogeneous, natural or synthetic, neutral or charged. Transport across the membrane can be active or passive; passive transport can be driven by pressure, concentration or temperature difference. Because of this variation, there are many ways to classify membranes, the first is by nature, i.e. biological or synthetic. This is the most obvious distinction possible and it is a very important one as these two types of membrane differ completely in structure and functionality. Biological membranes can be divided into living and non-living membranes. Synthetic membranes can be subdivided into organic (polymeric or liquid) and inorganic membranes. The most important class of membrane materials are organic, i.e. polymers or macromolecules. The choice of a given polymer as a membrane material is not arbitrary but is based on very specific properties, originating from the structural factors that determine the thermal, chemical and mechanical properties of the polymers. Such factors also determine the permeability, which is more or less an intrinsic property [17].

Inorganic materials generally possess superior chemical and thermal stability relative to polymeric materials. There are three different types of inorganic materials frequently used namely: ceramic membranes; glass membranes: and metallic membranes [16].

Membranes are also classified by their morphology or structure and this is important because the membrane structure establishes the separation mechanism and consequently the application. Solid synthetic membranes can be divided into two types: symmetric and asymmetric membranes and the two classes can be subdivided further [17].

The benefits of membrane technology are [18]:

- Separation can be carried out continuously
- Energy consumption is generally low
- Membrane can be easily combined with other separation processes
- Separation can be carried out under mild conditions
- Up-scaling is easy
- Membrane properties are variable and can be adjusted
- No additives are required

The disadvantages are:

- Concentration polarisation/membrane fouling
- Low membrane lifetime
- Generally low selective or flux
- Up-scaling factor is more or less linear

The other technical advantages of membranes separations, which result in economic advantages, are that they frequently achieve higher efficiency of separation, often yield faster separations and the simplicity of operation in modern compact modules means operation with small or large plant is relatively easy [19].

During the course of a typical permeation and separation process using membranes a variety of phenomena are important including: concentration polarization, adsorption and internal pore fouling influence the permeate rate. Fouling is one of the main factors responsible for the reduction of the flux through the membranes. The major modes of fouling include adsorption, chemical interactions, cake formation and pore blocking. The fouling rates are influenced by the nature of the solutes, their concentration, the membrane type and pore size distribution, water quality, hydrodynamic and surface characteristics of the membrane. The occurrence of fouling affects the performance of the membrane either by deposition of a layer onto the membrane surface or by blockage or partial blockage of the pores and this changes the effective pore size distribution [20].

Hence, membrane fouling and concentration polarisation are common and serious problems because they shorten the service life of membranes, restrict permeate fluxes and subsequently reduce the economic advantages of membrane efficiency. They also impose major limitations on the application and development of membrane processes.

5.3 COMPLEX FORMATION

5.3.1 The Chemistry of Complexation

Complexes are formed by the conjugation of a simple ion with another ion or molecule that may be of opposite charge or neutral. In complexation reactions that involve metals, one or more of the coordinated solvent molecules are replaced by other nucleophilic groups. The groups that are bound to the central ions are known as ligands and in aqueous solutions they are represented by the following equation (2) [15].

$$M(H_2O)_n + L \longrightarrow M(H_2O)_{n-1}L + H_2O \qquad (2)$$

Ligands are usually classified according to the number of attachments they have to the central metal ion, for example, a ligand that is bound to the central metal ion by only one bond (by donating a single pair of electrons) is known as a monodentate ligand. If the ligand molecule or ion has two atoms each with a lone pair of electrons (bidentate), then it becomes possible for the molecule to form two coordinate bonds with the same metal ion. Multidentate ligands contain more than two coordinating atoms per molecule.

5.3.2 Ethylenediaminetetraacetic Acid

Ethylenediaminetetraacetic acid (EDTA) is a synthetic amino acid and a powerful hexadentate chelating ligand. Its elemental formula is $C_{10}H_{16}O_8N_2$ $[(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2]$ with a molecular weight of 292.24. Its uses first were in the 1940's for the treatment of heavy metal poisoning. In industry, it is widely used to enhance metal solubility or to prevent the formation of insoluble metal compounds. When mixed with heavy metal ions, it has a tendency to produce strong complexes with a 1:1 metal:EDTA ratio.

The presence of EDTA in solution hinders metal recovery in the form of insoluble compounds, which is the common practice used in the treatment of spent solutions containing heavy metal ions. It has applications in many industrial processes e.g. metal treatment, photography, pharmaceutical products, industrial cleaning, water softening, textile, paper etc. In medicine it is used in the immediate treatment of hypercalcaemia and to control ventricular arrhythmias associated with digitalis toxicity [21].

EDTA is capable of producing very stable, water soluble complexes with a wide range of metal ions including radionuclides. It is only slowly biodegradable in soil and is resistant to decomposition by radiation, making it a persistent compound in the environment. EDTA is exceptional among chelating agents in that it reacts stoichiometrically and instantaneously with nearly every metal ion carrying more than unit positive charge, and even with certain of the alkali metals. Due to its acidic nature, it can form very soluble metal complexes allowing EDTA and its sodium based salts to dissolve many chemical compounds of the metals [21]. Ethylenediaminetetraacetic acid is usually used as its disodium salt, Figure 5.2.

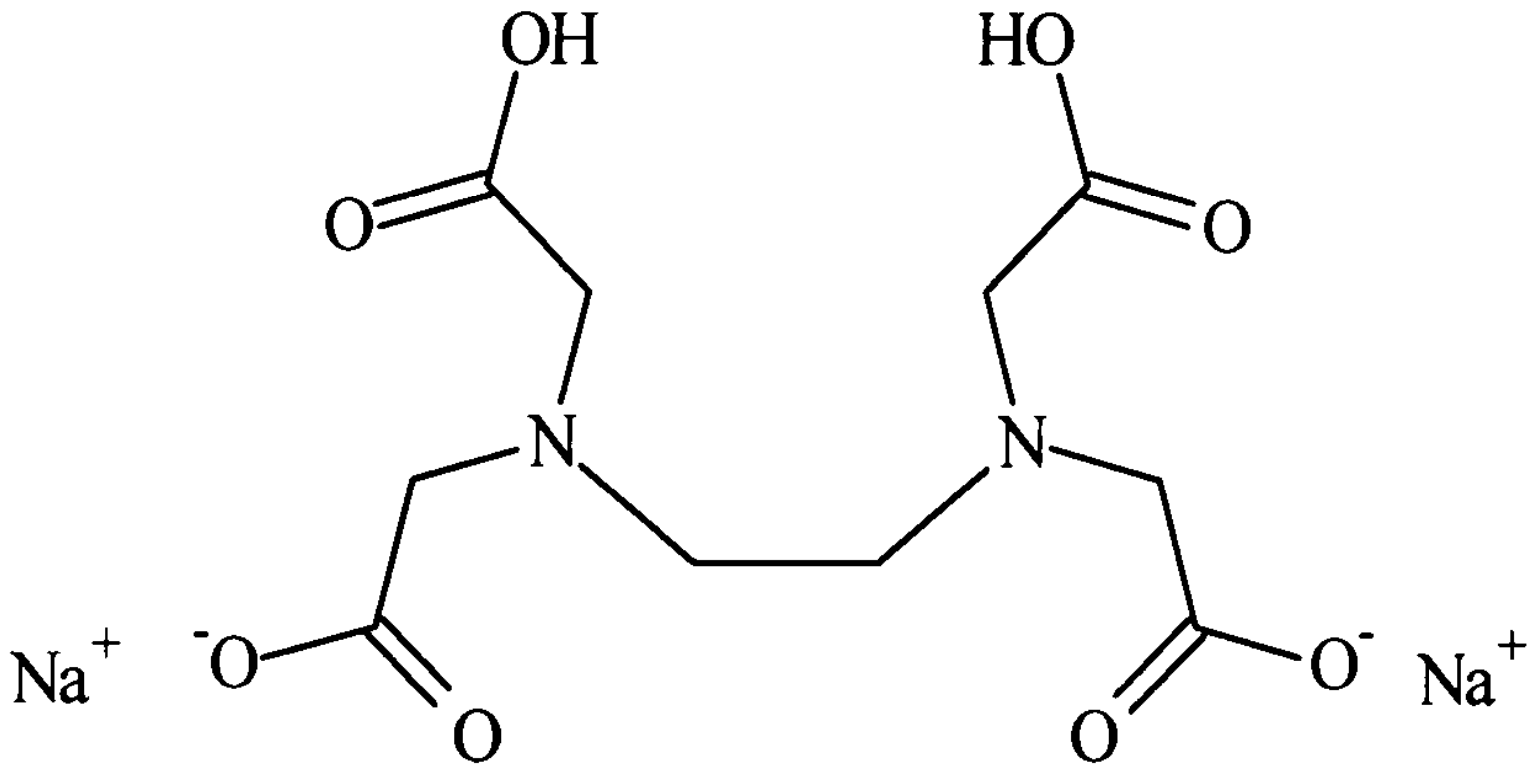


Figure 5.2: Ethylenediaminetetraacetic acid disodium salt $C_{10}H_{14}N_2O_8Na_2$ (Na_2EDTA)

The analytical potential of this group of reagents was first realised at the end of the 1940 by a Swiss chemist called Gerold Schwarzenbach. He applied the generic term "complexones" to the series of complexing agents to highlight the extraordinary ability of these substances to form stable complexes with most metal ions in solution [21].

The complexes formed by these reagents are very soluble: the overall complex remains anionic despite the fact that the metal ions are bound in ring structures. This type of chelate structure is most stable when there are five or six rings, therefore the most chelating agents are those that form the maximum number of such rings and fully saturate the co-ordination requirements of the ions in a one-step reaction. EDTA is an example of such a chelating compound. The complexing power of EDTA depends on bonding reactions of the metal, nitrogen atoms and the carbonyl oxygen of the acetic acid groups. Acetate ions form complexes with practically every metal ion and nitrogen atoms in amines have similar characteristics.

In EDTA, the donor ligands are built into a molecule which is flexible and in such a position that they are easily accessible and correctly spaced to ensure the formation of five-membered rings with cations both across the iminodiacetic acid groups and the ethylenediamine bridge [22]. The colour of EDTA complexes is mainly dependent on the metal ion. The divalent metals react with the disodium salt $Na_2H_2Y^{2-}$ according to equation (3). In this reaction, the metal is bonded to four oxygen atoms and the two nitrogen atoms as shown in Figure 5.3.

$$M^{2+} + H_2Y^{2-} \longleftrightarrow MY^{2-} + 2H^+ \tag{3}$$

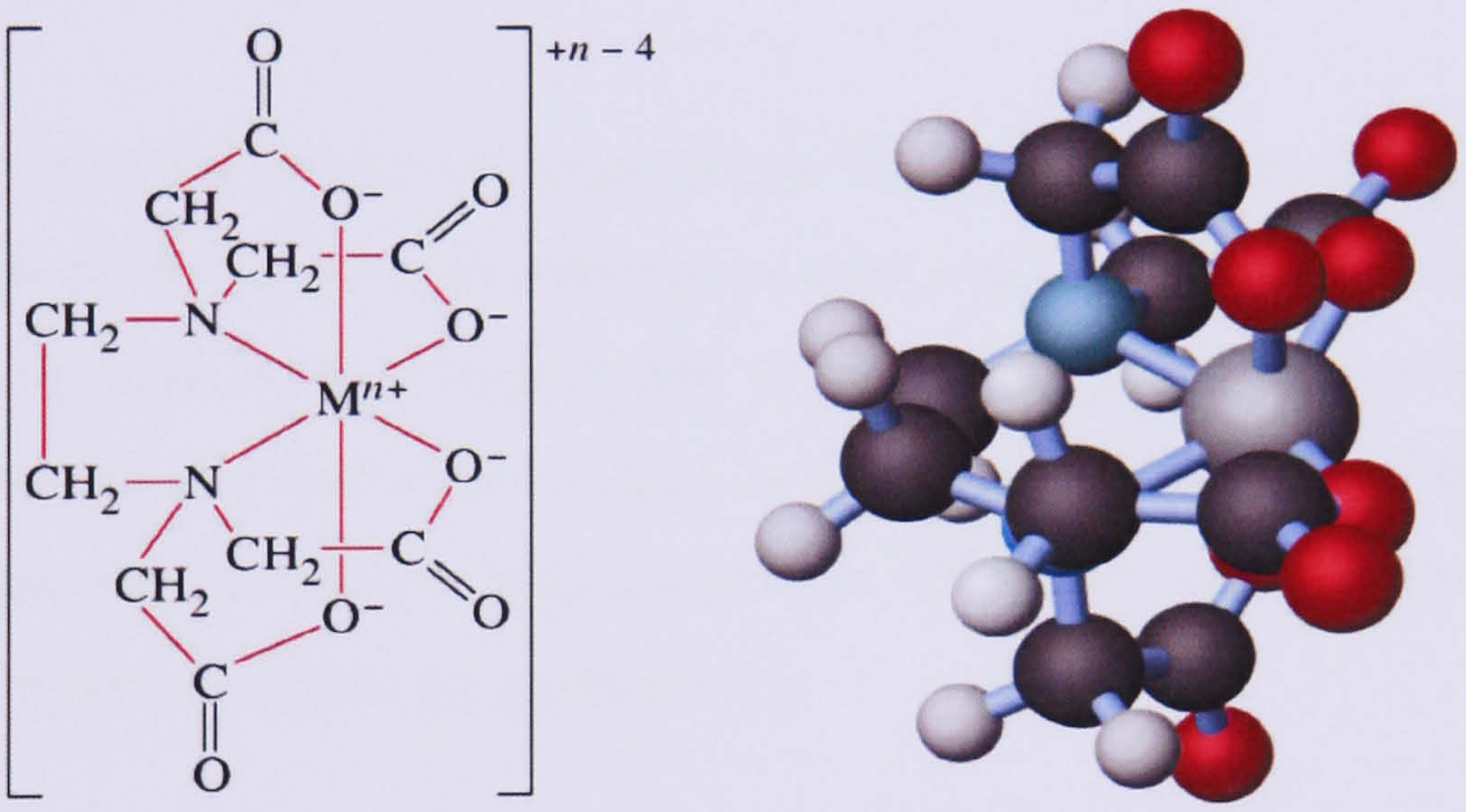


Figure 5.3: Schematic of a metal-EDTA complex structure

5.3.3 Stability Constants of EDTA Complexes

Stability / formation constants determine the stability of a particular complex [15]:

$$M^{n+} + Y^{4-} \longleftrightarrow (MY)^{(n-4)} \tag{4}$$

$$K = \left[(MY)^{(n-4)}\right] / \left[M^{n+}\right]\left[Y^{4-}\right] \tag{5}$$

Equation (5) makes the assumption that the metal ion M^{n+} is uncomplexed, i.e. once in an aqueous solution, the metal ion simply exists as a hydrated ion. However, if other compounds apart from EDTA are present, they can have a propensity to form complexes with the M^{n+} ion, thereby affecting the results. Also of note, in equation 5, only the Y^{4-} form of the ion has been taken into account, however at lower pH, other species such as HY^{3-}, H_2Y^{2-}, H_3Y^- and even undissociated H_4Y may be present. Table 5.1 provides the stability constants (expressed as log K) of some metal-EDTA complexes.

Changes in pH, as well as the presence of other complex forming agents, can alter the stability of the metal-EDTA complex. The dissociation of the complex is in part dictated by the acidity of the solution; a solution of low pH would cause a disruption of the metal-EDTA bond and reduce the stability of the complex to the point of complete breakdown. The minimum pH values for the existence of some metal-EDTA complexes are shown in Table 5.2. A pH lower than the minimum, would cause the destruction of the bonds within the complex and, therefore, the breakdown of the metal-EDTA complex.

Metals that form trivalent bonded complexes with EDTA tend to require more energy to disrupt and are therefore more stable when compared with those of divalent bonds, even in high acidic solutions. This is largely due to the strong chelating reaction of these metals [21]. Generally, the higher the charge on the metal and the higher the charge on the EDTA, the greater the stability constant will be. Therefore, the stability constant of metal-EDTA complexes is given by equation (6):

$$\log K_{HZ} = \log K - \log \alpha - \log \beta \qquad (6)$$

Where

K The stability constant of metal-EDTA

α The ratio of the total uncombined EDTA (in all forms) to the form Y^{4-}

β 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.

Table 5.1: Stability constants (as log K) of metal-EDTA complexes [15]

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

Table 5.2: Stability with respect to pH of some metal-EDTA complexes [15]

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

5.4 ELECTRODIALYSIS

5.4.1 The Theory of Electrodialysis

The use of electrolysis and dialysis was first proposed by Maigrot and Sabates in 1890 [23]. However the actual term; 'Electrodialysis' was proposed some 10 years later in a Patent by Schollmeyer (1900) to purify sugar syrup [23].

Essentially electrodialysis is a separation technique that uses an electromembrane to transport ionised species through ion-exchange membranes which are alternately arranged between the anode and cathode and are under the influence of an electric field. These ion exchange membranes can be divided into Anion Exchange Membrane (AEM) and Cation Exchange Membrane (CEM). The anion exchange membranes contain positively charged groups attached to a polymer, while the cation exchange membranes contain negatively charged groups [18]. Figure 5.4 shows, when a direct current is applied to a solution containing ionic species in a three compartment cell, anions migrate toward the anode passing through the anion-exchange membrane that is only permeable to anions and impermeable to cations; whereas, the cations migrate toward the cathode crossing the cation-exchange membrane which is permeable to cations and impermeable to anions.

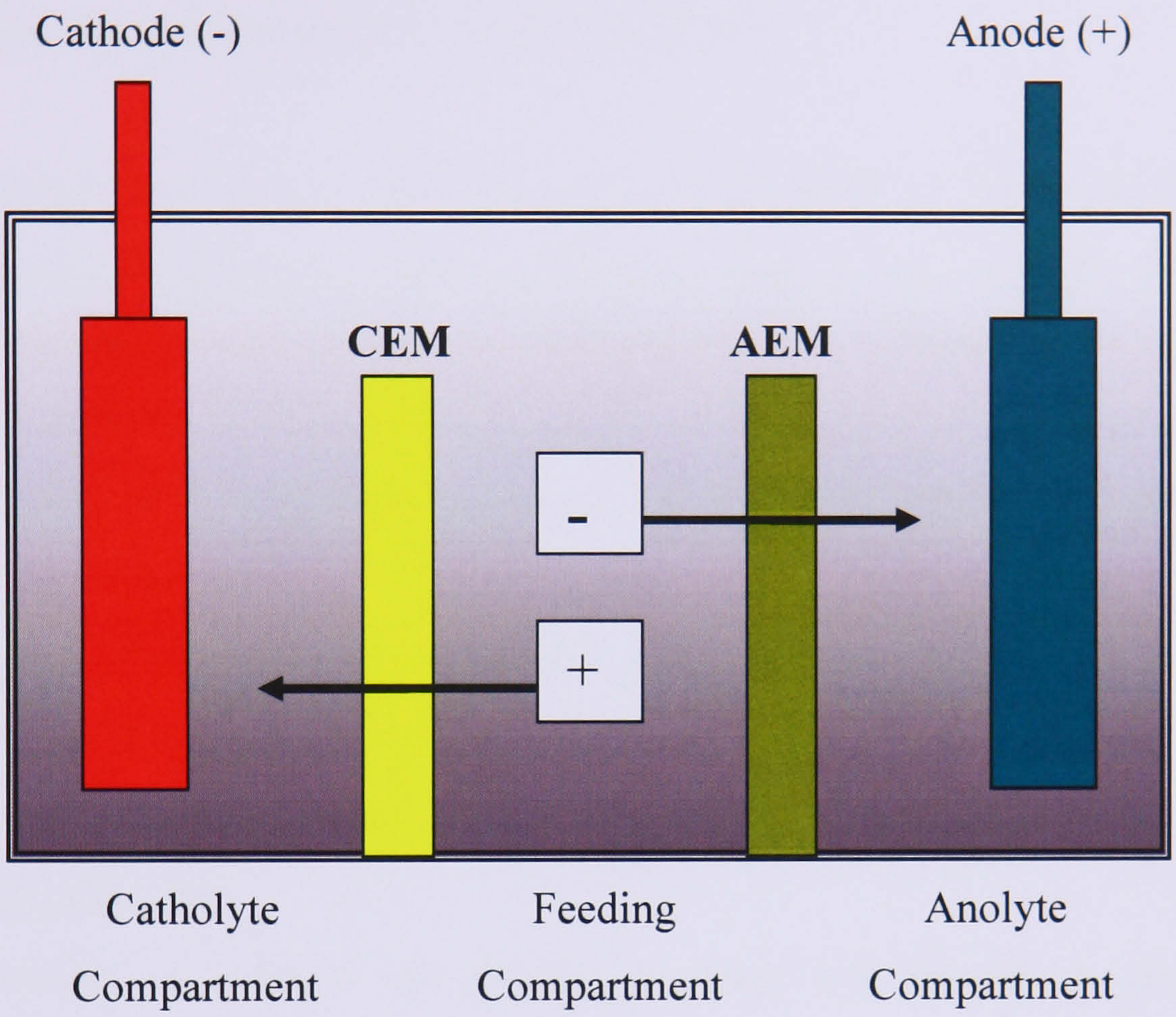


Figure 5.4: Schematic of an electrodialysis cell using both cation and anion exchange membranes

This means that overall effect is that the cationic and anionic concentrations increase and decrease respectively in compartments on either side of the membrane [17]. Hence, it is possible to impoverish or enrich a solution containing ionic species. Electrodialysis should thus permit concentration of metals ions from effluent through the use of high-performance membranes. The membranes are effectively impermeable to the hydraulic transport of water and other solvents.

Every membrane separation process is characterised by the use of a membrane to accomplish a particular separation. The membrane has the ability to transport one component more readily than other because of differences in physical and/or chemical properties between the membrane and the permeating components. Thus, transportation can be carried out through a cation exchange membrane or anion exchange membrane or both (above mentioned).

One of the most attractive features of electrodialysis is its energy efficiency. Because the membranes are not perfectly semipermeable, some co-ions diffuse across the membrane. Nonetheless, electrodialysis uses significantly less energy than competitive processes especially for low concentration feed solutions [24].

Since the membranes used in electrodialysis have the ability to selectively transport ions having positive or negative charge and reject ions of the opposite charge, useful concentration, removal, or separation of electrolytes can be achieved by electrodialysis, allowing the operator to directly influence the concentration of any desired electrolyte. Compared with other separation techniques, electrodialysis offers several significant advantages such as [19]:

- Energy efficient and low investment costs
- Yield a higher quality product
- Easy up and down scaling
- High selectivity
- Operating at ambient temperature avoiding any change or degradation of products
- Continuous operation
- No chemical regenerates or significant feed water pre-treatment
- Proven membrane life

Despite of all these advantages, there are some drawbacks of the membrane processes such as sometimes they require excessive pre-treatment due to their sensitivity to concentration polarization and membrane fouling due to chemical interaction with water constituents. In addition, membranes are mechanically not very robust and can be destroyed by a malfunction in the operating procedure.

Membranes are divided by the type of ions into cation-exchange membranes and anion-exchange membranes.

5.4.2 Electrodialysis with Cation Exchange Membranes

Nafion is a perfluorosulfonate ionomer that is widely used as a cation exchange membrane in a wide variety of electrochemical processes, such as fuel cells, water electrolysers,cholrakali and modified electrodes. It consists of Polytetrafluoroethylene (PTFE) backbone with several perfluorinated pendant side chains that are in turn attached to sulfonic groups $SO_3^-H^+$ which can be substituted by exchangeable cations, Figure 5.5. These structures give great thermal, chemical and mechanical stability, while the sulfonic groups permit it to have a high ionic conductivity. These properties are strongly influenced by the equivalent weight, water content, nature of solvent, exchanged cations and temperature.

Perfluorosulfonated ionomer membranes present a hydrophobic region largely due to the PTFE segments and a hydrophilic region consisting of ionic domains formed by pendant side-chains of perfluorinated vinyl ethers terminated by ion-exchanged groups. When the compound comes into contact with solvents or water, the compound sorbs these ions and incorporates them into its own clusters and channels, causing them to swell. Nafion's mechanical, thermal and chemical properties undergo significant change during cation exchange processes.

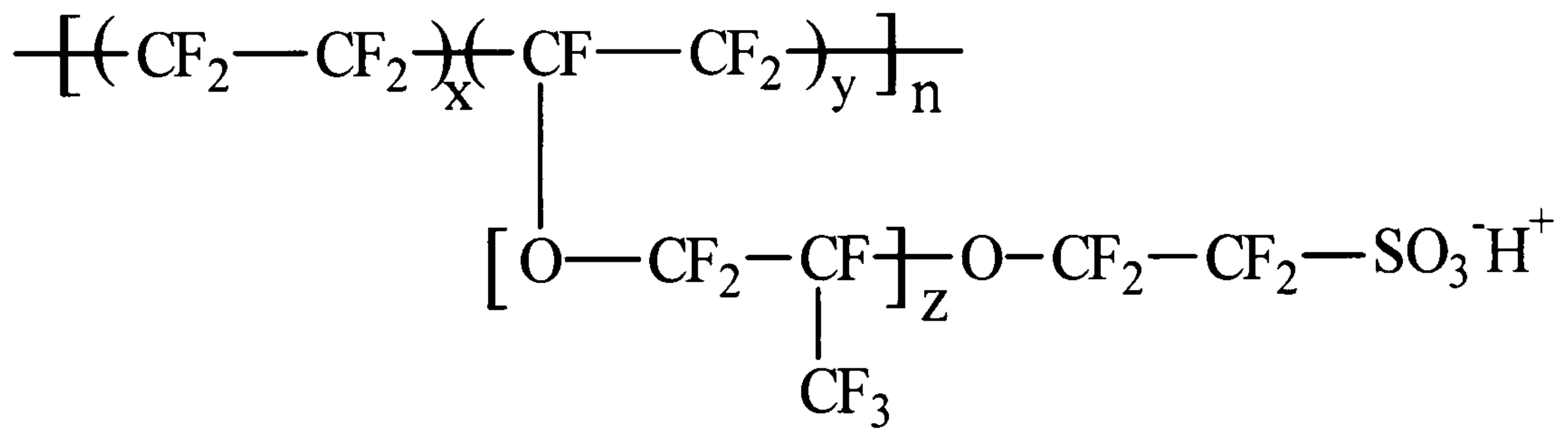


Figure 5.5: Schematic representation of Nafion cation exchange membrane

5.4.3 Electrodialysis with Anion Exchange Membranes

The anion exchange membrane used in this work was ADP anion exchange membrane from SOLVAY, Bruxelles. The membrane minimises the amount of energy required in electrolysis owing to its low electrical resistance. A fluorinated film is exposed to Beta irradiation to produce reactive radicals within the film. These sites are then used as anchors to attach an ion exchange site containing polymer. The irradiated film is then used for radiochemical grafting, which involves the exposition of the film to a monomer which in turn diffuses into the film and polymerises. This polymerisation reaction occurs at the site where the grafted polymer chains are being anchored by the free radicals. As a result, the film and the grafted polymer create a mutual network linked by anchoring points. The grafted film is then deemed functional to provide an ion exchange site. In the case of ADP membranes, the sites are trimethylammine groups [25].

5.4.4 Applications of Electrodialysis

The potential applications of electrodialysis are numerous in different areas. It is used in environmental treatment and materials recycling such as the concentration of electrolyte solutions and for the dilution, or de-ionising, of solutions. Also it is used for removal or recovery of ionic species. In addition, it is utilized in the metal-plating industry for effluent treatment and chemical regeneration from salt solution as well as using the process in the food and pharmaceutical industries [19]. Overall, the process of electrodialysis is used to perform several operations including [20]:

- Separation of salts, acids and bases from aqueous solutions
- Separation of ionic compounds from neutral molecules
- Separation of monovalent ions from ions with multiple charges
- Introduction of ionic moieties to generate new species

5.5 EXPERIMENTAL

5.5.1 Electrodialysis of Copper and Zinc

An electrochemical cell, Figure 5.6, was designed, constructed and used to carry out the experiments in this work. It was constructed from 5 mm width acrylic plates and consisted of three compartments, one for the cathode and catholyte with a capacity of 400 cm^3, a middle (feed) compartment designed to hold 150 cm^3 of the feed solution and a third containing the anode and the anolyte with a capacity of 400 cm^3. The cell was held together by eight 5 mm diameter stainless steel screws bolted at the ends. The anode was made of titanium mesh coated with mixed metal oxide and the cathode was a stainless steel plate. The overall interelectrode gap was 92 mm. The compartments of the cell were separated by a cation exchange membrane between the feed solution and the catholyte and anion exchange membrane between the feed solution and the anolyte.

The distance between the cathode and the cation exchange membrane was 28 mm which was equal to the distance between the anode and the anion exchange membrane. The distance between the two membranes was 36 mm. Figure 5.7 shows the three-compartment cell used in this study.

Two ion exchange membranes; a Nafion N-112 cation exchange membrane (CEM) separate the catholyte compartment from the middle compartment and an ADP Solvay anion exchange membrane (AEM) separates the anolyte compartment from the middle compartment in the sequence anode: anion exchange membrane: feed compartment: cation exchange membrane: cathode. The cation exchange and the anion exchange membranes have the same dimensions of 5 × 5 cm. Zinc and copper solutions were prepared from reagent grade zinc (II) sulfate ($ZnSO_4.7H_2O$), reagent grade copper (II) sulfate ($CuSO_4.5H_2O$) and 98% (w/w) sulfuric acid diluted at different molar concentrations. A current of 0.5 ampere was applied unless otherwise stated from a Thurlby power supply (30V, 2A) and the voltage was kept at a maximum. The chelating agent used in this work was Ethylenediaminetetraacetic acid (EDTA) $[CH_2.N(CH_2.COOH).CH_2.COONa]_2.2H_2O$ as the disodium salt.

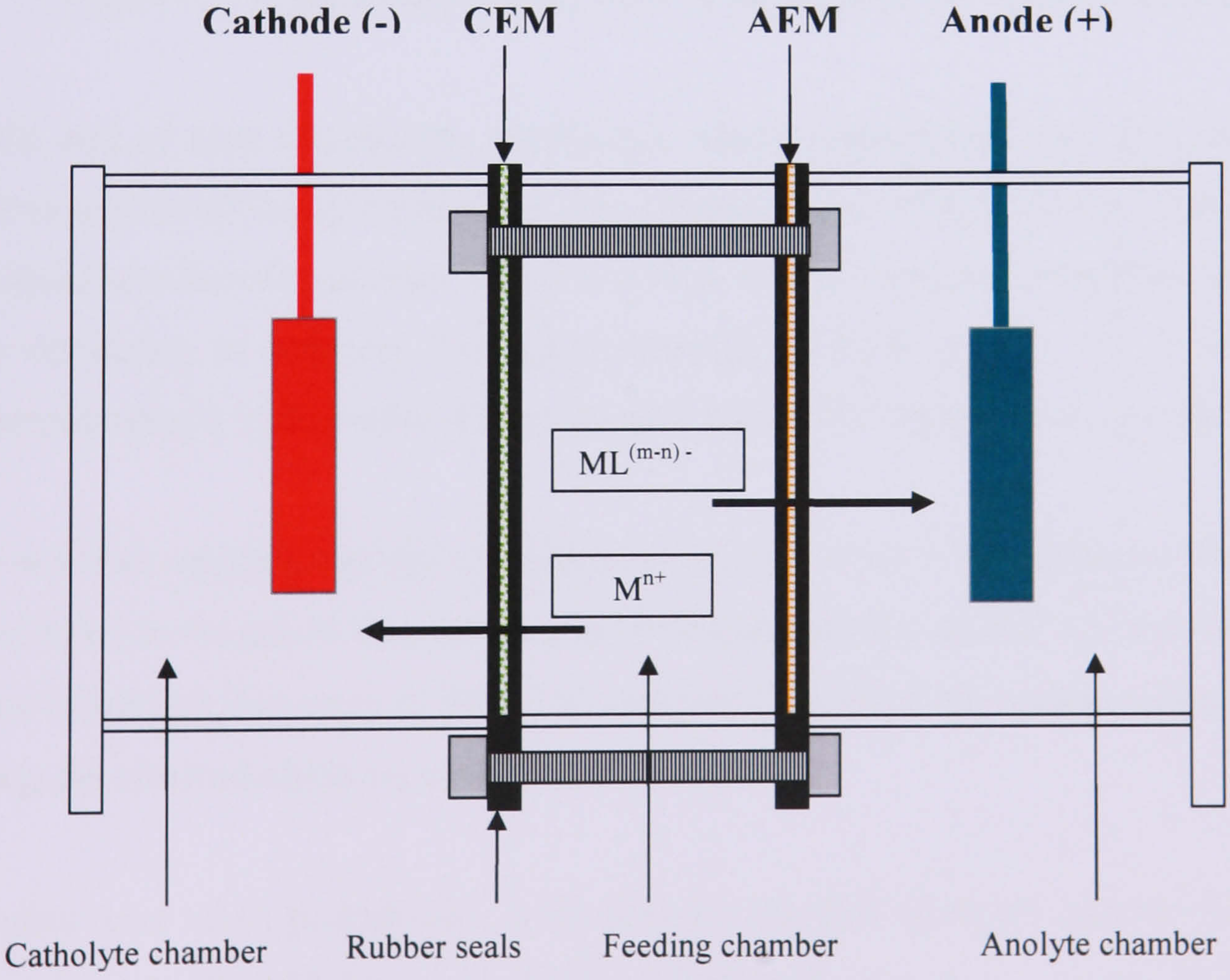


Figure 5.6: Schematic of the three-compartment cell

The initial electrolyte in the catholyte and anolyte compartments was 0.01 mol dm^{-3} H_2SO_4, and the initial feed solution consisted of copper and zinc ions in 0.01 mol dm^{-3} H_2SO_4 in the presence of the chelating agent EDTA-diasodium salt.

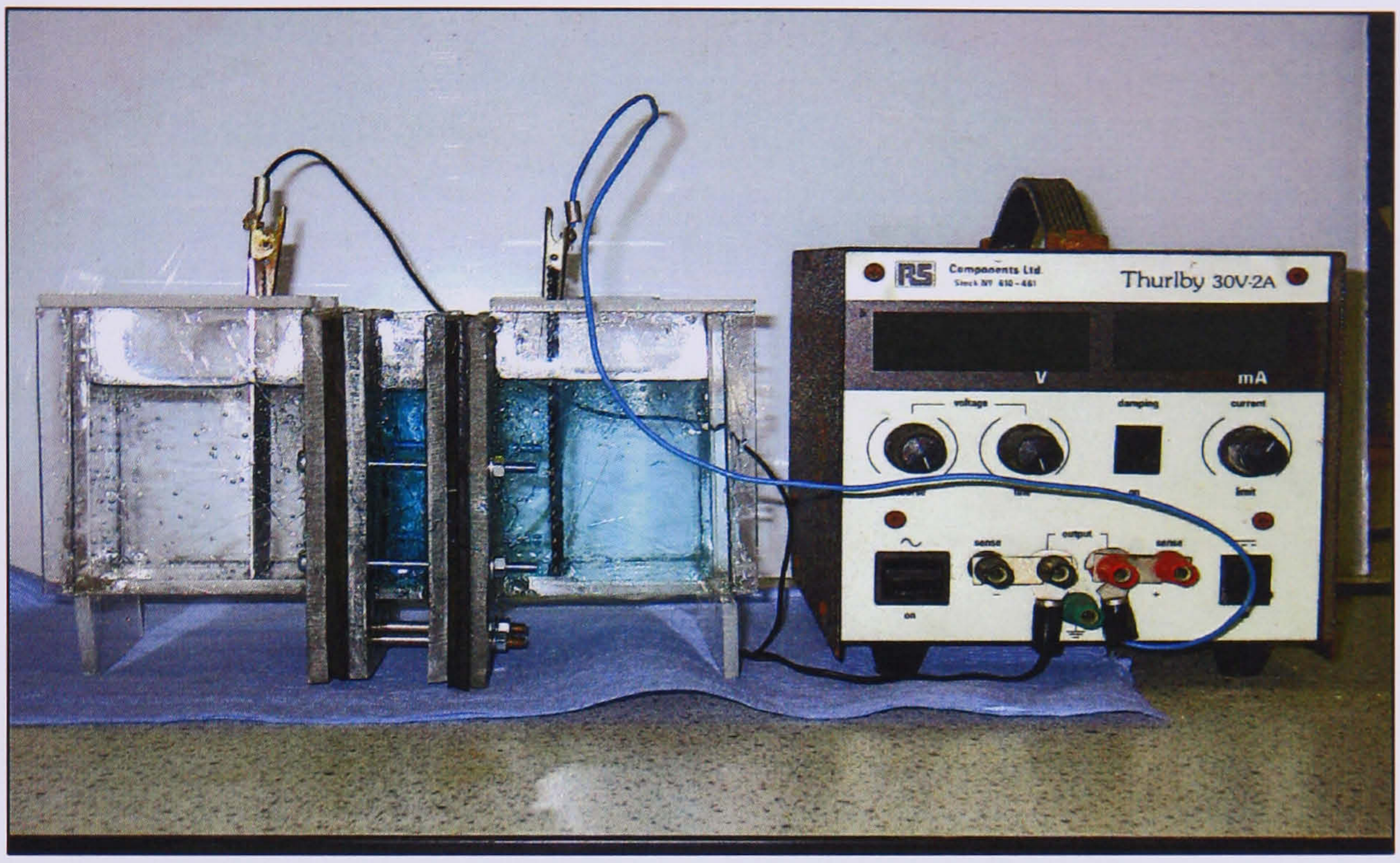


Figure 5.7: A photograph of the three-compartment cell used in this study

At the end of each experiment, membranes were washed twice with distilled water to remove any metal ions prior to reuse. The concentrations of the ions Cu^{2+} and Zn^{2+} were measured as a function of time, which was then used to calculate the percentage of metal ions remaining in solution. The concentrations of metal ions in the solutions were measured using a 3280 Perkin–Elmer Atomic Absorption Spectrometer (AAS).

It is worth to mention that the concentration of metal ions in the catholyte compartment is not equal to the actual amount of metal ions transferred from the feed solution and this is due to the fact that some of the metal ions will deposit on the cathode surface as metal during the electrodialysis process.

Samples were taken periodically every hour for the first six hours and the final sample was taken in after 24 hours for those experiments that were run to 24 hours. All experiments were performed in duplicate and were reproducible.

The effects of the following variables on the separation of copper and zinc were studied:

5.5.2 The Effect of EDTA on Copper-Zinc Electrodialysis

Two comparative experiments were performed to examine the effect of EDTA on the electrodialysis of a Cu-Zn mixture using the three compartment system.

5.5.2.1 The Effect of Presence of EDTA

Preliminary experiments were carried out to investigate the effect of EDTA on the separation of Cu and Zn. In each experiment, the concentration of Cu is equal to the concentration of Zn (500 mg dm^{-3}) in 0.01 mol dm^{-3} H_2SO_4. In the subsequent experiment, the conditions were the same as in the preliminary experiment except with the addition of 0.01 mol dm^{-3} EDTA.

5.5.2.2 The Effect of Changing the Concentration of EDTA

The effects of changing EDTA concentrations in the feed solution was investigated and the range changed between 0.005 – 0.0125 mol dm^{-3} with time on the separation and purification of both zinc and copper in the catholyte and in the anolyte compartments.

5.5.3 The Effect of Changing the Concentration of H_2SO_4

Two sets of experiments were carried out to investigate the effect of changing H_2SO_4 concentration in the middle compartment and all the compartments.

5.5.3.1 The Effect of Changing the Concentration of H_2SO_4 in the Middle Compartment

The effect of H_2SO_4 concentration was studied by changing the sulfuric acid concentration only in the middle compartment and in the range of 0.005–0.05 mol dm^{-3}.

5.5.3.2 The Effect of Changing the Concentration of H_2SO_4 in All Compartments

The effect of changing the concentration of H_2SO_4 in the three compartments was studied using different concentrations ranging from 0.005 to 0.05 mol dm^{-3}.

5.5.4 The Effect of Changing the Copper- Zinc Ratio

In some hydrometallurgical leach solutions the concentration of copper may be less than the zinc concentration. The following experiments were carried out to investigate the optimum conditions to separate small amounts of copper ions from zinc solution.

5.5.4.1 Optimising Removal of Low Levels of Copper from Zinc Solution

The optimum concentration of EDTA for the separation of small quantities of copper from zinc was studied using a Cu:Zn ratio of 50:500 mg dm^{-3} and different concentrations of EDTA (0.0005, 0.00078 and 0.001 mol dm^{-3}) in 0.01 mol dm^{-3} H_2SO_4. The effect of changing the EDTA concentration was studied to optimise the maximum amount of Cu and minimise the amount of Zn moving toward the anolyte compartment.

5.5.4.2 The Effect of Changing the Copper / Zinc Ratio on Copper Removal from Zinc Solutions at a Fixed EDTA Concentration

The effect of the Cu:Zn ratio was investigated by changing the copper concentration (300, 500 and 700 mg dm^{-3}) at a constant zinc concentration 500 mg dm^{-3} and 0.01 mol dm^{-3} of EDTA and 0.01 mol dm^{-3} H_2SO_4.

5.5.5 Electrodialysis of an Industrial Sample in the Presence of EDTA

The effectiveness of electrodialysis was studied on an industrial solution containing copper and zinc. The solution contained 300 mg dm^{-3} of copper and 600 mg dm^{-3} of zinc and the concentration of EDTA used was 0.005 mol dm^{-3}. The initial electrolytes in the catholyte and anolyte compartments contained 0.01 mol dm^{-3} H_2SO_4. The pH of the solution was adjusted to approximately (pH3) using few drops of sodium hydroxide.

5.5.6 Application of Electrodialysis to Different Metal Mixtures

The application of the three compartment membrane process used to separate copper and zinc described in details in section 5.5.1 was extended to separate other metals from mixed solutions. The experiments were carried out to establish the possible separation of metals in a solution of 500 mg dm^{-3} of metals sulfate from a feed compartment containing 0.01 mol dm^{-3} H_2SO_4 and 0.01 mol dm^{-3} EDTA. The initial catholyte and anolyte solutions were 0.01 mol dm^{-3} sulfuric acid. Electrodialysis was performed on the following mixed metal solutions:

- Ni – Zn Mixture in the Presence of EDTA
- Cd – Zn Mixture in the Presence of EDTA
- Cu – Cd Mixture in the Presence of EDTA

These experiments were carried out using the following reagent grade chemicals as source materials; zinc sulfate ($ZnSO_4.7H_2O$), nickel sulfate ($NiSO_4.6H_2O$), cadmium sulfate ($3CdSO_4.8H_2O$) and copper sulfate ($CuSO_4.5H_2O$).

5.6 RESULTS AND DISCUSSIONS

5.6.1 The Effect of EDTA on Copper-Zinc Electrodialysis

5.6.1.1 The Effect of EDTA

Table 5.3 shows that in the control experiment there was no separation of copper from zinc because no metal ions transferred to the anolyte compartment over 24 hours experiment.

Both metal ions copper and zinc were transported to the catholyte compartment and the reason for decreasing the percentage of copper ions in the catholyte compartment rather than zinc ions is because the electrodeposition process is pH dependant and therefore copper ions with an electrode potential of +0.34 deposit before the zinc ions with an electrode potential of -0.76. Figure 5.8 is a photograph shows the deposition of copper on the cathode plate in the control experiment.

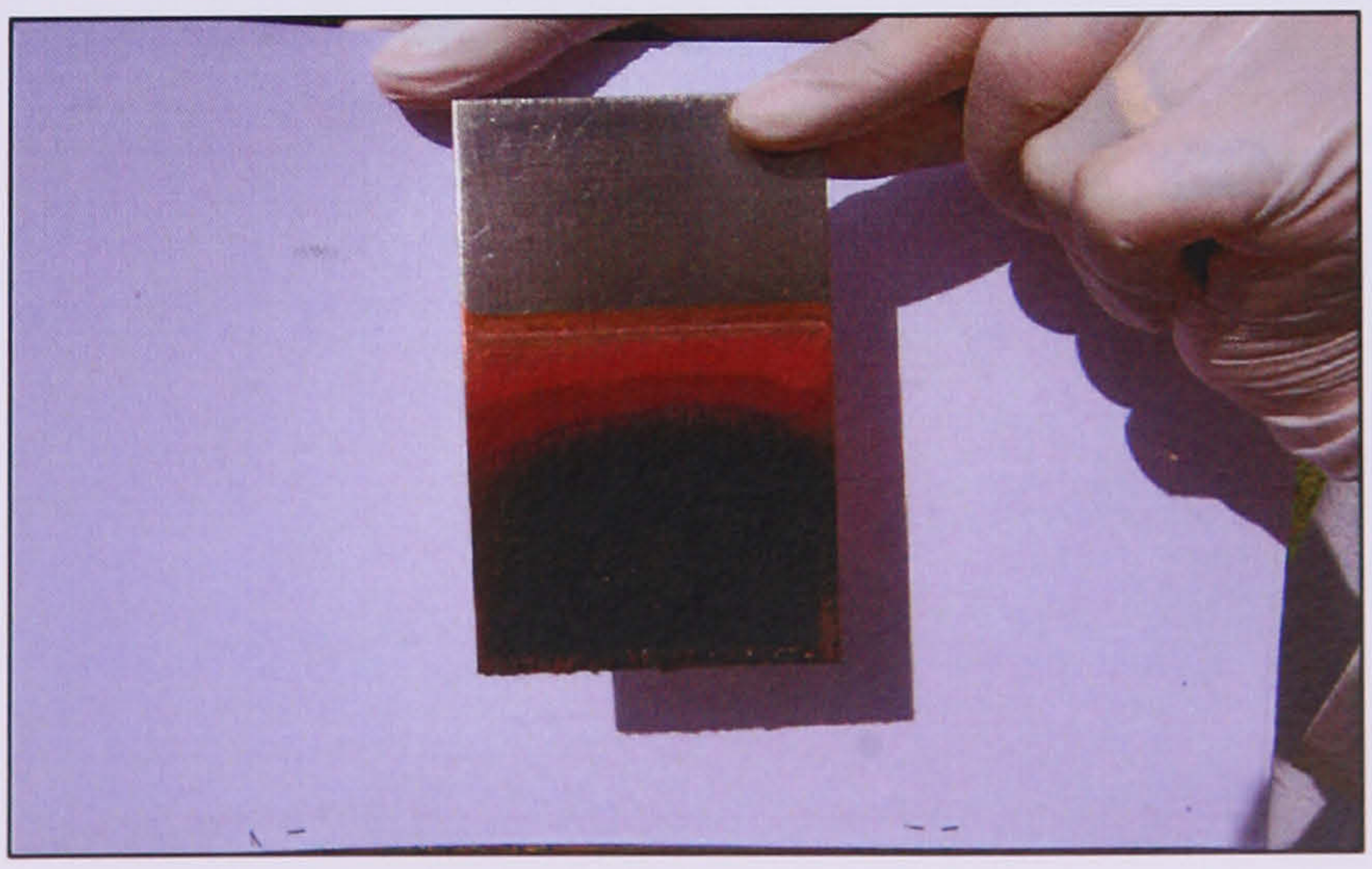


Figure 5.8: Shows the deposition of copper on the cathode plate

Figure 5.9 shows the influence of EDTA absence and presence on the separation of copper and zinc ions in the three compartments electrodialysis system. When EDTA is added, the percentage of metal ions transferred to the anolyte compartment increases with time, and is significantly higher for copper than zinc. This is because adding the EDTA to the solution leads to the formation of the Cu-EDTA complex with a stability constant of $10^{-18.8}$ in preference to Zn-EDTA with a stability constant of $10^{-16.7}$. The metal content in the catholyte compartment also increases predominantly with time, but with significantly greater amounts of zinc than of copper ions.

The anionic Cu-EDTA complex is transported to the anolyte compartment through the anion exchange membrane and degrades at the anode by the anodic oxidation process releasing hydrated copper ions [25]. These hydrated Cu cations cannot return to the middle compartment through the anion exchange membrane. On the other hand, the Zn ions are transferred to the catholyte compartment and some of the Cu is deposited on the cathode plate.

Table 5.3: The Electrodialysis of copper and zinc

Time (Hours)	Zinc percentage in solution			Copper percentage in solution		
	Catholyte	**Middle**	**Anolyte**	**Catholyte**	**Middle**	**Anolyte**
Control experiment (in the absence of EDTA)						
0	0.0	100	0.0	0.0	100	0.0
2	29.9 ± 1.5	35.0 ± 1.8	0.0	47.1 ± 1.3	37.2 ± 1.3	0.0
4	49.3 ± 2.8	15.0 ± 2.3	0.0	67.8 ± 3.8	18.2 ± 2.2	0.0
6	75.1 ± 1.6	1.4 ± 2.6	0.0	90.2 ± 2.1	2.1 ± 1.1	0.0
24	99.6 ± 0.4	0.4 ± 0.3	0.0	99.7 ± 0.3	0.3 ± 0.1	0.0
EDTA presence						
0	0.0	100	0.0	0.0	100	0.0
2	19.4 ± 1.7	51.1 ± 2.1	5.1 ± 1.1	0.5 ± 0.2	56.4 ± 1.3	24.7 ± 1.6
4	38.1 ± 2.2	30.8 ± 1.5	8.6 ± 0.6	0.8 ± 0.1	34.2 ± 2.1	46.3 ± 1.7
6	52.0 ± 1.8	18.3 ± 1.3	10.7 ± 1.0	1.0 ± 0.4	15.4 ± 2.5	72.9 ± 2.1
24	84.1 ± 1.2	0.5 ± 0.2	15.4 ± 1.2	2.2 ± 0.5	0.2 ± 0.06	97.6 ± 0.5

Control experiment: Zn=Cu = 500 mg dm^{-3}, 0.01 mol dm^{-3} H_2SO_4 and Current 0.5 A
EDTA presence: Zn=Cu = 500 mg dm^{-3}, 0.01 mol dm^{-3} H_2SO_4, Current 0.5 A and 0.01 mol dm^{-3} EDTA

The table above shows the concentrations do not up to 100%. This is most likely due to metal deposition on electrode.

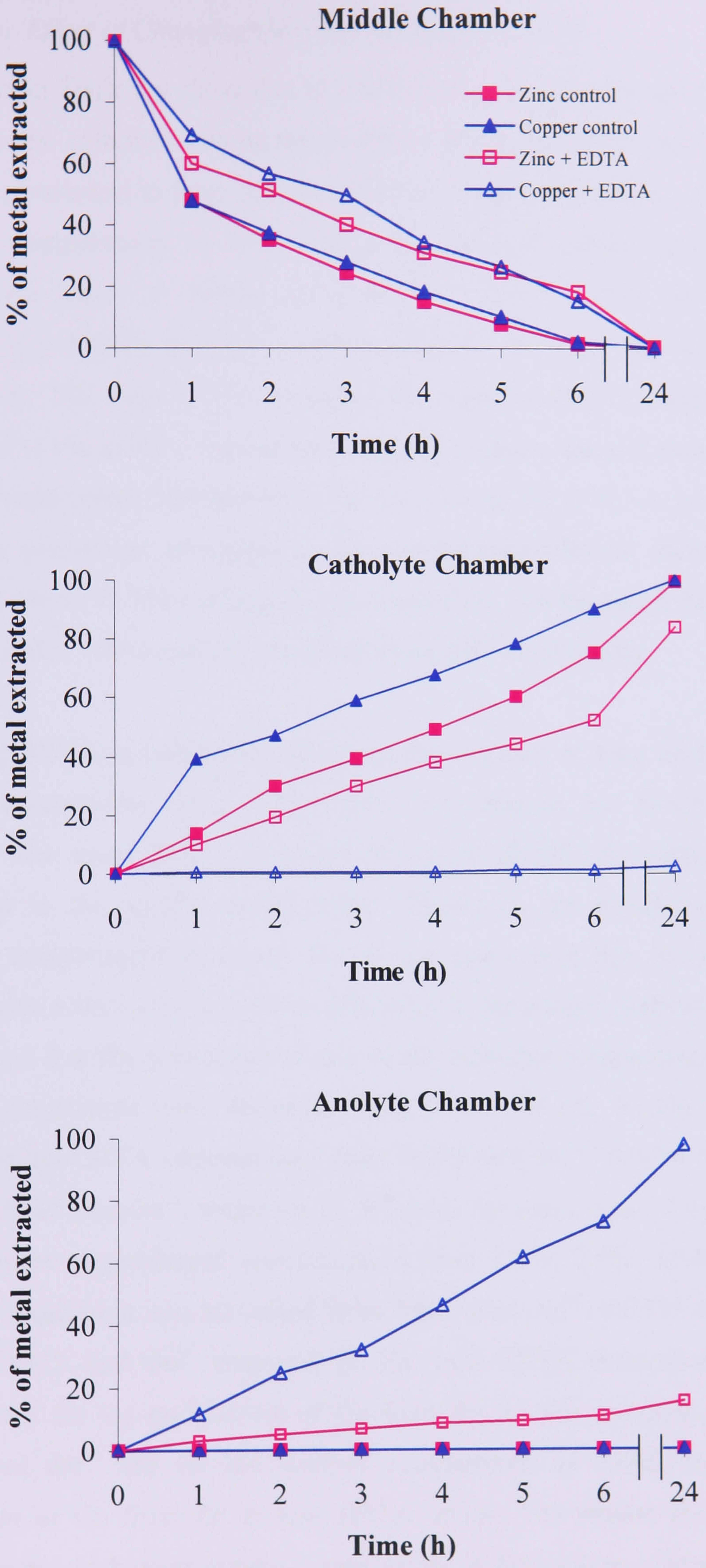


Figure 5.9: The effect of the presence of EDTA on the metal levels with time in the electrodialysis of Cu-Zn

5.6.1.2 The Effect of Changing the Concentration of EDTA

The results in Table 5.4 show that at low EDTA concentration some of the copper ions transfer to the catholyte compartment due to the insufficient amount of EDTA in the middle compartment to form complex with the copper ions. Hence the zinc purity in the catholyte compartment is low. The percentage of copper ions in the catholyte compartment after 24 hours, were 46.1%, 21.0%, 2.2% and 1.3% at EDTA concentration of 0.005 mol dm^{-3}, 0.0075 mol dm^{-3}, 0.01 mol dm^{-3} and 0.0125 mol dm^{-3} respectively. The more EDTA is added the more Cu-EDTA complex is formed and transferred to the anolyte compartment. For this reason, the percentage of copper in the anolyte compartment increases with the increase in the EDTA concentration. After 24 hours, the percentage of copper in the anolyte compartment increased from 53.3%, 78.6%, 97.6% to 97.1% when EDTA concentration was increased from 0.005 mol dm^{-3}, 0.0075 mol dm^{-3}, 0.01 mol dm^{-3} to 0.0125 mol dm^{-3} respectively.

Increasing EDTA concentration increases the amount of zinc ions transferred to the anolyte compartment along with copper ions due to the formation of Zn-EDTA complex. The more EDTA is added the more Zn-EDTA complex is formed and transferred to the anolyte compartment. Therefore, the purification of zinc in the catholyte compartment increases and at the same time this increase in the EDTA concentration reduces the separation efficiency in the anolyte compartment, Figure 5.10. It was found that the percentage of zinc in the catholyte compartment by the end of the 24 hours experiment were decreased from 98.4%, 96.8%, 84.1% to 48.5% with the increase in the EDTA concentration from 0.005 mol dm^{-3}, 0.0075 mol dm^{-3}, 0.01 mol dm^{-3} to 0.0125 mol dm^{-3}, respectively. Whereas the percentage of zinc ions transferred to the anolyte compartment was increased from 1.0%, 2.8%, 15.4% to 50.7% when EDTA concentration was increased from 0.005 mol dm^{-3}, 0.0075 mol dm^{-3}, 0.01 mol dm^{-3} to 0.0125 mol dm^{-3} respectively. The best EDTA concentration in the middle compartment for the purification of Cu from Zn for the catholyte compartment is at 0.0125 mol dm^{-3} and for the anolyte compartment is 0.005 mol dm^{-3} indicating purification of Cu from Zn at low EDTA levels. The results show that the EDTA concentration which gives greater copper purity in the anolyte compartment, results in a less pure zinc in the catholyte compartment, and vice versa. The use of EDTA at a concentration of 0.01 mol dm^{-3}, however, gives a good degree of copper separation from zinc and good purification of zinc in the catholyte compartment.

Figure 5.10: Effect of EDTA concentrations on the separation of copper and zinc in the copper-zinc mixture

Table 5.4: The effect of changing the EDTA concentration on the separation of copper and zinc

EDTA mol dm^{-3}	**Zinc percentage in solution**		**Copper percentage in solution**	
	Catholyte	**Anolyte**	**Catholyte**	**Anolyte**
0.005	98.4 ± 0.5	1.0 ± 1.0	46.1 ± 2.5	53.3 ± 1.3
0.0075	96.8 ± 2.4	2.8 ± 0.5	21.0 ± 2.1	78.6 ± 1.5
0.010	84.1 ± 1.2	15.4 ± 1.2	2.2 ± 0.5	97.6 ± 0.5
0.0125	48.5 ± 1.8	50.7 ± 2.4	1.3 ± 0.4	97.1 ± 1.0

Cu=Zn 500 mg dm^{-3}, 0.01 mol dm^{-3} H_2SO_4, current 0.5 A in 24 hours

5.6.2 The Effect of Changing the Concentration of H_2SO_4

5.6.2.1 In the Middle Compartment

The 24 hour data in Table 5.5 show that increasing the H_2SO_4 concentration from 0.005 mol dm^{-3} to 0.05 mol dm^{-3} decreases the percentage of copper transferred to the catholyte compartment from 4.3% to 0.6%.

It was found that an increase in sulfuric acid concentration increases the zinc purity in the catholyte compartment and, at the same time, it decreases the initial transportation of the zinc and copper ions towards the catholyte and the anolyte compartments respectively.

This reduction in the initial transportation is attributed to the fact that during the electrodialysis, the dissociation of water into hydrogen and hydroxyl ions and H_2SO_4 into hydrogen and sulfate ions can occur and, therefore, an increase in the sulfuric acid concentration will favour the transportation of small ions such as hydrogen and sulfate rather than larger ions such as zinc and the Cu-EDTA complexes across the cation and anion exchange membranes respectively. This effect can be followed by the change in pH of the middle compartment during the electrodialysis processes. The pH changed from 2.2 to 4.3 and from 1.5 to 3.4 after 24h in 0.005 and 0.05 mol dm^{-3} H_2SO_4 solutions respectively, Figure 5.11.

Table 5.5: The effect of changing the concentration of H_2SO_4 in the middle compartment

H_2SO_4 mol dm^{-3}	**Zinc percentage in solution**		**Copper percentage in solution**	
	Catholyte	**Anolyte**	**Catholyte**	**Anolyte**
0.005	83.5 ± 0.7	16.3 ± 0.4	4.3 ± 0.5	95.2 ± 0.8
0.01	84.1 ± 1.2	15.4 ± 1.2	2.2 ± 0.5	97.6 ± 0.5
0.03	81.4 ± 1.3	18.3 ± 1.0	1.0 ± 0.4	98.8 ± 0.8
0.05	83.8 ± 1.1	16.0 ± 0.7	0.6 ± 0.2	99.0 ± 0.5

Zn=Cu 500 mg dm^{-3}, current 0.5 A and 0.01 mol dm^{-3} EDTA in 24 hours

5.6.2.2 In All Three Compartments

The results show in Table 5.6 that increasing H_2SO_4 concentration in all compartments decreases the zinc purity in the catholyte compartment, for example at 0.005 mol dm^{-3} the percentage of zinc and copper in the catholyte compartment were 83.1% and 2.2% respectively. These figures reached 86.1% and 3.9% for Zn and Cu respectively when H_2SO_4 concentration was increased to 0.05 mol dm^{-3}.

Increasing the H_2SO_4 concentration slightly increased the separation efficiency in the anolyte compartment ranged from 16.7% and 97.6% for Zn and Cu at 0.005 mol dm^{-3} to 15.4% and 97.6% at 0.01 mol dm^{-3} respectively, and 13.4% and 95.1% when the H_2SO_4 concentration was increased to 0.05 mol dm^{-3}. Figure 5.12 demonstrates the effect of H_2SO_4 concentration on the separation of copper and zinc in the copper-zinc mixture in all compartments respectively.

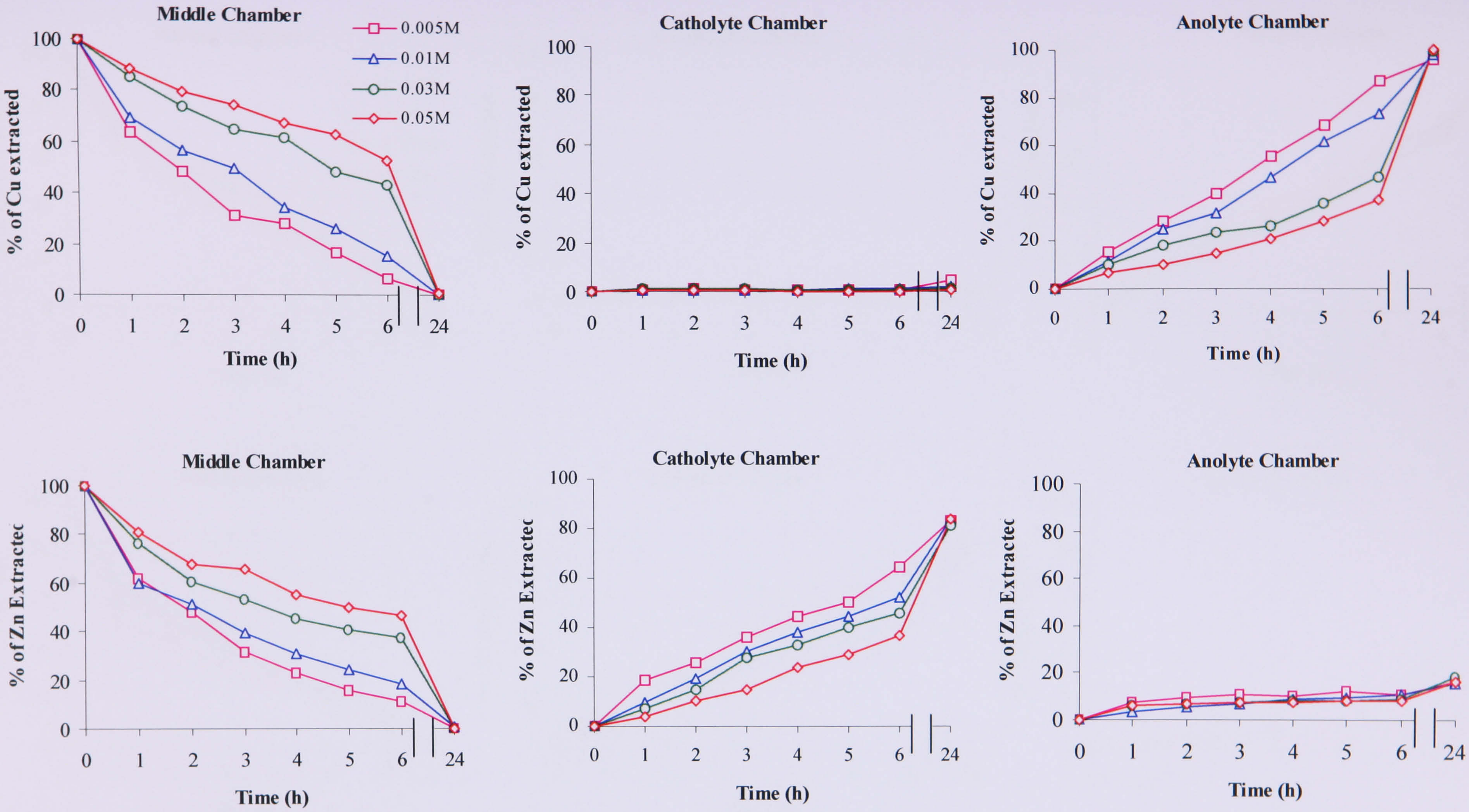


Figure 5.11: Effect of H_2SO_4 concentrations on the separation of copper and zinc in the copper-zinc mixture in the middle compartments

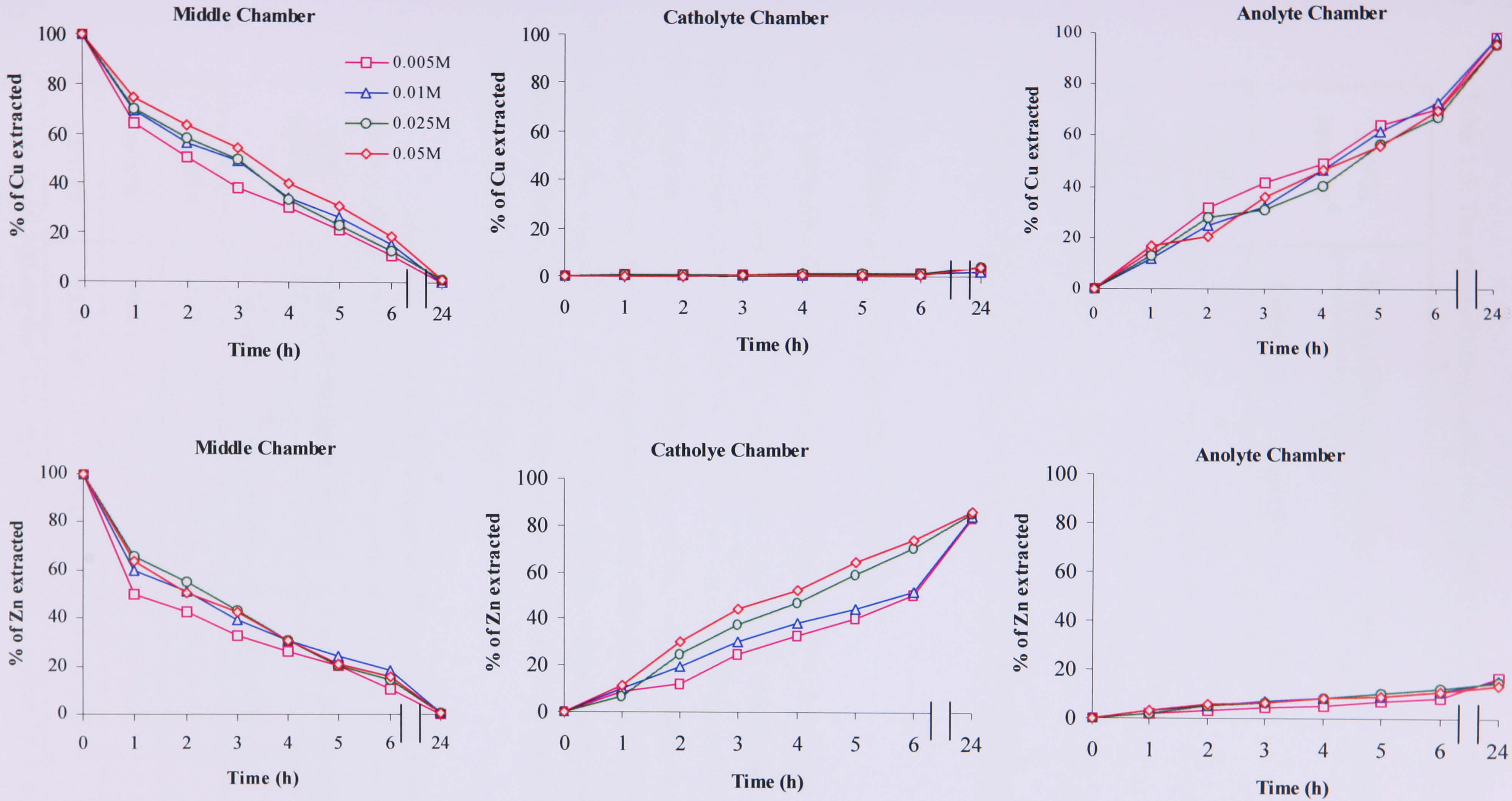


Figure 5.12: Effect of H_2SO_4 concentrations on the separation of copper and zinc in the copper-zinc mixture in all compartments

Table 5.6: The effect of changing the concentration of H_2SO_4 in all compartments

H_2SO_4 mol dm^{-3}	**Zinc percentage in solution**		**Copper percentage in solution**	
	Catholyte	**Anolyte**	**Catholyte**	**Anolyte**
0.005	83.1 ± 1.5	16.7 ± 0.5	2.2 ± 0.3	97.6 ± 1.1
0.01	84.1 ± 1.2	15.4 ± 1.2	2.2 ± 0.5	97.6 ± 0.5
0.03	85.0 + 0.4	14.6 ± 1.1	3.7 ± 0.5	95.3 ± 0.8
0.05	86.1 ± 1.0	13.4 ± 0.5	3.9 ± 0.5	95.1 ± 1.0

Zn=Cu = 500 mg dm^{-3}, current 0.5 A and 0.01 mol dm^{-3} EDTA in 24 hours

5.6.3 The Effect of Changing the Zinc-Copper Ratio

5.6.3.1 Optimising Removal of Low Levels of Copper from Zinc Solution

The results in Table 5.7 show that an increase in the EDTA concentration resulting in a slight increase in the transportation of the zinc ions toward the anolyte compartment. The highest percentage of zinc 96.8% in the catholyte compartment was obtained when a 0.00075 mol dm^{-3} EDTA concentration was used. Increase in the EDTA concentration increases the purification of zinc in the catholyte compartment and decrease the separation process in the anolyte compartment. Figure 5.13 show the effects of changing the EDTA concentrations in the separation process.

Table 5.7: The effect of changing the EDTA concentration

EDTA mol dm^{-3}	**Zinc percentage in solution**		**Copper percentage in solution**	
	Catholyte	**Anolyte**	**Catholyte**	**Anolyte**
0.00075	96.8 ± 0.8	3.0 ± 0.3	20.1 ± 1.1	79.7 ± 1.5
0.0010	96.0 ± 0.5	3.6 ± 0.3	6.1 ± 0.8	93.6 ± 0.5
0.00125	95.0 ± 0.5	4.4 ± 0.6	4.8 ± 1.2	94.5 ± 1.0

Cu:Zn 50:500 mg dm^{-3}. 0.01 mol dm^{-3} H_sSO_4 and current 0.5 A in 24 hours

Figure 5.13: The effect of changing the EDTA concentration on the transportation of copper and zinc in the copper-zinc mixture

5.6.3.2 The Effect of Changing the Zinc/Copper Ratio on Copper Removal from Zinc Solutions at Fixed EDTA Concentration

The results in Figures 5.14 show that an increase in the Cu:Zn ratio at a fixed EDTA concentration leads to a reduction in the purification of the zinc solutions in the catholyte compartment, but enhance the separation of Cu from Zn in the anolyte compartment. This is because at a ratio of 500:300 mg dm^{-3} most of the copper ions are complexed with the EDTA to form Cu-EDTA in the middle compartment and transferred to the anolyte compartment.

The data in Table 5.8 shows that some of the zinc ions will also transfer to the anolyte compartment after forming a Zn-EDTA complex. In the case of Zn:Cu ratios of 500:500 and 500:700 the uncomplexed copper ions are transferred to the catholyte compartment and consequently leads to a reduction in the purification of the zinc solutions in the catholyte compartment.

Table 5.8: The effect of changing the initial Zn:Cu ratio

Initial Zn:Cu mg dm^{-3}	**Zinc percentage in solution**		**Copper percentage in solution**	
	Catholyte	**Anolyte**	**Catholyte**	**Anolyte**
500:300	62.7 ± 2.5	37.0 ± 2.3	0.8 ± 0.2	98.1 ± 0.4
500:500	84.1 ± 1.2	15.4 ± 1.2	2.2 ± 0.5	97.6 ± 0.5
500:700	84.3 ± 1.3	15.5 ± 0.6	4.1 ± 0.5	95.7 ± 1.0

0.01 mol dm^{-3} H_2SO_4, current 0.5 A and 0.01 mol dm^{-3} EDTA

Figure 5.14: The effect of changing the Cu:Zn ratio in the separation of copper and zinc in the copper-zinc mixture

5.6.4 Electrodialysis of an Industrial Sample in The Presence of EDTA

The data in Table 5.9 show that a large percentage 94.1% of the zinc ions was transferred through the cation exchange membrane to the catholyte compartment during the 24 hours electrodialysis and 91.3% of the copper ions were passed through the anion exchange membrane as Cu-EDTA complex to the anolyte compartment. It can be noticed that some of the copper and zinc have been left in the middle compartment and it is assumed that the separation process might have needed extra time to separate the copper from the zinc.

5.6.5 The Application of Electrodialysis to Different Metal Mixtures

5.6.5.1 Electrodialysis of Ni – Zn Mixture in the Presence of EDTA

The results in Table 5.10 show that it is possible to separate nickel from zinc using the three-compartment cell. The percentage of zinc in the catholyte compartment was 48.7% in the second hour and increased to 79.9% in the 24 hour, it was also noticed that there was a slight increase in the percentage of nickel transferred to the catholyte compartment from 1.8 % in the second hour to 3.2% by the end of the 24hour.

Although a high percentage 96.2% of nickel in the anolyte compartment was obtained in the 24 hour, simultaneously there was an increase of the zinc ions transferred to the anolyte compartment from 7.7% in the second hour to 19.7% in the 24 hour. This increase in the zinc ions is attributed to the extra amount of EDTA present in the solution. Figure 5.15 shows these results graphically.

Table 5.9: The effect of electrodialysis on the separation of copper and zinc in the industrial sample

Time (Hours)	Zinc percentage in solution			Copper percentage in solution		
	Catholyte	Middle	Anolyte	Catholyte	Middle	Anolyte
0	0.0	100.0	0.0	0.0	100.0	0.0
2	8.7 ± 0.8	77.1 ± 1.6	0.4 ± 0.1	0.3 ± 0.08	66.8 ± 1.4	21.1 ± 2.1
4	20.1 ± 1.2	68.9 ± 1.5	0.5 ± 0.2	0.5 ± 0.2	59.3 ± 2.8	33.0 ± 1.6
6	33.4 ± 2.1	60.6 ± 1.2	0.6 ± 0.2	0.5 ± 0.3	45.0 ± 1.7	43.8 ± 2.3
24	94.1 ± 1.5	4.9 ± 0.8	1.0 ± 0.4	0.7 ± 0.1	8.0 ± 1.6	91.3 ± 1.5

Zn:Cu 600:300 mg dm^{-3}, Current 0.5 A and 0.005 mol dm^{-3} EDTA in 24 hours

Table 5.10: The electrodialysis of nickel - zinc mixture in the presence of EDTA

Time (Hours)	Zinc percentage in solution			Nickel percentage in solution		
	Catholyte	Middle	Anolyte	Catholyte	Middle	Anolyte
0	0.0	100.0	0.0	0.0	100.0	0.0
2	48.7 ± 2.4	39.6 ± 2.1	7.7 ± 0.5	1.8 ± 0.3	53.4 ± 1.5	37.6 ± 2.7
4	61.2 ± 1.6	25.3 ± 1.2	8.5 ± 0.4	1.9 ± 0.8	34.2 ± 0.8	57.1 ± 1.8
6	66.9 ± 1.6	14.4 ± 0.8	11.1 ± 1.4	2.0 ± 0.4	19.2 ± 1.3	77.7 ± 2.1
24	79.9 ± 2.7	0.4 ± 0.1	19.7 ± 1.2	3.2 ± 0.8	0.6 ± 0.2	96.2 ± 1.4

Zn=Ni = 500 mg dm^{-3}. 0.01 mol dm^{-3} H_2SO_4, Current 0.5 A and 0.01 mol dm^{-3} EDTA in 24 hours

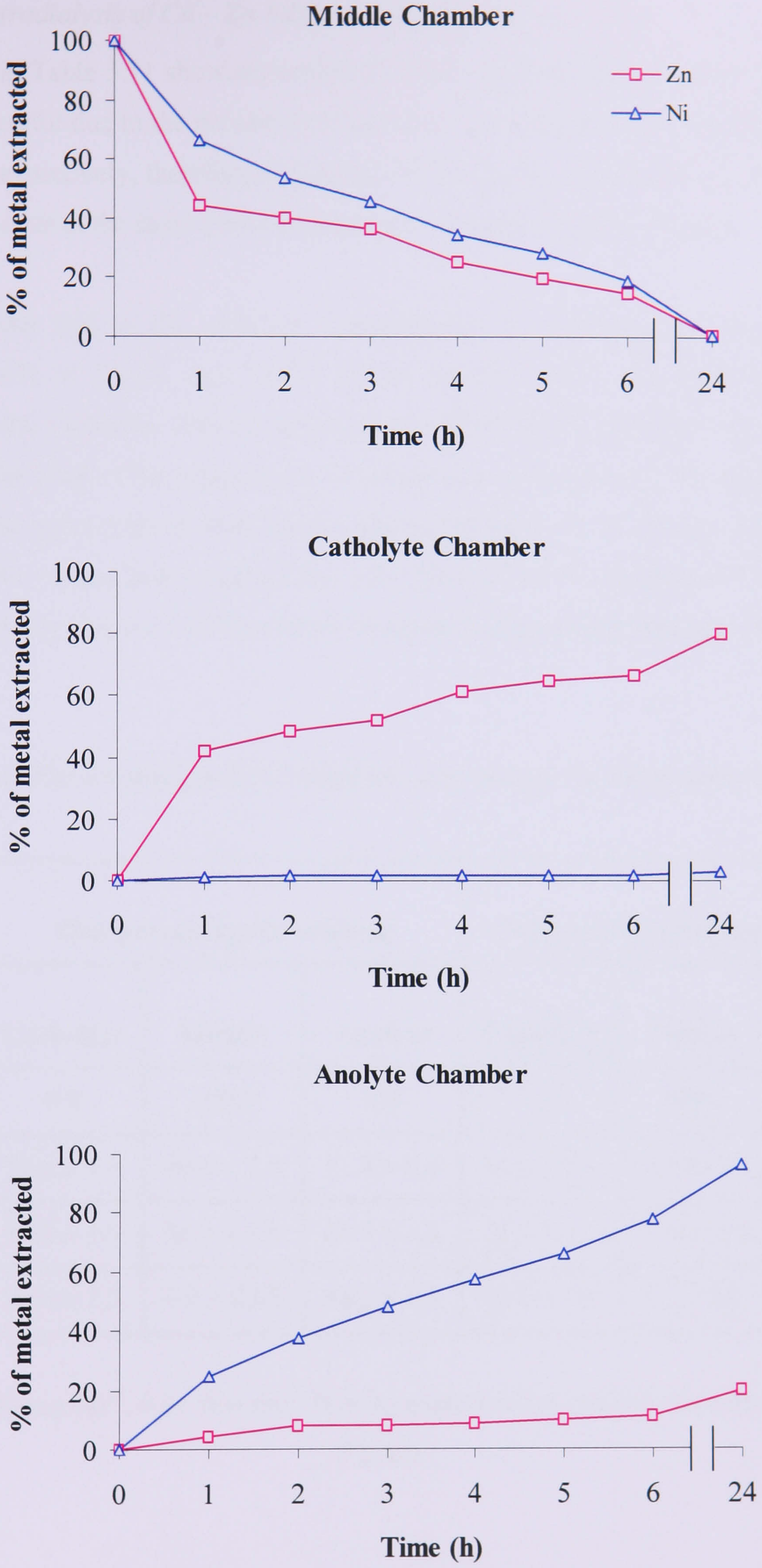


Figure 5.15: The effect of the presence of EDTA on the metal levels with time in the electrodialysis of Ni-Zn.

5.6.5.2 Electrodialysis of Cd – Zn Mixture in the Presence of EDTA

The results in Table 5.11 show separation of cadmium from zinc in a mixture of Cd:Zn was unsuccessful due to the proximity of stability constant for zinc and cadmium, $10^{-16.7}$ and $10^{-16.6}$ respectively, therefore adding the EDTA to the solution will form complexes with both metals at the same time and hence the separation will be difficult.

It was noticed that in the catholyte compartment, the percentage of zinc increases slightly 21.6% to 33.2% and 51.6% in the second, fourth and sixth hour of the electrodialysis. Cadmium behaves similarly as 16.8%, 28.6% and 40.0% in the second, fourth and six hour of the experiment. In the anolyte compartment, the results obtained show that the percentage of both metals was increased from 11.8% and 17.5% for Zn and Cd in the second hour respectively to 48.2% and 59.5% for Zn and Cd in the six hour respectively. Figure 5.16 illustrates the separation process of zinc and cadmium.

Table 5.11: The electrodialysis of cadmium - zinc mixture in the presence of EDTA

Time (Hours)	**Zinc percentage in solution**			**Cadmium percentage in solution**		
	Catholyte	**Middle**	**Anolyte**	**Catholyte**	**Middle**	**Anolyte**
0	0.0	100.0	0.0	0.0	100.0	0.0
2	21.6 ± 1.3	40.6 ± 1.5	11.8 ± 0.8	16.8 ± 0.9	39.6 ± 1.4	17.5 ± 1.1
4	33.2 ± 1.1	26.3 ± 1.6	28.5 ± 1.4	28.6 ± 1.2	17.8 ± 1.8	39.1 ± 1.5
6	51.6 ± 2.3	0.2 ± 0.05	48.2 ± 1.5	40.0 ± 1.6	0.5 ± 0.2	59.5 ± 2.1

Zn=Cd = 500 mg dm^{-3}, 0.01 mol dm^{-3} H_2SO_4, current 0.5 A and 0.01 mol dm^{-3} EDTA in 6 hours

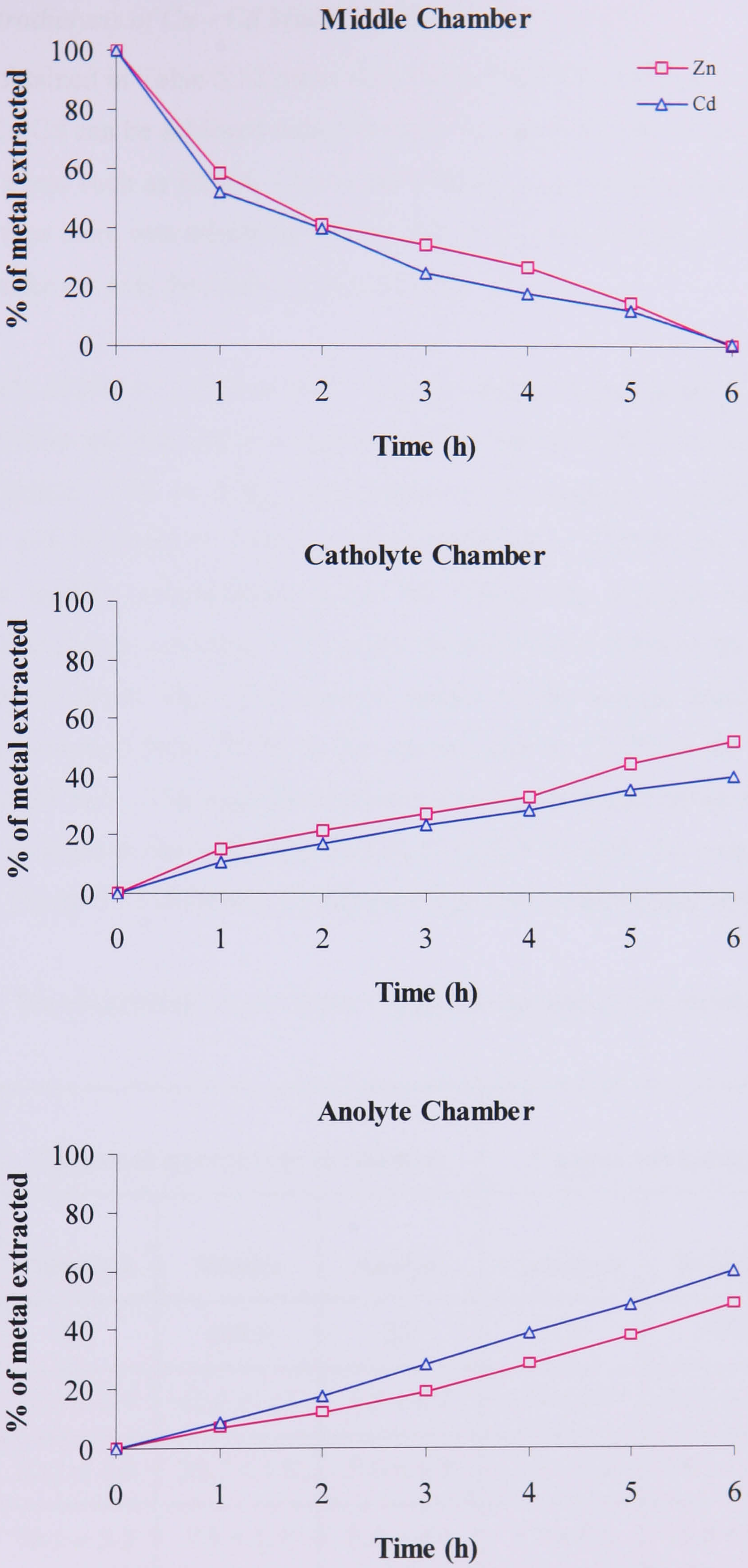


Figure 5.16: The effect of the presence of EDTA on the metal levels with time in the electrodialysis of Cd-Zn

5.6.5.3 Electrodialysis of Cu – Cd Mixture in the Presence of EDTA

The results obtained in Table 5.12 prove that a separation of copper from cadmium in a mixture of Cu:Cd can be achieved using the three compartment cell in the presence of a complexing agent such as EDTA. Due to the difference in the stability constant of the two metals, thus there was selectivity for the EDTA to form a complex with the copper ions and transfer towards the anolyte compartment.

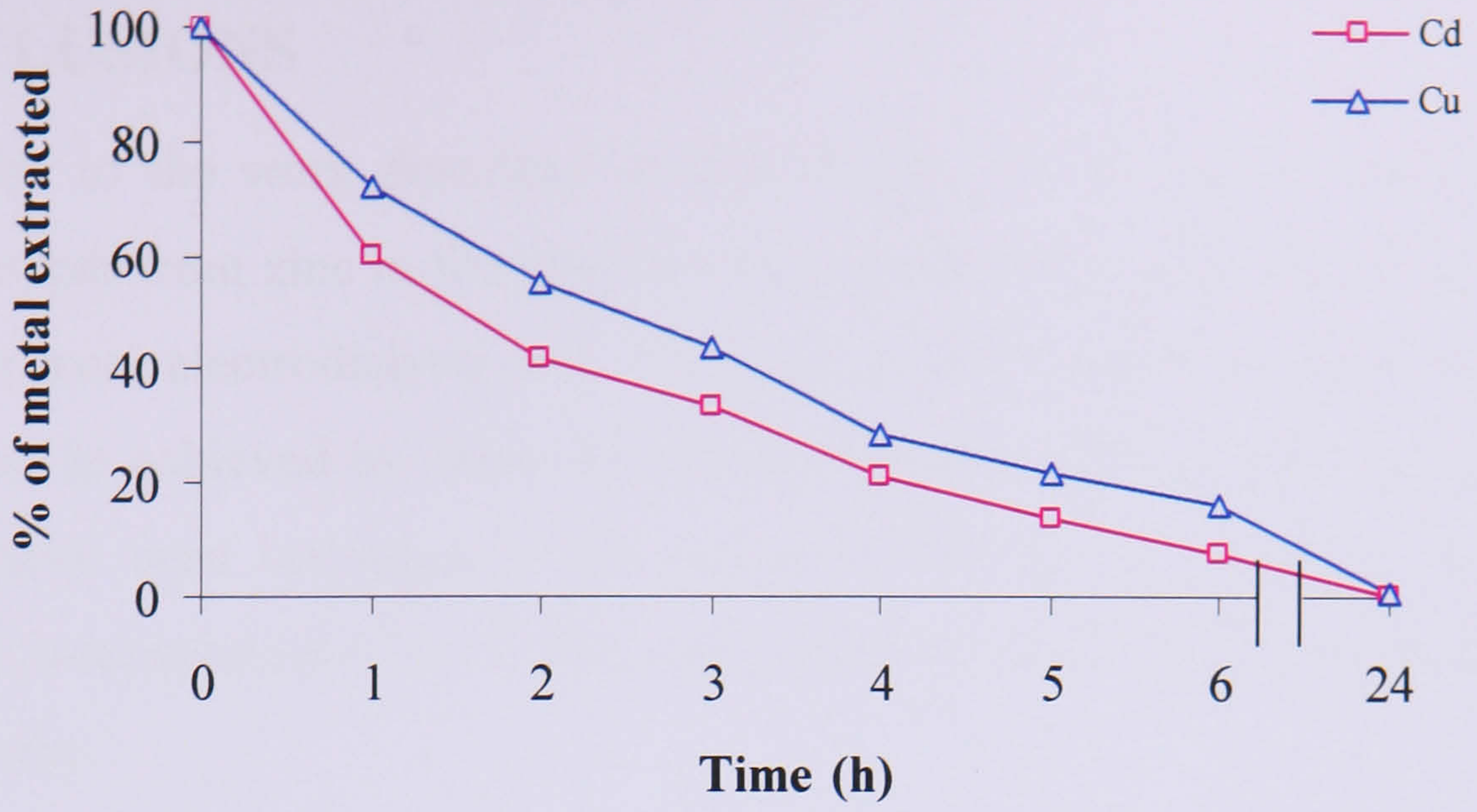
Approximately 35.6% of cadmium ions were transferred to the catholyte compartment in the second hour and this figure increased to 70.5% by the sixth hour and 87.5% in the 24 hour. Whereas, 1.3% of copper was present in the catholyte compartment in the second hour and increased to 3.7% in the six hour and to 5.2%.by the end of the 24 hour. In the anolyte compartment, it can be noticed that a slight increase in the percentage of cadmium occurred, 3.3% in the second hour to 6.5% in the six hour and 12.4% in the 24 hour. The percentage of copper in the anolyte compartment was significantly increased from 37.3% in the second hour to 73.1% in the six hour and 94.1% in the 24 hour. The separation process can be optimised using stoichiometric calculations to allocate the sufficient amount of EDTA to form the complex with the copper ions. Figure 5.17 illustrates the separation process of the copper and cadmium.

Table 5.12: The electrodialysis of copper - cadmium mixture in the presence of EDTA

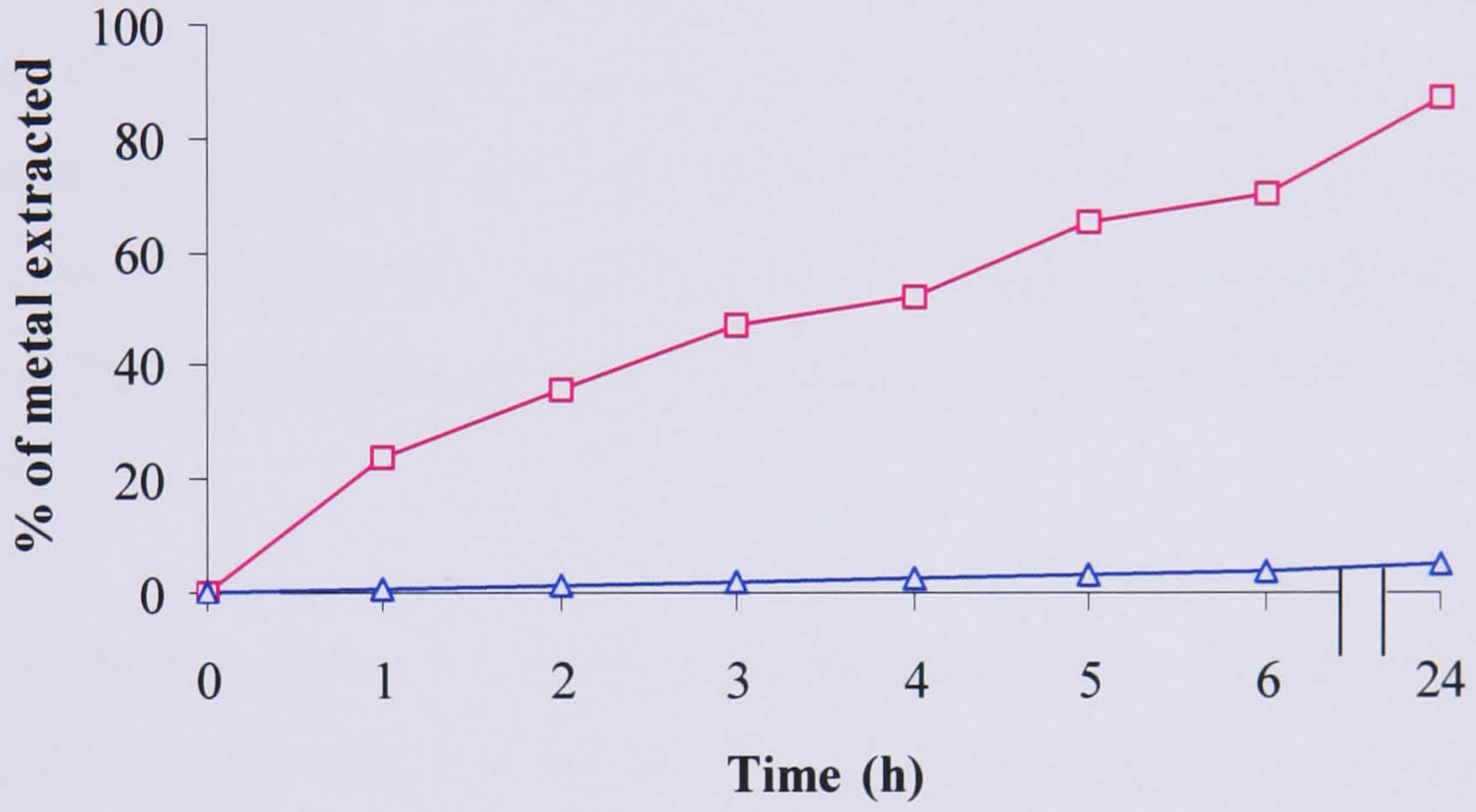
Time (Hours)	**Cadmium percentage in solution**			**Copper percentage in solution**		
	Catholyte	**Middle**	**Anolyte**	**Catholyte**	**Middle**	**Anolyte**
0	0.0	100.0	0.0	0.0	100.0	0.0
2	35.6 ± 2.4	41.6 ± 1.5	3.3 ± 0.3	1.3 ± 0.4	54.6 ± 2.1	37.3 ± 1.8
4	52.1 ± 1.8	20.7 ± 1.8	5.0 ± 0.9	2.5 ± 0.8	28.2 ± 1.4	64.0 ± 1.4
6	70.5 ± 2.3	7.1 ± 1.7	6.5 ± 0.6	3.7 ± 0.5	15.6 ± 0.8	73.1 ± 1.4
24	87.5 ± 1.5	0.1 ± 0.02	12.4 ± 1.2	5.2 ± 1.1	0.7 ± 0.02	94.1 ± 1.6

Cu = Cd = 500 mg dm^{-3}, 0.01 mol dm^{-3} H_2SO_4, current 0.5 A and 0.01 mol dm^{-3} EDTA in 24 hours

Middle Chamber



Catholyte Chamber



Anolyte Chamber

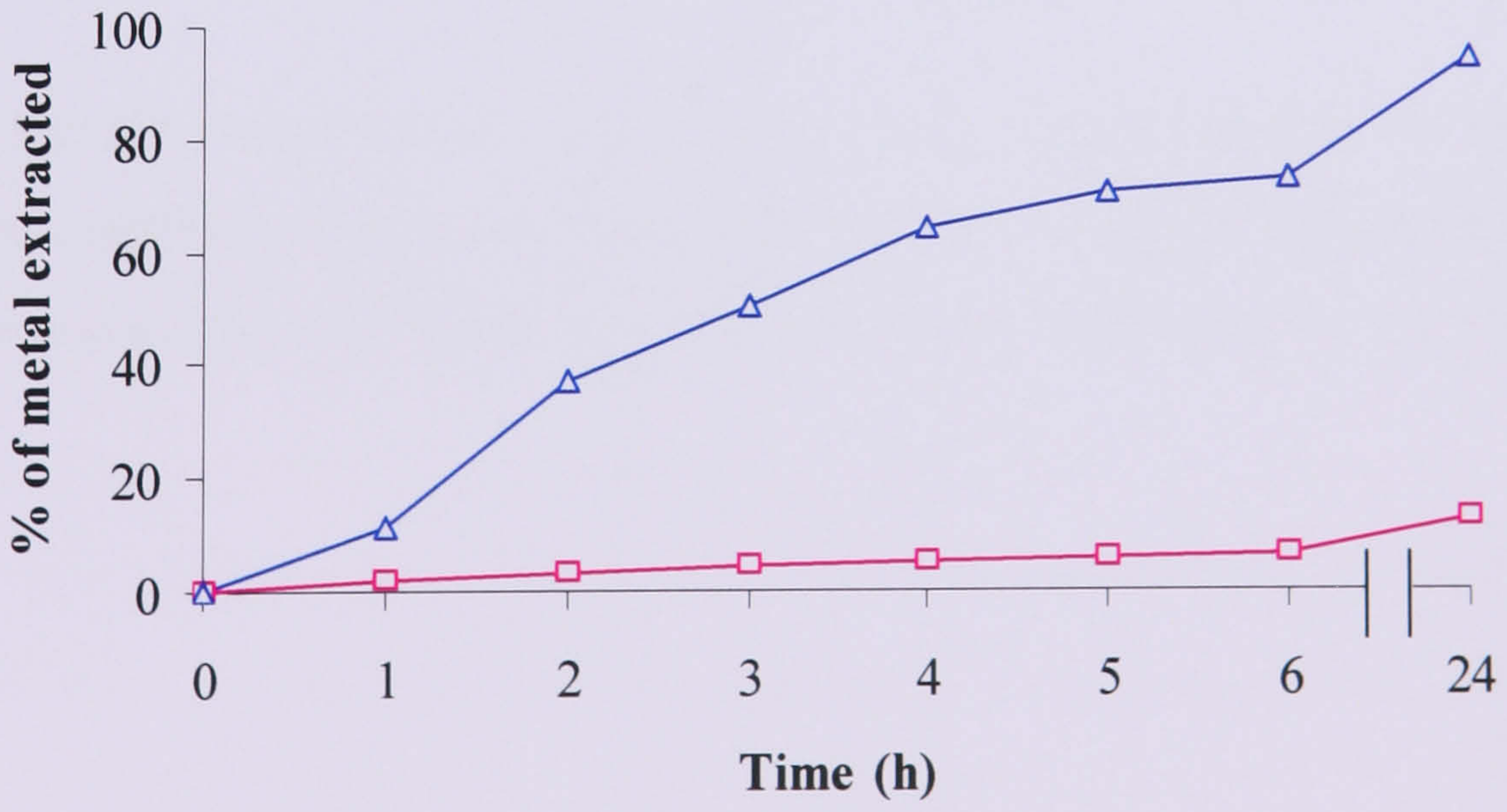


Figure 5.17: The effect of the presence of EDTA on the metal levels with time in the electrodialysis of Cu-Cd

5.7 CONCLUSIONS

The main aim of the work described in this chapter was to optimise the separation process of copper from zinc in the presence of a complexing agent such EDTA using a three compartment electrodialysis cell. The study proved that the separation of copper from zinc can be achieved by using the electrodialysis technique. Different separation parameters have been investigated and optimised during the processes such as the presence and concentration of the EDTA, the concentration of H_2SO_4 and the initial zinc and copper ratio.

The separation process carried out takes advantage of the stability constant of the formed Cu-EDTA complex which is greater than the stability constant of Zn-EDTA complex. The Cu-EDTA complex transferred to the analyte compartment crossing the anion exchange membrane and was then destroyed by oxidation at the anode releasing the Cu hydrated ions which can not passed through the anion exchange membrane. On the other hand the Zn ions pass through the cation exchange membrane to the catholyte compartment.

In addition, work included an investigation of this technique in the separation process of different metal mixtures. The results obtained show that nickel can be separated from zinc in a mixture of Ni:Zn. But the technique was not successful in the separation of cadmium from zinc due to the similarity in the stability constant of the metal complexes. The separation of copper and cadmium was achieved successfully.

Finally, an attempt was made to apply the process of electrodialysis to an industrial waste sample containing copper and zinc. The separation of individual metals from this mixture was successful but required longer time than that required for the standard solutions.

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CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS (METHANE AND ETHANE) USING RECYCLED TRANSITION METAL CATALYSTS

CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS (METHANE AND ETHANE) USING RECYCLED TRANSITION METAL CATALYSTS

6.1 INTRODUCTION

With increasing industrial development, air pollution has become a growing concern. In both developed and developing nations, there is a global problem with the emission of high concentrations of toxic substances into the atmosphere. These substances are a cocktail of many different carcinogenic, tetragenic or harmful compounds [1] largely in the form of nitrogen oxides (NOx), carbon monoxide (CO) and volatile organic compounds (VOCs). Such compounds which have adverse effects on humans and the local environment are produced in vast quantities, for example, approximately 235 million tonnes of VOCs are released into the atmosphere. Global hydrocarbon emissions are even greater at 830–2100 million tonnes per year [2].

These VOCs, including alcohols, alkanes and aromatics, are easily vaporized at ambient temperature and pressure and may pollute the atmosphere directly or indirectly as secondary pollutants [3]. The main source of these compounds are from industrial processes such as cosmetics & toiletries, household products, construction/DIY, car care products as well as traffic pollution, and with a rapidly developing global economy and a rising population, the problem is likely to be further compounded.

In the atmosphere, VOCs contribute to the destruction of the protective ozone layer in the stratosphere, contribute to the greenhouse effect and also tend to undergo a photochemical reaction with nitrogen oxides, causing the formation of ozone in the troposphere [4]. The compounds also contribute to the acidification of rain, which itself has detrimental affects on human, marine and animal biology.

In humans, the effects of such pollutants can be quite serious. Solvents can enter the body through inhalation, swallowing and skin contact, causing intoxication, dizziness and fatigue even at low concentrations [5]. Tropospheric ozone serves as a powerful oxidant that irritates the lining of the respiratory tract and can exacerbate pre-existing lung disease such as asthma and Chronic Obstructive Pulmonary Disease (COPD) [6]. VOCs also tend to have a negative impact on vegetation and contribute to global warming [7].

There are two main methods of controlling VOC emissions. The first is referred to as process and equipment modification, in which raw materials, processing and equipment are modified in order to reduce the overall emission of VOCs. Modifying equipment and processes can take many forms such as changing raw materials used, operating conditions, reaction vessels used etc. Monitoring programmes can be put in place to monitor potential leaks from valves, vessels, pipes and connections. The second is through 'add-on-control' techniques in which an additional process or technique is employed to regulate emissions. Ideally, the former should be employed as it is a more effective measure of reducing VOC emission. Add on control techniques take the form of two processes; destruction and recovery. These two can be further divided into several sub groups such as adsorption, absorption, biofilteration, thermal incineration and catalyst incineration. The choice of technique depends on the characteristics of the effluent to be treated. Figure 6.1 shows the methods which are commonly being used for the destruction and removal of VOCs [8].

Thermal incineration, the conventional method for methane destruction, requires very high temperatures (up to 1000°C) and normally produces noxious by-products such as NOx. An alternative method is thermal catalytic oxidation, which operates at much lower temperatures and hence forms nitrogen oxides in much smaller amounts. This method was shown to be effective in producing energy in gas turbine combustors, while reducing emissions.

The UK is a signatory to the United Nation Framework Convention on Climate Change (UNFCCC) and also the Kyoto Protocol, thereby it is obliged to reduce its VOC emissions by 12.5% of its 1990 levels by 2012. The six main greenhouse gases included in this agreement are carbon dioxide, methane, nitrous oxide, the chlorofluorocarbons, perfluorocarbons and sulfur hexafluoride. The target is calculated in equivalent terms of carbon dioxide. giving governments flexibility in the choice of implementing this reduction in any of the six main gases [9].

Two types of catalysts are used for the oxidation of VOC in air, noble metal and metal oxide catalysts. Noble metals are common oxidative catalysts that are widely used to control exhaust emissions such as HCs, CO and VOCs. They have the added advantage of having high catalytic activity. Moreover, they are far less likely to be poisoned by sulfur emissions than the metal oxide catalysts. Platinum and palladium are the two noble metals that are most commonly used. However, as useful as they are as catalysts, they are both also quite expensive metals. This coupled with their limited availability and their sensitivity to high temperatures has pushed for a search to find alternative catalysts.

The metal oxide catalysts have provided the best alternative solution. They are far cheaper than the noble metals and have significant activity, although they are generally thought of being as less active than the noble metals at lower temperatures. However, at higher temperatures this gap in activity between the two catalysts is almost entirely eliminated and the metal oxide catalysts have proven themselves to have similar activities to the noble metals. This similarity in activity and their relatively low economic cost has made metal oxide catalysts an attractive alternative to noble metal catalysts.

The aim of this work was to create a functional catalyst using the heavy metal solutions, obtained from leaching spent industrial catalysts with sulfuric acid, to prepare metal oxide support catalysts for the destruction of volatile organic compounds (methane and ethane) in air.

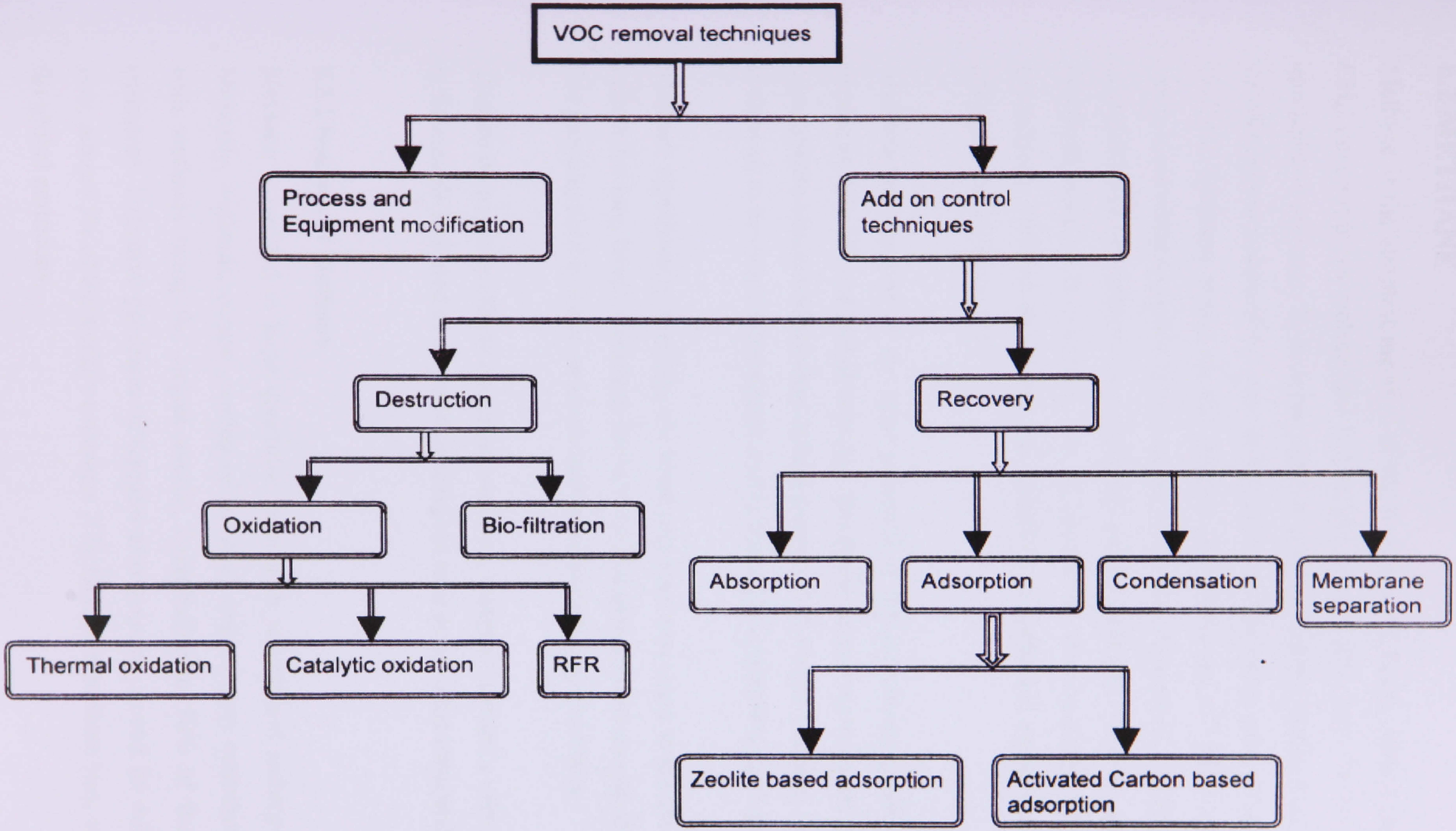


Figure 6.1: Classification of VOC control techniques

6.2 METHANE

Methane is the simplest member of the hydrocarbon family with a chemical formula CH_4, giving it a low melting and boiling point (−182.5°C and −164°C respectively) at atmospheric pressure. In its liquid form it does not readily undergo combustion unless subjected to pressures of 4-5 atm. In fact, methane has a very narrow flammability range (5-15%). Methane makes up the majority of natural gas (70-90%) while ethane and other, more complex hydrocarbons make up the rest. As a result, natural gas exhibits the characteristics of methane, i.e. colourless, denser than air, odourless and tasteless gas, (artificial odorant is added to gas to give it its characteristic smell, as a safety precaution). Methane has a very low solubility in water, but reacts very violently with halogens and oxidisers [10]·

Methane remains one of the most powerful of the greenhouse gases, contributing to approximately 20% of global warming, this being despite methane existing at far lower atmospheric concentrations than carbon dioxide [11]. Over a 100 year lifetime, methane is deemed to be over 23 times more potent than CO_2 in contributing to global warming.

Methane significantly alters the chemical processes that occur in the atmosphere and its effects are long lived. With such detrimental and potent effect on global warming, there is a pressing need to focus on immediate reduction of emission levels.

Despite its negative effects on global warming, methane remains a very valuable gas. It is flammable and used as a combustion fuel as well as for other industrial processes.

6.2.1 Sources of Methane

Methane is emitted in large quantities from both natural and anthropogenic sources. Naturally, wetlands, oceans, rearing of livestock and termites contribute to emissions, with wetlands being the largest source, contributing to 30% of the totally global emissions. Digestive processes of termites also generate around 20 million tonnes per year, almost 5% of the world's emissions [12]. Oceans contribute less, only about 2% of the global emissions.

However, in the UK, it is largely anthropogenic sources that contribute the most to methane emissions (around 60%). In 2002, 2.10 million tonnes of methane was emitted from anthropogenic sources in the UK [13]. Agriculture emission accounting for some 38% of the UK's production in 2006 [14], Rice production requires large areas of wetlands, with high moisture content and a high organic substrate and releases significant amounts of methane [15].

Landfill sites contribute to methane emissions through the action of methanogenic bacteria on organic substrate in an anaerobic environment. Such sites account for approximately 40% of the UK's total annual production in 2006 [14]. Anthropogenic methane emissions continue to rise, now estimated around 80-100 million tonnes per year. Figure 6.2 shows the different sources from which methane enters the atmosphere [16].

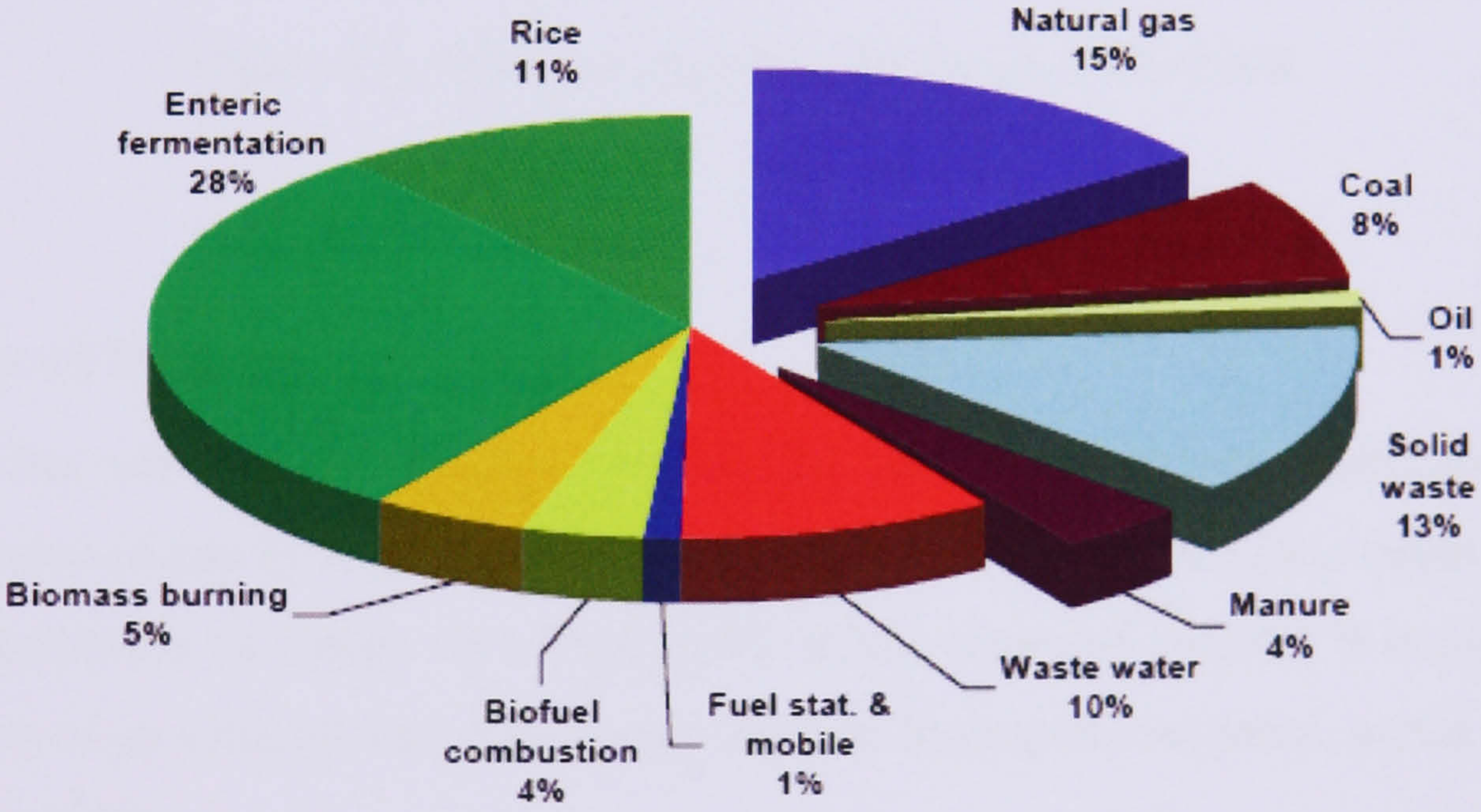
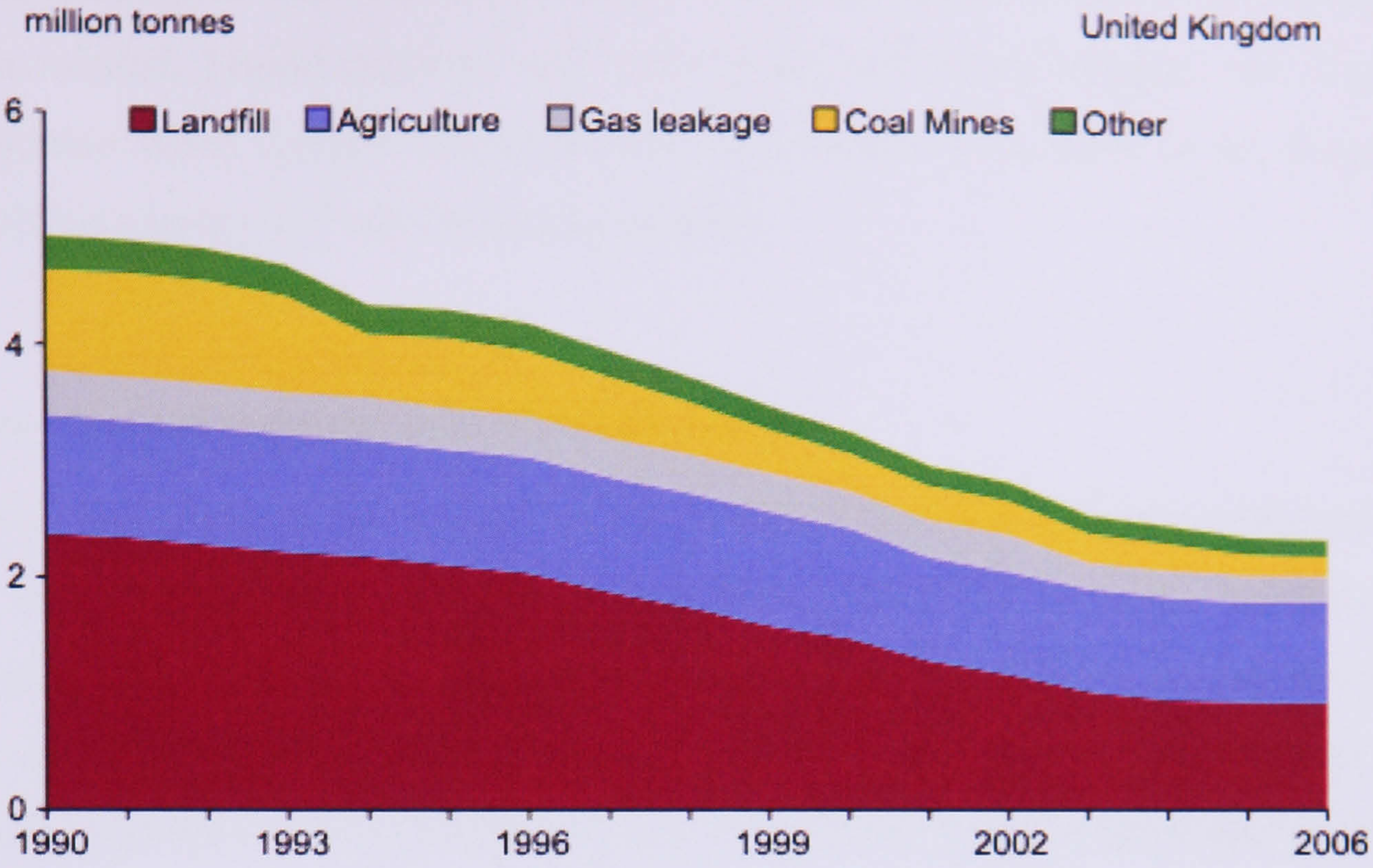


Figure 6.2: Global anthropogenic methane emissions by source

The natural estimated annual release of methane to the atmosphere was around 660 million tonnes. Of this approximately 450 million tonnes was from man made emissions. The UK accounted for less than 2.5 million tonnes in 2004. According to the figures drawn up in 2006, methane made up approximately 8% of the UK's greenhouse gas emissions. The contribution of various sources of methane emissions from1990 to 2006 in the UK is given in Figure 6.3 [14].



Data source: AEA Energy & Environment

Figure 6.3: Methane emissions by source 1990-2006

6.2.2 Uses of Methane

Methane has several uses in human society. Its ability to combust readily makes it a useful source of energy in many industrial processes as well as domestic needs and also for the generation of energy on a large scale. In the chemical industry it is used in the production of an element and compounds, such as hydrogen, methanol, acetic acid and acetic anhydride.

6.2.3 Environmental & Health Effects of Methane

Globally, methane has a significant impact on the environment [17]. It is a 'greenhouse gas' that is radiatively, 62, 23 and 7 times stronger than CO2 on a mass basis on a 20, 50 and 100 year time scales, respectively [18]. In the UK, around 2.4 million tonnes are produced each year [19], many other nations such as USA and China, produce far more than this. It is one of the six gases covered by the Kyoto Protocol to the United Nations Framework Convention on Climate Change that requires emissions of methane to be reduced. The annual rate of emission of methane into the atmosphere is increasing at a rate of almost 0.02 ppm/year [20]. Methane in itself is not toxic to humans when inhaled, although it will eventually cause suffocation by reducing the concentration of oxygen inhaled. Liquid methane will cause burns and tissue damage, but aside from asphyxiation when oxygen concentrations drop below 15%, there is no documented health effects associated with methane exposure.

6.2.4 The Benefits of Reducing Methane Levels

Reducing the overall methane emission has several important environmental, economic, safety and energy benefits. From an environmental point of view, methane is an extremely potent greenhouse gas, its reduction has obvious benefits for humans and the environment in terms of slowing the rate if not halting the 'global warming'. It is therefore important to reduce emissions as to decrease its subsequent global warming effects [11].

Methane is the main constituent of natural gas, its collection, storage and utilisation provides a valuable, clean burning and cheap energy source that can generate both revenue and energy in human communities. This utilisation of recovered methane can also help to reduce power plant emissions of carbon dioxide, sulfur dioxide and other pollutants. From a safety aspect, capturing methane from coal mines, will not only provide the before mentioned economic benefits but also help prevent or at least reduce the risks of explosions in coal mines.

6.3 ETHANE

Ethane is a compound that is a close relative of methane in the hydrocarbon family. It is the only alkane with two carbons and like to methane it is an entirely odourless and colourless gas but owing to it greater molecular mass, has a higher melting (-183.3°C) and boiling point (−88.63°C). It can be produced by 'cracking' from crude oil and is a by-product of many other chemical processes. Most of the ethane production is associated with gas and oil refineries and facilities. Like methane, the only real adverse health effect attributed to ethane is secondary to asphyxiation, i.e. depletion of oxygen concentration below 15%. High concentrations of ethane can have a mild anaesthetic effect, but the compound is essentially non-toxic.

6.4 CATALYST

6.4.1 Catalyst Design

Catalysts must be able to perform the desired reaction under cost effective conditions, i.e. those that do not require (costly) extreme conditions. Therefore a catalyst must be both highly active and very durable so that it is not easily poisoned or deactivated and can be used again. The catalyst must also be resistant to carbon, and itself must be non corrosive and non toxic [21].

Broadly, catalysts contain three main groups of components [22]:

- Catalytically active materials
- Catalyst supporters
- Promoters

Catalytically Active Materials

Different materials exhibit a specific spectrum of catalytic activity, for this reason, it is important to select the catalytic material carefully. There are many catalytic materials involving metals such as multi-metallic clusters, oxides, sulfides, acids, bases, chlorides, carbides, nitrides, borides, silicides, phosphides, molten salts, anchored homogeneous catalysts.

Many of the active metals used as catalysts are expensive metals, therefore, to maximise reactivity and decrease cost, the surface area of the catalyst and the reactants are increased. There are two ways of achieving this aim: one is to finely divide the metal or oxide in the unsupported powdered state, but there are problems associated with this method, as there is a limit to how finely divide the metal oxide can be made.

The other way, which overcomes this particle size problem, is to deposit and immobilise the small particles of the catalytically active phase onto a support such as alumina, silica and titania in order to slow down their aggregation. The bulk catalyst may be pelleted. granular, tabular, spherical or monolithic in form, thereby allowing gas to flow through the reactor under strictly controlled conditions. Such supports also control heat dissipation.

Catalyst Support

Most heterogeneous catalysts contain supports that are either very limited in their catalytic activity or are entirely inactive. Supports are chosen for their low catalytic activity, large surface area (and therefore great ability to stabilise support metal particles), optimum pore size and distribution, desired chemical properties of its surface, resistance to reaction media, good mechanical properties, thermal stability and resistance to sintering, stable behaviour and ability to regenerate and economic cost effectiveness.

Catalyst Promoters

Promoters are more often used such as alkali and alkaline earth metal cations, halides, additional transition metals and solvents. Usually more than one promoter is used to meet the set specification. Catalytic promoters can be classified into 4 main groups, according to their surface chemical properties:

- basic supports (MgO, CaO, BaO),
- acidic supports (γ-Al_2O_3, SiO_2, Al_2O_3/SiO_2, zeolites),
- neutral supports ($MgAl_2O_4$, $MgCr_2O_4$, $ZrCrO_4$, $ZnAl_2O_4$)
- amphoteric supports (α-Al_2O_3, TiO_2, CeO_2, ZrO_2).

Raw Materials for Catalyst Production

The catalyst quality and homogeneity depend on the criteria of the materials used in the catalyst production and also on the technique employed. These criteria include: particle size, absence of undesired components, equipments and price. Commonly, salts such as sulfates, chlorides, nitrates, carbonates and hydroxides are used for catalyst preparation. Solubility, thermal decomposition and environmental factors are important influencing features when considering the suitability of materials for the production of catalysts.

In the preparation of supported metal catalysts, there are four main stages [23]:

(i) The distribution of the precursor over the metal support
(ii) Drying
(iii) Calcination (not always necessary), and
(iv) Reduction (to get the active metallic state).

6.4.2 Impregnation

Many different methods can be used to prepare catalysts for use in the laboratory or on an industrial scale, including: impregnation, co-precipitation, ion exchange, deposition, colloidal method and sol-gel method. Due to the use of impregnation method in this study, it was, therefore, thought to be relevant to provide detailed information about this method.

This method involves a pre-formed, dried support being suspended in a solution of a metal salt from which the solvent is removed; leaving micro-crystals embedded into the support pores. Furthermore, by knowing the pore volume of the support, it is possible to add just the right amount of metal solution without exceeding the pore volume, thereby creating a paste. This method of impregnation is called incipient wetness. If excess solution is used, the method is referred to as a soaking method or wet impregnation. Incipient wetness impregnation process are technically simple, cheap and reproducible when it comes to metal loadings, their main disadvantage is that their metal loading is limited by the solubility of the metal precursor, although this can be overcome by varying the hydrolysis ratio.

The solution used determines the average particle size of the metal. Solutions high in metal, give larger particles, whereas low loading solutions give smaller particles. A slow drying process will cause the salt to move towards the external surface of the support particles. Therefore to ensure a uniform distribution of metal over the support, the drying should take place quickly.

Dry impregnation is useful for high metal loading systems, i.e. greater than 5% or when the support has a low adsorptive strength. Wet impregnation is used in lower metal loadings or when the support has greater adsorption properties. Generally, the impregnation technique is useful and widely used in the preparation of small quantities of catalyst, usually used for academic research or study.

6.4.3 Pre-Treatment of Catalyst

The pre-treatment of metal catalysts may require certain processes such as drying, calcination and reduction/oxidation.

6.4.3.1 Drying

The constituents are exposed to temperatures ranging from 75-225°C. Slow drying can be carried out in a controlled environment, medium-fast drying is usually done in fluidised bed dryers and fast drying is achieved in the spray process. In order to select the type of drying conditions that are best suited to a particular catalyst system, there are several factors to take into consideration, mainly the effect of the drying step on the distribution and the dispersion of the metal onto the support and the final pattern of dispersion of the metal in the catalyst.

Several problems can occur during the drying process, one of which is redistribution of the precursor compound, giving a distribution and dispersion pattern that is different to the one originally desired. This inadvertent redistribution occurs due to weak interactions between the support and the precursor metal compound. Another problem is the redistribution of the metal precursor towards the surface or the centre of the catalyst pellet which can occur due to the speed of the drying process or the pores on the support.

6.4.3.2 Calcination

Calcination usually requires medium to high temperature in the presence of air or O_2/N_2. During calcinations, the precursors decompose to oxides and an oxide bond formed, with the support. Sintering of the oxide occurs and impurities are eliminated by the release of volatile compounds, commonly SO_2, NO_2 and CO_2.

Calcination has a significant effect on distribution and dispersion of metal oxides within the support in the final catalyst [24,25]. High temperature treatment leads to a strong bond between the metal oxides and the support, creating stable solid solutions (spinels). In many instances, this strong, stable interaction between the support and the metal oxide is desired as it leads to a highly dispersed catalyst. However, in some cases, calcination causes the formation of large oxide particles which are naturally more difficult to disperse, resulting in low dispersion, and in these cases, calcinations should be avoided.

6.5 CATALYTIC OXIDATION

Catalytic oxidation is the process whereby oxidation reactions occur at the surface of a catalyst. The process has two primary benefits, one is that it is a useful method of pollution abatement and the other is that it is important for power generation. As a result of these advantages, it has stemmed a great deal of interest.

Catalytic systems work by the same method as thermal oxidisers. However, the systems can operate at far lower temperatures, thereby reducing the combustion energy required for VOC destruction. Thermal oxidisers function at temperatures above 980°C while catalyst based oxidisers function at temperatures of 260°C.

The catalytic systems work by passing a gaseous mixture of VOCs through the catalyst. Once inside the catalytic system, the reactants become adsorbed onto the catalyst surface, creating a temporary chemical bond for the reaction to take place. Finally, the resulting products desorb from the catalyst surface and are carried out of the system in the air stream, while a new batch of reactants are brought in. Such systems are capable of handling a capacity of 1000 to 100000 cubic feet per minute (cfm) and VOCs concentrations range from 100 to 2000 ppm [8].

At relatively low concentrations of VOCs deep oxidation catalytic systems are more selective and require less heating, making their use more cost effective than direct combustion [26]. However, catalytic deep oxidation also requires the reaction to be conducted at very high space velocities, (20,000-80,000 h^{-1}) [26,27] owing to the large volumes of gas that are required to be treated, in turn requiring a catalyst with high activity. There are additional complications of VOCs removal, mainly in that the vapour is usually a mixture of organic compounds of very different chemical properties. Therefore a good catalyst must be one that treats many different types of substances together simultaneously [27].

Catalytic systems are largely efficient, destruction levels upward of 90% are not uncommon [28], making them far more efficient than thermal methods [29]. This combined with the comparatively low energy levels required for reaction makes the process an attractive option; however replacement costs of catalyst remains high largely due to the material that they are made of, i.e. palladium. rhodium and platinum. The type of catalyst chosen depends on the application they are meant for, broadly, there are two main groups; (1) supported noble metals (Pt, Pd, Rh, Au),[30-33] and (2) transition-metals (Mn, Co, Cu, Fe, Ni) [34-37]. Among the metal oxides, copper oxide is often employed for its high activity and selectivity for VOC oxidation [38,39]. Furthermore, it is well known that supports play an important role in catalytic activity improvement, particularly in oxidation reaction [40].

Generally, the noble metals have a higher catalytic activity per site than the other metal catalysts and have a high activity in catalysing by-products of combustion reactions but obviously their manufacturing costs are higher and they are also susceptible to deactivation by 'poisoning' from compounds that contain sulfur, phosphorus, halogens and some other elements. Metal oxides are an inexpensive alternative to noble metals, especially with current costs of the noble elements. However, metal oxides do have the disadvantage of being inferior catalytic converters as they have a lower activity and a higher light-off temperature.

Platinum Group Metals (PGM) are routinely used in catalytic converters in automobiles to reduce exhaust emissions of VOCs while base-metal catalysts are used for ozone removal. Furthermore the structure of the catalyst system, i.e. whether it is in pellets, monolithic or beads are employed depending on the type of reaction and the catalytic strength of a metal is strongly depending on the particle shape, size and distribution. All such systems have their own advantages and disadvantages [41].

Catalytic converters, however, come with their own problems. They require changing regularly which can have significant economic impacts. They can also produce secondary combustion wastes and the catalysts have to be disposed of carefully as spent catalysts themselves can pose an environmental danger.

6.6 LITERATURE REVIEW

Several techniques including high temperature incineration, catalytic incineration and adsorption methods have been developed to reduce VOCs emission. Catalytic oxidations are by far the most energy efficient as they are able to operate at far lower temperatures. Usually precious metal systems are employed in such systems; however transition metal oxides can also be used, offering a cheaper alternative. Such base metals are usually used in higher concentrations in the catalytic system, leading to an increased number of active sites in the metal oxide bed resulting in a catalyst that is marginally less active than the Pt/Al_2O_3 systems for the destruction of VOCs. Heyes et al. [42] have found that CuO was just as effective as Pt for the incineration of n-butanol and methyl mercaptan with the order of $CuO = Pt > MnO_2 > V_2O_5 > Co_3O_4$. Further work by Pope et al. [43], has shown similar results with cobalt oxide and have found cobalt oxides to be more active than platinum based oxides for the catalysis of n-butanal and n-propylamine, but Pt to be superior for the conversion of acrolein, toluene, and butyric acid.

Ferrandon et al. [44] investigated the oxidation of methane, carbon monoxide and naphthalene in a simulated flue gas mixture from wood combustion using either manganese oxides, copper oxides, Pt, Pd or a combination of these metal oxides and noble metals supported on γ-alumina. The results showed that the MnO_x-Pt, CuO_x-Pt and CuO_x-Pd catalysts with metal oxide and noble metal loadings of 10 and 0.1 mol % respectively had the best combination of activity, thermal stability and resistance to sulfur poisoning.

Larsson et al. [45] found similar success with oxides of copper, ceria promoted copper, manganese and copper manganese Al_2O_3 for the incineration of CO, ethyl acetate and ethanol over $CuOx/Al_2O_3$ and $CuOx–CeO_2/Al_2O_3$, $CuMn_2O_4/Al_2O_3$ and Mn_2O_3/Al_2O_3 catalysts.

Rajesh and Ozkan [46] investigated several other metal oxides and reported complete VOCs oxidation with chromium and copper and were even more active than Pt/Al_2O_3 for the complete oxidation of ethanol.

Copper has been found to be a promising catalytic metal in other studies. In a study by Sang Chai Kim [47], several metals, including (Cu, Mn, Fe, V, Mo, Co, Ni, Zn)/γ-Al_2O_3 were compared for the oxidation of several VOCs including toluene, xylene and benzene. Copper was found to be most effective, although increasing the concentration of the reactant had a predictably inhibiting effect on the catalytic activity of the system. Alternative combinations of transitional metals as catalysts have also been investigated.

Work by Lu et al. [48] has also shown promising use for both cobalt and copper when combined with Activated Carbon (AC). Catalytic systems using AC impregnated with transition metals such as Cu, Co, Fe and Ni were used in the presence of 6% oxygen concentrations at low temperatures of (200–250°C). The results of the investigation were that Co/AC and Cu/AC systems were able to provide an activity of nearly 100% VOCs destruction, proving just as effective as noble metal catalytic systems. At 250°C, VOCs and AC were also found to reduce NO reduction in the presence of oxygen.

Further work by Ferrandon et al. [49] has also shown that for the oxidation of certain VOCs such as CH_4, the activities of the copper aluminium oxide catalysts were similar and in some instances even superior to that of Pt based aluminium oxides. Studies conducted by Li et al. [50] have also shown Ni/Al_2O_3 catalysts to be effective on CH_4 decomposition. They concluded that the reaction mechanism is significantly affected by the surface state of the catalyst.

The Partial Oxidation of Ethane (POE) has been studied by Iwasaki et al. [51] using cobalt mounted on various supports. It was found that the support grossly affected the activity of cobalt catalyse the POE. The order of activity was: Y_2O_3, CeO_2, ZrO_2, La_2O_3 > SiO_2, Al_2O_3, TiO_2 > MgO. The greatest activity was found with the use of Y_2O_3 but at the cost of greater carbon deposition at temperatures of 650°C after 2 hours. Other compounds that Co were loaded onto, such as CeO_2 (Co/CeO_2), gave a marginally lesser activity, although still high, without a significant carbon deposition at the same temperature. The catalytic reaction using these Co mounted catalysts appear to be a 2 step reaction: 1) the complete oxidation of ethane and 2) H_2O and CO_2 reforming reactions. Therefore, Co/CeO_2 was suggested to be a suitable catalyst for the partial oxidation of ethane. Other investigations on ethane have been conducted using different transitional metals mounted on SnO_2. Tahir et al. [52] used metals such as Mn, Co, Cu, Ce and Ni, and showed that Mn and Co oxides were the most active catalysts in the complete oxidation of ethane at temperatures ranging from 420-440°C.

The aim of the work described in this chapter is to prepare metal oxide supported catalysts using γ-Al_2O_3 spheres impregnated with heavy metals such as copper, nickel, iron and zinc. This research work has two primary objectives: (1) to prepare new supported transition metal catalysts using solutions attained from leaching spent catalysts with nitric and sulfuric acid, and (2) to study the activity of these new catalysts for VOCs emission control applications. Methane and ethane were used as indicators of volatile organic compounds during this study.

6.7 EXPERIMENTAL

6.7.1 Catalyst Preparation

The γ-Al_2O_3 support spheres (surface area of 120 m^2 g^{-1}) were obtained from Universal Oil Product Limited (UOP), Enfield, UK. The spheres were crushed to small particles less than < 0.5 mm in size to use as a support in the catalyst preparation.

The catalysts were prepared by using both nitrate and sulfate solutions containing metal ions and these solutions were prepared by a) dissolving the standard grade nitrate or sulfate compounds in distilled water and b) leaching the spent catalysts with nitric or sulfuric acid (Chapter 4). Supported metal catalysts were prepared by the impregnation method. The support (γ-Al_2O_3) was impregnated with an aqueous solution of metal precursors. The required weight of metal (in the form of nitrate or sulfate) was dissolved in a minimum amount of distilled water. The leached transition metal solutions or the aqueous of the metal precursor(s) were then added to the alumina support. The resultant metal salt(s) and alumina slurry were stirred well and the excess water removed by rotatory evaporator and then the product was dried overnight at 120°C. The dried material was then placed in a crucible for calcination and later calcined at 450°C (in case of nitrate precursors) or 650°C (in case of sulfate precursors) for 5 hours in air. The finished catalysts were in granular form and the active metal(s) on the surface of the support were in the oxide form. When heated in air, $CuSO_4$ undergo phase transitions and according to the literature it converts into CuO at 650°C [53,54].

The metal concentration is as a percentage. N: represents nitrate metal precursors and S: represents sulfate metal precursors. Total metal content in the catalysts is presented in weight %. The metal loadings were determined by atomic absorption spectrophotometery. Catalysts were characterised by X-ray diffraction (XRD).

The following catalysts have been prepared in this work, and were made from two different precursors:

1. leached solutions obtained by leaching the spent catalysts with nitric and sulfuric acids (see chapter four)
2. standard solutions prepared by dissolving metal nitrate or sulfate in distilled water.

- ***Cat-1**: 2.2% Cu - 4.6% Zn – N / γ-Al_2O_3 catalyst*

A 100 cm^3 aliquot of nitrate leached solution containing 2.3115 g/l Cu and 4.990 g/l Zn was placed in a conical flask and concentrated to a 50 cm^3 by evaporation. 9.32 g of granular γ-Al_2O_3 was added into the flask and the resulting mixture was stirred to ensure complete homogeneity. After carrying out the impregnation process (see procedure in section 6.7.1), the solid product was dried overnight at 120°C, and then calcined at 450°C for 5 hours. The final catalyst will contain 2.2% Cu and 4.6% Zn.

- ***Cat-2**: 2.2% Cu - 4.8% Zn - S / γ-Al_2O_3*

A 100 cm^3 aliquot of sulfate leached solution containing 2.341 g/l Cu and 5.090 g/l Zn was placed in a conical flask and concentrated to a 50 cm^3. To this solution, 9.30 g of granular γ-Al_2O_3 was added and the mixture was stirred to obtain homogeneous slurry. After carrying out the preparation process (see section 6.7.1), the solid product was dried overnight at 120°C, and then calcined at 650°C for 5 hours. The final catalyst will contain 2.2% Cu and 4.8% Zn.

- ***Cat-3**: 2.2% Cu – S / γ-Al_2O_3*

A known volume of sulfate leached solution, containing both Cu and Zn, was used to obtain pure copper solution by using a three compartment membrane system (see chapter five for detail). A 200 cm^3 aliquot of sulfate leached solution containing 0.367 g/l Cu and 0.006 g/l Zn was placed in a conical flask and concentrated to a 50 cm^3. To this solution, 9.78 g of granular γ-Al_2O_3 was added and the mixture was stirred to obtained homogeneous slurry. After carrying out the impregnation procedure (see section 6.7.1), the solid product was dried at 120°C, and then calcined at 650°C for 5 hours. The final catalyst will contain 2.2% Cu and 0.03% Zn.

- ***Cat-4**: 2.2% Cu – N / γ-Al_2O_3*

The required amount of Cu in the form of $Cu(NO_3)_2.3H_2O$ from Aldrich was dissolved in a minimum amount of distilled water in a conical flask. To this solution, 9.8 g of γ-Al_2O_3 was added and the mixture was stirred to obtained homogeneous slurry. After carrying out the impregnation procedure (see section 6.7.1), the solid product was dried overnight at 120°C, and then calcined at 450°C for 5 hours. The final catalyst will contain 2.2% Cu.

- ***Cat-5**: 5.0% Cu – N / γ-Al_2O_3*

The required amount of Cu in the form of $Cu(NO_3)_2.3H_2O$ from Aldrich was dissolved in a minimum amount of distilled water in a conical flask. To this 9.5 g of γ-Al_2O_3 was added and the mixture was stirred to obtained homogeneous slurry. After carrying out the impregnation procedure (see section 6.7.1), the solid product was dried overnight at 120°C, and then calcined at 450°C for 5 hours. The final catalyst will contain 5.0% Cu.

- ***Cat-6**: 4.6% Zn – N / γ-Al_2O_3*

The required amount of zinc in the form of $Zn(NO_3)_2.6H_2O$ from Aldrich was dissolved in a minimum amount of distilled water in a conical flask. To this solution, 9.5 g of γ-Al_2O_3 was added and the mixture was stirred to obtained homogeneous slurry. After carrying out the impregnation procedure (see section 6.7.1), the solid product was dried overnight at 120°C, and then calcined at 450°C for 5 hours. The final catalyst will contain 4.6% Zn.

- ***Cat-7**: 0.11% Cu - 1.9% Ni - 0.3% Fe - 0.14% Zn – N / γ-Al_2O_3*

A 200 cm^3 aliquot of nitrate leached solution containing 0.063 g/l Cu, 0.956 g/l Ni, 0.174 g/l Fe and 0.070 g/l Zn was placed in a conical flask and concentrated to a 50 cm^3. To this solution, 9.74 g of granular γ-Al_2O_3 was added and the mixture was stirred to obtained homogeneous slurry. After carrying out the preparation process (see section 6.7.1), the solid product was dried overnight at 120°C, and then calcined at 450°C for 5 hours. The final catalyst will contain 0.11% Cu, 1.9% Ni, 0.3% Fe and 0.14% Zn.

The following three catalysts have been prepared as references for the purposes of the XRD analysis:

- ***Cat-8**: 2.2% Cu - 4.6% Zn - N / γ-Al_2O_3*

The component of this catalyst was the same as the component in **Cat** 1. The required amount of copper and zinc in the form of $Cu(NO_3)_2.3H_2O$ and $Zn(NO_3)_2.6H_2O$ from Aldrich were dissolved in a minimum amount of distilled water in a conical flask. To this solution, 9.3 g of γ-Al_2O_3 was added and the mixture was stirred to obtained homogeneous slurry. After carrying out the impregnation procedure (see section 6.7.1), the solid product was dried overnight at 120°C, and then calcined at 450°C for 5 hours. The finished catalyst contained 2.2% Cu and 4.6% Zn.

- ***Cat-9**: 2.2% Cu - 4.8% Zn - S / γ-Al_2O_3*

The component of this catalyst was the same as the component in **Cat** 2. The required amount of copper and zinc in the form of ($CuSO_4.5H_2O$) and ($ZnSO_4.7H_2O$) from Aldrich were dissolved in a minimum amount of distilled water in a conical flask. To this solution, 9.3 g of γ-Al_2O_3 was added and the mixture was stirred to obtained homogeneous slurry. After carrying out the impregnation procedure (see section 6.7.1), the solid product was dried overnight at 120°C, and then calcined at 650°C for 5 hours. The finished catalyst contained 2.2% Cu and 4.8% Zn.

- ***Cat-10**: 0.11% Cu - 1.9% Ni - 0.3% Fe - 0.14% Zn – N / γ-Al_2O_3*

The component of this catalyst was the same as the component in **Cat** 7. The required amount of copper, nickel, iron and zinc in the form of $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$, $Fe(NO_3)_2.9H_2O$ and $Zn(NO_3)_2.6H_2O$ from Aldrich were, respectively, dissolved in a minimum amount of distilled water in a conical flask. To this solution, 8.7 g of γ-Al_2O_3 was added and the mixture was stirred to obtained homogeneous slurry. After carrying out the impregnation procedure (see section 6.7.1), the solid product was dried overnight at 120°C, and then calcined at 450°C for 5 hours. The finished catalyst contained 0.11% Cu, 1.9% Ni, 0.3% Fe and 0.14% Zn.

6.7.2 Catalytic Activity Measurement

The activity of the prepared metal oxide supported catalysts in the destruction of volatile organic compounds (methane and ethane) was investigated using a fixed-bed bench-scale activity rig, Figure 6.4.

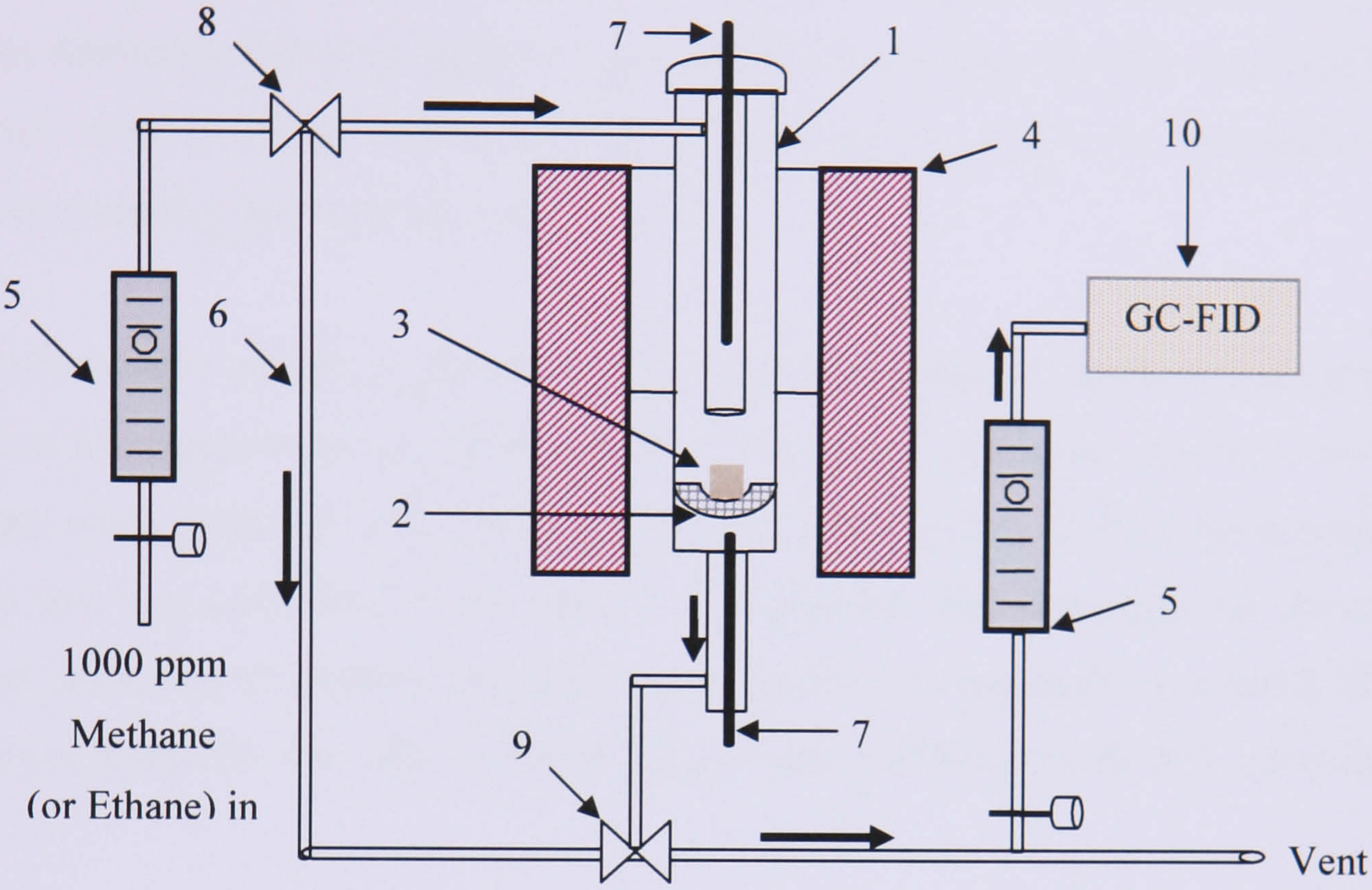


Figure 6.4: A schematic diagram of the activity rig used in the study
1) Reactor 2) Catalyst holder 3) Catalyst 4) Furnace 5) Flow meter
6) Bypass 7) Thermocouples 8&9) Valves and 10) Flame Ionisation Detector (FID)

The activity rig used, Figure 6.4, consisted of a silica tube reactor (1), having an internal diameter of 1.5 cm, containing an inner silica cup (2) to hold the catalyst (3). The reactor was housed in a furnace (4). The activity performance of each catalyst was investigated by increasing the furnace temperature at a rate of 5°C/min for up to a maximum temperature of 600°C. The flow of a continuous stream of the test gas mixture was controlled by a flow meter (5) and allowed to pass through the bypass (6) or through the reactor (1) at atmospheric pressure. The test gas mixtures contained 1000 ppmv methane or ethane in air. Thermocouples (7) monitored the inlet and outlet temperatures of the test gas mixture. Valves (8) and (9) were used to allow the test gas mixture to pass through the reactor or the bypass line. In control experiments, the test gas mixture was passed through the reactor, in the absence of the catalyst, and the product exiting the reactor were analysed.

In separate test experiments, the test gas mixture was passed through the reactor, in the presence of the catalyst, and the products exiting the catalyst were also analysed.

Each experiment was performed using 2 ml catalyst at atmospheric pressure and a space velocity of 20,000 h^{-1} to monitor the catalytic activities of different catalysts. A portion of the exit gas was passed through an on-line flame ionisation detector (FID) system (10) to determine the total hydrocarbons that have not reacted. The feed and product samples were analysed during the run using a GC to detect the formation of any products resulting from partial oxidation.

For each catalyst sample a plot of the extent of conversion of methane and ethane as a function of temperature was constructed; conversion/temperature curves of the typical S-shape were obtained. The VOCs conversion was calculated from the percentage of VOCs that was converted in the reactor. The product selectivity data for the catalysts did not show any detectable formation of undesirable compounds as a result of partial oxidation reactions. The only products formed were carbon dioxide and water in all the tests.

The results for the 7 catalysts (section 6.7.1) are given in Tables 6.1 – 6.4 and are compared in Figure 6.6 – 6.9.

6.8 RESULTS AND DISCUSSION

Extensive data on the activity of these catalysts has been procured. The effect of temperature on the conversion efficiency of a fixed concentration of VOCs in air over the catalysts was tested on the bench scale rig in a continuous stream at atmospheric pressure.

This effect is illustrated by the rise in conversion efficiency for the VOCs species, which occurs with increasing catalyst inlet temperature. The first inflection point on the curve is the point at which the reaction starts. The temperature at which 99% conversion was achieved was readily determined from the curve. The T_{10}, T_{50} and T_{90} are the temperatures at which 10, 50 and 90% conversion were achieved: these were readily determined from the curves and listed in Tables 6.1 – 6.4. The extent to which homogeneous oxidation occurred with this reaction mixture was determined by using an empty silica reactor.

No oxidation of methane or ethane occurred in the range of temperature where most of the heterogeneous work was carried out.

The catalyst activity was expressed in terms of conversion efficiency in percentages.

$$\text{Conversion efficiency (\%)} = \frac{C_i - C_o}{C_i} \times 100$$

Where, C_i = inlet concentration of the VOC in the feed

C_o = outlet concentration of the VOC in the effluent.

The effect of increasing inlet temperature from 250 to 600°C on methane (or ethane) conversion using Cu, Cu-Zn and Zn supported γ-Al_2O_3 catalysts create S shape curves.

6.8.1 Catalyst Characterisation with XRD

XRD analyses were carried out for the prepared catalysts in this study. Figure 6.5a shows the XRD patterns for catalysts 1, 2, 3, 4, 5, 8, 9 and pure compounds of CuO and γ/Al_2O_3. It was observed from the XRD patterns of the pure compounds of CuO and γ/Al_2O_3 that they are in crystalline forms. However, the patterns for catalysts 1, 2, 3, 4, 5, 8, 9 show no CuO crystalline form which means that the CuO may be highly dispersed or amorphous on the alumina surface.

Figure 6.5b shows the XRD patterns for catalysts 1, 2, 6, 8, 9 and pure compounds of ZnO and γ/Al_2O_3. In this figure, the pure compounds ZnO and γ/Al_2O_3 are shown in crystalline form, whereas, catalysts 1, 2, 6, 8 and 9 show no ZnO in crystalline form. This means that the ZnO either highly dispersed over the alumina support or it was in amorphous form.

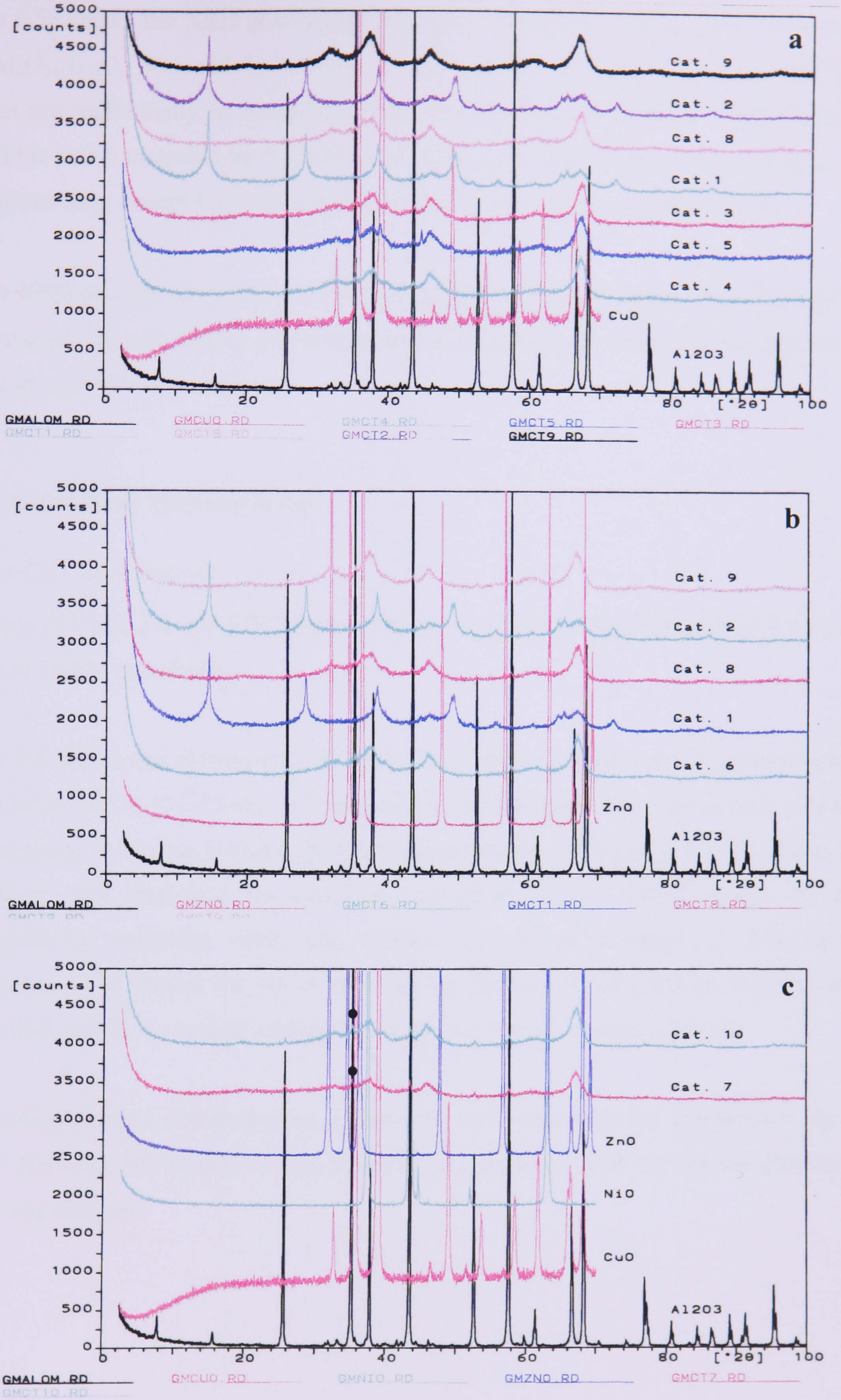


Figure 6.5: XRD patterns for various catalysts with pure compounds. a) CuO, b) ZnO and c) NiO (•)

Figure 6.5c shows the XRD patterns for catalysts 7 and 10 as well as pure compounds of γ/Al_2O_3, CuO, NiO and ZnO. It can be noticed that γ/Al_2O_3, CuO, NiO and ZnO patterns are individually in crystalline form. The patterns for catalysts 7 and 10 show that all the active materials on the surface of γ/Al_2O_3 are either highly dispersed or are in amorphous form except for a trace amount of NiO in a crystalline form at 35° 2θ.

All the XRD patterns show that use of the recycled heavy metal solutions can be used to prepare catalysts with highly dispersed active materials on the surface of the support at the recommended concentrations

6.8.2 Oxidation of Methane in Air

6.8.2.1 Cu – Zn Catalysts

Catalysts of Cu (2.2% and 5.0%) and Zn (4.8%) were prepared using granular Cu or Zn nitrate or sulfate precursors.

Figure 6.6 shows the conversion efficiency as a function of inlet reaction temperature over a series of Cu, Cu-Zn and Zn supported γ-Al_2O_3 catalysts as well as pure γ-Al_2O_3 with methane in air gas mixture (methane concentration 1000 ppm). It also illustrates that there was basically no methane conversion below 290°C. Most of the heterogeneous oxidation work was carried out within a range of 300–600°C temperature. The reason for not continuing the destruction of gases at temperatures higher than 600°C is to avoid melting of the reactor (which is made of silica).

Pure γ-Al_2O_3 coded **Cat-0** showed no activity with increasing the temperature up to 500°C. Between 500 to 600°C inlet reaction temperatures a low conversion efficiency of 1% was obtained.

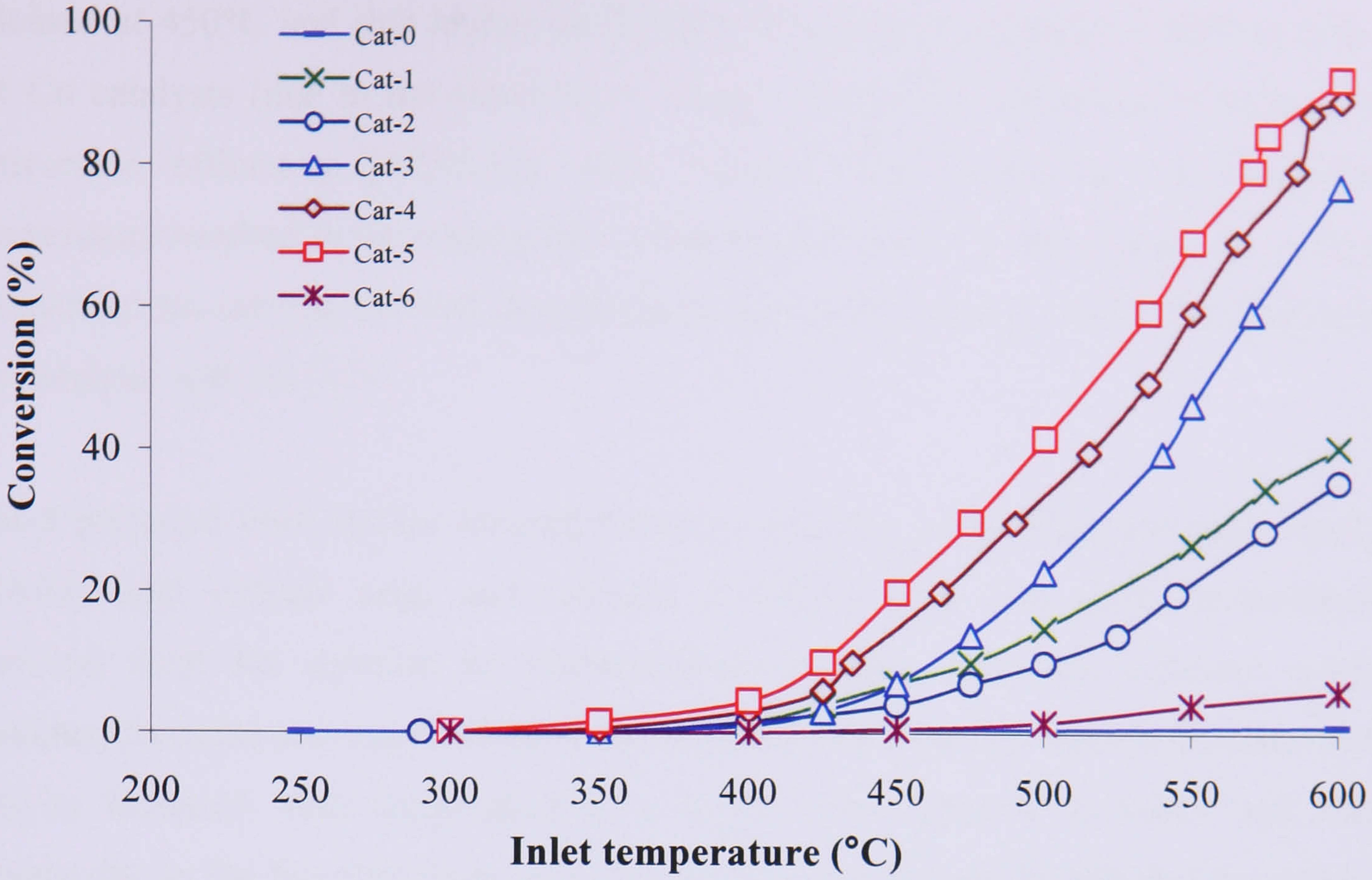


Figure 6.6: Oxidation of methane using Catalysts

It was noted from Figure 6.6 that with raising the inlet reaction temperature, all catalysts show an increase in activity but with different rates of increase.

Cat-1 contains Cu-Zn oxides which were prepared from nitrate leached solution, obtained by leaching the spent catalyst (HA02) with nitric acid, and calcined at 450°C. The results obtained showed an increase in activity with increasing inlet temperature but the maximum methane conversion was around 40% at 600°C.

Cat-2 contains Cu-Zn oxides with same metal composition as in **Cat-1** but prepared from sulfate leached solution, obtained by leaching the spent catalyst (HA02) with sulfuric acid, and calcined at 650°C as the Cu and Zn sulfate precursors required higher temperature to decompose to their oxide forms. **Cat-2** showed an increase in activity with increasing temperature but the rate of increase was similar to **Cat-1** which reached approximately 35% methane conversion at 600°C, i.e. **Cat-1** showed higher activity by 5% than **Cat-2.** The lower activity for both catalysts is due to the large concentration of Zn oxide which is inactive and possibly covers a large portion of the surface area of the support as well as the Cu oxide. Also, the 5% difference in activity is possibly due to the difference in the calcinations temperature as **Cat-2** is calcined at 650°C while **Cat-1**

calcined at 450°C and this higher calcination temperature reduced the surface area of the Cu catalysts (due to the sintering of catalyst materials) and therefore reduced the conversion efficiency [47,55,56]. Kim reported that increasing the calcinations temperature resulted in decreasing the conversion of toluene in air over the Cu /γ-Al_2O_3 catalyst as the catalyst showed decreasing in the surface area of catalyst. subsequently the catalytic activity [47].

Cat-3 prepared from sulfate leached solution, obtained by leaching the spent catalyst (HA02) with sulfuric acid, and calcined at 650°C. Zinc ions were predominantly removed from the solution by electrodialysis (chapter five), the resultant catalyst contains Cu oxide and traces of Zn oxide supported on γ-Al_2O_3. The results showed the activity increases with temperature of a higher rate compared to **Cat-1** and **Cat-2** largely due to the fact that there was little or no Zn metal and despite that the catalysts having been calcined at 650°C, at 600°C inlet reactor temperature, the methane conversion was about 78%.

To check the validity of the above results, three more catalysts were prepared by using copper nitrate precursor to make **Cat-4 and Cat-5** calcined at 450°C and using zinc nitrate to prepare **Cat-6** which was calcined at 650°C. The catalysts were tested for their ability to destroy methane in air.

Cat-4, which contains 2.2% Cu in oxide form showed high efficiency in the conversion of methane with increasing inlet reactor temperature and reached 90% conversion at 600°C. Both catalysts **Cat-3** and **Cat-4** contained the same amount of Cu as oxides, and showed the same trend in that both increased in their activity as the temperature increased, but **Cat-3** showed 78% conversion at 600°C and **Cat-4** showed 90% conversion at 600°C, i.e. **Cat 4** is more active than **Cat-3**. A possible explanation is that **Cat-3** was prepared using the leached Cu sulfate and needs higher temperature to decompose in order to produce copper oxide while **Cat-4** was prepared using copper nitrate which can decompose at lower temperature than the sulfate precursor. This change in temperature probably affects the surface area of the copper oxide and the alumina support. i.e. 650°C calcination temperature probably reduces the surface area compared to 450°C and this will affect the conversion efficiency level.

Cat-5, which contains 5% Cu as oxide, showed higher activity with increasing temperature as 93% of the methane was converted. Xiao et al. [57] reported the complete methane conversion to CO_2 at 600°C during the oxidation of methane over Co/Al_2O_3. The conversion efficiency for **Cat-5** with increasing temperature was always higher than **Cat-4** by a few percent. This increase in activity is due to the higher Cu metal loading in **Cat-5** than **Cat-4** and this is in agreement with the results reported by Kim [47] who found that the 5% Cu supported on $Cu/\gamma\text{-}Al_2O_3$ showed highest activity in the destruction of toluene in air.

Cat-6, which containing only Zn metal as oxide, showed very low activity even at higher temperatures, e.g. 6% at 600°C. This explains why the Cu-Zn catalysts (**Cat-1** and **Cat-2**) showed low activity (see Figure 6.6) although they contain around 2% Cu as oxide on the surface of the alumina support. The catalysts which contain only Cu metal as oxides showed very high activity in the destruction of methane in air. The reason that **Cat-1** and **Cat-2** showed low activities is that the Zn metal as an oxide possibly covered the Cu metal, i.e. the Zn metal is preventing the methane molecules gaining contact with Cu during the reaction period. Kim [47] reported that the 15 wt% $Zn/\gamma\text{-}Al_2O_3$ catalyst showed no destruction of toluene in air at a reaction temperature of 350°C.

Cat-5, which was prepared from nitrate precursors, was able to convert more than 90% of the methane gas at temperature of 600°C. Meanwhile, **Cat-3** which was prepared from sulfate precursor was able to convert 78% of the methane gas at a temperature of 600°C.

Table 6.1 represent the temperatures of the destruction of methane in air at 10, 50 and 90% conversion and these results were extracted from Figure 6.6. For all catalysts, no detectable oxidation of methane was achieved below 300°C, and the minimum T_{50} shown by **Cat - 5** was 515°C.

Table 6.1: Catalytic oxidation of methane in air at 10%, 50% and 90% conversions

Catalyst	**Composition**	**T_{10}(°C)**	**T_{50}(°C)**	**T_{90}(°C)**
Cat-0	Pure γ-Al_2O_3	n.d	n.d	n.d
Cat-1	Cu(2.2%)+Zn(4.6%)-N/γ-Al_2O_3	477	n.d	n.d
Cat-2	Cu(2.2%)+Zn(4.8%)-S/γ-Al_2O_3	502	n.d	n.d
Cat-3	Cu(2.2%)-S/γ-Al_2O_3	468	548	n.d
Cat-4	Cu(2.2%)-N/γ-Al_2O_3	434	531	600
Cat-5	Cu(5.0%)-N/γ-Al_2O_3	423	515	584
Cat-6	Zn(4.8%)-N/γ-Al_2O_3	n.d	n.d	n.d

n.d.: not determined.

6.8.2.2 Cu-Ni-Fe-Zn-N/γ-Al_2O_3 Catalyst

Figure 6.7 shows the conversion efficiency as a function of inlet reaction temperature for **Cat-7.** Temperature above 300°C was needed to start the methane conversion in the presence of air into CO_2 and H_2O. It is noticeable from Figure 6.7 that **Cat-7** is more active and achieved complete conversion of methane at lower temperature than the Cu metal Catalyst. **Cat-7** contains large amount of nickel metal as oxide, in addition, the loading of Cu, Fe and Zn as oxides in small quantities enhanced the oxidation process at lower temperature. The >99% conversion efficiency for this catalyst was obtained at 575°C. Table 6.2 represents the temperatures of the destruction of methane in air at 10, 50 and 90% conversion. The results were extracted from Figure 6.6. Gluhoi and Nieuwenhuys [58] reported that the addition of oxides of iron and manganese to Au/Al_2O_3 led to improve the catalytic activity in both methane and propane oxidation.

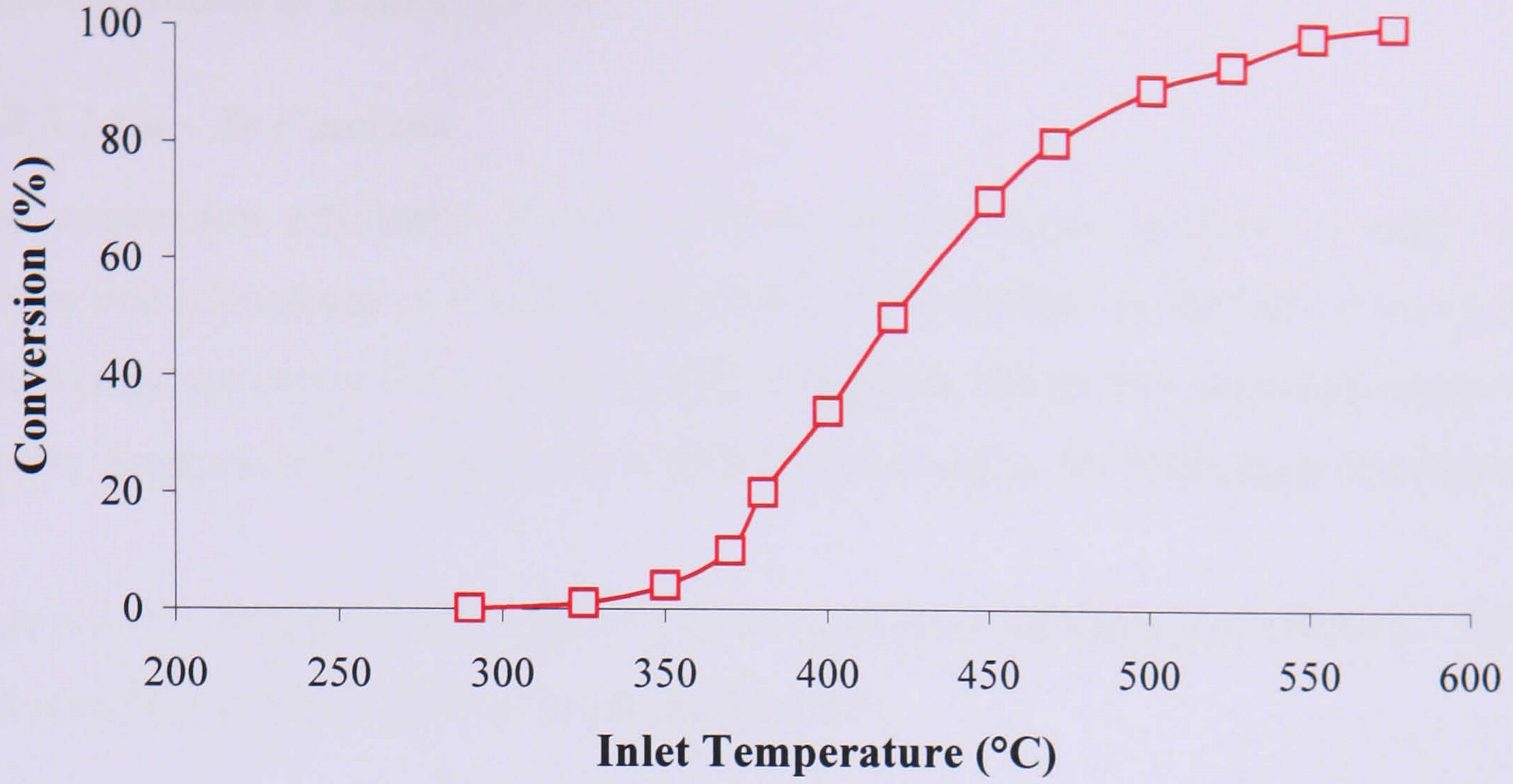


Figure 6.7: Total oxidation of methane using **Cat 7** Catalysts

Table 6.2: Catalytic oxidation of methane in air at 10%, 50% and 90% conversions

Catalyst	**Composition**	**T_{10}(°C)**	**T_{50}(°C)**	**T_{90}(°C)**
Cat-7	0.11%Cu-1.9%Ni-0.3% Fe-0.14%Zn -N/γ-Al_2O_3	370	420	525

For the methane destruction, the minimum T_{50} for Cat-7 was 420°C. The activities of different catalysts studied in this work decreased in order:

Cat-7 > Cat-5 > Cat-4 > Cat-3.

Cat-0, Cat-1, Cat-2 and Cat-6 showed low activities and they have not reached 50% conversion of methane with increasing the temperature up to 600°C.

6.8.3 Oxidation of Ethane in Air

6.8.3.1 Cu – Zn Catalysts

The conversion efficiency of ethane in air for the same catalysts as used for the destruction of methane is shown in Figure 6.8. It was found that the trend for conversion efficiencies for ethane was similar to that of methane, albeit they were more active with ethane. Temperatures between 300 to 600°C were used in the destruction of ethane.

Pure γ-Al_2O_3 coded **Cat-0** showed very low conversion efficiency of ethane 2 - 3% only between 500 to 600°C inlet reaction temperatures.

Cat-1 and **Cat-2** showed conversion efficiency around 55% and 50% respectively at 600°C. The reason for these low activities is due to the presence of a large amount of Zn metal on the surface of the support which is not active in first place for the destruction of ethane in air as well as the possibility of covering the Cu oxide active site on the surface of the support. Also, the reason for the 5% differences in activity at 600°C is possibly due to the differences in the calcinations temperatures as **Cat-1** calcined at 450°C and **Cat-2** calcined at 650°C.

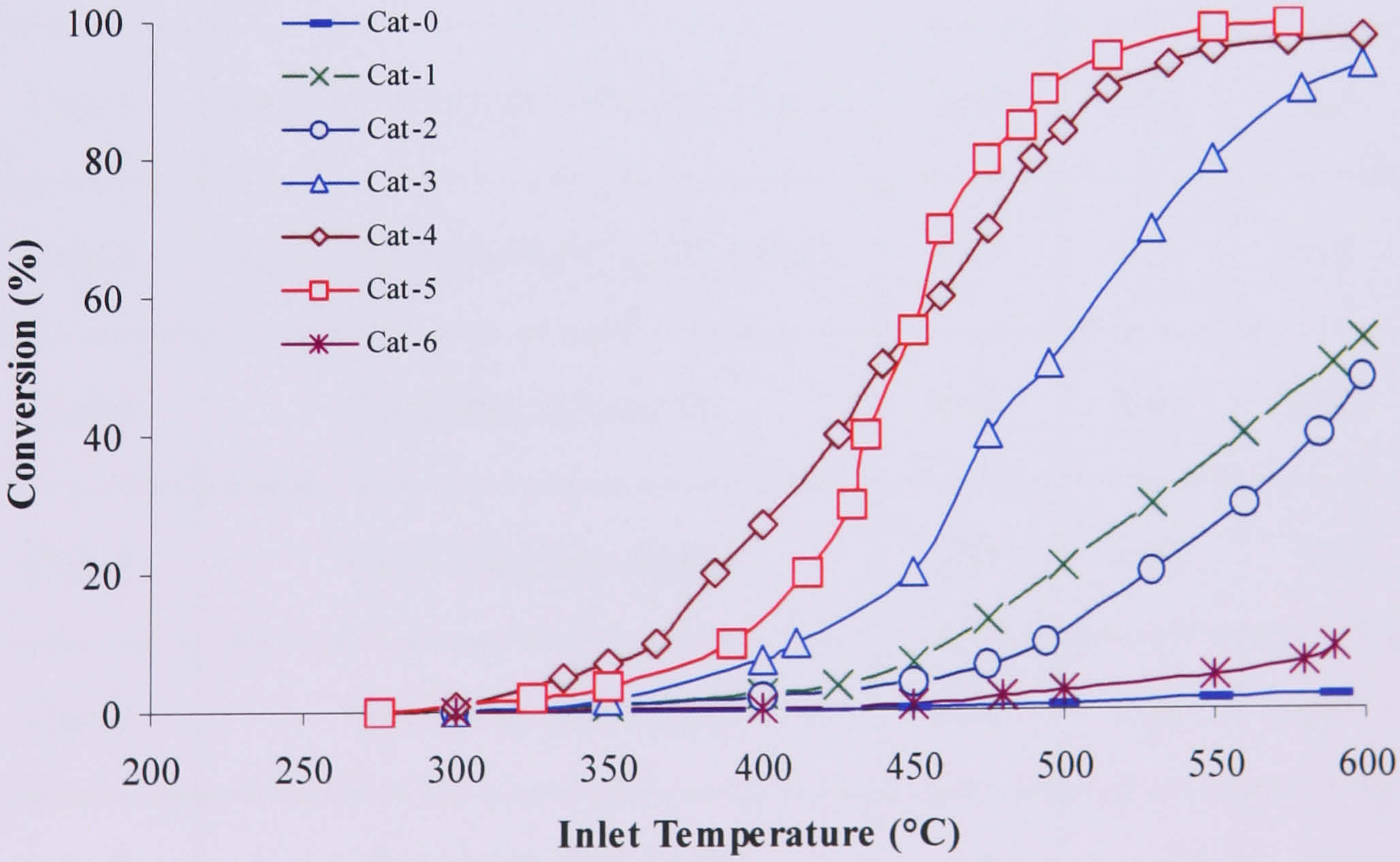


Figure 6.8: Total oxidation of ethane in air (1000 ppm ethane in air) using Cu-Zn Catalysts

Cat-3, prepared from the leached solution after removal of Zn ions, gave a loading, after calcinations of about 2.2% copper metal as oxide which gave a conversion rate of 92% at 600°C. **Cat-4**, as for methane, caused a conversion of 98% at 600°C and **Cat-5** with higher Cu metal loading gave >99% conversion at 575°C. Therefore, it can be deduced that increased Cu loading led to an increase in the activity at lower temperatures. **Cat-3** showed lower activity than **Cat-4** by 6% and this is due to the fact that **Cat-3** was calcined at 650°C while **Cat-4** was calcined at 450°C which possibly affected the surface area of Cu oxide on the surface of the support [47,55,56]. Wang et al. [59] reported that the $CuO/\gamma\text{-}Al_2O_3$ catalyst was the best active transitional metal oxide among Fe, Mn, Cr, Co, Mo and Ni for the catalytic oxidation of toluene. With Cu fixed at 5% as the active species of four supports (CeO_2, c-Al_2O_3, TiO_2 and V_2O_5), the CeO_2 support produced the highest catalytic activity, followed by $\gamma\text{-}Al_2O_3$.

Table 6.3: Catalytic oxidation of ethane in air at 10%, 50% and 90% conversions

Catalyst	**Composition**	**T_{10}(°C)**	**T_{50}(°C)**	**T_{90}(°C)**
Cat-0	Pure $\gamma\text{-}Al_2O_3$	n.d	n.d	n.d
Cat-1	Cu(2.15%)+Zn(4.57%)-N/$\gamma\text{-}Al_2O_3$	460	588	n.d
Cat-2	Cu(2.15%)+Zn(4.57%)-S/$\gamma\text{-}Al_2O_3$	494	n.d	n.d
Cat-3	Cu(2.2%)-S/$\gamma\text{-}Al_2O_3$	410	496	583
Cat-4	Cu(2.2%)-N/$\gamma\text{-}Al_2O_3$	365	440	513
Cat-5	Cu(5.0%)-N/$\gamma\text{-}Al_2O_3$	390	445	490
Cat-6	Zn(4.8%)-N/$\gamma\text{-}Al_2O_3$	n.d	n.d	n.d

n.d.: not determined

Cat-6 as with methane, showed a low activity even at higher temperatures. This was again reported by Kim [47], who confirmed that Zn/γ-Al_2O_3 catalyst showed no conversion of toluene in air at a reaction temperature of 350°C, despite the fact that toluene oxidise at lower temperature compared to methane.

The results with **Cat-6** again gives a clue why **Cat-1** and **Cat-2** showed lower activity despite the presence of Cu in the catalyst. Table 6.3 represents the temperature of the oxidation of ethane in air at 10, 50 and 90% conversion and these results were extracted from Figure 6.8.

6.8.3.2 Cu-Ni-Fe-Zn-N/γ-Al_2O_3 Catalyst

Figure 6.9 shows the conversion efficiency as a function of inlet reactor temperature for **Cat-7.** Temperature above 280°C was needed to start the ethane conversion in the presence of air into CO_2 and H_2O. Figure 6.9 shows that **Cat-7** achieved complete conversion of ethane at lower temperature than the Cu metal Catalyst and is therefore more active. Since **Cat-7** contained substantial amounts of nickel metal as oxide, it again acted as a promoter and accelerated the oxidation process, even at low temperatures.

At a temperature of 525°C, >99% conversion efficiency for this catalyst was obtained. Ethane tends to break down to CO_2 and H_2O more easily than methane using **Cat-7**. Table 6.4 represent the temperature of the destruction of ethane in air at 10, 50 and 90% conversion. The results were extracted from Figure 6.9.

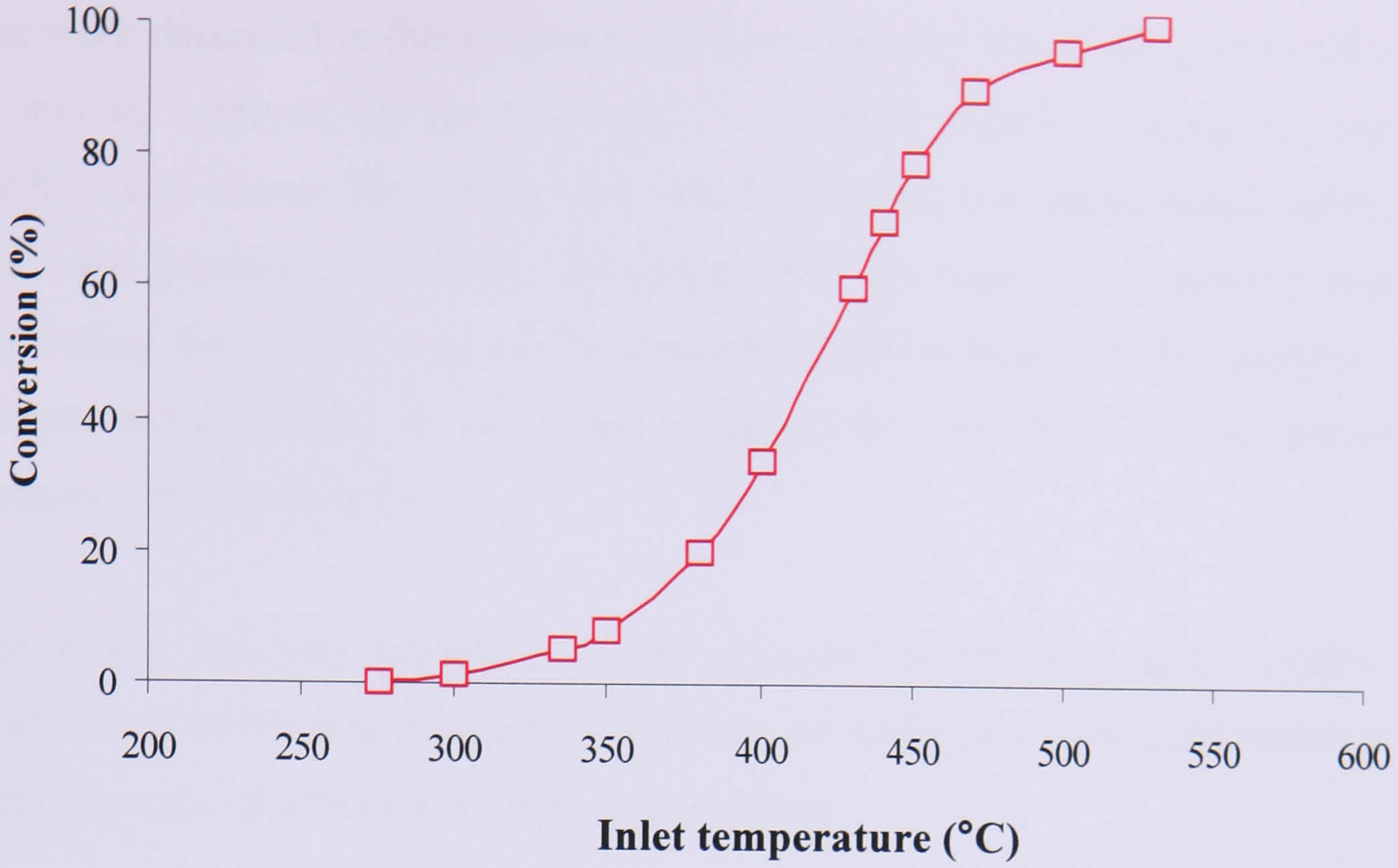


Figure 6.9: Total oxidation of ethane using Cu-Ni-Fe-Zn Catalysts

The minimum T_{50} shown by Cat-7, was 420°C: activities decreased in order:

Cat-7 > Cat-5 > Cat-4 > Cat-3 > Cat-1.

Cat-0, Cat-2 and Cat-6 showed low activities and they have not reached 50% conversion of ethane with increasing the temperature up to 600°C.

Table 6.4: Catalytic oxidation of ethane in air at 10%, 50% and 90% conversions

Catalyst	**Composition**	**T_{10}(°C)**	**T_{50}(°C)**	**T_{90}(°C)**
Cat-7	0.11%Cu-1.9%Ni-0.3% Fe-0.14%Zn -N/γ-Al_2O_3	355	420	470

6.9 CONCLUSIONS

The work described in this chapter emphasized the benefits of using recycled solutions in making catalysts for the destruction of volatile organic compounds, particularly methane and ethane. The results show that Cu/γ-Al_2O_3 and mixed metals catalysts were the most promising catalysts. Increasing the calcinations temperature resulted in decreasing the surface area of the catalysts and consequently the catalytic activity. Copper metal loading on the γ-Al_2O_3 support had an effect on the destruction of methane (or ethane) in air.

The mixed catalysts benefit from the presence of different metal oxides for the oxidation of methane and ethane (as they act as catalyst promoters) and hence lead to an increase in the destruction of methane and ethane.

The results revealed that amongst catalysts for the destruction of methane, Cu/γ-Al_2O_3 (**Cat-5**) achieved 93% conversion at 600°C and the mixed metal catalysts (**Cat-7**) was able to attain higher conversion than the copper catalyst by producing >99% conversion at a lower temperature of 575°C. The two catalysts **Cat-5** and **Cat-7** were both able to attain maximum conversion of >99% in the destruction of ethane at temperatures of 575°C and 525°C respectively.

Results also showed that catalytic activity is reduced as a result of decreasing the surface area. This decrease in surface area is due to an increase in the calcinations temperature. Copper metal loading on the γ-Al_2O_3 support had an effect on the destruction of methane (or ethane) in air as higher loading of copper catalyst (5%) achieved 93% conversion compared to the 90% attained by the 2.2% copper catalyst.

Zn (4.8%)-N/γ-Al_2O_3 (**Cat-6**) which contains only Zn metal as oxide showed very low activity 6% even at temperatures of 600°C and this is in agreement with the results obtained by other researchers in previous studies. An increase in the destruction of methane and ethane in the multi metal catalyst (**Cat-7**) is due to the availability of different metal oxides (within the mixed metals) which act as catalyst promoters.

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Chapter 7

CONCLUSIONS

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CONCLUSIONS

Due to the rapid growth in industrial activities, substantial amounts of solid wastes containing sources of heavy metals such as spent catalysts have annually been generated. In such wastes, metals are usually present in the form of their basic element, oxides or more complicated compounds. Most of the metal bearing wastes are not recycled in many countries especially in the developing world, but they are disposed off in landfill even if they contain high amounts of relatively easily extractable metals. An attractive approach to minimize the environmental problem associated with spent catalyst is to treat and stabilise them to reduce their hazardous potential before disposal in landfill or alternatively to recycle the valuable materials and this can contribute in alleviating the pressure on conventional resources.

Both nationally and internationally there is increasing interest in exploring the resource potential of waste. This is for example reflected in the European Union's approach to waste management. The waste management hierarchy, states that prevention and reduction of waste production has highest priority and recovery of waste by means of recycling, reuse and reclamation has the second highest priority.

The overall aim of this research work was to develop sustainable and economically viable treatment technologies that can be applied on an industrial scale to combat the environmental pollution problems associated with the management of wastes containing heavy metals.

The specific objectives of this work were:

- To investigate the leachability of metals from insoluble chemical compounds under different environmental and landfill conditions.

- To optimise the dissolution process and determine the best leaching conditions for metal extraction from waste using conventional method and then compare the findings with the results obtained by the microwave extraction technique.

- To design, develop and optimise a three compartment membrane technology for the separation of metals from a solution containing two metal ions.

- To make use of the industrial spent catalyst in making new catalysts containing heavy metals for the oxidation of volatile organic compound (methane and ethane) in air.

All these objectives have been achieved and the main conclusions of this work are now summarised in the following sections.

7.1 INVESTIGATION OF THE SOLUBILITY AND BIOAVAILABILITY OF DIFFERENT METALS UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

The aim of this work was to investigate the possibility of heavy metals migration under different environmental and landfill conditions. Four leaching media were selected to investigate the solubility of some selected heavy metals from their elemental and chemical compounds forms. The risk of heavy metal release from solid waste may be estimated using a modified Toxic Characteristic Leaching Procedure Test. All the heavy metals studied (Co, Cu, Cd, Ni, Pb and Zn) were extracted by different leaching solutions representing different environmental conditions such as water, HCl/NaCl, acetic acid and nitric acid using conventional method and microwave extraction.

The results show that the leached concentration for almost all the metals have exceeded the concentrations set by the World Health Organisation (WHO) for the studied metals, even when deionised water was used as a leaching medium. In particularly, the use of acetic acid (main acid generated from biodegradable of waste in landfill), as a leaching medium, was able to extract high concentrations of different heavy metals. In most cases the concentration was hundred times higher than the trigger levels. Therefore, under no circumstances waste containing these metals should be mixed with biodegradable waste in landfill. One way of achieving this is by taking into account the impact of the waste generated from the residential areas, shops and local authorities. It is imperative for the population to be aware of the necessity to change the practice of sorting waste that could contain hazardous and non- hazardous materials and encourage them to segregate the materials before the waste is collected from their premises and taken to landfills. This in turn would separate sources of metals such as cans, metal containers, batteries, paint, dyes, DIY tools and materials...etc that are currently mixed with biodegradable waste. By this practice the amount of waste containing biodegradable and heavy metals will be mixed less and consequently less pollution after disposal in landfill.

This allows a more reliable assessment of the environmental risks due to the mobility and availability of the different forms of metals.

The concentration of heavy metals in a leaching medium mimicking the gastric condition was also very high and these results showed that consumption of food or water contaminated with these metals by humans might have adverse health effects.

The extraction of heavy metals in different leaching media was increased when the experiments were carried out using a microwave extraction system. These results confirmed that temperature and pressure have a great influence on the extraction process as more metals were released from the samples in the extractions carried out with microwave extraction technique compared to the extractions carried out with the traditional method. The solubility of metals depends not only on the pH and temperature but also on the physicochemical forms in which metals are associated with solid particles.

7.2 OPTIMISATION OF LEACHING CONDITIONS FOR METAL RECOVERY

This chapter focused on the optimisation of leaching conditions for metal recovery. Traditional and microwave acid extractions were employed to evaluate the leaching efficiency of metal from solid industrial waste. Factors affecting traditional extraction like nature of solvent, leaching temperature, leaching time, acid volume and concentration were studied in detail. In addition, microwave extraction was also investigated and the optimizations of parameters influencing microwave extraction were elucidated.

Leaching experiments were optimized to increase the amount of solubilised metals and to formulate a leaching process scheme for samples containing valuable metals such as copper, cobalt, zinc, nickel and iron.

Sulfuric acid was selected as the extractant for the study because it is cheap and also to avoid the possible production of nitrogen oxides and chlorine from nitric and hydrochloric acid. The sulfuric acid leaching of the solid samples was found effective for the dissolution of the metals. An increase in the sulfuric acid concentration increases the solubility of the metals and it was considerably high at sulfuric acid concentration up to 2 mol dm^{-3}.

The effect of solid/liquid (S/L) ratio was examined by carrying out a series of experiments. The results show that in all the cases the dissolution of the metals was not affected by the S/L ratio.

The effect of the temperature on the extraction process was found considerably important for the dissolution of all the metals. The extractions carried out at ambient temperature were low and enhanced with increasing the temperature. Recoveries of more than 90% for almost all the metals were obtained at temperature of 50°C.

The kinetic study for the conventional extraction was carried out and the activation energy was calculated: 8.5 KJ mol^{-1} for Fe, 20.8 KJ mol^{-1} for Ni, 26.9 KJ mol^{-1} for Cu, 20.0 KJ mol^{-1} for Zn and 19.5 KJ mol^{-1} for Co for sample HA04. All the experimental data from the conventional method were found to fit the equation describing as the diffusion of the acid through the inert layer.

In the extraction carried out using microwave technique, parameters like temperature, time and sulfuric acid concentration had considerable effects on the extraction of copper and zinc. The efficiency achieved for the extraction of Cu and Zn in sample HA01 using microwave heating technique showed an extraction of copper which ranged from 79.2% at 10 min with 0.5 mol dm^{-3} H_2SO_4 and 150°C to 97.8% when the acid concentration increased to 2 mol dm^{-3}. The extraction percentage of zinc ranged from 80.7% at 10 min with 0.5 mol dm^{-3} H_2SO_4 and 150° C to 96.8% when the acid concentration increased to 2 mol dm^{-3}.

Comparing the microwave extraction technique and conventional method in the samples studied, both methods led to attain similar results with shortening the extraction time required to obtain maximum metal extraction from 60 to 10 minutes in the microwave heating.

Table 7.1 show the optimal leaching conditions for the extraction process in the conventional method. The recovery values of metals were found to be influenced by extraction temperature and sulfuric acid concentration.

Table 7.1 the optimum leaching condition for the industrial spent catalysts

Sample	**Metal**	**% Extracted**	**Condition of extraction**
HA01	Cu	97.6	1 g of sample, 50°C, 1 hour, 25 cm^3 of 2 mol dm^{-3}
	Zn	95.1	
HA02	Cu	96.0	1 g of sample, 50°C, 1 hour, 25 cm^3 of 2 mol dm^{-3}
	Zn	95.5	
HA03	Cu	94.6	1 g of sample, 50°C, 1 hour, 25 cm^3 of 2 mol dm^{-3}
	Zn	95.4	
	Ni	94.7	
	Fe	95.1	
HA04	Co	94.4	1 g of sample, 75°C, 2 hour, 25 cm^{-3} of 3 mol dm^{-3}
	Cu	94.4	
	Zn	93.1	
	Ni	97.1	
	Fe	95.7	

Figure 7.1 illustrate that in the conventional method the recovery of copper and zinc from sample HA01 at 50°C with 1:25 g/cm^3 solid to liquid ratio and acid concentration of 2 mol dm^{-3} in 60 minutes were 97.6% and 95.1%, respectively. Whereas. in the microwave extraction technique, the conversion recovery was 59.8% and 65.4% for copper and zinc respectively, at 50°C with 1:25 g/cm^3 solid to liquid ratio and acid concentration of 2 mol dm^{-3} in 10 minutes. Increasing the temperature to 150°C led to higher extraction of 97.8% and 96.8% in the same time, respectively. This means that the conventional method is slow and tedious. The data in Table 7.2 demonstrate a comparison between microwave and conventional method.

It can be seen from the calculation of the activation energy for the chemical controlled reaction and the diffusion controlled reaction under the microwave leaching that it was implausible to consider the reaction to be a rate controlled by the reaction on the surface of the spent particle, or to be consider as a diffusion controlled process. Both models were used and showed fair fitting and revealed rate constants $k_{RPS} = (16.05 \pm 1.02) \times 10^{-3}$ min^{-1} and $k_{DTL} = (49.01 \pm 5.82) \times 10^{-3}$ min^{-1} for Cu. The activation energy were found to be $\Delta E_{RPT} = 29.94 \pm 1.02$ KJ mol^{-1} and $\Delta E_{DTL} = 51.48 \pm 1.41$ KJ mol^{-1}. The corresponding values for Zn were: $k_{RPS} = (20.44 \pm 2.88) \times 10^{-3}$ min^{-1} and $k_{DTL} = (10.00 \pm 1.27) \times 10^{-3}$ min^{-1}, and the corresponding activation energy were found to be $\Delta E_{RPS} = 27.25 \pm 1.65$ KJ mol^{-1} and $\Delta E_{DTL} = 45.84 \pm 5.58$ KJ mol^{-1}.

Finally, the findings of this work show that the microwave extraction technique allows us to obtain similar results to the conventional method with significantly reduced extraction time. In addition, the sample throughput is increased as several samples can be extracted simultaneously. Therefore, the microwave extraction technique could be considered as a useful alternative to the conventional extraction procedure in the study of recovery of metals from waste.

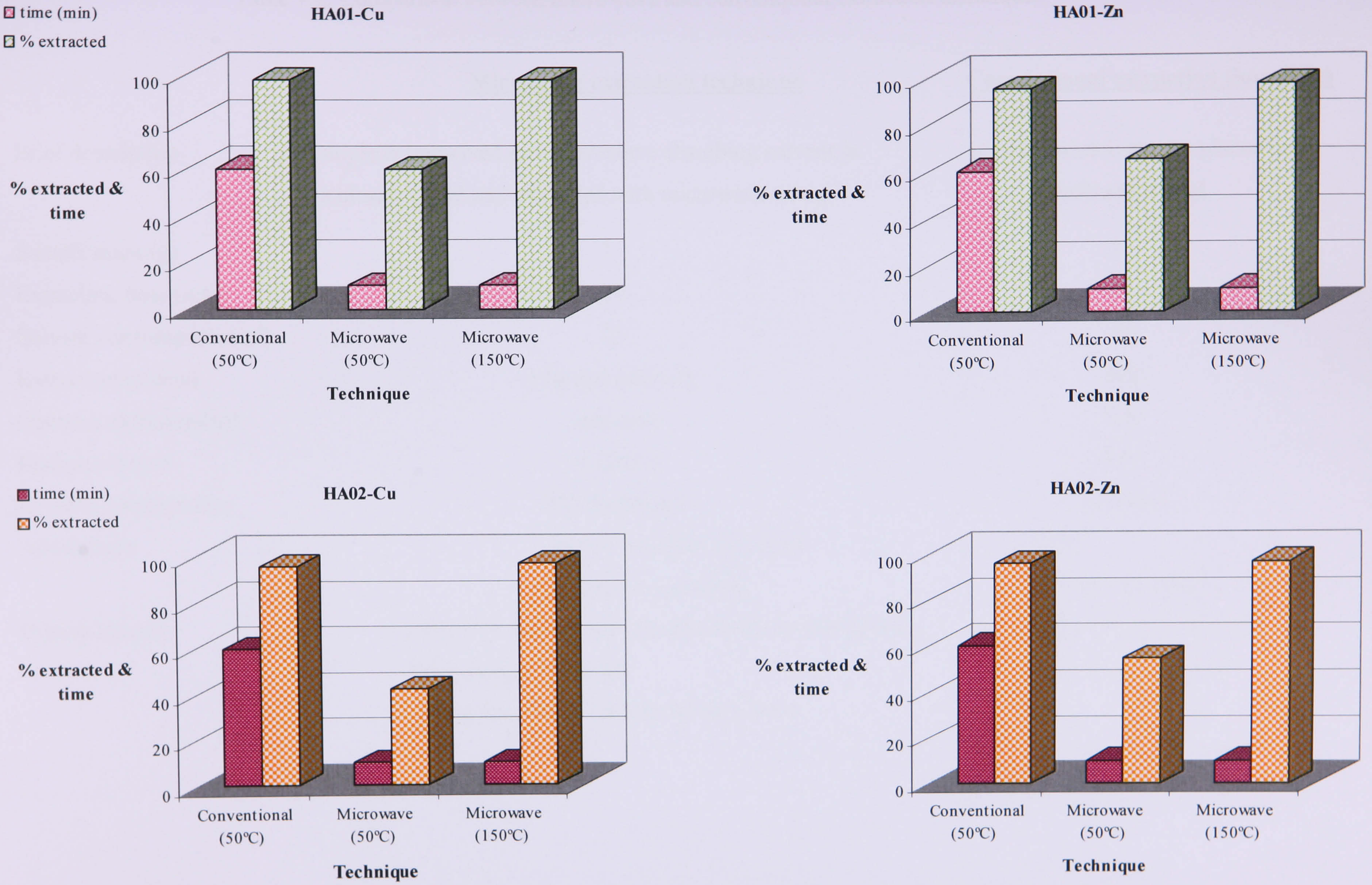

Figure 7.1: Comparison between conventional and microwave extraction methods

Table 7.2: Comparison between microwave and conventional extraction techniques

	Microwave extraction technique	**Conventional extraction (hot plate)**
Brief description	sample is immersed in a microwave absorbing solvent in a closed vessel and irradiated with microwave energy	sample and solvent are placed in a flask and heated
Sample mass (g)	1	1
Extraction time (min)	10	60
Solvent consumption (ml)	25	25
Extraction method	heat and pressure	heat
Operator skill required	moderate	low
Equipment cost	moderate	low
Level of automisation	fully automated	minimal
Advantages	- fast and multiple extraction - elevated temperature	- slow - room temperature
Disadvantages	- Extraction solvent must be able to absorb microwaves - clean up step extraction - waiting time for the vessels to cool down	- large solvent volumes - long extraction time

7.3 PROCESS OPTIMISATION FOR THE SEPARATION OF DISSOLVED METALS USING ELECTRODIALYSIS SYSTEMS IN THE PRESENCE OF EDTA AS A CHELATING AGENT

This chapter explores a logical approach to the treatment of metal-contaminated waters and this is to combine metal removal for clean up purposes with metal recovery, the metal then being available for reuse in industry. By adopting such a strategy the wastewater is converted into two valuable end products, the clean water and the metal. whilst environmental liabilities are greatly reduced. Expenditure on waste disposal is therefore also minimised.

Electrodialysis of copper and zinc sulfate has been achieved using cation and anion exchange membranes. The effect of different parameters such as the EDTA concentration, changing the concentration of H_2SO_4 and changing the copper and zinc ratio, has been evaluated through the performance of the electrodialysis system. Electrodialysis of mixed Cu and Zn ion solutions showed the feasibility of separating copper from zinc by employing an appropriate complexing agent (EDTA) and membranes.

The separation process takes advantage of the stability constant of the Cu-EDTA complex which is greater than the stability constant of Zn-EDTA complex. The Cu-EDTA complex transferred to the analyte compartment crossing the anion exchange membrane and was then destroyed by oxidation at the anode releasing the Cu hydrated ions which can't pass through the anion exchange membrane. On the other hand the Zn ions pass through the cation exchange membrane to the catholyte compartment.

In addition, novel investigations of this technique for the separation of several different metal mixtures are reported. The results showed that nickel can be separated from zinc in a mixture of Ni:Zn. However, the technique was not successful for the separation of cadmium from zinc due to the similarity in the stability constant of the two metals. The separation of copper and cadmium was achieved successfully.

An attempt was made to apply the process of electrodialysis to an industrial waste sample containing copper and zinc. The separation of this mixture was successful but required longer time than that required for model solutions prepared by using laboratory chemicals. Figure 7.2 shows the separation of copper from zinc in the industrial sample (HA01).

Finally, the application of membrane techniques to the treatment of wastewater as a replacement for or an aid to traditional methods seems to be an attractive suggestion. The present study suggests that membrane processes are very successful techniques for the removal of heavy metals such as Cu and Zn from wastewater streams. They are capable of reducing the heavy metal concentration in the effluent stream to low levels that are accepted and recommended by local standards for industrial wastewater discharge.

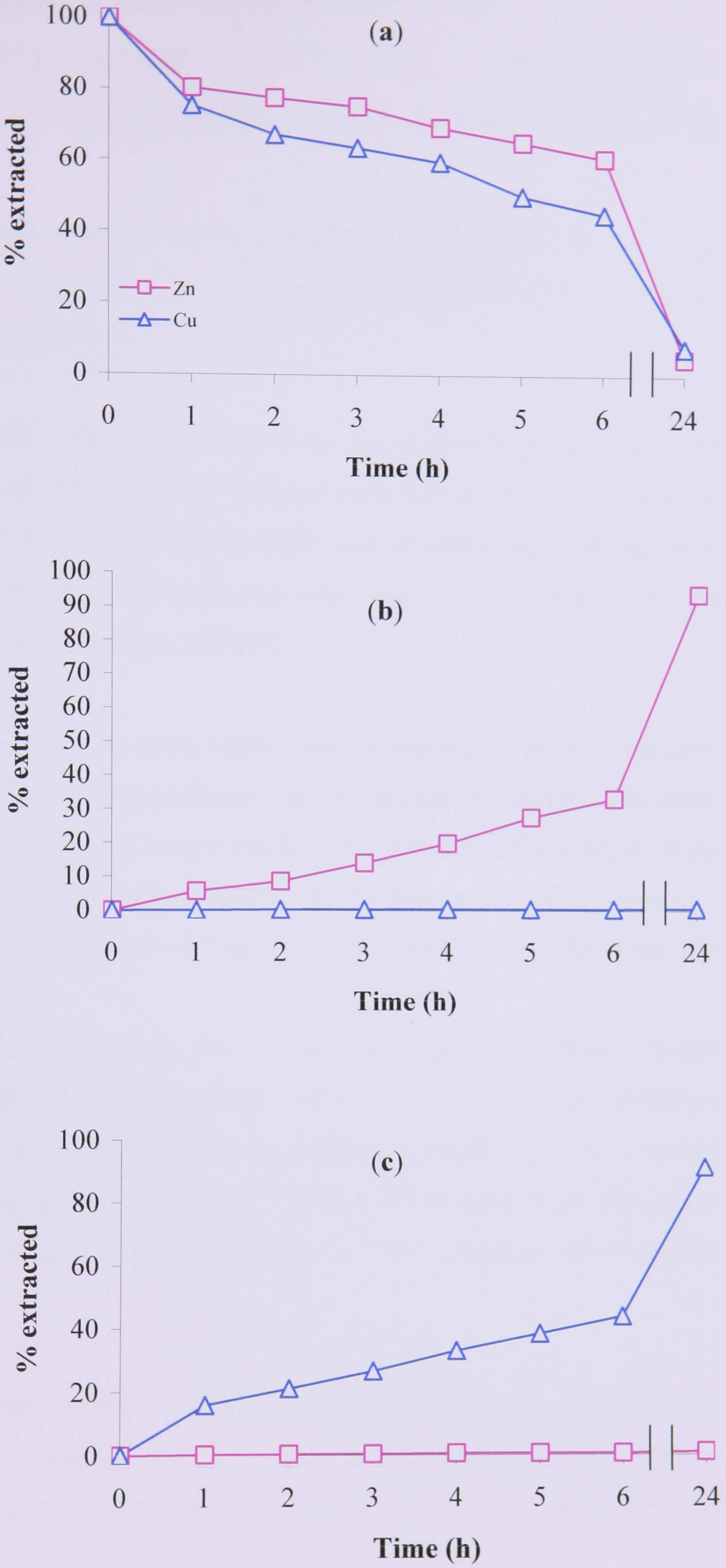

Figure 7.2: The effect of electrodialysis in the separation of Cu-Zn in industrial sample HA01 in the **a**) middle chamber, **b**) catholyte chamber and **c**) anolyte chamber

7.4 CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS (METHANE AND ETHANE) USING RECYCLED TRANSITION METAL CATALYSTS

The re-cycled leached solutions of transition metals as sulfate or nitrate were used as precursors in preparation of supported metal oxide catalysts for use in the destruction of methane and ethane in air.

$CuO/\gamma\text{-}Al_2O_3$ catalyst was found to be the most promising catalyst with respect to the activity in the destruction of methane (and ethane) in air to carbon dioxide and water. The copper loadings on $CuO/\gamma\text{-}Al_2O_3$ had an effect on the catalytic activity and 5wt% $CuO/\gamma\text{-}Al_2O_3$ catalyst (**Cat-5**) was observed to be the most active and achieved 93% conversion at temperature of 600°C.

The presence of zinc (zinc oxides) on the surface of $\gamma\text{-}Al_2O_3$ support with the copper (copper oxides) decreased the activity of the copper catalysts. The more zinc metal (zinc oxides) loading on the copper catalyst, the less active the catalyst. Supported zinc oxide catalyst (**Cat-6**) showed no activity in the destruction of methane (or ethane) in air at low temperature but showed some activity around (6%) in the range of 450°C to 600°C.

The mixed Cu-Fe-Ni-Zn metal oxides supported on $\gamma\text{-}Al_2O_3$ (**Cat-7**) showed high activity in the destruction of both methane (>99% at 575°C) and ethane in air (>99% at 525°C). These catalysts showed higher activities than $CuO/\gamma\text{-}Al_2O_3$ because the presences of Fe and Cu led to an increase in the activity of the catalyst. The Zn metal (oxide) loading is low and possibly has little negative affect on the activity on the catalyst.

Increasing the calcinations temperature up to 650°C in case of the catalyst obtained from sulfate precursor in order to convert the copper sulfate to copper oxide(s) resulted in some decrease in the surface areas of the catalysts and consequently the catalytic activity.

7.5 FINAL REMARK

Heavy metals are a useful group of elements used in human society. However, their disposal has also become a burden. The disposal of metals can either be in landfills where they inevitably end up as part of the leachate and cause significant environmental and health problems at a substantial economic cost or alternatively the waste can be treated with either conventional or microwave leaching techniques to recover some if not all of these metals. Both techniques give similar amount of metal recovered, however microwave techniques appears to provide a less time consuming route for the recovery of such metals.

Recovered metals can be used in the production of catalysts and re-introduced back into industrial processes, metal oxide catalyses have wide application in the petroleum and chemical industries. Supported metal oxides are used as selective oxidation catalysts by the chemical industry, pharmaceutical companies and petroleum industry to selectively transform undesirable pollutants to nonnoxious form, for example, for the removal of VOCs (which are in itself harmful to the environment). Or the recovered metals can be separated using membrane techniques and used as raw materials for the creation of new products.