IRON AND MANGANESE OXIDES IN THE SOIL-WATER ENVIRONMENT

A thesis submitted for the degree of Doctor of Philosophy

By

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Abstract

The importance of iron and manganese oxides in soil-water environments and their roles in controlling the availability and mobility of contaminants and nutrients are determined. Sorption is simulated using the synthetic iron and manganese oxides: goethite (α-FeOOH), birnessite ($Na_4Mn_{14}O_{27}.9H_2O$) and magnetite (Fe_3O_4) which are analogous to natural soil components.

Goethite is investigated in the three possible modes of occurrences in soil: colloidal, aggregate, and as coatings on inert materials. The adsorption of cadmium and cobalt onto goethite occurs in a narrow pH range between 6.5 and 7.5. Metal retention increased with both temperature and contact time. A tenfold decrease in ionic strength has no effect on the adsorption pH. Goethite pellets have a different pattern of adsorption due to reduction in surface area and granulation. The sorbing capacity of goethite coated sand is lower than that of the colloidal goethite but has a similar adsorption curve. The coated material is shown to have potential in industrial applications and notably in effluent treatment.

Cobalt and cadmium uptake on to hydrated suspensions of birnessite occur in a pH range (3.0-8.0) with sigmoidal shapes for the percent of adsorption curves. Birnessite uptake capacity increases with increasing pH with a maximum at about 6.4 pH. The pH, contact time and the surface area of the oxide are the main factors that control the uptake.

The adsorption of coloured species and organic colloids on magnetite was investigated in which magnetite is used both as an adsorbent and as magnetic material. Colour species and organic colloids adsorbed in acid pH and the adsorption decreases with increasing alkalinity. Dissolutions of the magnetite itself increases in low and high pH conditions.

The results of investigations of sorption of contaminants and nutrients onto iron and manganese oxides have been applied to shed light upon the behaviour of contaminants and nutrients in soil in the light of soil resource management. The importance of a detailed understanding of contaminant and nutrient transport behaviour in soil-water systems to achieve effective environmental management is demonstrated. Although soil pollution is of major environmental concern, it is probably the least understood source of pollution in terms of both transport of contaminants and remediation.

The studies carried out in this work have indicate the types of information required to permit the development of soil management and remediation protocols that will assist in technical management of issues related to soil resources. Detailed knowledge from experimental work must form the scientific basis for the development of contaminated soil assessment and management in an integrated approach.

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1.0 SOIL CONTAMINATION: INTERDEPENDENCE OF SCIENCE AND SOIL RESOURCES MANAGEMENT

1.1. Introduction

Contaminants in soils are an inevitable part of human activity. They are either a by-product of initial production processes, or they arise when objects or materials are discarded after they have been used. In a similar way, contaminants are also an inevitable part of natural processes. Thus environmental problems arise when Nature cannot cope with these added contaminants.

An ecosystem which is the combination of plants, animals, soil and climate that interacts together in an environmental medium is a starting point for any understanding of environmental problems; an ecosystem will reflect the problems that contaminants can cause, and the ways in which they can be treated. The processes in the system are complex and there are many species and components that are in continuous interaction with one other. The stability that appears in nature is not the outcome of a static situation, but of a dynamic equilibrium. As a result, radical changes in an ecosystem can occur even if only one small component is disturbed.

Soil and groundwater contamination is among the most technically complex and challenging environmental problems being addressed by most developed countries. As a result, there is an ongoing need to develop more reliable, cost-effective technologies to tackle these problems. The challenge is not only to develop appropriate techniques but also to transfer the information to others responsible for making decisions and implementing remedial measures. Transferring the information to end-users would, however, be of little value unless their appreciation and active involvement were secured.

Overall attitudes have varied from country to country for political and economic reasons. Secrecy has sometimes affected the community perceptions of the severity of soil pollution problems and conditioned demands for change as observed in Britain. Although pollution in most European cites has its origin in the industrial revolution, it is only relatively recently that proper consideration has been given to remediation. After the changes which took place about the beginning of the eighteenth century, collectively called the industrial revolution, the release of contaminants began to increase in amount and to change in content as industrial activities grew in importance. The process of industrial change has gathered momentum in the past three decades and many of the former heavy industries have closed and their sites have become disused or have been converted to alternative uses and have exposed the severity of soil contamination.

Many communities have become increasingly aware of and concerned by environmental pollution in relation to their everyday lives. Earlier, regulatory instruments emphasised aspects of food, water and air quality, but the current move is geared towards giving greater attention to soil. This arises from recognition of the role of the soil (1) as a repository of contaminants; (2) as a transmitter of contaminants to the groundwater; (3) as a supplier of contaminants and nutrients to plants and animals. This recognition has occured because of incidents of contamination, scarcity of usable land and increased general concern about the effect of industrial activity on the environment [1].

Concern about soil pollution increased in the 1960s when the writing of two famous activists came to public attention. Rachel Carson's [2] prophetic book, "SILENT SPRING" exposed the use of toxic chemicals and their effects on the environment; Galbraith [3], also showed how the ever-increasing demands of our society places a burden on the environment. Concern intensified in the 1970s, following the discovery of problems created by chemical waste materials in urban areas. This has brought the issue of contaminated land to the attention of the general public through sites such as Love Canal, near Niagara in the USA and Lekkerkerke in the Netherlands. Many other similar situations have been reported in different countries.

The history of Love Canal dates back to May of 1892 when William T. Love purchased a piece of land between the upper and lower Niagara River to construct a hydroelectric power plant. Love began digging one of several planned canals; unfortunately, economic hard times and the advent of alternating current ended Love's electrical endeavor and ultimately drove him to bankruptcy. For nearly fifty years, the canal was used as a neighborhood swimming hole until Hooker Electro-Chemical Company bought the canal and acquired the proper permits to begin dumping chemical wastes in the canal. A total of 21,800 tons of 200 toxic chemicals were dumped by Hooker, as well as by the Army, in the canal until 1953 when Hooker officially closed the dump, sealing it with a clay cap [4].

The following year, an Elementary School was built on the center of the landfill, and sewers and roads crossed the property. However, the primary disruption in the clay cap was caused by the construction of the LaSalle Expressway along the southern end of the canal. The expressway construction blocked the natural flow of groundwater. Ensuing rains effectively overflowed the clay basin in which the toxic chemicals rested, carrying the contaminants through the upper silt layer to sewer lines and basements of houses and schools situated to the north, east, and west of the canal. By 1977 the buried chemicals had begun to migrate as the drums containing them began to disintegrate, some were beginning to seep into basements and people were beginning to experience unexplained illnesses. In 1978 the school was closed and 235 families who lived within 120 m of the former canal were evacuated. The following year families with children under two and pregnant mothers were moved from the southern part of the site and the remaining families were advised not to initiate pregnancies[4, 5]. As a result of the cocktail of toxic chemicals greater than average health problems were experienced. The cost in terms of human misery was immense and the Love Canal disaster was largely responsible for persuading the US government to release funds to implement the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) known popularly as Superfund.

At Lekerkerke in the Netherlands, houses were built upon an old dump containing waste materials from a dyestuffs factory. The factory which had produced these wastes had been demolished and was so contaminated that material from the demolition was dumped in the Atlantic, but the waste remained buried. The waste included drums of toluene, xylene, and compounds of lead, cadmium and zinc. Three hundred houses had to be evacuated and 1.5 million tonnes of polluted soil removed from beneath the houses before the inhabitants could return safely [6].

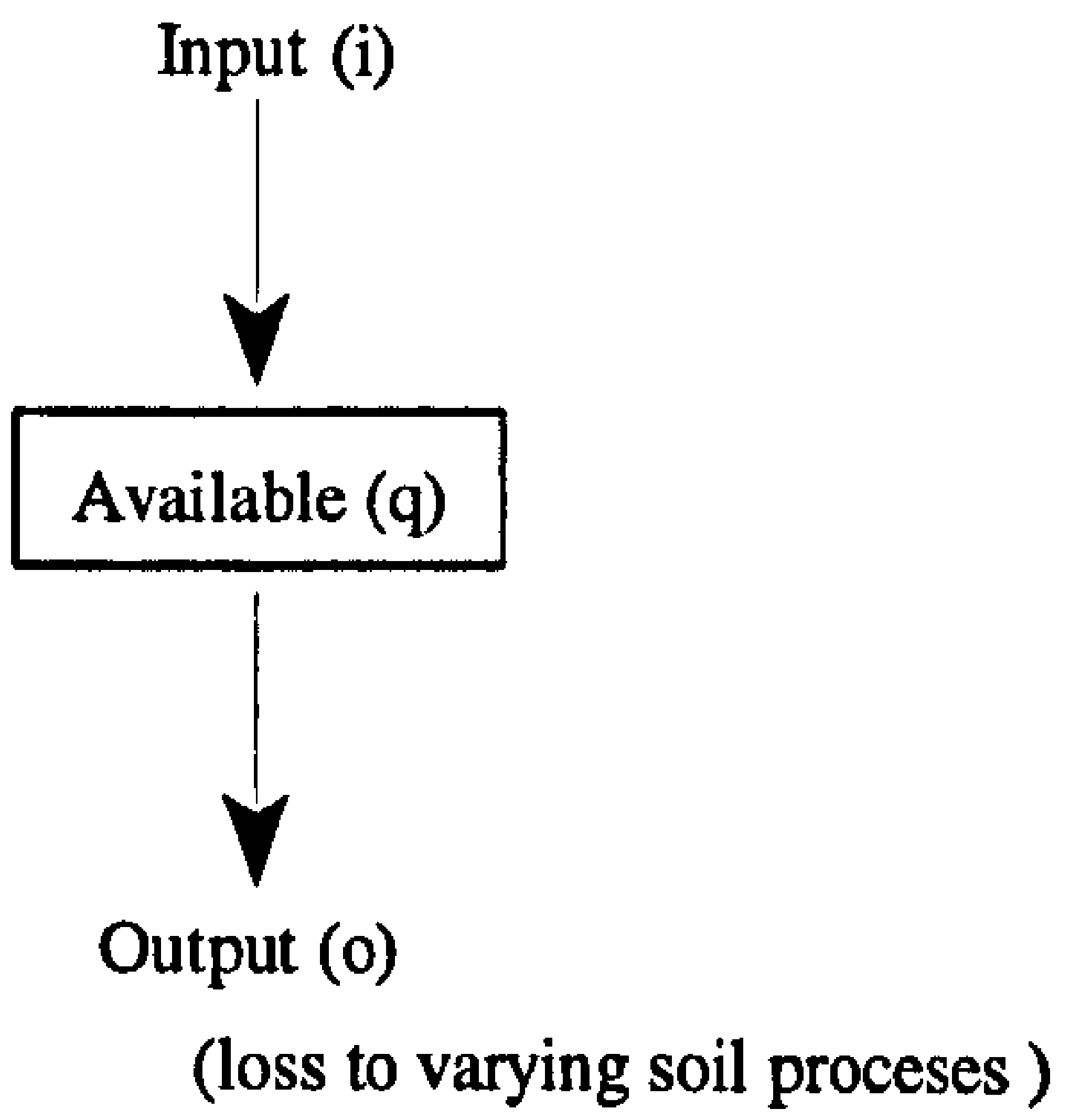
Because a large number of highly contaminated sites exist, throughout the world and in response to increasing public pressure, the problem has now received much more governmental attention in many developed market economies. As a result, policies are under development at both national and international level with the intention of protecting the soil environment from further contamination. In a number of industrialized nations, legislation exists, either in force or proposed, which aims to investigate, remediate and protect land. Development of effective investigative methods and remediation techniques for contaminated land are underway but much remains to be done to optimise decontamination processes at both research and operational levels. All these measures and developments show how contaminated land is currently an area of much activity in scientific, technical and legislative spheres [7-10].

1.2 Nature and sources of soil contamination

There are some major processes involved in the flow of contaminants and nutrients through the soil-water system. These include accumulation, transformation and transport which vary with the type of soil horizon and the nature of soil components. This can be described by a generalized input/output model as shown in Figure 1.1. The contaminants contained in a soil will be related to their rate of input and the rate of output. The outflow can be due to volatilisation, dilution, degradation, neutralisation, adsorption, complex formation etc. and may be quantified by a rate constant for loss, the reciprocal of which is the residence time. In equilibrium the critical factor is the rate constant for loss.

Changes in the chemical balance due to addition of contaminants may present a hazard to construction works, toxicity to flora and fauna or may lead to the accumulation of contaminants in vegetables making them unsuitable for human consumption. Flux between surface soils and dusts may influence exposure of the population and particularly of young children to toxic levels. Thus the complex nature of the problem demands an understanding of dynamics and mobility of the contaminants in soil and the main factors that affect the bioavailablity of the contaminants.

Figure 1.1 Generalized input-output model



If λ = rate constant for loss (with units of t^{-1})

$$\frac{dq}{dt} = i - \lambda q$$

At equilibrium

$$q = \frac{1}{\lambda}$$

To deal effectively with the problem of contaminated soil our understanding of soil processes needs to include contaminant levels, contaminant speciation and the effects of the contaminants on different components of an ecosystem. Besides considering the traditional soil parameters such as structure, organic matter content and nutrient levels, we need to consider a fundamental shift in the way we view soil, from a medium that supports human activities to a dynamic multi-functional ecological phase that is critical to sustaining the current and future uses of the environment. Soil must pose no harm to any normal use by humans, plants or animals and, although, it must not adversely affect natural cycles or functions, and it must not contaminate other components of the environment [11-12].

Contaminated soil results from a wide range of natural and anthropogenic activities including: effluent discharge, waste disposal, atmospheric deposition, capillary groundwater movement, irrigation with contaminated water, lateral flow of landfill leachates; application and spills of pesticide, percolation of petrol and other organic compounds etc. Contaminants are transported in soil by mass flow, fracture flow, and molecular diffusion of dissolved species. They can also be mobilized by vapour diffusion of gaseous species and by particle migration, colloid migration and mechanical mixing of sorbed species. Accordingly, heavy industrial and agricultural land use frequently leaves behind complex contaminants and environmental problems which require remediation before the site can be used for alternative purposes. Among the contaminants can be heavy metals, organics, pesticides, diesel or fuel oils and explosives The major industries likely to increase contamination of soil are listed in Table 1.1.

Apart from human activities, natural phenomena such as flooding, landslides, volcanic eruption and mineralisation can upset the balance of contaminants in the soil environment. Management of contaminated soil is an evolving practice. In spite of a long history of contamination, it is a relatively new field and there are many differences in understanding and tackling the problem between institutions and countries. This is evident from different definitions of the term “contaminated land." Because of such problems, most countries have adopted guidelines, regulations and laws that suit their respective political and economic goals that are not in line with the current knowledge of science.

Table 1.1 List of major industries likely to increase soil contamination [13].

Acid/alkali plant and formulation
Airports
Asbestos production and disposal
Chemicals manufacture and formulation
Defence works
Drum reconditioning works
Dry cleaning establishments
Electrical manufacturing (transformers)
Electroplating and heat treatment premises
Engine works
Explosives industry
Gas works
Iron and steel works
Land fill sites
Metal treatment
Mining and extractive industries
Oil production and storage
Paint formulation and manufacture
Pesticide manufacture and formulation
Pharmaceutical manufacture and formulation
Power stations
Railway yards
Scrap yards
Service stations
Tanning and associated trades
Waste storage and treatment
Wood preservation

There are broadly three levels in nature that are important in considering the effects of any potentially toxic species in soil *viz.* background levels, tolerable levels and harmful polluting levels. For the purposes of this work contaminated soil is considered as that containing tolerable levels of potentially toxic species, and polluted soil as that containing harmful levels of toxic species[1].

In this context the definition of 'background' in relation to 'contamination' and 'pollution' is given as follows. Many accept a 'contaminated' soil as presenting a hazard due to the addition of a potentially undesirable substance without any requirement of health or environmental impact. A 'polluted' soil indicates addition of a contaminant which results in a possible health or environmental risk. This implies a continuum of concentration from the pristine state though contaminated to a polluted situation. The boundaries between these three categories in terms of total concentration of a contaminant will depend on the nature of the substance considered, its bioavailability as determined by the chemical species involved, its interaction with the particular soil type, and the critical pathways contributing to assessed risk. The existence of near pristine soils which are more 'contaminated' (i.e. have higher concentrations) than some industrially affected soils deemed, by regulatory guidelines to be contaminated, can create some perceptual problems, especially in communities attuned to the view that natural must be healthy [13].

There are, however, problems even in deciding on background levels of, for example, heavy metals in the soil. Total analytical heavy metal content would include both metal species available to biota and the metal fixed in minerals which would under normal circumstances, not be available to plant and animal species. It is therefore important in deciding the background levels of heavy metals that the data quoted are for available species, essentially those soluble in dilute acids such as acetic, hydrochloric and sulphuric and not total heavy metal concentrations. The retention, volatilization and toxicity of many elements in soils depends on the speciation of the element. Many methods have been employed to identify the species of heavy metals and metals can exist in combination with both inorganic and organic materials, with species distribution primarily influenced by pH and dissolved organic carbon (DOC). High pH and high DOC favoures the formation of organic complexes[14-15]. The importance of speciation is perhaps best exemplified by mercury. The metallic and cationic forms of Hg are not particularly hazardous whereas methyl mercury in the environment has proven deadly [14]

Knowledge of the exact nature of the contaminating species present in the soils and the reactions and transport of these species through soils is vital to the development of remedial techniques. Polluting species can react with soil components in a number of ways: by adsorption on the surface of soil particles, by exchange with hydroxide and other groups in clays and aluminosilicates, by interaction with organic soil components such as humic acids, by reactions with the aqueous component of the soils leading to precipitation and dissolution of derivatives of the contaminating species and uptake by microorganisms and plants. Transfer of contaminating species in soils is further complicated by the physical nature of the soil, particularly the extent of a fissury which will affect the transport of dissolved and suspended species through the soil to the aquifer[1].

An aspect of transport of heavy metals that must be addressed is their availability to biota. The ability of living matter to take up potentially toxic species, depends upon a number of factors including the nature of the polluting species and the metabolism of the organisms. Toxicity is, of course, dose-dependent and many organisms can adapt to the levels of available heavy metal species. There are, for example, a number of plants native to Africa which are hyperaccumulators of cobalt. The soils in which they grow can contain up to 1% cobalt which is extremely poisonous to most plant life but the hyperaccumulators can concentrate cobalt in their leaves to very high levels. Pollutants generally present in the environment in very dilute concentration, they can be harmful even at these low levels. We are, however, faced with the fact that there is a lack of detailed knowledge of the fundamental properties and the behaviour of potentially toxic species in very low concentration in complicated systems such as soils [16].

The increased understanding of soil contamination processes presents a challenge to soil scientists, chemists, biologists, physical scientists, ecotoxicologists, human health experts and policy makers and related management professionals. The array of contaminants that must be addressed includes: heavy metals and toxic elements, excess nutrients, volatile and non-volatile organics, explosives, radioactive isotopes and inhalable fibres. In addition, the links between a contamination and its intrinsic hazard and risks are not always obvious. For example, humans eat plants grown on soil, drink water that passes through the soil and inhale air that exchanges with soil air. Humans also inadvertently eat and inhale some soil directly. Therefore the pathway has a potency for delivering the hazard, and this potency is highly dependent on a number of factors[11].

1.3 Remediation techniques

Contaminated soil is an unwanted legacy of industrial activity in developed nations with a long industrial heritage. In the developing countries it is the result of continuous civil war and legal and illegal dumping of toxic chemicals. The development of commercially viable soil remediation techniques is, therefore, an important area of current research and development. Many techniques used to remediate contaminated soil have been developed from knowledge and experience in other disciplines, especially mining, where low grade ores are treated to obtain a concentrate for smelting or hydrometallurgy. Furthermore, the multifaceted nature of the problem has benefitted from the input of several disciplines.

Because of the emergence of the new remediation techniques, and tighter environmental legislation, the traditional solutions of removal and/or encapsulation of the contaminated soil are also being questioned. Removal to landfill, while creating a potentially clean site, is seen as transferring unresolved contamination problems to another site. Encapsulation by covering, capping or vertical barriers renders a site safe for the immediate user, but further work may be necessary in the future if a change of use of the site occurs, or if the barrier systems fail.

As an alternative to traditional methods, a range of innovative clean-up technologies has been developed for treating contaminated soils and groundwaters. These techniques treat contamination by such processes as separation and removal, destruction, stabilisation, or transformation of pollutants into a less toxic and/or less mobile form. These technologies can be broadly classified according to the amount of site disturbance required and their degree of technological sophistication.

Remedial techniques can be classified [17] under three headings *viz. in situ*; prepared bed; and in-tank reactors; within these techniques the separation process involved can be physical, chemical or, biological. The prepared bed and in-tank reactors are defined here as *ex situ*. These methods and their appropriate processes aim to achieve separation, volume reduction, immobilisation and detoxifications depending on their general operating principles; for instance: biological, chemical, physical, solidification and thermal [17-19]. The soil remediation matrix is shown in Table 1.2.

Technology	Description	Applicable contaminants	benefits	Constraints	Relative cost
Immobilization Stabilization/ solidification	●waste is mixed with binding agent to immobilize contaminants ●reduces mobility without causing significant contaminant destruction or removal	primarily inorganics some organics	●Reduces pollutant mobility ●improves handling and physical characterisation ●basic process is familiar, i.e. mixing, curing and deposition	●incompatible waste reduction effectiveness ●organics can be a secondary environmental problem ● longevity still at issue ●results in volume increase (20 -80%)	medium
Vitrification *in situ*	●exposure of waste to temperatures that melt the waste to point of fusion, process includes chemical incorporation and physical encapsulation ●heat generally applied by electric current	inorganics, possible for organics	●Results in continous monolith, long term durability ●no pretreatment required	●not applicable for large volumes ●results in volume reduction (20-40%) ●site condition critical, i.e. soil type groundwater moisture content ●may have overmelt	medium-high

Table 1.2 Contaminated soil remediation technologies matrix [19]

Technology	Description	Applicable contaminants	benefits	Constraints	Relative cost
Thermal Incineration	●Controlled high temperature combustion to destroy or detoxify hazardous waste ●complete combustion converts contaminants to carbon dioxide and water ●consists of feed, primary chamber, secondary chamber air emissions control and residual management	organic	●proven technology for wide range of waste ●complete destruction ●human health risks seem minimal	difficult to handle inorganic/salt and heavy metals needs air pollution control for off-gas treatment type of waste can cause a handling problem needs residual management public perception	high
Pyrolysis	●converts contaminants to carbon dioxide and water in an oxygen-starved system at temperatures that pyrolyse the contaminants	organic	●reduce concerns for volatilization of metals ●air pollution control needs minimized	●high fuel requirements ●greater uncertainty for incomplete destruction	high

Table 1.2 continued

Technology	Description	Applicable contaminants	benefits	Constraints	Relative cost
Physical/chemical contaminant extraction	•physical transfer process •Mobilization of contaminants using washing fluid-surfactant, acid and bases, water. • *in situ* flushing • *ex situ* flushing	organics, certain inorganics	•offers treatment for inorganics that can reduce/concentrate contaminant •demonstrated removal efficiencies range from 70-99% depending on contaminant •may produce usable clean soil potential recycle of wash fluid •equipment available	•*in situ* flushing requires well-defined ground water flow pattern •may need a physical barrier •soil characterisation critical technology still being proven •water treatment needed •residual disposal needed	medium
stripping-vapour extraction, thermal desorption (hot air steam)	•physical transfer process •Contaminants are driven off through the application of induced air flow, (heat and/or mechanical) to volatilize contaminants into a gas steam	•volatile and semi-volatile organics •certain volatile metals •usually applied to vadose zone	•well proven for highly volatile organics in a vadose zone •inexpensive •minimal site disruption •demonstrated removal efficiencies range from 65-99% depending on contaminant •ease of installation •flexible operation	•soil type critical •treatment needed for extracted contaminats •may need a cap to reduce air releases •estimating cleanup time	

Table 1.2 continued

Technology	Description	Applicable contaminants	benefits	Constraints	Relative cost
Bioremediation	●bioremediation is a destruction process that uses bacteria, fungi and yeasts to degrade organic contaminants ●can be accomplished by aerobic and anaerobic processes'	organics	●demonstrated for certain organics, i.e. petroleum contaminants, benzene, phenol ●can degrade wide range of organic compounds ●single application	●environmental factors critical ●ability to deliver oxygen and nutrients ●metabolic byproducts ●added substances may react with the soil components ●time frame	low

Table 1.2 continued

An *in situ* method treats contaminated soil in the place where the contamination is located without excavation. Conceptually, this method appeals most, since it entails the minimum disturbance of the ground. The prepared bed method deals with contaminated soil in one or two ways: (1) by physically moving the contaminated soil for on-site treatment to avoid transport of contaminants; (2) by provisional removal of soil from the site in order to prepare the site for use, then return of the soil after treatment is complete. The bed contains the soil to be treated within a lining of clay or plastic to prevent the outward migration of contaminants. It can also be achieved by adding "clean soil" to provide a favourable medium for treatment. As with the *in situ* method, chemical, physical or biological techniques or any combination of these, can be used to improve treatment. The in-tank method uses industrial processes in which the soil is removed off-site to be treated in an enclosed reactor. The soil may be in an unsaturated or a saturated form, and treatment techniques include composting, slurry-phase and solid-phase methods.

Biological processes depend on the biological transformation or mineralisation of contaminants to a less toxic form and/or mobilising them to increase their availability to other treatment processes. Biological processes can also be used to fix and accumulate contaminants in harvestable biomass. Currently, treatable organic contaminants are limited to those which are readily biodegradable. *Ex situ* methods include traditional approaches such as land farming and composting, and more recent developments such as using aerobic or anaerobic bioslurry reactors, for example, for the treatment of organic contaminants in clays and silts. *In situ* methods include pump and treat systems where the natural biodegradation process is enhanced and controlled by the supply of oxygen and nutrients.

Chemical processes destroy, fix or neutralise toxic compounds. Most treatments in this category have been developed for groundwater clean-up. Processes have been developed *ex situ* for the remediation of organic and inorganic contaminants by oxidation or reduction to a more stable, immobile, and less toxic form. Examples include: the reduction of chromium (VI) to chromium (III) using ferrous ammonium sulphate [20], and the reductive dehydrochlorination of halogenated organic compounds. Chemical extraction processes can be used to transfer the contaminant from the soil to a leachate which can be collected, concentrated and treated. This approach can be used to deal with both organic and inorganic contaminants, using extraction agents such as organic solvents, acids and alkalis, surfactants, and supercritical fluids. Successful extraction requires conditions of intimate mixing between the soil and the liquid.

Physical processes remove contaminants from the soil matrix as concentrates which then require further treatment (for example chemical or thermal) or are disposed of to landfill. Soil washing is an *ex situ* technology which is most likely to be successful where there is distinct partitioning of contaminants. Soil vapour extraction, or soil venting, is an *in situ* physical treatment, in which volatile organic contaminants are volatilised from the soil by blowing air through the subsurface [17]. Electroremediation can be applied to the treatment *in situ* of soils with a relatively high content of clays or peat, and mainly for soils contaminated with heavy metals. An embedded electrode array induces contaminant migration through a combination of electrolysis, electro-osmosis and electrophoresis. The area around each electrode is washed with circulating fluid to transfer the contaminants to an above ground leachate treatment plant.

Solidification processes encapsulate contaminated material in a monolithic solid of high structural integrity. Where solidification is accompanied by chemical fixation of contaminants, it is also called stabilisation. Vitrification is related to solidification in that high temperatures are used to fuse contaminated materials into a glass. Materials used for solidification and/or stabilisation purposes include traditional civil engineering materials such as cement, clay, fly ash and lime. Newer developments in this area include the possibility of long term fixation of low levels of toxic organic compounds. Additives have been developed for cement-based solidification which overcome the inhibiting effects of high levels of organic compounds on the cement hydration [18].

Thermal systems make use of elevated temperatures (800- 2500°C) to induce physical and chemical processes, such as volatilisation and combustion, for eliminating toxic substances from the polluted soil. Thermal systems are commonly used to treat soils contaminated with toxic organic compounds, which are destroyed at high temperatures. Volatile heavy metals, such as mercury, can also be removed from soils by thermal processes [18], although they are not destroyed and have to be condensed downstream of the process. Thermal systems can treat almost any type of contaminated soil, although soils with high contents of clays and moisture require higher energy input and are difficult to handle. The majority of thermal processes, such as incineration, gasification and pyrolysis, are applied to excavated soils although a number of *in situ* applications exist.

Overall, soil remediation processes can be relatively expensive and several important contamination problems remain difficult to treat, notably: low level or deeply buried contamination; contamination in clay and peat- rich soils; and many mixtures of organic and inorganic contaminants. As a result there is often considerable difficulty in achieving successful treatment of sites which have complex contamination problems [18,21], for example, where a range of contaminants or contaminated materials is present and where this places limits on the technology to achieve effective remediation of soil within an acceptable cost margin.

As our understanding of contaminants in soil is evolving, it has presented both scientific and regulatory challenges. Technologies for remediation of contaminated soils are being developed rapidly although more will have to be achieved. Effective remediation, however, also requires the concomitant development of a methodology that incorporates social, political and scientific dimensions with proper appreciation of scientific and technological findings. This will enable the regulatory scientists, research scientists and industries to act in good time in their respective areas for a common goal. It should also be stressed that the remediation techniques have to be practical and scientifically defensible.

Because restoration to pristine levels is in most instances not feasible, remediation guidelines and regulations should aim to achieve some defined level of environmental and human protection.

1.4 Assessment approaches to contaminated soils

Soil is one of the most complex of biosystems on earth. It is in and on the soil that essential processes of the biosphere take place, especially the pathway back from an organic to an inorganic state of the chemical elements. Soil quality can be assessed in different ways: structure, composition of minerals, and biological elements.

Until the 1970's the problem of contaminated soil and its remediation had not received much attention. Serious contamination incidents resulting from abandoned landfill sites in the United States, the Netherlands and Germany acted as a trigger for legislative action. These incidents led to the contamination of nearby land, buildings and groundwater directly threatening human health and the environment. Because of such problems, most industrialised countries have adopted laws, regulations and guidance on the identification and assessment of contaminated soils and its remediation. Different approaches have been taken in the regulations pertaining to contaminated soil in different countries. Most countries use soil criteria strictly or as a support to decision making where it can be used in conjunction with soil characteristics and/or designated site use. Others rely entirely on toxicological and cancer risk assessment or complete subjectivity.

The 1980's was the decade of aggressive action in the USA, the Netherlands and Germany where the pro-active approaches were adopted. These countries have managed to bring under control cases of an immediate threat to human health and the environment, although many sites still need remediation, involving considerable time and financial resources. On the other hand, countries such as the UK and Canada have opted for a reactive approach. This approach especially in the UK is justified by its proponents, (1) on the geological setting of the country, (2) on the controlled waste disposal system and (3) on the lack of major incidents. Although the Lasoe incident of 1986 caused by a methane gas explosion is among the few publicised incidents in the UK, it was not of the same magnitude as that of the Love canal in the USA or Lekkerkerk in The Netherlands. The reactive approach, however, underestimates the problem, with the hidden motive of policy makers being to avoid blight, litigation and huge remediation cost[1].

The following section considers the range of approaches to the assessment of contaminated soils in different countries. Soil quality criteria provide the technical basis for all guidelines or other related official enforcement or legal instruments. They are mostly based on considerations of perceived risk, intended land use, political and economic factors, technical feasibility and related cost factors. The summary of the approaches adopted is in Table 1.3; The Netherlands, UK and Canada situations are discussed as an example.

The current guidelines in many developed countries are complicated and categorising them in a meaningful way is difficult. Most, however, fall into two categories: generic and site-specific [11]. Generic guidelines refer to maximum levels of contaminants in soil that generally will not harm human health and the environment, and are applicable to a broad range of sites. They are sometimes referred to as 'absolute', because they are independent of mitigating factors and are straight forward to legislate. Site-specific, guidelines are based on a diverse group of methods that analytically weigh many factors relevant to each site. Typically, they require detailed characterization of the site and computer models to estimate the fates and consequences of contaminants. They may also include cost-benefit and social issues. The use of site-specific guidelines is broadly advocated. It is difficult to track their development because they have largely been conducted in an ad hoc fashion, using a number of different models and different toxicological data and assumptions. The approach of the United States Environmental Protection Agency (USEPA) uses site-specific information to estimate doses that site users could receive via various pathways. Standard exposure scenarios are specified and guideline soil concentrations corresponding to a maximum acceptable health risk are computed [22].

Table 1.3 Summary of contaminated soil remediation programmes in different countries[11]

USA	Federal (Superfund) program for clean-up of major uncontrolled hazardous waste sites initiated in 1981 and amended in 1986.
Canada	National program (NCSRP) for cleanup of contaminated sites initiated in 1989. Provincial programmes were initiated: Ontario, 1984; Alberta. 1985; Quebec,1986; and British Colombia, 1989.
UK	Guidance documents issued in 1987 by the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL), laws enacted in 1990,1992 & 1995 but not yet functional.
Netherlands	Nationally initated programme of "soil clean-up" act in 1983 and the " soil protection act " in 1994.
France	No specific national legislation or directives. National level guidance and cleanup supervision provided in the form of document entitled "Analysis and treatment of polluted soils" in 1984.
Germany	General state level programs initiated in 1970's Federal guidance and research funding in 1983 and adoption of "Conception of soil protection" in 1985. In 1987, the Federal cabinet approved amendment of relevant laws and regulations to incorporate soil protection.
Australia	Draft " Australian guidelines for the assessment and management of contaminated sites" issued in 1990 by the Australia and New Zealand Environment Council (ANZEC); some states have enacted specific legislation and directives.
Denmark	National legislation enacted in 1983. No specific program or directives but a risk assessment procedure is being formalized by the National Agency for Environmental Protection.
Sweden	National legislation enacted in 1988. However, there are no specific programmes or approaches for assessing the significance of contamination and setting cleanup goals.
Finland	No specific legislation or directives. National inventories and informal guidance provided through the National Board of Waters and the Environment. Standard approaches to setting cleanup goals under development.
Norway	No specific legislation or directives. National level inventories are in progress and informal guidance is provided.

Risk assessment is becoming increasingly complex, and although it is supported by a host of sophisticated models it can be inconsistent in application and results. There are many sources of variation, including definition of the level of "acceptable' risk, choice of model, choice of parameter values for the model, quantification of potential exposure pathways, uncertainties in interpretation of toxicological data, and variation in the way the overall method is applied [19]. Because protection of human health may not ensure adequate environmental protection, there has been a recent emphasis on the development of ecological risk-assessment methods. These methods must consider a variety of receptors and endpoints at population, community and ecosystem levels, as well as a variety of exposure pathways.

Increasingly, it is recognized that generic and site-specific guidelines are compatible and essential components in any comprehensive approach to soil quality protection and clean up. The scientific information required by both approaches is basically similar.

1.4.1 The United Kingdom approach

In the United Kingdom, guidelines prepared by ICRCL (Inter-Departmental Committee on the Redevelopment of Contaminated Land) are the only soil quality guidelines [23]. The guidance notes which draw heavily on the gas-work experience gives guidance on when levels may require action to be taken by setting "trigger values".

For any contaminant addressed a “threshold” and action or “trigger” levels are specified, effectively setting three ranges of concentrations. At levels below the threshold the site can be regarded, for practical purposes, as uncontaminated; between the threshold and the trigger level treatment may be necessary, and above the trigger level treatment is unavoidable.

For each contaminant, several sets of trigger values are provided, depending on the intended use of the site; thus a site may be contaminated for some end uses such as recreation, but not for others. This is the main difference between the British and Dutch approach which advocates 'fit for the purpose' and 'multi-functionality' respectively. These values are based largely on professional judgement, but consider a range of factors including ingestion of soils, consumption of contaminated plants, skin exposure, phytotoxicity, corrosion, and even explosions. Trigger concentrations were also specific to land uses such as domestic gardens, parks, playing fields [23]. In the UK, options are being considered for changing the current guidelines but no progress has been reported to date.

1.4.2 The Netherlands approach

The Netherlands has carried out much research on the assessment and cleanup of contaminated soils. This was in response to their estimate of more than 100000 contaminated sites which require clean up [24].

In 1983 the Netherlands passed the "Soil Clean Up" Act [25-27] and issued a comprehensive list of "ABC" Guidelines for assessing the severity of soil contamination. The "A" value (reference value) describes the upper limit of the natural background range was not based on ecotoxicological effects. The A- value was viewed as a desirable aim for clean up which would permit a flexible, unrestricted or multi-functional use of the land. A second indicative level, B-value, was the trigger value for further investigation. The investigation would use available site and soil factors to determine bioavailablity, transport of pollutants, critical pathways in relation to the desired land use. A third indicative value, C-value, described a limit which requires cleanup. Table 1.4 shows the concentration of the the three indicative levels for several heavy metals.Values for various other inorganic pollutants. The C-values for cleanup incorporate human-toxicological data but are not based on any accepted risk assessement methodology. Empirical experience and 'expert' judgement were important. The Dutch approach has had an enormous impact world wide.The authorities are progressively upgrading their soil quality criteria in the light of new scientific work especially in relation to ecotoxicology. The revisions will be based on the general 'risk'of contaminants to human health and the environment and on background levels of contaminants in rural soils [24].

Table 1.4 Netherlands's Standard for inorganic contaminants in soil

Contaminant	**A** **(mg/kg)**	**B** **(mg/kg)**	**C** **(mg/kg)**
Arsenic	15	30	50
Barium	200	400	2000
Cadmium	0.4	5	20
Cobalt	20	50	300
Copper	15	100	500
Chromium	50	250	800
Lead	50	150	600
Mercury	0.2	2	10
Molybdenum	10	40	200
Nickel	10	100	500
Tin	20	50	300
Zinc	50	500	3000

A: Reference level
B: Levels that require scientific judgment
C: Levels for detailed investigation for redevelopment
L: Weight percentage of clay in the soil
H: Weight percentage of organic matter in the soil

1.4.3. The Canadian approach

The first soil quality guidelines in Canada were developed in 1984 by the Ontario Ministry of the Environment[11]. The values and approach were markedly different from those of the Netherlands or the UK. Up to four values were recommended for each substance, to apply to two broad categories of land use and two categories of soil texture. Based largely on professional judgement, they considered background concentrations, health of grazing animals, phytotoxicity and human health.

A review by Environment Canada [28] concluded that most of the international generic guidelines had no clear supporting scientific rationale and did not address all the issues deemed important. The inadequacies are well recognized, and consequently, most generic guidelines have been introduced on an interim basis. Generic guidelines can be important: they provide a common basis for comparison among sites, they streamline the initial or screening-phase assessment of contaminated sites. They facilitate communication between interested parties and foster broad-based soil protection programs. The International Organization for Standardization [7,8] Technical Committee on Soil Quality are working to address virtually all the problems associated with contaminated soil, from terminology and sampling through to analysis and bioassays.

Most regulatory and *de facto* guidelines that have emerged, are extremely fragmented, inconsistent and incomplete. Most rely on professional judgements ranging from the criteria used to accept data through to decisions made virtually in the absence of data. Considerable information has been acquired from basic and applied researches on soil pollution. The applied research in the future must, however, consider the needs of regulators. The policy makers and regulators also need to view in a balanced way research findings and economic factors. This will enhance research and will create an interface between policy makers, regulators, industry and the research establishments.

Although soil pollution is a major environmental concern, it is probably the least understood source of pollution in terms of both transport of contaminants and remediation. The current knowledge of soil processes and the situation in remediation techniques and legislation highlights the need for an additional endeavour. It must be realised that most of the processes which caused contamination in the past are continuing even if in a number of cases activities have been stopped.

Increased community concern in recent years has resulted in a major upsurge in the investigation and remediation of contaminated soils. This has led to a concomitant reassessment and development of regulatory procedures, and the establishment of some new environmental agencies. Assessment of contaminated sites has been largely based on a site-specific approach relevant to each country's soils and in a web of complex social, economic and political spheres.

Remediation of contaminated soil is a rapidly developing activity. Nevertheless, the attitude of many countries to environmental pollution overall does not adequately reflect the great commitment and enthusiasm within the political and industrial establishment. The strong move for a rational approach to the assessment and management of contaminated sites requires the active participation and commitment of regulatory scientists, research scientists and management professionals.

There is a complex web of political, social and legal concerns, as well as limitations imposed by the technology available to remediation of soil. There is an increasing demand in practice for an approach that is scientifically and economically defensible. Therefore, the soil assessement and remediation require a new way of thinking and acting. It requires the concerted action of those who must be prepared to use their responsibility for the common interest through integrated action. Narrowing the gap in the way of thinking between the scientists and the policy maker is important.

More detail on the management and control of contaminated and polluted land is given in reference [1] which is given as appendix to this thesis.

A major problem concerned with the control of contaminated land lies in the lack of understanding of many soil processes. One of the functions of the work carried out in this thesis is to increase our knowledge of reaction between soil components and metals and organic species being transported in the aqueous phase of the soil. This chapter is followed by a general review of soil oxides in pollution control in Chapter II and in chapter III, IV and V by descriptions of the interactions between goethite and metals, birnessite and metals and magnetite by metal and organic species.

1.5 References

1 Tadesse, B. Donaldson, J.D. & Grimes, S.M. (1994) Contaminated and polluted land: A general review of decontamination management and control, J.Chem. Tech. Biotechnol. 60, 227-240

2 Carson, R., (1962) Silent Spring. Penguin, London,

3 Galbraith, J.K., (1969) The Affluent Society. Penguin, Suffolk

4 Newton, L.H.&. Dillingham,C.K (1994) Watersheds; Classic Cases in Environmental Ethics. Wadsworth, New York.

5 Hoffman, A. (1995), An Uneasy Rebirth at Love Canal, Environment, 37, 5-31.

6 Bins-Hoefnagels, I.J.M., & Molenkamp, G.C., (1986) Case studies in soil pollution in some Dutch urban areas, In: Assink, J.W., & van der Brink, W.J., (eds) contaminated soil '86, 769-779, Martinus Nijhoff, Dordecht.

7 Hortensius, D., Meinardi, C.R.& Bayveye, P. (1989), ISO/TC 190 and the development of an international standardized approach to soil quality problems, Water Int. 14, 89-90

8 Hortensius, D., & Nortcliff, S. (1991) International standardization of soil quality measurement procedures for the purpose of soil protection. Soil use manage., 7, 163-166

9 NATO Committee on the challenge of modern society (1990) Demonstration of remedial action technologies for contaminated land and groundwater, Final report, United States Environmental protection Agency Report EPA/600/R-93/012, EPA, Wahington D.C.

10 Visser, W.J.F. (1995), Contaminated Land policies in Europe, Chemistry & Industry, 13, 496-499.

11 Sheppard, S.C., Caudet, C. Sheppard, M.I., Cureton, P.M.. and Wong, M.P. (1992) The development of assessement and remediation guidelines for contaminated soils, a review of the science. Can. J. Soil Sci. 72, 359-394

12 Moen, J.E.T. (1988). Soil protection in the Netherlands, In Wolf, K.,. Van den Brink, W.J. & Colon, F.J. (eds) Contaminated soil '88, 1495-1503, Kluwer, Dordrecht,

13 Tiller, K.G (1992) Urban soil contamination in Australia, Aust. J. Soil Res., 30, 937 - 957

14 D'Itri, F.M. (1991), Mercury contamination - what have we learned since Minamata?

Environ. Monit. Assess. 19, 165-182

15 Dufy, S.J., Hay, G.W., Micklethwaite, R.K., and Vanloon, G.W. (1989), Distribution of classification of metal species in soil leachates, Sci. Tot. Environ., 87/88, 189 -197

16 Donaldson, J.D.,Clark, S.J., Grimes,S. M., (1986) Cobalt in Medicine, Agriculture and the Environment. Cobalt institute, London,

17 Sims, R. C., (1990) Soil remediation techniques at uncontrolled hazardous waste sites: a critical review. Journal of air and waste management association.40, 704-732.

18 Martin, I. & Bardos, P. (1994) Recent developments in contaminated land treatment technology, Chemistry & Industry, 6 June , 411- 413

19 Air and Waste Management Association (1991) How clean is clean? cleanup criteria for contaminated soil and groundwater. AWMA, Pittsburgh.

20 Jacobs, J.H. (1992), Treatment and stabilisation of a hexavalent chromium containing waste material, Environmental Progress,11,123-126

21 Cairnes, J. (1989) Restoring damaged ecosystems:Is predisturbance condition a viable option? Environ. Professional 11, 152-159

22 United States Environmental Protection Agency (1989) Risk assessement guidance for superfund, EPA/540/I-89/001, EPA, Washington DC.

23 ICRCL(1987), Guidance on the assessment and development of contaminated land. Guidance note 59/83 2nd edition. Department of environment, London

24 Keuzenkamp, K.E., Von Meijenfeldt, H.G., & Roels, J.M (1990)., Soil protection in the Netherlands .In: Ardent, J. (ed), Contaminated soil '90, 3-10, Kluwer, Dordrecht.

25 Gravestlyn, L.T.J., (1990) Contaminated industrial sites in the Netherlands. In: Ardent, J. (ed), Contaminated soil '90, 17-18, Kluwer, Dordrecht.

26 Ministry of housing, physical planning and environment, (1984) Soil clean up (interim) act. Central department for information and international relations, The Hague

27 Denneman, C.A. J. & Robberse, J.G., (1990) Ecotoxicological risk assessement as a base for development of soil quality crietaria, In: Ardent , J. (ed) Contaminated soil '90, 157-164, Kluwer, Dordrecht,

28 Environment Canada (1991) Review of recommendations for Canadian interim environmental quality criteria for contaminated sites. Scientific Series No.197, Inland Waters Directorate , Water Quality Branch, Ottawa

2.0 ROLE OF SOIL OXIDES IN POLLUTION CONTROL

2.1 Introduction

The release of contaminants into an ecosystem can alter the nature of the environment and restrict the use of the natural resources available to plants, animals, and humans. Soil and water are among the resources that are vital to ecosystems; since the start of the industrial revolution human activity has significantly changed the material balance of parts of the planet and in certain areas disrupted the equilibria of ecosystems, to an extent that there is now universal recognition of potential environmental hazards. In spite of this recognition, however, many economic and social factors have combined to reduce the effectiveness of attempts to curb environmental pollution.

The growing awareness of the effects of environmental pollution, the increasingly affluent lifestyles in developed countries, and the rapid growth of world population have accelerated the recognition of the dangers of soil pollution and its impact on the environment. It has been accepted that soil plays a major role as a repository of many contaminants and as a pathway for the transport of contaminants to ground and surface waters, and as a source of toxins as well as nutrients to the food chain. Soil is also an essential component in plant growth and the degradation and recycling of biomass. Moreover, it is a medium in which interaction between the hydrosphere, atmosphere and biosphere can take place because it is an interface between ground water and surface water and between the biosphere and atmosphere. A detailed knowledge of its direct and exchange reactions with other environmental components, therefore, is important in understanding the dynamics of the soil in any given environmental system. An increased understanding of the dynamics of soil system will not only enable researchers, industrialists and regulators to appreciate the effects of pollution but will also assist in endeavours towards pollution prevention and control.

2.2 Objective of the investigation

The aim of the research described in this thesis is to study the adsorption of pollutants on to soil particles to gain information on their transport in soils and to assess the possibility of increased use of soil oxides in clean and clean- up technology based on their soil chemistry and physics.

To this end the following tasks were carried out:

- Preparation and characterization of Goethite (α-FeOOH), Birnessite ($Na_4Mn_{14}O_{27}.9H_2O$) and Magnetite (Fe_3O_4), as precipitates, coprecipitates, and coatings on inert material.
- Investigation of the sorption capacity of goethite and birnessite for cations such as Cd^{2+} and Co^{2+}.
- Investigation of the ability of magnetite to remove coloured species and organic colloids from acidic and alkali media.
- Investigation of the electrokinetic behaviour of the precipitates in electrolyte solutions.
- Use of the technical results to further knowledge in the interface between the soil chemistry and soil resource management.

2.3 Background

A literature review is presented here under the headings soil-sorption processes, soil-water reactions, and solute transport in soil.

2.3.1 Soil sorption processes

The term soil pollution is controversial, and it should be noted that it is used in this thesis to imply presence of some unwanted materials in the soil which have arisen through a variety of processes that can be natural or anthropogenic in origin. Pollution infers the presence of such materials in concentrations that provide a significant risk of damage to users of the soil or at least sufficient to restrict its free use. The risks include: damage to human, animal and plant health, damage to engineering structures and contamination of water resources that come into contact with the soil[1-2].

To curtail these pollution problems, a number of research projects have been undertaken and many remediation processes have been developed. In spite of an increased general knowledge of soil processes in relation to pollution there is still a need for detailed knowledge of the processes involved to fully understand the problem[2]. It is particularly important to increase our understanding of the behaviour of pollutants in the soil-water system because of the dynamic and heterogenous nature of soil.

The terms "heavy metal" and "trace metal" are used in this work based on the definition of Alloway and Sposito [3-4]. Heavy metal denotes metals with a density which is greater than 6g cm^{-3} and the term trace metal is used when the soil solution concentration of the metal is below 1mM. Accordingly the term "heavy metal" includes most transition metals.

Soil is an open system which consists of a heterogeneous mixture of interacting organic and organometallic substances, clay minerals, oxides of iron, aluminium and manganese, and other solid components as well as a variety of soluble substances. It forms horizons which support life and accumulate soil mineral oxides and clays. These oxide and clay minerals play a major role in static and dynamic processes in the soil. The uniqueness of soil is augmented by the complex biological, chemical and physical processes operating within it under varying conditions.

Above all soil is both the source of nutrients and toxic elements, and also serves as a sink. The nutrients are usually present in ionic form in aqueous solution. Among them cobalt, zinc, copper, iron and manganese can be cited as essential but it should be noted that even these metals, when they are present above the required level, can be a toxicity risk. On the other hand elements like cadmium and lead can be considered as nonessential and, depending on their concentration and availability, can constitute a risk. The distribution of these elements in the soil is said to be controlled by soil minerals which in turn regulate the availability of the metal to the biota. A study of trace elements of the soil should, therefore, involve a study of the physico-chemical processes in the soil and their effects on the fauna and flora which form the basis of the food chain for the system as a whole.

The binding mechanisms for contaminants and the uptake of nutrients are manifold and vary with the composition of the soils, the soil reaction, and redox conditions. Thus a metal may form different species according to which soil component or other species it is bound in the soil-water system.

Regardless of the heterogeneity of the soil, its constituents can be subdivided into a coarse fraction (>2µm), a colloid fraction (<2µm), and an organic fraction. The coarse fraction consists of 5-90% (dry weight) of soils and may be separated into gravel, sand and silt. This fraction is primarily responsible for the filtration mechanism of soil. The colloidal fraction constitutes 10-80% (dry weight) of most soils and is responsible for the colour, texture, and surface reaction properties of most soils. In addition to these inorganics, soil also contains 1- 40% (dry weight) organic matter. Soil organic matter is composed of plant and animal residues and products of their biological, physical and chemical transformations. It is a highly complex mixture of carbon compounds that contain N, S, and P. Organic matter is made up of humic substances and biochemical compounds. Humic substances are operationally defined as based on the procedure generally used for their extraction from the soils and their fractionation. Thus, we can identify: (1) humin, the fraction which is not extracted from the soil with either acids or bases and remains after humic and fluvic acid extraction; (2) humic acids, insoluble in acid solution but soluble in bases; (3) fulvic acids are part of the humus but are soluble in acids and bases. In many soils 90-99 per cent of the total carbon, nitrogen and sulphur is bound in the humus fraction. Humus particles are colloidal, bind strongly to clays and hydrous oxides and have cation exchange properties. From an environmental quality standpoint, organic matter is both beneficial and detrimental as it can adsorb heavy metals and pesticides. The detrimental effect of soil with high organic matter is that it may require higher pesticide applications. This can lead to pesticide leaching into water or being transported by wind. The organic matter present in soil is predominantly acidic. The major effect of the presence of these acids is to lower the soil solution pH, and increase the rate of a soil component dissolution by chelation which facilitates the solubility of both nutrients and contaminants [5-6].

The composition of soil changes with depth from surface to subsurface horizons. Especially under humid climatic conditions, precipitation percolates through soil and may transport soluble pollutants with the soil solution. The concentration of heavy metals in the solution phase is of major importance for all ecological considerations because plants take up the available metals from the soil solution, and the transport of metals within the soil or even to the groundwater depends on the metal concentrations in the solution phase. However, the total process which determines the concentration of heavy metals in the soil solution is not yet fully understood. A change in the composition of soil solution can induce a non-equilibrium situation which in turn alters (1) the activities of microorganisms which influence redox processes; (2) the contents of chelating agents; (3) the composition of soil atmosphere. All these factors exert influence on the system and their combined and individual roles need to be considered. The processes that moderate the reaction of contaminants such as precipitation-dissolution, adsorption-desorption, and complex and ion pair formation in relation to the pH, influence the distribution of the various metal species in the solid phase of the soil and in the solution.

As an example we can consider the fate of heavy metals in the soil-water system. They are influenced by many factors including: pH, temperature, redox potential, cation exchange capacity of the solid phase, and ligation by anions. In the aqueous medium, heavy metals may exist in (a) true solution as free or complexed ions and (b) as particulates due to precipitation and adsorption onto other particles, or incorporation into the biomass of the living organisms and inorganic precipitates such as hydroxides, carbonates, sulphides and sulphates. Many metals are present as very insoluble sulphides (Zn, Ag, Hg, Cu, Cd, Pb) and oxides (Cr, Fe), while some oxides (Ni, Co, Mn) are relatively soluble. The free and complexed metal ions may be removed from solution by adsorption and precipitation mechanisms, while the particulate heavy metals may be transformed by dissolution of the heavy metals and by the filtration mechanism of soils.

Increased understanding of the mechanisms regulating the distribution process between the solid interface and aqueous solutions is of considerable importance. This is best exemplified by the role of soil oxide minerals. The adsorption of inorganic and organic ions on hydrous oxides of iron, manganese, aluminium, silica, etc. has been the subject of investigation, mainly because of the ubiquitous presence of these soil minerals in soils and natural water systems. These oxides not only act as pollutant scavengers, but are also a potential mineral source for example as ferro-manganese nodules in the ocean floor and iron oxides in the lithosphere. The hydrous oxides play a vital role in scavenging the pollutants from soil-water system through adsorption onto their surfaces. To understand the phenomenon of uptake of metal ions by the hydrous oxides it is essential to understand the surface chemistry of these compounds in electrolyte solutions and the reactions involving dissolved and adsorbed species.

2.3.2 Soil-water reactions

The chemical and hydrodynamic processes involving soil oxides and solution occur both at a macroscopic and microscopic scale. However, the macroscopic dispersal of contaminants is controlled by microscopic scale processes that occur mainly at the soil solid component/ water interfaces. Ions and molecules in a solid or liquid phases are surrounded by similar ions or molecules. Thus, at different phases of the system, physical and chemical forces are balanced. The polar solvent water interacts with the surface structure of the solid and can envelop charged sites creating regions where physical and chemical properties vary gradually [7]. This can, therefore, change the distribution of contaminants between the phases and facilitate contaminant transport through aqueous media.

2.3.2.1 Sorption phenomena

Sorption processes involve the interchanges of mass which have an impact on the fate and transport of contaminants. The effects can be complex, given the diversity, magnitude and activity of chemical species, phases and interfaces present in the soil-water environment.

When a contaminant enters a soil-water system, it tends to distribute itself between the two phases until thermodynamic equilibrium is reached. This distribution process, called sorption-desorption, may involve different mechanisms. The different mechanisms which may be involved in the sorption of contaminants include: (1) cation exchange (non-specific adsorption); (2) specific adsorption; (3) migration into a crystal lattice; (4) organic complexation. These processes occur in conjunction with each other depending on the microchemical environment. However, although the extent of sorption can be measured and isotherms derived, it is frequently difficult to be precise about which particular process is responsible for the retention of contaminants. Distinguishing between physical and chemical adsorption is not always easy. Because of the difficulties associated with direct measurements at the interface [8] information on the attainment of the sorption equilibrium is generally derived from measurements of the contaminant concentration in the mass of the phases involved C_{soil} and C_{water}. From an operational point of view, the equilibrium state can be described by the distribution coefficient K_d, defined as:

$$K_d = \frac{C_{soil}}{C_{water}} \tag{2.1}$$

The experimental procedure for K_d measurements can be divided into three steps. First, the water/contaminant/soil mixture is reacted either under static or dynamic conditions. After a defined contact time, the solid is separated from the solution either by centrifugation or filtration, and the residual concentration of the contaminant is measured analytically [9]. Although this procedure is very simple, it is often difficult to ascribe a thermodynamic meaning to the measured K_d values [10]. The main drawback with sorption models is the assumption that systems are at equilibrium, a situation which can rarely be achieved. An additional problem is the assumption that the separation of the liquid from the solid corresponds to distinct, well-defined physical entities. Instead, the existence of colloidal suspension makes it difficult to establish the boundary between the solid and the true solution. This distinction is generally made on an operational basis, because it depends on the efficiency of the filtration or centrifugation system used. The molecules of the contaminant sorbed on suspended particles are then considered as soluble[11].

The results of adsorption measurements at constant temperature are usually reported by plotting a graph of moles of concentration per unit weight or per unit area of soil as a function of the residual concentration in the solution. This graphical representation is known as an adsorption isotherm, which is sometimes based on theory, but more often, is empirical in nature. The term sorption is therefore being used as a generic definition [12]. The interactions which occur between the solutes in the aqueous phase and the solid surface involve: chemical, electrochemical and physico-chemical forces. However, sorption relates a solute to a solid independent of the reaction mechanisms. Sorption phenomena significantly affect the transport and ultimate fate of trace elements which include both nutrients and contaminants in soil-water system. Sorption determines the relative significance of other reactions and transport processes occurring in the subsurface environment.

The two broad categories of sorption phenomenon, adsorption and absorption can be differentiated by the degree to which the sorbate molecule interacts with and is free to migrate to and from the sorbent phase. Adsorption indicates solute accumulation or concentration generally restricted to a surface or interface between the solution and the adsorbent. In contrast absorption is a process in which solute penetrate the sorbent phase by at least several nanometres. Along the lines of processes involved in the binding of the solutes to the soil solid component, Sposito [13] draws a distinction between outer sphere and inner sphere complexation as equivalent to nonspecific and specific adsorption respectively. The adsorption reactions that occur between metallic ions and the charged surfaces of soil components may involve either the formation of relatively weak outer sphere complexes through exchange of cation reactions or the formation of strongly bound inner sphere complexes through ligand exchange reactions. The actual nature of the association between the charged surface and the counter ion depends on the mechanism of retention of the counterion with the surface; the extent of adsorption depends on either the respective charges on the adsorbing surface and the metallic cation or the intrinsic formation constants for the complexation reactions. The adsorption of weak acid cations (Co, Cd, Cu, Zn, Pb) on soil oxide surfaces is termed as specific adsorption or ligand exchange and the non-specific adsorption of ions refers the mechanism created to balance the charge developed by the adsorption of H^+ and OH^- (potential determining ions) on the oxide surfaces due to specific adsorption. Positively charged cations in solution are attracted by electrostatic or coulombic forces to the negatively charged edges and surfaces of soil particles. If the cations do not form covalent bonds with the surface, thereby retaining their water of hydration to form only outer sphere complexes, a weak association is formed between the adsorbed ion and the soil particle. Because of this weak association, the adsorbed ions are easily exchanged by other cations that similarity form only outer sphere complexes with the surface. Such bonding is referred to as non-specific adsorption.

Cation exchange is a particularly important mechanism of retention for many of the alkali and the alkali earth metals such as Na^+, Ca^{2+}, and Mg^{2+}, and to a lesser extent for ion pairs such as $CaCl^+$ and $MgCl^+$. For those cations involved in ion exchange reactions, the process is rapid and readily reversible.

The inner sphere complexation includes both physical and chemical adsorption. Most contaminants can form inner sphere complexes with the charged soil surfaces through a process of ligand exchange. These types of complexes occur in most oxide and hydroxide surfaces of soil. The specific adsorption of inner sphere complexes involves the formation of covalent bonds, so the adsorbed species are not readily displaced. Although most of the more abundant soil cations, such as Ca^{2+}, Mg^{2+}, Na^+, and K^+, are weakly held by soil surfaces as exchangeable ions, many other cations can form inner sphere complexes with variably charged soil surfaces and are therefore strongly held. The specific adsorption of metallic ions occurs most readily for metals that hydrolyse in water. The adsorption reaction generally involves the formation of an inner sphere complex between the hydroxo-metal complex and the negatively charged surfaces of soil oxides, hydroxides, and oxyhydroxides.

Accordingly, three types of loosely defined categories of adsorption: (1) ion exchange, (2) physical adsorption, (3) chemical adsorption are traditionally distinguished according to the class of attractive force which predominates.

Ion exchange refers to the exchange between counter-ions balancing the surface charge on the soil solid component and the ions in the solution. In the case of cations, it is the negative surface charge on soil oxides which is responsible for exchange of cation. The extent to which adsorbing soil constituents can act as cation exchangers is expressed as the cation exchange capacity (CEC) measured in meq of cation per 100g of a sample. Ion exchange process are generally reversible and proceed stoichiometrically. One significant difference between adsorption and ion exchange lies in the fact that the exchanging cations are necessary components of the soil sorption complex and they might be substituted by cations of other types, but they cannot be removed all together.

Physical adsorption results from the action of Van der Waals forces which comprise both London dispersion forces and electrostatic forces. The sorbate is bound to the surface by relatively weak forces that are of the same nature as the intermolecular forces of cohesion which operates in the solid, liquid, and gaseous state. As a result the chemical nature of adsorbed molecules remains unchanged.

Chemical adsorption or chemisorption, however, involves a reaction through the exchange or sharing of electrons between the adsorbate and the adsorbent. The bond formed between the two is essentially a chemical bond and is therefore much stronger than that in physical adsorption processes. Chemical adsorption sometimes requires a certain amount of its energy for its operation. Such a process is called activated adsorption.

The different nature of the forces that cause physical adsorption and chemisorption makes them two distinct processes; the most usual difference between them is in the magnitude of the heat of adsorption evolved during the interaction of adsorbate and adsorbent. A further point of difference is the activation energy. Physical adsorption does not require any activation energy [14]. The rate of physical adsorption is almost independent of the temperature and process is completed in a very short time. On the other hand the rate of chemisorption is dependant on temperature and several other factors including activation energy.

Accordingly, it is believed that adsorption can prevent or prolong the bioavailability of contaminants and nutrients and also decomposition of organics. It can also retard the mobility of contaminants through an unsaturated zone to a saturated zone. On the other hand, recent work has suggested that mobile colloidal soil components may facilitate the long distance transport of heavy metals and inorganics in soil, surface water and ground water [15].

Since soil contains considerable amounts of Ca and Mg, the heavy metals adsorbed by electrostatic forces compete with alkaline earth elements. It is reported that at low pH values some nutrients and contaminants like Co and Cd compete with Ca for the available sorption sites and exhibit similar adsorption affinity[16]. A recent review of soil chemisorption processes suggests the following indirect evidence of chemisorption[17]: (1) divalent metal ions (M^{2+}) exchange with up to two H^+; (2) soil oxides exhibit highly specific sorption preferences towards certain nutrients and contaminants; (3) metal adsorption causes a change in oxide surface charge.

Specifically adsorbed cations occur at isolated sites on the surface and can also migrate into the crystal lattice as opposed to ions bound nonspecifically to layer silicate clays. Surface precipitation may also take place in addition to specific interactions of ions with some soil oxides. Heterogenous nucleation is a significant process contributing to crystal formation and precepitation because nucleation can be catalysed by mineral surfaces [18]. Braumer and co-workers[19] have suggested that precipitation may take place at a concentration far below that of the solubility product. In addition to surface precipitation, solid solution formation can contribute to the retention of trace metals. In contrast to precipitation, solid solutions do not have constant solubility products. Solid solutions are mixtures of two solutes in the solid phase where the composition of the solid phase is dependent on the composition of the aqueous phase. Solid solution formation is aided by the fact that some trace metal ions are of the same size as Mg^{2+} and may, therefore, form a mixed hydroxide interlayer in layer silicate clays [17]. It was reported that uptake of heavy metals including Cd is affected by the Ca concentration in the soil-water system. At low Cd loadings the affinity of the soft base Cd towards soft acidic surface functional groups is very high and therefore Cd is preferentially adsorbed. In contrast, at high Cd loadings Ca can compete with Cd for harder bases such as carboxylate ligand groups [20-21].

In contrast to soil minerals, organic matter is characterised by its structural complexity and heterogeneity, which manifests itself in the diversity of possible reaction sites. Humic substances can act as both oxidizing and reducing agents, depending on environmental conditions. Humic substances have been shown to reduce Hg^{2+} to volatile Hg^0 under natural pH conditions. They also play a role in reducing the toxicity of certain heavy metals to aquatic organisms. Thus humus strongly influences the sorption capacity of soil, thereby providing a pathway for the mobilization and retention of contaminants and nutrients [22].

The oxidation-reduction process occurs continually during the course of humification of plant remains and other substances entering the soil system. Besides the purely chemical processes, biochemical processes of oxidation and reduction in soil are quite common. Therefore, redox reactions may contribute to the changes of the soil-solution metal ion status. The redox potential can directly change the oxidation state of heavy metals. Furthermore in oxygen-deprived areas microorganisms undergo biological processes that contribute significant control over the solubility and mobility of trace metals[23].

The numerous different surface functional groups of the inorganic and organic substances in soil as well as the various bonding mechanisms suggest that no single theoretical model can describe the sorption processes of heavy metals in soil. Nevertheless, predicting the fate of these metals in soil requires a quantitative description and models of the adsorption and desorption processes. Retention of contaminants may be explained in terms of the following: (1) well-defined chemical reactions of several species in solution with different sorption sites, e.g. precipitation of a pure compound or inner sphere complexation at the solution/soil mineral interface; (2) sorption of two or more competing ions regardless of the nature of the reaction; (3) sorption of a single solute on one (or more) reaction site(s). Well-defined reactions have been described by either chemical models based on molecular hypotheses or models based on thermodynamic data of the formation of pure solids and of complex formation in the aqueous solution [13].

Currently, considerable attention is being paid to the speciation of contaminants because of the importance in understanding the fate and effects of contaminants in the environment. The total concentration of a contaminant in an environmental medium is needed for mass balance calculations but, knowledge of the physico-chemical form of the contaminant is also required. Therefore, an evaluation of the fate of contaminants in the soil-water system requires detailed consideration of the chemical, physical and biological processes. Considering the complexity and difficulty of the subject, computer programs are being used for solving problems related to chemical speciation in soil and water environments. The two major categories which are in use to determine the equilibrium species concentration are: (1) Those involving a system of nonlinear equations derived from mass and/or charge balance expressions applied in programs such as SOILCHEM, MINTEQA2, WATEQ2, and PHREEQE [24], (2) Those involving minimisation of the change of Gibbs free energy of the overall reaction as applied in CHARON [25]. It is worth noting that computer programs such as SOILCHEM and MINTEQA2 offer the option to use one or more surface complexation models [26].

The physicochemical complex interactions in the retention and release of contaminants may also be described using models such as adsorption models, surface complexation models constant capacitance models and ion exchange models. Adsorption and ion exchange models are widely used in providing information on the distribution of contaminants in the soil-water system.

The adsorption of ions in soil is significantly affected by competitive adsorption from other ions. Generally the sorption behaviour can be described in terms of ion exchange selectivity coefficients. Multiple ion exchange sites can also be used to describe ion exchange in heterogeneous soil systems. The author of a review of ion exchange equilibria of some heavy metals in soils [27], has suggested that the presence of more than one reaction site is needed to explain the high affinity of heavy metals at low concentration. The general assumption is that specific sorption at the oxide/hydroxide surfaces and broken edges of clay minerals can be attributed to the high affinity for heavy metals in soils.

The widely used method for describing contaminant and nutrient distribution in a solid-solution phase is using adsorption isotherms. The two widely used isotherm equations are Langmuir and Freundlich isotherms. The Langmuir isotherm was originally designed to describe adsorption at the gas-liquid interface. The general form of the Langmuir equation is [28]:

$$N = \frac{K\ C\ Nx}{1 + K\ C} \tag{2.2}$$

Where

N is the quantity adsorbed per unit weight of adsorbent
C is the aqueous concentration of the adsorbing solute
N_x is the adsorption maximum which corresponds to monolayer coverage
K is an empirical constant

There are many assumptions inherent in this theory which may be questionable in a natural system. The basic assumptions of the Langmuir isotherm are: (1) sorption up to monolayer coverage, (2) no adsorbate-adsorbate interactions, (3) homogeneity of the surface sites, and (4) the heat of adsorption that is independent of surface coverage.

The Freundlich isotherm equation may be written [29]:

$$\frac{W}{M} = K\ C^n \tag{2.3}$$

Where

W is the weight adsorbed,
M is the mass of the sorbent
K and n are empirical constants

Freundlich and Langmuir isotherm equations gave very similar results for identical data [14,29]. Problems with these isotherm models arise when conditions such as pH, ionic strength, concentrations and types of computing species, or complexation are altered. These models do not account for most properties of the sorbent, and for different solution conditions, for which constants must be changed. The adjustable parameters in the Langmuir isotherm equation are K, which is related to the binding energy, and N_x , the adsorption maximum.

When experimental adsorption data are plotted against the concentration of the adsorbate at the equilibrium, a graph is obtained called the adsorption isotherm. Adsorption isotherms were classified into four main types according to the initial slope near the origin and the shapes of the upper parts of the curves as follows [30]:

The S-curve (normal) isotherm is characterised by an initial slope that increases with the concentration in the soil solution. This suggests that the relative affinity of the soil solid phase for the solute at low concentration is less than the affinity of the soil for the solvent.

The L-curve (Langmuir type) isotherm is characterised by an initial slope that does not increase with the concentration in the soil solution. This behaviour equates to the high relative affinity of the soil solid phase at low concentration and to a decrease of the free adsorbing surface.

The H-curve (high affinity) isotherm is characterised by a large initial slope which indicates the high affinity of the soil solid phase for the adsorbate.

The C-curve (constant partition) isotherm exhibits an initial slope that remains independent of the concentration in the solution under the possible experimental condition. This type of isotherm suggests a constant partitioning of a solute between the solvent and the adsorbing surface and may be due to a proportional increase of the adsorbing surface.

The most common curve in soils is the L-curve (Langmuir type) isotherm, which exhibits a concave shape with respect to the solution concentration axis.

It should be noted that both Langmuir and Freundlich isotherms were originally developed to describe gas adsorption on metal surfaces. The Langmuir equation was derived on the basis of the kinetics of monolayer adsorption. The Freundlich equation is used where the adsorption enthalpy exhibits a logarithmic change with increasing sorption due to surface heterogeneity. It was shown that both Langmuir and Freundlich equations can represent ion exchange if the concentration of the ions of heavy elements is very low when compared with the other ions present in solution [32,33]. It should be stressed here, however, that soil as a whole and most soil minerals cannot be considered as uniform surfaces. The parameters obtained by curve fitting on these models should, therefore, be viewed as pure empirical constants. To this effect it has been demonstrated that sorption isotherms cannot be used to distinguish adsorption from surface precipitation [8].

Many published studies describe the use of Langmuir and Freundlich isotherm equations to model heavy metals retention in soils. It has been suggested suggested that the Langmuir and Freundlich equations are not the best mechanistic tools for data interpretation or for describing sorption of heavy metals in the soil-water system [34]. Nederlof et. al. [35] discussed methods for the determination of adsorption affinity functions for a heterogeneous surface like soil from single component adsorption data. They showed that an approximation of a local isotherm can be used to solve the integral adsorption equation for the distribution function without making prior assumptions about the distribution.

The concept of multiple sites is relevant when dealing with soil organic substances. In this case one can assume continuous or discrete situations for the distribution of the affinity coefficients of multiple sites[36]. High concentration of heavy metals is another determining factor in the choice of an empirical adsorption isotherm. If high concentration is envisaged in an alkaline soil one may also have to consider the possible precipitation of heavy metals. In this situation BET [37] or the Farley-Dzombak-Morel (FDM) [38] equations may be used. FDM is a model for a continuum between surface reactions and precipitation. The model extends the surface complexation approach by considering the precipitation on the solid to be described by the solid solution whose composition varies continuously between that of the original solid and pure precipitate of the sorbing cation.

2.3.2.2 Adsorption kinetics

The soil-water system is a chemically reacting system where chemical transfer and transformation occur. The soil solid phase contains minerals, amorphous inorganic and organic components, while the soil liquid phase contains dissolved chemicals in free and complexed form as well as chemicals associated with colloidal particles. Thus, the contaminant availability and mobility in the system are dependent on contaminants in soil solution. Measuring chemical intensity in the soil-water system is critical for understanding contaminants in the system. Soil solution analysis yields information of both a static and a dynamic nature, depending on experimental design and modelling scale, for describing the nature, direction, extent and rate of chemical reactions. Chemical dynamics deals with kinetics, and movement within systems, and offers insight into the soil-water contaminant process. Accordingly kinetics entails motions and forces among microscopic particles involved in chemical reactions. Contaminant chemical dynamics attempts to understand the transition process from one state of the system to another and the time-dependence of the transition. The study of sorption from a kinetic perspective can lead to a better understanding of the mechanism of the process.

The complexities of kinetic theory, however, make accurate application of chemical dynamics difficult, for heterogenous reactions to soil-water contaminant reactions. The current understanding is based on the long time observation that the adsorption of contaminants on the soil solid phase is not necessarily instantaneous although there are reactions reported to be very fast, and practically instantaneous [39-40].

Kinetic processes can be viewed from the time domain consisting of fast and slow activities. The ion exchange process is diffusion-controlled and the reaction rate is limited by mass transfer phenomena that are mostly film-diffusion controlled with a half life of 10 seconds [40]; the reaction process is so rapid that the kinetics may be difficult to define. These same phenomena are also observed in work related to inner sphere complex formation on oxyhydroxides of iron and aluminum. On the other hand, processes considered as slow are: recrystallisation on surfaces, diffusion into micro pores, surface diffusion, and solid phase diffusion [41- 42]. The complexity of soil environments with its solid-liquid phase requires the combined use of empirical and semi-empirical methods for the kinetic study of related heavy metals and organics sorption.

The mobility of solutes in soil has been studied using empirical models. Because the system is not in equilibrium, the concept of a two-site model was developed. Two-site models consider that two phenomena take place, namely slow sorption and fast sorption processes. It was suggested that four categories of sites should be considered [43-44]: (1) reaction sites defined on a molecular basis; (2) different sites due to different accessibility; (3) different sites due to different sorbents, and (4) different sites due to different reaction mechanisms.

It is important to take into account the overall structure of the soil as well as the microstructure of the soil particles. The soil particles are composed of inorganic and organic constituents which exist discretely or clustered into aggregates. When the solute enters the soil, it diffuses through the pores into aggregates and particles to the available sorption sites. Therefore, the soil structure dominates to a large extent the accessibility of the sorption sites so that diffusion-controlled processes are often rate-limiting in soils.

The diffusion processes of solute in soils follow four steps [44]. The first is the rapid diffusion of a solute through the bulk solution. Then, passage of the solute from the bulk solution through a film that surrounds the soil particles or aggregates; this is known as film diffusion. The third step is the diffusion within the particle or aggregate, known as particle diffusion. The fourth step is the sorption process on the surface. The particle diffusion can be further classified into diffusion within the solution of the aggregate (pore diffusion) and diffusion on the surface of the solid material (surface diffusion). In surface diffusion sorption takes place before the diffusional process. Surface diffusion was suggested as a possible mechanism on the sorption study of zinc on to goethite [45]. All processes involve the break up and formation of bonds, although the last three processes can be assumed as chemical non-equilibrium, because ions may form chemical bonds on the surface and may be transported on a surface or within a solid [46].

Modelling heavy metal-laden solute mobility and reaction mechanism is very difficult, the main difficulty being the inability to collate the geometry of the reaction particles and reaction mechanism. The above two factors are related to microscopic phenomena which are not easy to measure. Barrow et. al., [47] modelled sorption of zinc on oxide minerals, such as goethite and haematite using second order kinetics. They also observed continuous sorption which started with fast initial sorption and continued for over two weeks. They suggested diffusion of zinc into the solid phase as an explanation for the process mechanism.

Many studies of the kinetics of heavy metal reactions in soils have found that the reaction is fast in the beginning but slows over the following days and weeks. For this reason single-site models have a limited use in explaining the sorption kinetics in soil. To overcome this, multi-site models have been suggested to explain kinetic behaviour of some heavy metals[47]. The fast kinetics takes place between minutes and a few hours and slow kinetics can extend to weeks depending on the nature of soil and soil materials.

2.3.3 Solute transport in soil

The contaminants in the soil-water system that have undergone transformation or have been retained by soil components are redistributed in the system. The extent and kinetics of mobility is controlled by both soil and contaminant properties, and the environmental media. Solutes are transported by molecular diffusion and mass flow, whatever their properties are. For contaminants with low solubility and for soil with high adsorption capacity, the rate - limiting parameters are dissolution, desorption and diffusion. Hydrodynamic dispersion determines solute spreading in soil and other porous media in accordance with water velocity variations. Contaminants adsorbed on soil solid components do not move freely with water through the soil. It was shown that the travel time for an adsorbed contaminant, t_A, is related to the travel time for a non-adsorbed or mobile contaminant, t_M, by [48]:

$$t_A = 1 + \rho_b \frac{K}{\Theta} t_M \equiv R\, t_M \tag{2.4}$$

Where ρ_b is the soil dry bulk density

K is the solid/liquid partition or distribution coefficient

Θ is the volumetric water content

R is the generalised sink term modified for specific reactions (mass /volume/time)

In actual field conditions, the movement of contaminants often does not follow the anticipated general pattern. Soils with high clay content may shrink and crack when subjected to wetting and drying cycles. Then, when a contaminant is applied and followed by a rainfall or irrigation, the pollutant will partially leach into the soil through cracks, only a portion of the solid phase coming into contact with the solute and the amount retained on the soil being relatively small.

The description of the transport of a contaminant in a porous system requires a mathematical expression establishing a relationship between the concentration of the contaminant adsorbed on the soil, and the concentration in the moving solution. The simplest is assumed to have a linear relationship with fast and reversible sorption kinetics, although mobility of solutes is a complex phenomenon.

The mobility of ions that interact with soil particles determines the fate of these ions in soil-water systems. Several authors have reviewed mobility models that incorporated adsorption, ion exchange, and chemical transformations. Many models have also been developed to describe the movement through a soil system [49-51]. Most models involve complicated equations, and powerful computers. The models contain unknown system parameters for reactive and non-reactive solutes. The parameters are mostly obtained by comparing theoretical results against laboratory or field data. Estimating the parameters accurately and predicting the behaviour of the system using estimated parameters under conditions different from that used for parameter estimation is problematic.

A knowledge of the distribution coefficient K_d would allow the prediction of the rate of movement of the contaminant under dynamic conditions. The hypothesis underlying this treatment of data, is that the sorption process can be described by a linear K_d model. Alternatively, solute mobility can be described by a breakthrough curve using a retardation factor. The retardation factor is an index calculated from the ratio of velocity of water to contaminant in a soil column. Modelling of breakthrough curves with the appropriate transport equation would yield effective porosity, dispersivity and mass recovered. The breakthrough curves for a step input of the solute are often sigmoidal in shape. Two regions of mobile-immobile approach models are commonly used. They are based on either a mass transfer expression, usually first order kinetics, or a discrete geometric description of the soil aggregates. The mass transfer approach requires the measurement of mass transfer coefficient [52]. Though valuable advances have been reported in this line of research, much more information needs to be accumulated in order to benefit from the use of models for the transport phenomena.

2.4 Iron and Manganese oxides in soils

Iron and manganese belong to the subgroups VIII and VIIA of the periodic table and exist in a number of oxidation states. In soils the compounds of Fe are represented in the most typical oxidation state Fe (II) and Fe (III). For Mn the characteristic states are (II) and (IV) and (III) is less stable. Manganese compounds of a higher degree of oxidation such as (V), (VI) and (VII) are not widely available in soils.

The importance of soil iron and manganese oxides in pollution control is attributed to their common occurrence as coatings, concretions and as colloids in soil-water systems, and their influence on the bioavailablity of nutrients and toxicants. The ubiquitous occurrence and chemical reactivity of these oxides has engendered a number of research projects on their ability to control pollutants in soil and water.

There are about 13 oxides, oxyhydroxides and hydroxides of iron, and about 36 known oxides of manganese. Tables 2.1 and 2.2 list the major iron and manganese oxides. Many iron and manganese oxides occur in soils as oxides and hydroxides under normal aerated conditions[53-56]. The mode of their occurrence is shown in Figures 2.1 and 2.2. The absence of iron oxides, or their occurrence in trace amounts, is usually due to strong reduction and removal from the profile or the absence of Fe-bearing primary minerals in soil parent materials. Iron oxides in soils can be differentiated by their susceptibility to chemical extraction. Acid ammonium oxalate extracts amorphous Fe oxides as well as some organic-chelated Fe, whereas sodium dithionite extracts both amorphous and crystalline oxides to varying degrees[57]. This division, based on chemical extractability, is only relative in as much as the transition from the amorphous Fe oxides through cryptocrystalline forms to the crystalline Fe oxides is by no means clearly defined. The amorphous Fe oxides are more chemically reactive than are the crystalline Fe oxides[58].

Average soils contain greater amounts of Fe oxides than Mn oxides but the Mn oxides exhibit greater chemical reactivity and more complex mineralogical composition than do the Fe oxides. The chemical reactivity of Mn oxides is related to some specific features of Mn: (1) Mn can exist in several oxidation states, (2) Mn forms non stoichiometric oxides with variable valence states, (3) Mn in its higher valent oxides exists in several crystalline or pseudo crystalline forms, and (4) Mn oxides form coprecipitates and solid solutions with Fe oxides [59]. A study conducted using X-ray diffraction on Mn nodules, concretions, and stains from soil samples has identified lithiophorite ($(Al,Li)MnO_2(OH)_2$), birnessite, ($Na_4Mn_{14}O_{27}.9H_2O$), hollandite ($(Ba,K)_{1-2}Mn_8O_{16}.xH_2O$), todorolite ($(Na,Ca,K,Ba,Mn^{2+})_2)$ $Mn_4O_{12}.3H_2O$), and pyrolusite (β -MnO_2) [60-63].

Fe and Mn oxides exhibit a marked tendency to form coprecipitates or mixed oxides. Ponnamperuma et. al. [63] attributed this association to (1) similarities in some chemical properties of the higher oxides of Fe and Mn, including reversible oxidation-reduction, and the presence of pH-dependent electric charges; (2) the closeness of the ionic radii of Mn^{2+} (0.80Å) and Mn^{3+} (0.66Å) to those of Fe^{2+} (0.76Å) and Fe^{3+} (0.66Å), respectively; and crystal lattice-induced valence changes.

The occurrence of hydrous oxides of Fe and Mn as coatings on other soil matrix surfaces, and as colloids and aggregates enables them to exert a major influence on chemical species. In addition to soils, the adsorption capacity of these oxides to many heavy metals is observed in sediments and ferromanganese nodules in ocean-floors.

Some analytical techniques for the determination of trace metals utilize the adsorption property of manganese oxides. In fact their capacity as cation scavengers has been documented by Burke [64] who described the use of manganese oxides for the chemical analysis of the eleven metallic elements Fe, Zn, Sb, Sn, Mo, As, Pa, Pb, Ce, Ga, and Bi.

The role of hydrous oxide of manganese and iron in pollution control and the availability of micronutrients can be best understood in terms of the factors which influence the sorption and desorption of metals by these oxides. The adsorption on to soil oxides is mainly a solid-liquid interfacial phenomenon resulting from the physicochemical behaviour of the oxides. The adsorption on to the oxides regulates the mobility and availability of chemical species in the environment. Examples are the retention of cobalt from soil and the transport of heavy metals and pesticides from soils into the aquatic systems.

Oxyhydroxides		Oxides	
Formula	**Mineral**	**Formula**	**Mineral**
α- FeOOH	Goethite	Fe_3O_4	Magnetite
β -FeOOH	Akaganeite	α-Fe_2O_3	Hematite
γ- FeOOH	Lepidocrocite	γ-Fe_2O_3	Maghemite
δ'-FeOOH	Feroxyhyte	β-Fe_2O_3	
$Fe_5HO_8.4H_2O$	Ferrihydrite	ϵ-Fe_2O_3	
Fe $(OH)_3$	Bernalite	Feo	Wüstite
Fe $(OH)_2$			

Table 2.1 The major iron oxides and hydroxides [54]

Oxides		hydroxides	
Formula	**Mineral**	**Formula**	**Mineral**
β -MnO_2	Pyrolusite	$(Na,Ca,K,Ba,Mn^{2+})_2Mn_4O_{12}.3H_2O$	Todrokite
MnO_2	Ramsdellite	$(Na_{0.7}Ca_{0.3})Mn_7O_{14}.2.3H_2O$	Birnessite
$(Mn^{2+},Mn^{4+})(O,OH)_2$	Nsutite	(Ca,Mn) $Mn_4O_9.3H_2O$	δ-MnO_2(disordered birnessite)
$(Ba,K)_{1-2}Mn_8O_{16}.xH_2O$	Hollandite	$Na_4Mn_{14}O_{27}.9H_2O$	Synthetic birnessite ("7Å Manganite)
K_{1-2} $Mn_8O_{16}.xH_2O$	Cryptomelane	(Al,Li) $MnO_2(OH)_2$	Lithiophorite
$Pb_2Mn_8O_{16}$	Coronadite	$Na_4Mn_{14}O_{27}.9H_2O$	Buserite
$(Ba, K, Mn, Ca)_2$ $Mn_5O_{10}.xH_2O$	Romanéchite (psilomelane)	$ZnMn_3O_7.3H_2O$	Chalcophanite
MnOOH	Manganite		

Table 2.2 The major manganese oxides and hydroxides[55]

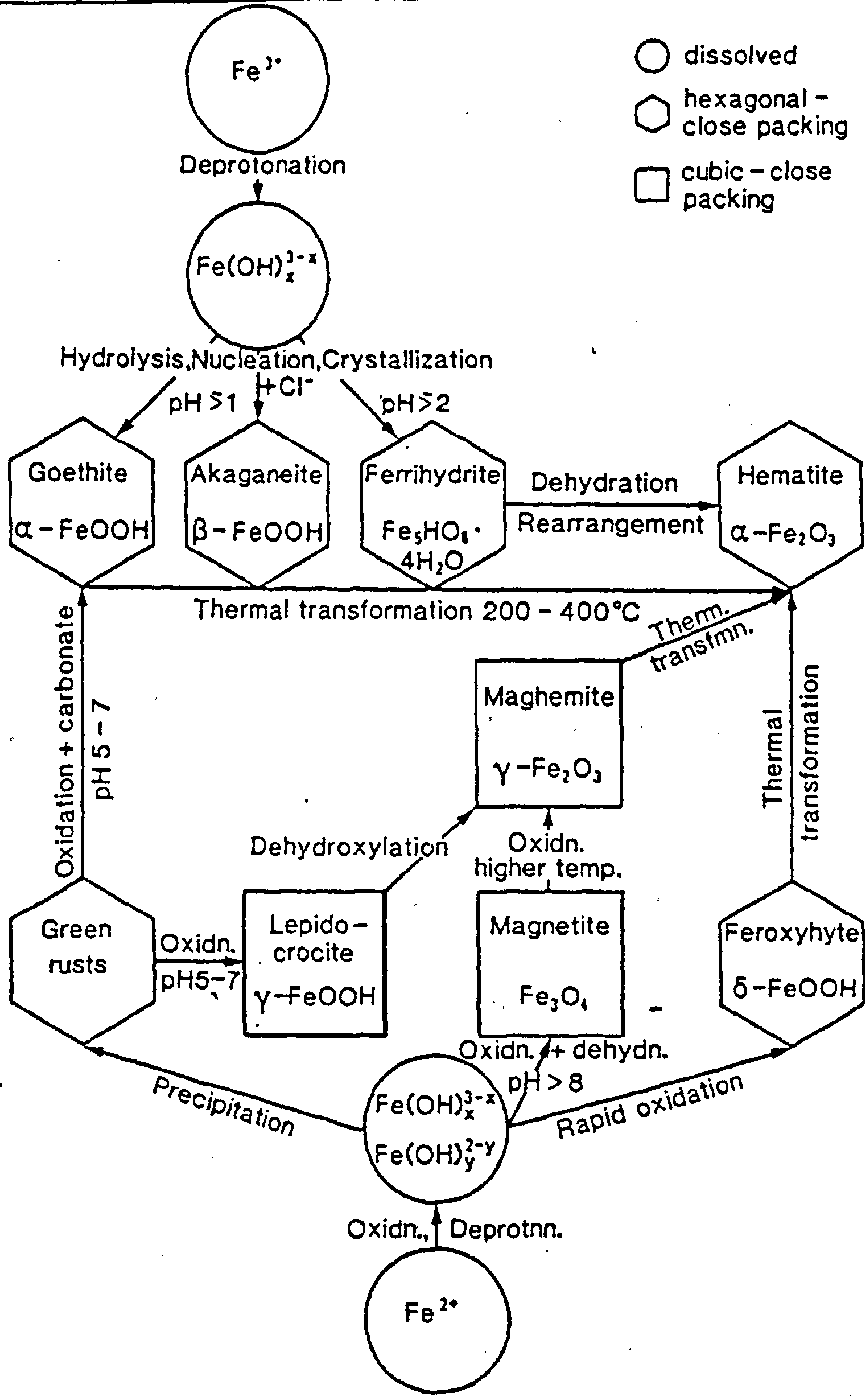


Figure 2.1 Schematic diagram of formation pathways of iron oxides [53]

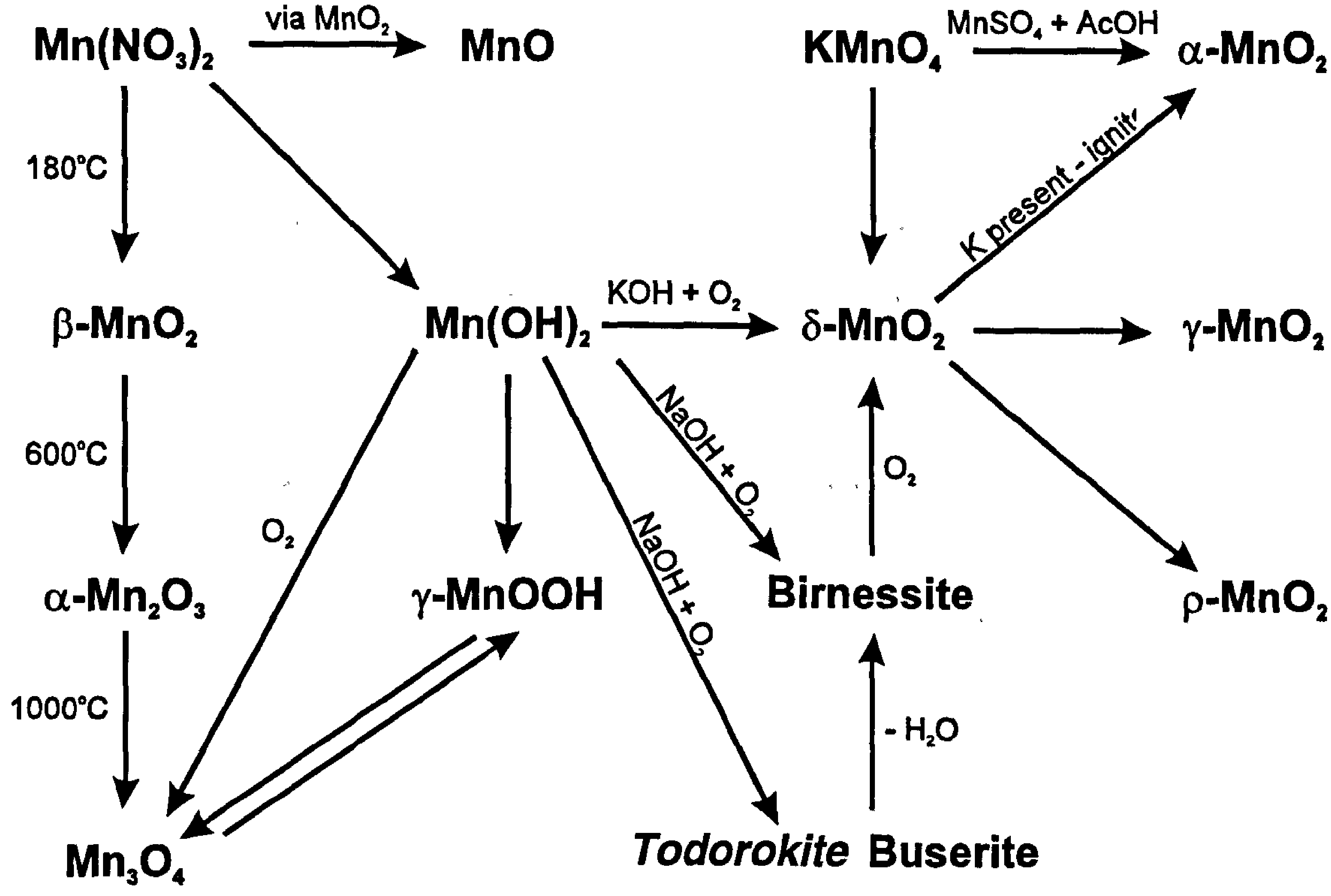
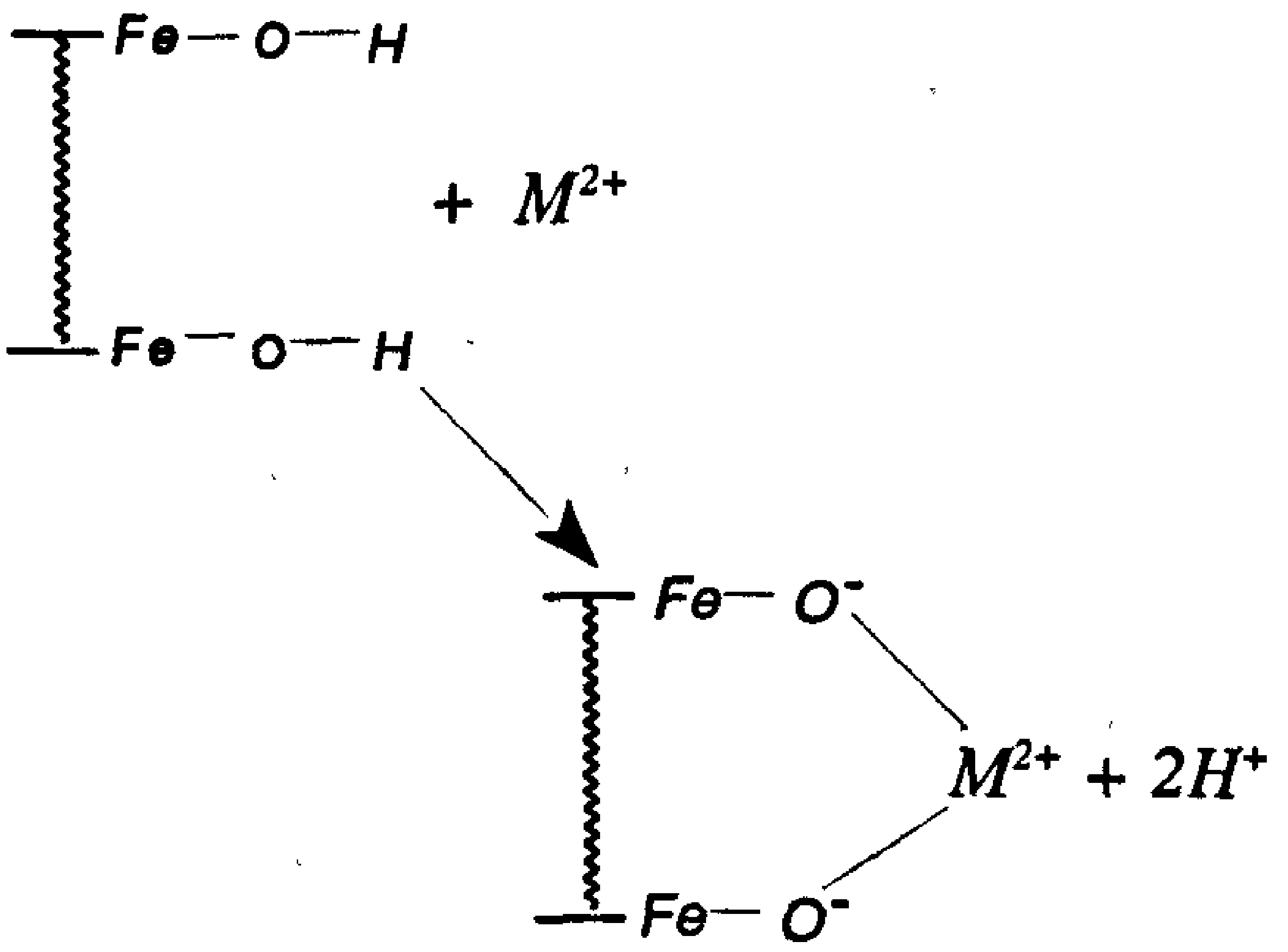


Figure 2.2 Relationship between the various synthetic oxides [63]

The adsorption of heavy metals by these oxides may take place by one of or any combination of the following mechanisms: (1) adsorption, (2) ion exchange, (3) surface complex formation, (4) coprecipitation, and (5) penetration into the crystal lattice. Coprecipitation may occur under certain conditions where Fe and Mn oxides are precipitated out of solution along with other metals, for example, the case of a subsurface solution entering into an oxidative environment.

The surfaces of the oxides are generally not homogenous but are composed of heterogenous sites. Some Fe and Mn oxides have surface areas as high as a few hundred square metres per gram and have a larger cation exchange capacity than some clay minerals. They also have open structures with both external and internal surfaces and the readily available sites due to crystal imperfections tend to make these oxides effective scavengers for pollutants [65-67]. The adsorption of metal ions by Mn and Fe oxides, determined in the laboratory under constant pH, can often be described by the Langmuir or Freundlich equations. A part of the adsorption is attributed to ion exchange through electrostatic attraction or surface complex formation. A relatively large proportion of the sorption, however, has been explained on the basis of the existence of specific adsorption that entails inner sphere surface complexes[68].

Adsorption of cations on hydrous oxides can be explained as specific adsorption that involves the deprotonated surface with hydroxyl group to form inner sphere complexes as shown in Figure 2.3 (a similar scheme can be used to explain Mn hydrous oxides).



(2.3)

Where M^{2+} is divalent cation

Figure 2.3 Sorption of metals on iron and manganese oxides

Implicit in the above model is pH dependence of the adsorption of metal ions by hydrous Mn and Fe oxides and the release of H^+ ions as a result of the adsorption [68]. Anderson et al. [69] found that Ag adsorption maxima appeared to vary with the amounts of Na and K that existed within the structure of poorly crystallized Mn oxides. The uptake of Ag by these oxides is considered to be by surface exchange for Mn, K, and Na as well as exchange for structural Mn, K, and Na. Mackenzie, [70] studied the adsorption of Co, Cu and Ni from solution by several synthetic Mn oxides; he found that the initial rapid uptake of all three ions by replacement of readily exchangeable Mn^{2+}, K^+, and H^+ was followed by a period of slow uptake. The slow phase of the reaction was attributed to the exchange with ions in the crystal lattice, which he called "diffusion exchange" or "penetration of the crystal lattice."

The colloidal properties of Fe and Mn oxides in aqueous media are extremely complex. The hydrous oxides of Mn and Fe can be considered as hydrated solid electrolytes with a variable space lattice in which the proportion of different ions, cations as well as anions, are variable within the limit of electrical neutrality of the solid [65]. Under natural conditions, organic matter is another complicating factor. The organic matter produces a periodic reducing environment, which maintains Mn and Fe oxides in a hydrous microcrystalline condition [56]. The presence of organic matter may solubilize these oxides under prolonged reducing conditions, and may chelate metal ions, thereby changing their mobility and dispersion. The study of the adsorption of metal ions by soil oxides requires a knowledge of the factors affecting the formation and reactivity of Fe and Mn oxides.

It is difficult to generalize about the relative importance of Mn oxides versus Fe oxides as effective pollutant adsorbents. A study of New Zealand soils showed that cobalt was concentrated in the Mn-rich phase rather than in the Fe-rich phase of Fe-Mn concretions [69]. The determining factors for the relative importance of Mn oxides and Fe oxides in adsorption are (1) redox conditions, (2) the reactivity and degree of crystallinity of the oxides formed at the time when a given metal ion is introduced, (3) the relative abundance of the oxides, (4) the post- retention chemical changes of the oxides, and (5) the presence of organic matter as a chelating and fixing agent in competition with the oxides. Jenne [56] reported that the slope of plots of the extraction rate versus time (with dithionite-citrate) for Co from the <60 mesh extraction of a stream sediment was closer to that of Mn than that of Fe, indicating that more of the Co had been adsorbed by Mn oxides than by Fe oxides. Thus it was indicated that Mn oxides, as a group, are better scavengers for heavy metals than Fe oxides. The greater adsorbing capacity of Mn oxides for heavy metals can be explained, at least in part, on the basis of the extremely complex mineralogical structure of Mn oxides and the wide range of zero point of charge (z.p.c.), parameters related to their surface and interface properties [66].

2.5 Cadmium and cobalt in Soil

Cadmium and cobalt belong to groups IIb and VIII of the periodic table with atomic numbers of 48 and 27 respectively. The sources of cadmium and cobalt in soils are from natural and anthropogenic accumulations. Cadmium is nearly always present at lower concentrations than cobalt. Anthropogenic sources of cadmium in soil are primarily airborne deposition, sewage sludge, composted refuse, and phosphate fertilizer. The highest amounts can be found in sewage sludge where the cadmium content ranges from 1 to 3410μg/g [3]. In contrast to cobalt, cadmium is not an essential element for plants, animals or humans. Cadmium may lead to toxic effects at critical soil total concentrations of 3 μg/g. On the other hand cobalt is a component of vitamin B_{12} , which is essential for sheep, cattle humans and all mammals. Although the amount of cobalt required is very small, deficiency syndromes in animals pastured in cobalt-deficient soil have been reported in certain regions. In naturally cobalt-rich regions, the cobalt contents of accumulating plants such as *Astragalus sp.*may range from 2.3 to 100μg/g dry matter [71].

The capacity of soil oxides and soil in general to adsorb cadmium and cobalt depends on the interfacial reactions that formulate the sorption mechanism. The affinity of most divalent metals to soils and their components can be compared on the basis of theoretical considerations from different physical and chemical parameters. Table 2.3 lists the major properties and order of affinity [72]. The ionic potential (charge/radius) describes the likelihood of a metal ion being adsorbed by electrostatic forces. The electronegativity and the 'softness' parameter are a measure of covalent contributions in a chemical bond. Electronegativity refers to the potential of an atom to attract an atom to itself. Softness refers to a readily deformable electron sheath characterised by "soft sphere" cations. The Irving-Williams series is a general complex stability sequence which is derived from the observation of complex stability of transition elements with different organic ligands.

Table 2.3 Predicted affinity sequences of divalent metals for oxides based on several metal properties [17]

Property	Predicted order of affinity
Ionic potential (Z^2/r)	Ni > Mg > Cu > Co > Zn > Cd > Sr> Pb
First hydrolysis constant	Cu > Pb ~ Nl > Co ≥ Zn > Mg > Cd > Sr
Electronegativity (Pauling)	Cu > Ni > Co > Pb > Cd > Zn > Mg > Sr
Softness	Pb > Cd > Co > Cu > Ni > Zn > Sr > Mg
Irving Williams series	Cu > Ni > Zn > Co > Mg > Sr

Predicted affinity order when compared with reported works indicated some discrepancies [54,72-73]. In particular the ionic potential does not agree with the observed sequences for soil oxides. The electronegativity and the softness parameter are slightly better in predicting the affinity sequence, but covalent bonding alone cannot explain the observed sequence. Therefore, a combination of both electrostatic and electron-sharing properties are significant for the sorption sequence.

2.5.1 Cadmium

Cadmium is a transition metal of Group IIB which also includes zinc and mercury. Cadmium is a soft silvery metal with an atomic weight of 112.41; it tarnishes in air and is soluble in acids but not in alkalis. It is mainly found in zinc, lead-zinc and lead-copper-zinc ores, and its concentration is usually related to the zinc content. It is also found in varying amounts in rocks, soil, water, air, plant and animal tissues. Its chemical behaviour is similar to that of zinc because of the similar electron structures and ionization potentials of the two elements. In nature cadmium is nearly always present in the Cd^{2+} oxidation state and there are eight naturally occurring isotopes of which ^{112}Cd and ^{114}Cd are the most common. Radioactive isotopes with mass numbers ^{104}, ^{105}, ^{107}, ^{109}, ^{111}, ^{113}, ^{115}, ^{117}, ^{118} and ^{119} have been made artificially, of which ^{113} Cd has the longest half-life of 5.1 years [74].

Cadmium has an ionic radius of 1.03Å, similar to that of Ca^{2+} (1.06Å) and Na^+ (0.98 Å).

Cadmium, like zinc, is found in ferro-magnesian minerals. The average concentration of cadmium in the earth's crust has been reported as 0.15 μg/g and 0.11μg/g in the upper lithosphere. Igneous and metamorphic rocks contain from 0.1 to 1μg/g Cd; in contrast sedimentary rocks may have up to 11μg/g Cd. Of the sedimentary rocks, bituminous and carbonaceous shales may contain abnormally large concentrations of cadmium, which may in turn be reflected in the weathering cycle and provide significant pathways to uptake by plants and animals [3,74].

The total cadmium in non-contaminated soils ranges from < 0.1 to 10μg/g. The average contents of cadmium reported in surface soils from many parts of the world, lie between 0.07 and 1.1μg/g all values more than 0.5μg/g are thought to reflect anthropogenic inputs. Cadmium is fairly mobile in the soil profile and is almost uniformly distributed; its contamination induces an enrichment in cadmium content of the upper layers of the soil [71, 75-76].

Soils tend to reflect the chemical composition of the parent materials from which they were derived. Where residual soils are formed *in situ* from the underlying bedrock, the trace metal content of the soil may be directly related to bedrock geochemistry which may be modified to varying degrees by pedogeneic processes leading to the mobilization and redistribution of elements both within the soil profile and between neighbouring soils. Although during leaching cadmium goes readily into solution, the main factor determining the cadmium content of soil is the chemical composition of the parent rocks.

Cadmium enters the soil-water environment mainly as soluble compounds (the hydrated Cd^{2+} ion) during weathering of cadmium-containing rocks or minerals. Then, the important factors controlling the mobility of cadmium in the environment are pH and oxidation potential. Cadmium may also form several complex ions ($CdCl^+$, $CdOH^+$, $CdHC0_3^+$, $CdCl_3^-$ $CdCl_4^{2-}$, $Cd(OH)_3^-$ and $Cd(OH)_4^{2-}$) and a variety of chelated and organometallic complexes resulting from the decay of plants and animal matter[74].

Contaminant fate mathematical modelling in soil-water systems is an area of current active research. These models are called equilibrium or speciation models. A chemical equilibrium-based computer model known as GEOCHEM employed on two Californian soils predicted the principal aqueous species of cadmium as Cd^{2+}, $CdSO_4^0$ and $CdCl^-$ [4]. It may be possible that under strongly oxidizing conditions, cadmium may form oxide and carbonate minerals, and under reducing conditions can also utilize H_2S produced by bacteria during the decay of organic residues and precipitate as a sulphide. Cadmium precipitated in soils and sediments may be mobilized again by bacteria, probably in both inorganic and organic forms, and released to soil, air and water [74]. The properties of the soil solid phase and the composition of the soil solution together with initial Cd concentration as well as the environmental factors define the species of Cd.

Unpolluted waters contain cadmium below 1μg/l but concentrations in rivers and estuaries range from 10 to 1000μg/l. Waters in the vicinity of cadmium-bearing mineral deposits may even contain higher values [77]. The input of cadmium into waters originates directly from wastewater and precipitation from the atmosphere, and indirectly from weathering of minerals, leaching from sewage sludge and waste dumps.

Cadmium is generally considered as a non-essential for both plants and animals, and is said to be as one of the most dangerous environmental pollutants. Cadmium toxicity primarily affects kidneys, but other organs can also be affected. The "itai-itai" disease observed in Japan was derived from soil pollution and was mainly caused by intake of Cd in the rice grain from Cd-polluted fields. Cadmium is mostly absorbed by plant roots, but a part of Cd found in plants can also be attributed to airborne origin.

Factors influencing the availability and uptake of cadmium into biological systems are the chemical species of the cadmium in soil-water and the complex interactions within the system that depends on the environmental factors. A generalised cadmium cycle in the environment depicting major components is shown in Figure 2.4.

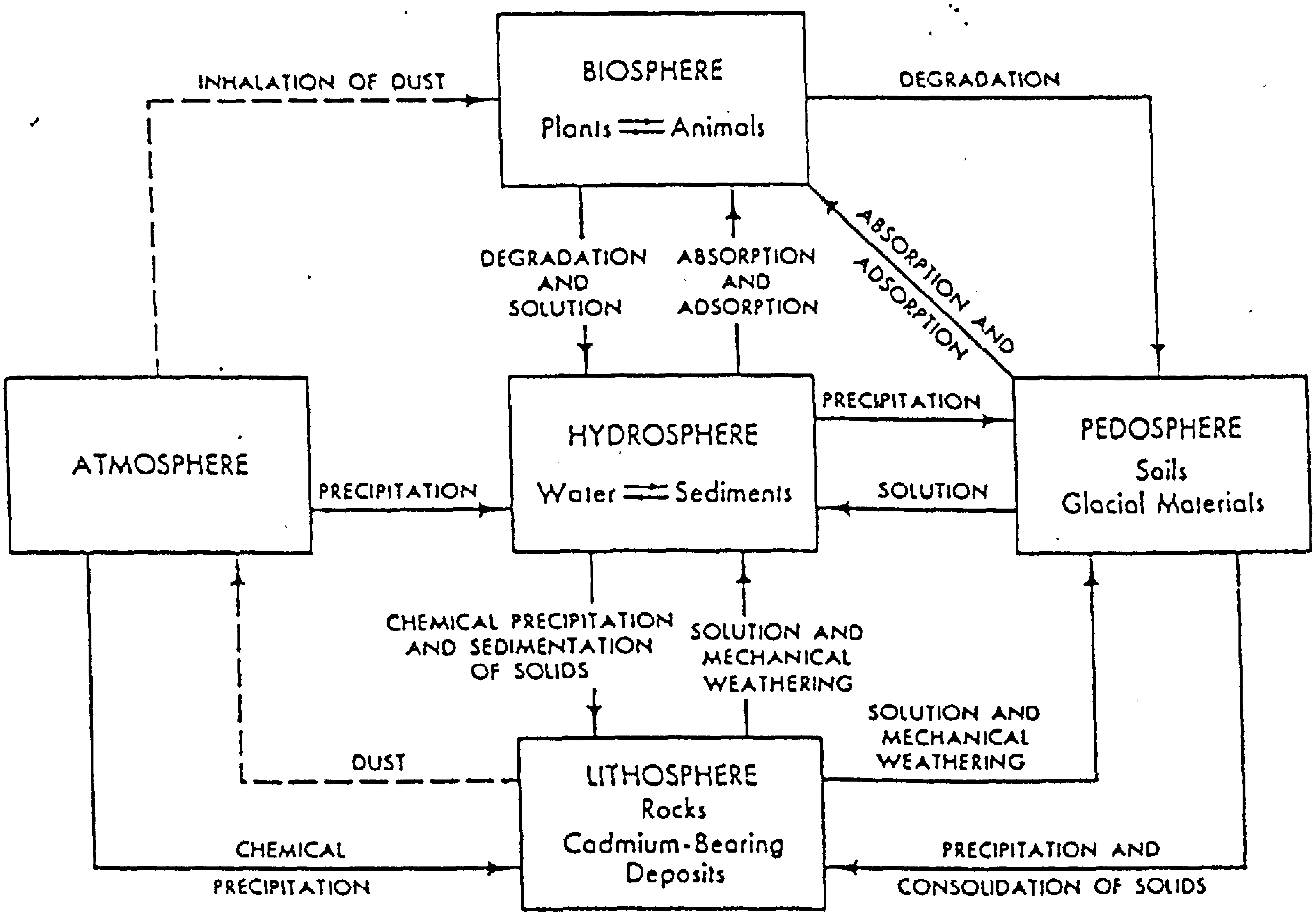


Figure 2.4 Major components of cadmium cycle in the environment [77]

2.5.2 Cobalt

Cobalt is a transition metal of group VIII, located between iron and nickel. Cobalt closely resembles these two metals in both its pure and combined states. Cobalt is a lustrous, silvery- blue hard metal with atomic mass of 58.93; stable in air and slowly attacked by acids. The main oxidation states of cobalt are Co^{2+} and Co^{3+}. However, compounds of Co^{0} and Co^{+} are also known. Its atomic nucleus normally contains one stable isotope, ^{59}Co. However, radioactive isotopes such as ^{60}Co, ^{57}Co, ^{58}Co have been detected in atomic fallout and in marine organisms exposed to fallout. Cobalt is a rare element, ranking 32nd in abundance on the earth's crust, mostly in sulfidic copper ores[79].

Cobalt is widely diffused and traces of cobalt are found in many rocks, minerals and soils. The average cobalt content of the earth's crust is 18μg/g. Cobalt usually occurs together with nickel and iron. The average content of igneous rocks is 25µg/g, of shales 19µg/g, and of sandstone and limestone 0.3 and 0.1µg/g respectively; the average Co content of soil is 8 µg/g [78-79]. Fresh waters which are uncontaminated range in cobalt concentrations from 0.1 to 10 µg/l, and ocean water is reported to have concentrations of 0.002µg/l. However, in waters of polluted rivers high cobalt levels up to , 4500µg/l, have been reported [80-81]. The solubility of cobalt is pH - dependant. In acid soils, cobalt is more mobile than in alkaline soils. Annually, approximately 21000 tons of cobalt are transported by rivers to the oceans and about the same amount is deposited in deep-sea sediments, whose cobalt content is in the order of 74 µg/g [81].

Unlike cadmium, cobalt is essential for all higher animals including humans, but for higher plants it has not been definitely established although cobalt is required by Rhizobia for nitrogen fixation and thus indirectly by leguminous plants. Some species of nitrogen-fixing blue-green algae also need cobalt for their normal growth.

Cobalt is a component of vitamin B_{12}, which is associated with the ruminant stomach. Cobalt constitutes 4.35% by weight of vitamin B_{12} . Ruminants have a special requirement for dietary inorganic cobalt required for bacterial vitamin B_{12} synthesis in the rumen. It is now known that B_{12} is a coenzyme in a number of biochemical processes. The most important is the formation of erythrocytes. Accordingly, an adequate amount must be present in the feed of ruminants. In non-ruminants, it is assumed that the vitamin B_{12} complex must be present in the diet, for instance the human body contains 2-5 mg concentrated in the liver. Although the amounts of cobalt required are very small, deficiency syndromes occur in different countries where the soil is cobalt deficient. The known symptoms in the ruminants are: loss of appetite, progressive emaciation, retarded sexual development and anaemia. The disease is known by various names: *pin* in Scotland, *salt sickness* in Florida, *nakuruitis* in Kenya, *wasting disease /coast disease* in Australia and *bush sickness* in New Zealand. Sheep are usually affected more than cattle, and young stock more than old[76,82]. Pasture cobalt levels below 0.1µg/g are likely to lead to deficiency in lambs and calves, while prolonged confinement to pastures containing below 0.07µg/g of cobalt can be expected to produce widespread deficiency. A soil is regarded as cobalt deficient if the cobalt level is below 5μg/g dry matter; only about 6% of the total cobalt present is bioavailable[78]. In general, grasses contain more cobalt than grain crops; both of these are exceeded by legumes.

Cobalt has a low order of toxicity to all species studied and it is not a practical problem under natural conditions. The farm animals in some regions of cobalt deficiency are protected by adding 1 to 2 kg of cobalt sulfate per hectare of land every 3 to 5 years. In others cobalt is supplemented by adding cobalt oxide, carbonate, chloride, acetate, or sulphate to the feed, to fertilizers, salt-licks, or in the form of pellets which are placed in the rumen. It was reported that daily doses of 3mg Co/kg body weight can be tolerated by sheep for many weeks without toxic effect. There are differences of opinion as to whether, in curing cobalt deficiency, it is better to apply cobalt to the soil or whether it should be given directly to livestock[82]

Agricultural deficiency of cobalt is relatively widespread; it is most likely to become a problem in the near future, as the natural cobalt content is low. Depletion of cobalt occurs through agricultural practices and natural processes like sorption, weathering, erosion, and leaching. As resources are limited, cobalt deficiency could eventually develop on a much greater scale. In fact one of the objectives of this research is to look at factors that influence sorption which affect the bioavailablity of cobalt in the soil-water system.

Cobalt also poses a risk to humans, mostly from mining activities and widespread industrial use that can produce cobalt- containing dust. The risk is primarily to metal workers exposed to the dust who suffer damage to lungs and heart.

2.6 References

1 Finney, E.E. (1987) Incidental and accidental soil pollution. In: Barth, H. and Hermite, P.H. (eds) Scientific basis for soil protection in the European Community. 259-280, Elsevier, London.

2 Tadesse, B., Donaldson J.D., and Grimes S.M. (1994) Contaminated and polluted land : General review of decontamination management and control. J. Chem. Tech. Biotechno. 60, 227-240.

3 Alloway, B.J., (1990) Heavy metals in soils. John Wiley, New York

4 Sposito, G., (1983). The chemical forms of trace metals in soils: In:Thornton, I. (ed.) Applied environmental geochemistry, 123-170, Academic Press, London.

5 Gamble, D.S., and M. Schnitzer, (1974). The chemistry of fulvic acid and its reaction with metal ions In: Singer, P.C. (ed) Trace metals and metal organic interactions in natural waters,265-290, Ann Arbor Science, Michigan.

6 Schnitzer, M. (1971) Metal organic matter interaction in soils and waters. In: Faust, S. and Hunter, J.V (eds) Organic compounds in aquatic environment. 297-310, Marcel Dekker, New York.

7 Marshall, C.E. (1964) The physical chemistry and mineralogy of soils, volume I, John Wiley, New York.

8 Sposito,G.,(1986) Distinguishing adsorption from surface precipitation. In: Davis,J.A. and Hayes, K.F. (eds), Geochemical Processes at Mineral Surfaces, ACS Symposium Series 323, 217-228, American Chemical Society, Washington.

9 Schweich D. and Sardin M., (1981) Adsorption. partition, ion-exchange, and chemical reaction in batch reactors or in columns: a review, J. of Hydrol. 50, 1-33.

10 Morel F.M.M. and Geschwend P.M., (1987) The role of colloids in the partitioning of solutes in natural waters. In: Stumm, W. (ed.), Aquatic Surface Chemistry, 405-422, John Wiley, New York.

11 Benes P. and Majer V.(1980) Trace chemistry of aqueous solutions, Elsevier , New York.

12 Georgievics, G.V. (1913) Adsorption in solutions IV significance of x in the disrtribution formula; V solution, adsorption, chemical combination adhesion.

Montash, 34,733-757.

13 Sposito, G. (1984) The surface chemistry of soils. Oxford University Press. New York.

14 Hayward,D.C. and Trapnell, B.M. W. , (1964) Chemisorption, Butterworth, London.

15 Macarthy, J.F. and Zachara J.M. (1989) Subsurface transport of contaminents. Environ. Sci. Tech. 23, 496-502.

16 El-Sayed, M.H., Burau, R.G. and Babcock, K.L.(1970). Thermodynamics of copper(II)-calcium exchange on bentonite clay. Soil Sci. Soc. Am. Proc. 34, 397-400

17 McBride, M.B. (1989). Reactions controiling heavy metal solubility in soil. Advances in Soil Science, 10, 1-56.

18 Stumm, W., and Morgan, J.J., (1981) Aquatic chemistry. John Wiley, New York

19 Brümmer,G., Tiller, K. G., Herms, U. and Clayton, P.M. (1983). Adsorption - desorption and/or precipitation-dissolution process of zinc in soils. Geoderma 31,337-359

20 Davis, J.A., Fuller, C.C. and Cook, D A., (1987) A model for trace metal sorption processes at the calcite surface: Adsorption of Cd and subsequent solid solution formation. Geochim. Cosmoehim. Acta 51,1477-1490.

21 Hendrickson, L.E., and Corey, R.B. (1981). Effect of equilibrium metal concentrations on apparent selectivity coefficients of soil complexes. Soil Sci. 131,163-171.

22 Oades, J.M. (1989). An introduction to organic matter in mineral soils. In: Dixon, J.B. and Weed, S. B. (eds.). Minerals in soil environments, 81-159 Soil Sci. Soc. Am., Madison.

23 Domsch, K.H. (1989). Microbiological aspects of heavy metal and toxic chemical behaviour in porous media, In:Bar-Yosef, B., Barrow,N.T., and Goldschmidt T. (eds.) Inorganic contaminants in the vadose zone. Ecological Studies 74, 81-159 Springer-Verlag, Berlin.

24 Bonzanountas, M. ,(1987) Chemical fate modelling in soil systems : a state-of-the art review. In:Barth, H., and Hermite, P.H. (eds) Scientific basis for soil protection in the European Community, 487-566, Elsevier, London.

25 Bril, J., de Rooij N.M., and Smits J.G.C. (1986). Modeling heavy metals in the top soil of a harbour sludge depot. In: Assink, J.W. and van den Brink,W.J. (eds.). Contaminated Soil '86, 33-47, Martinus Nirhoff, Dordrecht.

26 Dzombak, D.A., and Morel, F.M.M., (1990)Surface complexationmodeling. Hydrous ferric oxide, John Wiley, New York

27 Sposito, G. (1981) The thermodynamics of soil solution. Oxford University Press. New York.

28 Harter, R.D., & Baker, D.E., (1977) Applications and misapplications of the Langmuir equation to soil adsorption phenomena, Soil Sci. Soc. Am. J. 41, 1077-1080

29 Soldatini, G.F., Riffaldi, R., & Levi-minzi, R. (1976) Pb adsorption by soils 1. Adsorption as measured by the Langmuir and Freundlich isotherms. Water, Air Soil Poll., 6, 111-118.

30 Giles, C.H., MacEwan T.H., Nakhawa S.N., and Smith D.. (1960). Studies in adsorption. Part XI: A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J. Chem. Soc., 3973- 3993.

31 Sposito, G. (1985). Chemical models of inorganic pollutants in soils, CRC Critic. Rev. Environ. Control 16, 1-24.

32 Elprince, A.M., and Sposito, G. (1981). Thermodynamic derivation of equations of the Langmuir type for ion equilibria in soils, Soil Sci. Soc. Am. J. 45, 277-282.

33 Sposito, G. (1989), The chemistry of soils. Oxford University Press. New York,

34 Kinniburgh, D.G. (1986). Multipurpose sorption isotherms. Environ. Sci. Technol. 20, 895-904.

35 Nederlof, M.M., van Riemsdijk, W.H. and Koopal, L.K. (1990) Determination of adsorption affinity distribution: a general frame work for methods related to local isotherm approximation. J. Colloid Interf. Sci. 135, 410-426.

36 Sposito, G., (1986), Sorption of trace metals by humic materials in soils and natural waters CRC Critical Rev. Environ. Control 16, 193-229.

37 Brunauer, J., P.H. Emmett, and E. Teller.,(1938) Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60, 309-315.

38 Farlly, K.J., Dzombak, D.A. and Morel,F.M.M.,(1985) A surface precipitation model for sorption of cations on metal oxides. J. Colloid. Interf. Sci. 106:229-242.

39 Sparks, D.L. (1989) Kinetics of soil processes, Academic Press, San Diego.

40 Sparks, D.L., and Zhang, P.C. (1991) Relaxation methods for studying kinetics of soil chemical phenomena. In Sparks, D.L.. and Suarez, D.L. (eds.) Rates of soil chemical proeesses.Spe. Publ. No.27, 61-94. Soil Sci. Soc. of America, Madison.

41 Aharoni, C., and Sparks, D.L. (1991) Kinetics of soil chemical reactions - A theoretical treatment. In Sparks, D.L. and Suarez, D.L. (eds.) Rates of soil chemical processes. Spe. Publ. No.,27, 1-18, Soil Sci. Soc. of America, Madison.

42 Skopp, J., (1986) Analysis of time-dependent chemical processes in soils. J. Environ. Qual. 15,205-213.

43 Brusseau, M.L., and Rao, P.S.C., (1989) Sorption non-ideality during organic contaminant transport in porous media. Criticl Rev. in Environ. Control 19:33-99.

44 Rubin, J. (1983). Transport of reacting solutions in porous media: relation between mathematical nature of problem formulation and chcmical nature of reactions. Water Resour. Res. 19,1231-1252.

45 Brümmer, G.W., Gerth, J., and Tiller,K.G., (1988). Reaction kinetics of adsorption and desorption of nickel, zinc, and calcium by geothite, I Adsorption and diffusion of metals. J. Soil Sci. 3, 37-51

46 Stumn, W., and Wollast, R. (1990) Coordination chemistry of weathering: Kinetics of surface controlled dissolution of oxide minerals. Rev. of Geophys., 28, 53-69

47 Barrow, N.J., Gerth, J., and Brummer, G.W. (1989). Reaction kinetics of the adsorption and desorption of nickel, zinc and calcium by goethite. II Modelling the extent and rate of reaction. J. Soil. Sci. 40, 437-450.

48 Jury, W. A. (1983), Chemical transport modeling: current approaches and unresolved problems. In: Shawhney, B.L. & Brown, K., (eds) Chemical mobility and reactivity in soil systems, Spec. Publ. No. 11, 49-64, Soil Sci. Soc. of America, Madsion.

49 Nielsen, D.R., van Genuchten, M.Th. and . Biggar, J.W (1986) Water flow and solute transport processes in the unsatutated zone. Water Resour. Res. 22:89S-108S.

50 Jury, W.A, and Roth, K. (1990). Transfer functions and solute movement through

soil. Birkhäuser Verlag, Basel.

51 Skopp, J., Gardner,W.R. and Tyler, E.J. (1981) Solute movement in structured soils: two-region model with small interaction . Soil Sci. Soc. Am. J. , 45, 837-842

52 van Genuchten, M.Th., and Dalton,N. (1986) Models for simulating salt movement in aggregated field soils. Geoderma 38, 165-183.

53 Schwertmann, U., and Cornell R.M. (1991) Iron oxides in the laboratory preparation and characterization, VCH, Wienheim- New York- Basel-Cambridge.

54 Schwertmann, U., and Taylor, R.M. (1989) Iron oxides In: Dixon, J.B., & Weed, S.B. (eds) Minerals in Soil Environments, 379-438, Soil sci. soc. Am. Madison.

55 Mckenzie, R.M. (1989) Manganese oxides. In: Dixon, J.B. and Weed, S.B. (eds) Minerals in Soil Environments, 439-465, Soil Sci. Soc. America, Maidson.

56 Jenne, F. A., (1968) Controls on Mn,Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role ot hydrous Mn and Fe oxides, Advances in Chemistry Series 73, 337-388.

57 McKeague, J. A., Brydon, J. E., and Miles, N. M., (1971), Differentiation of forms of extractable iron and aluminum in soils, Soil Sci. Soc. America Proc., 35, 33-38.

58 Ponnaperurna, F. N., Tianco, E.M. , and Loy, T., (1967) Redox equilibria in flooded soils: I The iron hydroxide systems, Soil Sci., 103, 374-382.

59 Chao, T.T. and Theobald, P. K., (1976), The significance of secondary iron and manganese oxides geochemical processes. Economic Geology, 77, 1560-1569.

60 Taylor, R.W., McKenzie,R.W.,and Norrish, K., (1961) The mineralogy and chemistry of manganese in some Australian soils, Aust. Jour. Soil Sci., 2, 235-218.

61 Taylor, R.W., (1968), The association of manganese and cobalt in soils-further observations: J. Soil Sci., 19, 77-80.

62 Mckenzie, R.M. (1971) The synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese, Mineralogical magazine, 38, 493-502

63 Pomlamperuma, F. N., Loy, T., and Tianco, E.M. (1969), Redox equilibria in flooded soils: II The manganese oxide system,Soil Sci., 108, 48-57.

64 Burke, K. E., (1970), Study of the scavenger properties of manganese (IV) oxide with atomic absorption spectrometry, Anal. Chemistry, 42, 1536 - 1540.

65 Morgan, J. J., a nd Stumm, W., (1964) The role of multivalent metal oxides in limnological transformations as exemplified by iron and manganese: Proc. of second International Conference on Water Pollution Research, Tokyo, 1, 1-16.

66 Wadsley, A. D., and Walkley, A., (1951), The structure and reactivity of the oxides of manganese, Rev. Pure Applied Chemistry, 1, 203-213.

67 Gadde, R. R., and Laitinen, H. A., 1974, Studies of heavy metal adsorption by hydrous iron and manganese oxides, Anal.Chemistry, 46, 2022-2026.

68 Anderson, B. J., Jenne, E. A., and Chao, T. T., (1973) The sorption of silver by poorly crystallized manganese oxides, Geochim. et Cosmochim. Acta, 37, 611-622.

69 McKenzie, R.M., (1970) The reaction of cobalt with manganese dioxide minerals, Aust. Jour. Soil Research, 8, 97-10.

70 Childs, C. W., 1975, Composition of iron and Manganese concretions from some New Zealand soils, Geoderma, 13,141-152.

71 Kabata-Pendias, A., and Pendias, H. (1984). Trace elements in soils and plants. CRC Press, Boca Raton,

72 Gerth, J., and Brümmer, G. (1983). Adsorption und Festlegung von Nickel, Zink und Cadmium durch Goethit (a-FeOOH). Fresenius Z. Anal. Chem. ,316,616-620.

73 Mckenzie, R.M. (1980) The adsorption of lead and other heavy metals on oxides of manganese and iron. Aust. J. Soil. Res., 18, 61-73

74 Thornton, I. (1986), Geochemistry Cadmium, In:Mislin, H.,& Ravera,O.(eds) Cadmium in the Environment, 7-12, Birkhäuser, Basel-Boston-Stuttgart.

75 Adriano, D.C. (1986) Trace elements in the terrestrial environment, Springer, Berlin.

76 Sillanpää, M., and Janson, H. (1992) Status of cadmium, lead, cobalt and selenium in soils and plants of thirty counties. FAO soils bulletin 65, FAO, Rome.

77 Bowen, H.J.M., (1966) Trace elements in biochemistry. Academic Press, London

78 Bowen, H.J.M., (1979) Environmental chemistry of the elements Academic Press, London

79 Donaldson, J.D., Clark,S.J., & Grimes, S.M., (1986) Cobalt in Medicine, Agriculture and the Environment. The Cobalt Development Institute, London.

80 Foerstner, U. and Wittmann, G.T.W. (1981) Metal pollution in the aquatic

environment, Springer verlag, Berlin-Heidelberg-New York .

81 Knauer, G.A., Martin, J.H., and Gordon, R.M. (1982) Cobalt in Northeast Pacific waters, Nature, 297, 49-51

82 Young, R.S. (1979), Cobalt in Biology and Biochemistry, Academic Press, London

3.0 ADSORPTION OF CADMIUM AND COBALT ON TO GOETHITE

3.1 Introduction

There are many different iron oxide minerals in soils, each with unique properties. Many of these minerals have properties that are useful in adsorbing contaminants and limiting the availability of trace metals essential for metabolic processes. Most of these oxides have high specific surface area and conductive surfaces to attract a number of contaminants, including natural organic matter and many heavy metals. The adsorption reactions are pH-dependent, so that contaminants that are adsorbed at one pH can often be released when the solution is adjusted to a different pH. Overall, anions are bound at lower pH values and released at higher pH values, while cations behave oppositely. This pH dependency is an important characteristic of the contaminant-surface interaction. The exact pH range where contaminants are adsorbed or desorbed depends on the nature of the ion itself and the nature of the adsorbing surface.

The adsorption of trace and toxic cations by soil oxides is an important mechanism that controls trace metal concentration and bioavailablity in the soil [1-2]. The soil oxide surfaces are capable of adsorbing metals from the aqueous solutions at the oxide-solute interface [3-8]. Furthermore, adsorption of divalent cations on to oxides, clays, and soil results in a drop in the pH of the solution, indicating a release of protons from the adsorbing surface [9-13].

A wide variety of theories have been developed to account for adsorption of dissolved ions onto oxides and hydroxides [14-18]. Experimental data show that a simple partition between solid and liquid, expressed by a distribution coefficient (K_d), $K_d = C_{aq}/C_{adsorbent}$, is applicable only for the specific solution and adsorbent concentration at which it is measured [19-21] and that simple Freundlich and Langmuir isotherms and similar relations are valid only as special cases. Recent research shows that surface complexation models incorporating a double or triple layer surface can explain many sets of experimental adsorption measurements [22] but that the true nature of the phenomenon is probably more complex than any existing model [23]. Nevertheless, many aspects of adsorption investigations have been explained on semi-quantitative predictions with extrapolations for natural conditions.

The objective of the present investigation is mainly to elucidate the main factors that may affect adsorption, so that their possible effect on experimental conditions can be considered as the basis for recognizing the interaction in natural systems. The study involves a system of contact of an adsorbing ferric oxide (α-FeOOH) phase and a solution that contains an electrolyte ($NaNO_3$) and traces of Cd (II), or Co (II) metal cations. It is considered that the following factors have a major effect on the adsorption process.

1 The pH of the solution

The hydrous metal oxides, particularly those of iron, manganese and aluminium sorption capacity have been found to be strongly pH dependent. The importance of pH as a factor controlling the adsorption of divalent metal cation, or other metal species and hydroxy species from solution can be described in relation to the exchange of protons from OH^- or OH_2 groups of oxide surfaces.

Oxides and hydrous oxides in aqueous solution show ion exchange properties which arise from their pH- dependent surface charge. At hydroxylated or hydrated surfaces, positive or negative charge is created by an adsorption or desorption of H^+ or OH^- resulting in a surface potential. Surface charge and surface potential vary with concentration of $H^-$and OH^- ions in solution. Thus, the oxide and hydroxide surfaces are capable of adsorbing or dissociating H^+ from a surface OH group to acquire a net surface charge. The surface charge is a result of ionization of the surface function groups as shown in equation 3.1 and 3.2

$$S \sim OH + H^+ \rightleftharpoons S \sim OH_2^+ \qquad (3.1)$$

$$S \sim OH \rightleftharpoons S \sim O^- + H^+ \qquad (3.2)$$

Where

$S{\sim}OH$ indicates a surface site occupied by OH

$S{\sim}OH_2^+$ and $S{\sim}O^-$ charged sites affected by the pH of the solution

These charged sites affect the electrostatic attraction for other cations on or near the surface of the solid and create sites for further reaction as presented by Davies et.al. [24]

$$S \sim OH + H^+ \leftrightharpoons S \sim OH_2^+ \qquad (3.1)$$

$$S \sim OH \leftrightharpoons S \sim O^- + H^+ \qquad (3.2)$$

$$S \sim OH + M^+ \leftrightharpoons SO^- \sim M^+ + H^+ \qquad (3.3)$$

$$S \sim OH + MOH^+ \leftrightharpoons SO^- \sim MOH^+ + H^+ \qquad (3.4)$$

$$S \sim OH + A^- + H^+ \leftrightharpoons SO \sim H_2^+ + A^- \qquad (3.5)$$

Where

S = surface site of an adsorbent
M^+ = divalent cation (Cd^{2+}, Co^{2+})
M = monovalent cation
A^- = univalent anion (Cl^-, NO_3^-)

The pH of the solution is also important in the formation of hydroxy complexes in solution for example:

$$Cd^{2+} + H_2O \leftrightharpoons CdOH^+ + H^+ \qquad (3.6)$$

$$Co^{2+} + H_2O \leftrightharpoons CoOH^+ + H^+ \qquad (3.7)$$

These complexes, like simple ions, can be adsorbed on the surface but with differing affinity.

As a result of these pH effects, adsorption experiments with specific concentrations of cations commonly show adsorption over a relatively small increase in pH, to form an adsorption edge. Anion adsorption shows the opposite behaviour.

2 Concentration of the metals.

If we consider reactions 3.3 and 3.4 above, the extent of adsorption is clearly dependent on the concentration of an adsorbate in the system. Increasing the concentration of the metal tends to increase the pH at which a given percentage of a cation is adsorbed.

3 Temperature.

Temperature is an important factor in soil-water systems. In certain places, the summer temperature can reach 50°C and can also fall substantially in winter. These variations can affect the availability of both pollutants and trace metals.Temperature may have effects on: (i) the proportions and activity of ions present in the solution ,(ii) the affinity of ions for the goethite surface and (iii) the charge and therefore the potential of the surface. These can be attributed to affect the position of an adsorption equilibrium or may cause an increase in the rate of reaction. In general, adsorption is expected to increase with increasing temperature, but specific changes cannot be predicted.

4 Concentration of adsorbent

This is expressed as surface area of solid adsorbent per unit volume of iron oxide dispersion. If only a small amount of adsorbing surface is available, the effects of adsorption will be small. Conversely, if the adsorbing surface is large, adsorption is potentially extensive.

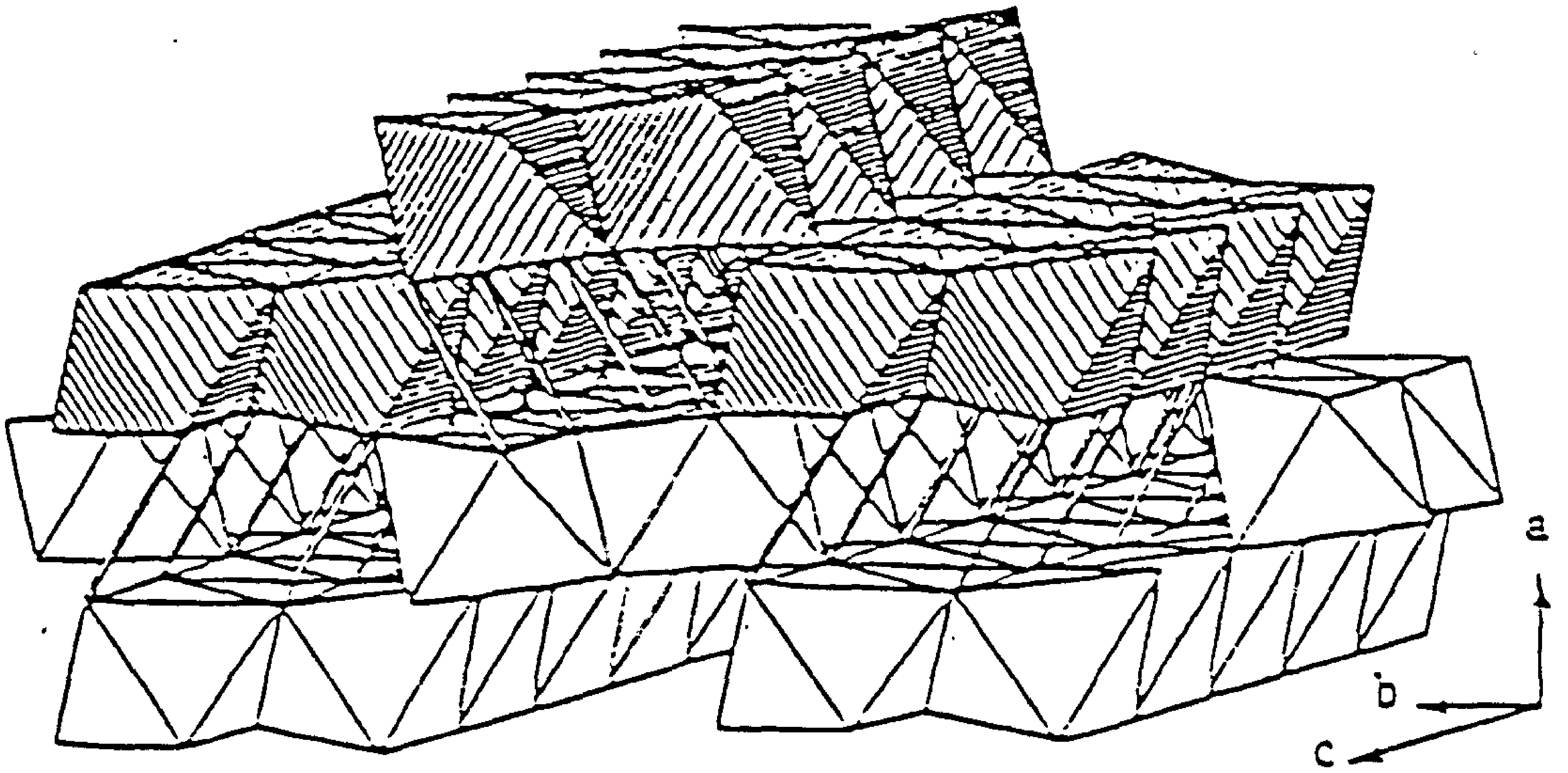
5 Surface properties of the adsorbent

The properties of the phases in the soil including crystallinity, granulation and coated forms of the adsorbing phase, need to be considered.

Goethite (α-FeOOH) is the most common of the iron oxides and it is available in small quantities in all soil types and climatic regions. In addition to its high adsorbing capacity it is also responsible for the brownish to yellow colour of many soils. It was named after the German mineralogist and poet J.W. V. Goethe in 1806 [25].

The goethite structure consists of double chains of linked $FeO_3(OH)_3$ octahedra extending along the crystallographic c-axis and the double chains are also further cross-linked to adjacent double chains through corner sharing of oxygen atoms to give orthorhombic symmetry as shown in Figures 3.1 (A) and 3.1 (B) [26].

(A)



(B)

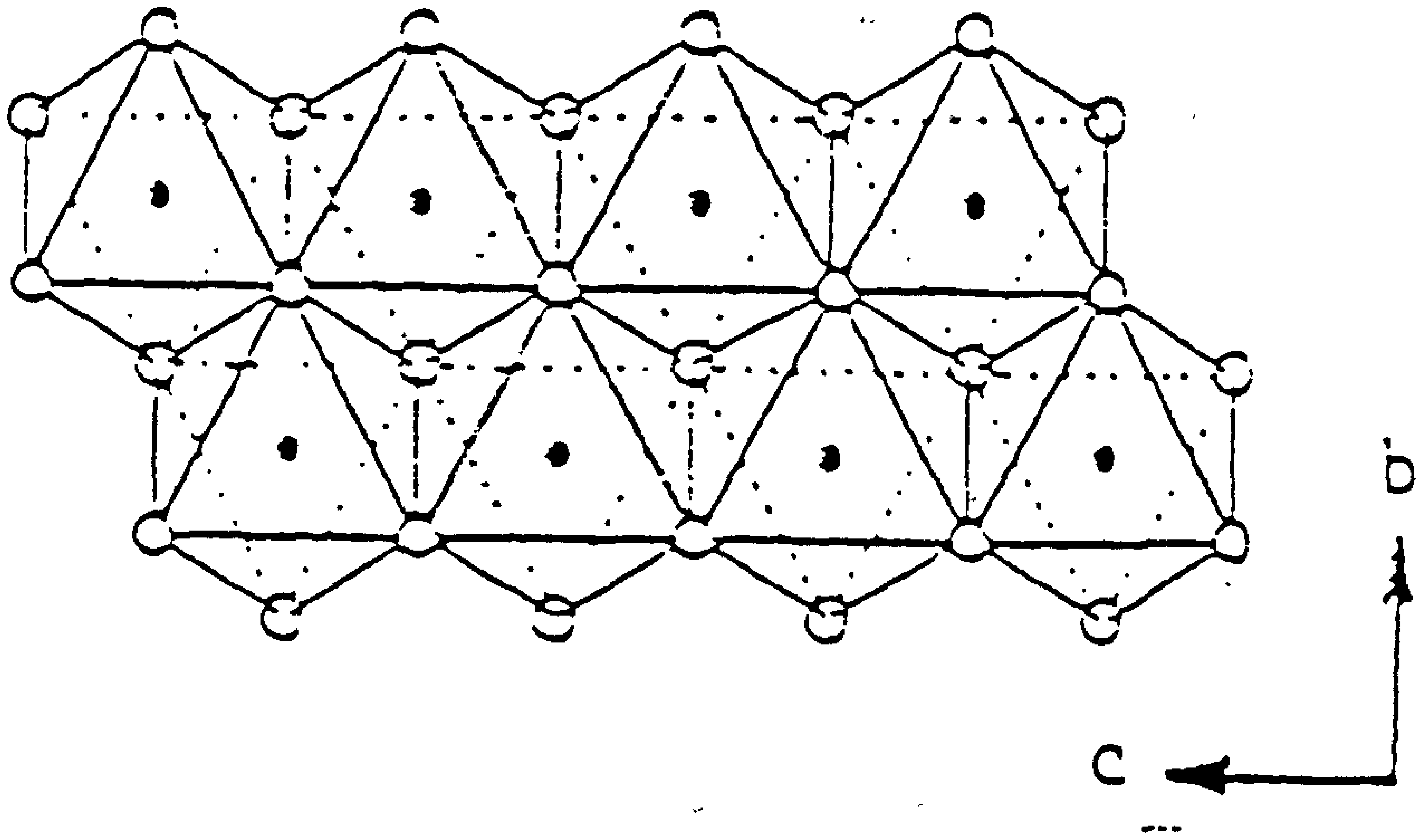


Figure 3.1 Structure of Goethite (α- FeOOH) (A) The way in which double chain of octahedra are linked to the neighboring double chains and (B) The double chain unit of the octahedra [26]

Synthetic goethite crystals are acicular with the needle axis lying along the c-axis. This acicular morphology is found in soils but is often less well developed and can be simulated in synthesis experiments under appropriate conditions. Fibrous goethite was detected in a number of soils from Japan and Scotland [27], and from Australia [28]. Under the scanning electron microscope, grassy types of goethite aggregates also can be found. Often, however, the crystals are mono-dimensional and irregularly shaped.

Goethite (α-FeOOH) was used in this study because of its vital role in the soil-water system. Interest in the preparation and use of goethite as a model adsorbent has also increased recently. This chapter describes an investigation of three preparations of goethite that simulate the soil materials *viz.* goethite colloids, goethite coated on sand and goethite pellets (aggregates), and their use in a study of effects of pH and metal concentration of the solution, concentration of an electrolyte, anion type of electrolyte, amounts of goethite, and contact time on the adsorption of cadmium and cobalt on to goethite.

The pH ranged from 4 to 11, cadmium and cobalt concentration ranged from 4.45×10^{-6} to 7.10×10^{-5} M and 8.48×10^{-6} to 1.36×10^{-4} M respectively. The amount of goethite used, expressed in terms of surface area, ranged from 40 to 300 m^2/l, except for goethite coated sand where it is expressed in weight for convenience; although the surface areas studied were adjusted to similar values and the electrolyte concentration ranged from 10^{-3} to 10^{-1} M of $NaNO_3$. The effects of chloride and nitrate electrolyte and contact time (4 to 120h) were also investigated. .

3.2 Materials and Methods

3.2.1 Reagents and labware

Hydrated iron (III) nitrate [($Fe(NO_3)_3.9H_2O$ Analar minimum assay =99 %)], were supplied by BDH, Poole. England; Cadmium nitrate tetrahydrate [($Cd(NO_3)_2.4H_2O$) assay >99%] and Cobalt (II) nitrate hexahydrate [($Co(NO_3)_2.6H_2O$, assay >99 percent], were supplied by Fluka; Sodium nitrate, as pellets (99.6 percent), was supplied by Fisons, Loughborough, England: Sodium hydroxide as pellets "Analar" supplied by BDH.Technical grade nitric acid (assay 69%), and hydrochloric acid (assay 37%), all supplied by BDH were used. Cadmium and cobalt standard solution, (1000 ppm spectrosol), suitable for atomic absorption spectroscopy were also supplied by BDH. The water used in this study was doubly deionized water processed by the Milli-Q system.

Cadmium and cobalt stock solutions were prepared by diluting cadmium and cobalt standard solutions (1000 ppm spectrosol). The solutions were also prepared from their respective nitrate salts by dissolving in a minimum amount of concentrated nitric acid and then diluting with the required amount of deionized water. The standard solution and the nitrate salt solutions were compared by atomic absorption spectroscopy and were found to be close within experimental error (±1.5%).

All reaction glassware and plasticware are usually stained with the goethite following use. The vessels were cleaned by overnight immersion in 4M hydrochloric acid. Containers used to contain Cd or Co solutions were also soaked in a dilute hydrochloric acid bath at room temperature. After removal from the baths, containers were rinsed repeatedly with deionised water. Soaking baths were changed every two days.

3.2.2 Preparation of goethite

3.2.2.1 Goethite suspension

Goethite (α-FeOOH) was prepared by hydrolysis and ageing of a ferric nitrate solution using the following steps based on the methods of Atkinson et. al. [29] and Forbes et. al. [30].

100 g of ferric nitrate were dissolved in 450 ml of deionized water in a polypropylene container and the pH was adjusted between 1.5 to 2 with 2.5M sodium hydroxide solution. The suspension obtained was then aged at room temperature for 24 hours. Agitation of the mixture with an overhead mixer or teflon coated magnetic stirrer was necessary during the precipitation to maintain suspension of the solid. After the first ageing sufficient 2.5 M sodium hydroxide solution was added dropwise with stirring to bring the final pH of the suspension to about 12.0. The resulting suspension was aged at 70°C in an oven for 90h. During the second ageing process, the voluminous, red brown suspension was

converted to a compact, yellow-brown precipitate of goethite. The resulting goethite precipitate was dialysed in acetate tubing against doubly deionised water until the pH of the suspension was between 7.5 and 8.0 and the conductance of the suspension reached 150μS m^{-1}. The precipitate was then finally washed with deionized water by centrifugation and decantation. Part of the goethite produced was dried and ground gently in an agate mortar and passed through a 200 mesh (75μ) sieve. The other half was stored as a suspension in a polyethylene container.

3.2.2.2 Goethite coated sand

The goethite coated sand was prepared using a modification of the procedure of Wangen, et.al. [31]. To a 1M solution of $Fe(NO_3)_3.9H_2O$ sufficient 2M sodium hydroxide solution was added to obtain a pH of 1.9. The mixture was allowed to react for 60 hours at room temperature, and the pH adjusted to 11.7. The mixture was placed in an oven at 70°C for 72 hours to give a gelatinous precipitate of iron (III) hydroxide. This material was washed three times with deionised water by centrifugation and decantation. The precipitate was then dispersed to form a colloidal suspension, which was adjusted to pH 7 with a 0.1M nitric acid solution to give a mixture that separated into aqueous and gelatinous solid phases. After removal of the liquid phase the gelatinous material was combined with 500 g of acid washed sand and heated in an evaporating dish until nearly dry.

Prior to mixing with the iron (III) hydroxide, the silica sand was washed in 1.0 M HNO_3 suspended for 24 hours in the acid, and finally rinsed in distilled water.

The iron (III) hydroxide - sand mixture was vacuum dried at 60°C for 72 hours, and the coated oxide was scraped from the sand and analysed. Analysis of the coatings by X-ray diffraction confirmed that goethite was the only iron- containing crystalline phase present.

3.2.2.3 Wet-pelletised goethite

The goethite pellet was prepared by mixing goethite (40g) in a polyethylene bowl prepared by the method described in 3.2.2.1 above with the following binding materials:

Material	**Wt %**
Bentonite	2
Starch (dextrin)	2
Sodium carbonate	1
water	~18

The binder composition is based on those used for pelletizing iron ores and zinc ferrite and related observations [31-34]

This resulted in a moist mixture, which was pelletised with a mini bench disc-pelletiser fabricated in the university workshop. In the process of pelletisation speed was adjusted and the mixture was also sprayed with deionized water to facilitate pellet formation. The pellets obtained were approximately 2 mm in diameter and were oven dried at 110°C for 24 hours. The BET-N_2 surface area analysis gave a value 4 m^2/g for the pellets in comparison with $48m^2/g$ for the material obtained when the pellets were provided after crushing them in an agate mortar.

3.3 Characterization of the goethite

3.3.1. Potentiometeric titration

Potentometric titration is the equilibrium electrochemical technique most often used to determine, the zero point of charge (ZPC) of oxides and other materials [35-39]. The zero point of charge is the pH value at which a solution is in equilibrium with a particle whose net charge from all sources is zero. An isoelectric point (IEP) is a zero point of charge from interaction of H^+, OH^-, the solid and water. The ZPC of oxides serves as a convenient reference for predicting how the surface charges of oxides depend on pH. ZPC can be determined by electrokinetic and equilibrium electrochemical methods. In certain circumstances filtration rate can also be used in determining ZPC[40]

Electrokinetic methods include microelectrophoretic and streaming potential techniques. They are based on the determination of the zero point of a material that depends on the presence of an electric double layer. The filtration rate technique is based on the principle that at the ZPC, no net charge exists on the oxide particles to repel each other, resulting in maximum flocculation of particles.

In the present work ZPC measurements were made using potentiometric titrations. Potentiometric titration involves the measurement of H^+ or OH^- at different pH and at different electrolyte concentration. Because of the characteristics of the amphoteric surfaces, there is a pH at which the different curves intersect. This is a point at which adsorption of protons is independent of electrolyte concentrations.

The second method, ion adsorption, involves the measurement of retention of an indifferent ion (adsorbed into the surface by electrostatic attraction) such as Na^+, K^+, NO^-_3 and Cl^- as a function of pH at a fixed electrolyte concentration. This method provides an estimate of cation exchange capacity (CEC) and anion exchange capacity (AEC) as well as the net charge (AEC - CEC) at each pH and is considered to measure zero point of net charge (ZPNC).

In general the method relies on the assumption that if the oxide is prepared at its ZPC and then dialysed and dried, when it is placed in a solution of the same pH as the ZPC it will cause no change in that pH, irrespective of the electrolyte concentration. Since one does not know the ZPC at the beginning of the exercise, the following procedure is adopted.

A known mass, m, of the oxide is added to a known volume, V, of the electrolyte of the known concentration. The initial pH (called pH_0) is noted and the sample is then titrated with acid or base and the volume required to achieve each solution pH is recorded. A suitable time must elapse after each addition to establish equilibrium with the surface. In parallel the titration without the oxide will also be recorded. The difference between the two titrations *volume*, v_d ,corresponds to the amount of a titrant taken up by the oxide surface in order to establish equilibrium with a solution of $pH = pH_d$.

The surface charge on oxides is due to adsorption or desorption of H^+ and OH^- ions consequently;

$$\sigma_o = F(\Gamma_H{}^+ - \Gamma_{OH}{}^-) = F(\Gamma_{HCl} - \Gamma_{KOH}) \tag{3.8}$$

Where Γ, is the surface excess concentration, F, is Faraday constant. The expression in (3.8) is the actually measured one: if a proton adsorbs on the surface, a counter ion, OH^- in this case is accompanying it [38].

The net increases in (negative) surface charge, per unit area is therefore[36]:

$$-(\Gamma_+ - \Gamma_-) = \frac{10^{-5} v_d}{mA} \tag{3.9}$$

where v_d is cm^3

A area per unit mass

The quantity obtained from equation (3.9) is the relative amount of OH^- adsorbed at pH_1. If this calculation is repeated for all pH > pH_0 and the comparable data for acid titration are also obtained a plot of relative charge against pH for electrolyte can be constructed. The same procedure is then be repeated in diffrent electrolyte concentrations. When all the data are plotted together, one hopes to obtain the intersection point. The point where all three isotherms cross one another can be identified as the ZPC, because only at that point is the surface charge independent of the concentration of the supporting electrolyte.

1.5 g of goethite was suspended in 15ml of 0.1, 0.01 and 0.001 KCl and the pH adjusted to a range between 4 and 10 with the measured amounts of 0.1M HCl and 0.1M KOH and the solution was mixed using a teflon coated magnetic stirrer in polyethylene bottles and flushed with wet CO_2-free N_2 gas. The suspension was kept at room temperature in capped 20 ml plastic vials and shaken twice daily over a three day period. After this time the pH values of the supernatant liquid were recorded. Blank titrations were obtained using equal volumes of KCl solution in the absence of the oxide. The amounts of H^+ and OH^- adsorbed by the goethite samples were estimated from the amount of acid or base necessary to bring test suspension to the particular pH values, minus the amount necessary to bring 15 ml of a blank solution (KCl solution without goethite) to the same pH. Adsorption densities ($\Gamma_{H^+} - \Gamma_{OH^-}$) micro equivalents per gram of oxide were calculated using equation (3.9) and relative ZPC values located by the common point of intersection of titration curves at different ionic strengths. The isoelectric point of the goethite as determined by acid-base titration was found to be 7.2 as shown in Figure 3.2

3.3.2 X-ray powder diffraction

X-ray powder diffraction is an essential tool for the identification of the product and in determining its degree of purity. The samples obtained were characterised by X-ray diffraction (XRD) using CuKα 1.5406 Å radiation and a Philips PW 1050 X-ray diffractometer automated and computer controlled by Sietronics software. The sample was scanned in the range 18 - 75° 2θ. X-ray powder diffraction patterns showing the main peaks at 4.979, 4.184, 2.693 and 2.448 Å, compared to the literature values [41] of 4.98,4.18, 2.69, and 2.45 Å and confirmed that the sample was α-FeOOH. The instrument is calibrated with compacted silicon powder periodically and the accuracy for d-spacing is ± 0.005Å.

3.3.3 Scanning electron Microscopy

This is another useful technique which enables crystal dimensions and also crystal morphology to be measured directly. It is also useful for indicating the presence of amorphous material or traces of iron oxides not detectable by XRD. Scanning electron micrographs were obtained using a Jeol JXA 840A electron probe microanalyser. This confirmed the acicular nature of the crystals as shown in Figure 3.3.

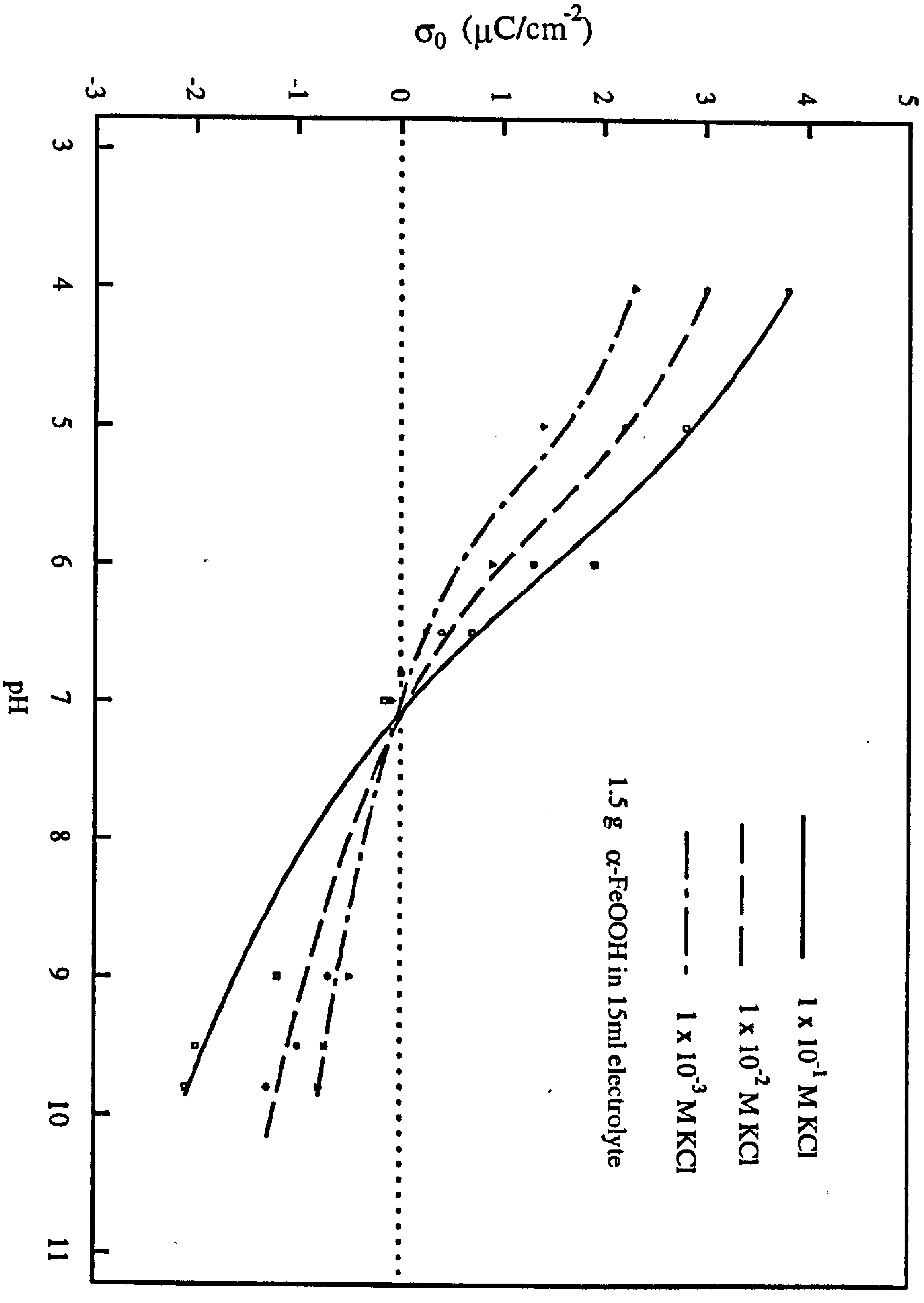


Fig 3.2 Zeta potential measurements of α-FeOOH

Standard		Sample	
dÅ	**Intensity**	**dÅ**	**Intensity**
4.98	12	4.979	8
4.183	100	4.184	100
3.383	10	3.378	9
2.693	35	2.693	36
2.583	12	2.582	15
2.489	10	2.49	10
2.450	50	2.448	50
2.303	1	2.31	5
2.253	14	2.255	10
2.190	18	2.192	16
2.089	10	2.09	4
1.920	5	1.919	5
1.802	6	1.8	10
1.7192	20	1.72	34
1.6906	6	1.691	7

Table 3.1 XRD results as compared to results from XRD data file [41]

3.3.4 Surface Area

The most widely used method for determining the surface area of iron oxides is the Brunauer-Emmett-Teller (BET) method. The area determination is based on the fact that if a gas is brought in contact with a powdered solid at a temperature near the condensation temperature of the gas, part of the gas is physically adsorbed on the surface of the solid. If the volume of gas adsorbed at a series of known gas pressures is measured, it is possible to determine the surface area of the solid by means of the BET isotherm:

$$\frac{p}{v\,(p_0 - p)} = \frac{1}{v_m \,.\, c} + \frac{(c - 1)\,.\,p}{V_m \,.\, c \,.\, p_0} \tag{3.10}$$

Where

v is the volume of gas adsorbed at pressure p,

p_0 is the saturation vapour pressure of the gas

v_m is the volume of adsorbate required to cover the adsorbent with a monolayer,

c is a constant for any given system and is related to the heat of liquification of the gas.

The monolayer volume v_m, is found from the slope and intercept of the linear part of the curve obtained by plotting $p/v\,(p_0 - p)$ verses p/p_0.

N_2, the gas used in the study, has a molecular cross section of 0.162 nm^2. The surface area of the solid is calculated from the value of v_m and the cross section of the molecule of the adsorbate,

Samples need to be evacuated overnight before an adsorption test is carried out at a temperature between 100 - 150 °C to remove physically adsorbed water, otherwise there would be interference with the surface area determination.

Surface area measurements were carried out on the samples by the application of the B.E.T. equation to the conventional volumetric data for nitrogen adsorption of goethite after 100 °C outgassing overnight using Micromeritics A S A P 2000. The results obtained in duplicate were as given below and duplicate 1 results are considered as representative.

	Duplicate 1 (m^2/g)	**Duplicate2(m^2/g)**
goethite suspension	75 ±0.93	74.8±0.93
goethite pellet	4 ± 0.0640	3.9 ± 0.0640
crushed goethite pellet	48 ± 0.532	47.4 ±0.45
sand coated goethite	6 ± 0.085	6 ± 0.010

The values are in line with reported observation of effect of granulation on soil oxides surface area [42-43]. The surface area for sand-coated goethite was measured by scraping the goethite from the sand surface and outgassing overnight as with the other three products.

3.3.5 Thermogravimetry (TGA)

This is another technique that provides information about the adsorbed and structural water present in the sample and also about phase-specific changes and transformations,. A sample is continuously heated at a constant rate (2-10°C min $^{-1}$) and its weight loss is measured using a balance. Fe oxides containing structural OH, lose weight between 250 and 400°C via the dehydroxylation reaction

$$2OH^- \rightarrow O_2 + H_2O \qquad (3.11)$$

All fine grained material contains adsorbed water and additional weight loss stems from the loss of adsorbed water at a characteristics' temperature of between 100 - 200° C.

TG curves for goethite samples were obtained in triplicate using a Stanton Redcroft STA-780 series thermo-balance linked to a BBC SE 460 chart recorder. The analysis conditions were

Sample weight	15 mg
Gas	Nitrogen
Flow rate	25ml min^{-1}
Temperature	20 - 600° C
Heating rate	10° C min^{-1}
Crucible type	Aluminum

The goethite samples mass loss was measured from each TG curve and averages for the triplicate samples were 2.1 and 10.6% for adsorbed water and crystalline water respectively. The instrument is calibrated for temprature accuracy and weight accuracey using magnetic alloy wires and calcium oxalate respectively. The accuracy for temperature is ±2°C and 0.5% for weight.

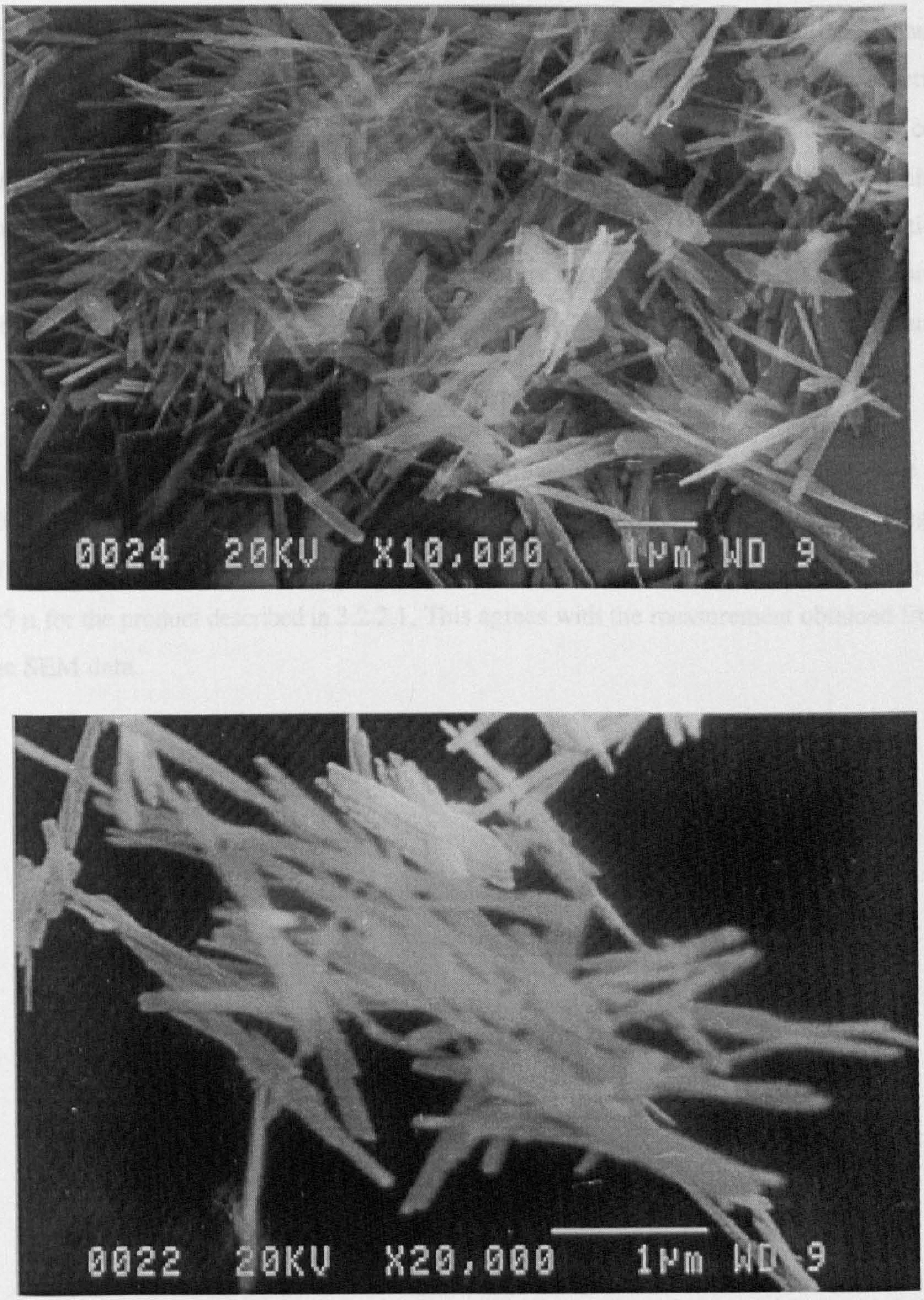


Figure 3.3 Scanning electron micrograph of goethite (α-FeOOH.)

3.3.6 Particle size

The technique used in this work was light scattering. Monochromatic light from a laser source is passed into the index-matching chamber containing the sample in a cuvette, usually of optical quality quartz, or a suitable plastic. The beam enters and leaves the cell through flat optical windows. The chamber is filled with a suitable refractive index matching fluid, such as filtered water or other organic solvents. This fluid also performs the function of thermally coupling the cuvette to the temperature regulation system in the cell housing which enables the contents to be kept to within ± 0.1 °C of the measurement temperature.

A goethite sample was dispersed in a 10^{-3} M solution of $NaNO_3$ as electrolyte in an ultrasonic bath. Particle size measurements were then carried out in triplicate using a Malvern Zetasizer III. The average size from the three runs for the goethite suspension is 1.5 μ for the product described in 3.2.2.1. This agrees with the measurement obtained from the SEM data.

The main characterisation results are given in Table 3.2

Property	Value
Goethite powder	
PZC	7.2 (pH)
surface area (BET)	75 ± 0.93 m^2/g
particle diameter	1.5μm
particle geometry	acicular crystals
adsorbed H_2O (TGA)	2.1%
crystalline H_2O (TGA)	10.6 %
X-ray Diffraction pattern	Goethite
Goethite-coated silica sand	
pH of slurry	-
surface area (BET)	6 ± 0.085m^2/g
particle diameter (Malvern)	-
particle geometry	-
adsorbed H_2O (TGA)	-
crystalline H_2O (TGA)	-
X-ray Diffraction pattern	Goethite
Goethite pellet	
pH of slurry	-
surface area (BET)	4 ± 0.0640m^2/g
particle diameter (zeta sizer)	-
particle geometry	-
adsorbed H_2O (TGA)	2.1%
crystalline H_2O (TGA)	10.6 %
X-ray Diffraction pattern	Goethite

Table 3.2 Summary of properties of goethite preparations

3.4 Analytical Methods

3.4.1 Cation analysis

Cadmium and cobalt concentration in the solutions was analysed by a Perkin Elmer Atomic Absorption Spectrophotometer -AAS-, model 2380, and Inductively-coupled plasma emission Spectrophotometer -ICP-, model 40. Prior to each analysis the spectrophotometers were calibrated using standard solutions for each run.This is obtained by using the instrument supplier procedure for checking the accuracy of the instrument using standard solutions set for both cadmium and cobalt before a batch of every analysis.

3.4.2 pH measurement

The pH of the suspension was measured with a Mettler pH meter Delta 320 using Ingold Inlab combination electrode 405, with an integral temperature sensor and multiple connector. BDH; pH 4, 7, and 10 buffers were used for calibration. Goethite suspension pH measurements were made on 1:10 goethite/deionised water suspensions, shaken for 30 minutes in an end-to-end-shaker at 250 throws per minute.

3.5 Experimental procedure

Batch adsorption experiments on goethite preparations were carried out as follows. A known amount of goethite was suspended into a 125 ml polypropylene centrifuge bottle containing 25 ml of 1×10^{-2} M $NaNO_3$ solution and equilibrated overnight at the desired pH. After adjustment to the same pH as the suspension, 25 ml of the required sorbate solution in 1×10^{-2} M $NaNO_3$ was added to the suspension. The suspensions were then adjusted serially with small amounts of HNO_3 or NaOH to achieve a pH range between 4 and 10. The sorbate solution was prepared freshly for each batch by diluting cadmium or cobalt stock solutions (1000 ppm). Adsorption studies were carried out at different initial concentrations between 4.45×10^{-6} and 1.4×10^{-4} M [Cd] and 8.48×10^{-6} and 2.7×10^{-4} M [Co] and at varying solid solution ratios. Regulators use ppm (mg/l) in setting consent levels so that in this work initial solutions of cobalt and cadmium had the same initial concentrations in ppm. In terms of transport of metals in soil again the requirement is again for a knowledge of the concentration in ppm. The suspension was shaken on an end- to- end shaker at 250 throws min^{-1} for a predetermined time. For experiments designed to investigate the effect of temperature an overhead stirrer at 250 rpm was used. Following sorbate addition the pH of the suspension was carefully readjusted with addition of small measured quantities of 1×10^{-2} M NaOH or 1×10^{-2} M HNO_3 periodically throughout the contact time. The amount of sodium hydroxide or nitric acid used did not significantly change the electrolyte strength of the suspension.

Adsorption distributions were studied by shaking suspensions for contact times of 4,8, 36, and 120 h at room temperature using initial Cd and Co concentrations of 1.78×10^{-5} M [Cd] and 3.39×10^{-5} M [Co] in 0.01 M $NaNO_3$. In order to determine the effect of temperature on adsorption processes experiments were carried out at 12, 24,35,and 45 ± 1 °C for goethite powder only. For practical convenience the bulk of the experiments were run at room temperature with a 4 h contact time.

After the adsorption period, the final pH of the suspension was measured, and the suspension centrifuged and decanted.The supernatant was filtered through a 0.45μ Whatman membrane filter and the clear supernatant solution was analysed for the metals. To achieve uniformity all the standard solutions and blank solutions were also filtered through the same filter material. The results of the metal content in the bottles with different pH values were combined as a unit to give a complete curve of adsorption vs pH for each initial concentration of metal ions.

Similar procedures were applied,with a modification, for goethite-coated sand and goethite pellets. Since the amount of ferric oxide in sand-coated goethite is about 2.5% of the reaction volume, the volume of solution was adjusted to 200ml instead of 50ml for goethite coated sand and goethite pellets preparations. The reacting mixtures were equilibrated for 4 h after which the solids were separated by centrifugation and then filtration of the supernatant solution with 0.45μ Whatman membrane filter. The filtered supernatant solution was analysed using atomic absorption and an inductively coupled plasma emission spectrometer. It should be noted that goethite pellet and goethite-coated sand were investigated only for the effect of metal concentration as a function of pH at constant goethite concentration.

Standards to calibrate atomic absorption spectrophotomete and inductively-coupled plasma emission spectrophotometer were prepared from the stock solutions of cadmium and cobalt standards, (1000 ppm spectrosol). A fresh standard was prepared for each series of measurements. Results are reported as percentage adsorbed (metals) as a function of pH for various initial metal concentrations, contact time, electrolyte concentration, electrolyte composition, temperature and oxide concentrations expressed in terms of m^2/g depending on the type of preparations used. A control solution was prepared from the stock solution in an identical method to the experimental solution in the absence of goethite.

3.5.1 Adsorption of cadmium and cobalt on container walls

Cadmium and cobalt adsorption on reaction bottle walls was investigated for aqueous solutions of 1×10^{-2} M $NaNO_3$. The solutions were prepared as described earlier, except that no goethite was added; the only adsorbent was the bottle wall. No significant cadmium or cobalt loss from adsorption on bottle walls was detected .

3.5.2 Calculation of Percent Cd (II) and Co (II) Adsorbed on to Goethite

Total cadmium and cobalt present in the experimental system was distributed in three reservoirs: metal in solution, metal adsorbed on goethite, metal lost as a result of adsorption on container walls. Because loss of metal on the container walls was found to be negligible, metal adsorbed onto goethite can be calculated as

$$M^{2+}_{ads} = M^{2+}_{t} - M^{2+}_{aq} \tag{3.12}$$

$$\%M^{2+}_{ads} = 100 * M^{2+}_{ads} / M^{2+}_{t} \tag{3.13}$$

3.5.3 Establishing the Time Required for Equilibration

To determine the time required to attain equilibrium, ten adsorption experiments were conducted at contact times ranging from 15 min to 8 h, with 4.45×10^{-5} M[Cd], 8.48×10^{-5} M [Co] and goethite surface area =75 m^2/l. The adsorption process was fast, and equilibrium was established within 80 minutes. Several works reported equilibrium times of varying length from 30 min to several hours [29-30]. To ensure equilibration and for operational convenience, a contact time of 4 h was used for all the subsequent experiments except those run to study the effect of contact time.

3.5.4 Reversibility

This was designed to give an insight into the reversibility of the adsorption reaction at a 1.78 x 10^{-5} M [Cd]and a 3.39 x 10^{5} M [Co] concentration. Two duplicate sets of experiments were run. The first set (set I) consisted of 1.78 x 10^{-5} M [Cd] and 3.39 x 10^{-5} M [Co] within a pH range of 4 - 10, and a second set (set II) was prepared along with the first in the same pH range. After 8 h contact time the first set (set I) was analysed for cation adsorption. The second set (set II) continued to be shaken without removing aliquots for metal analysis. Instead, the suspensions were readjusted as follows: suspensions with an original pH of 4 - 7 were readjusted to a pH of 7 - 10, and suspensions with an original pH of 7 - 10 were readjusted to a pH of 4 -7. The suspensions were then allowed to react for an additional 8 h and were analysed for cadmium and cobalt adsorption. The results of the two sets of experiments showed that the adsorption of cobalt and cadmium onto goethite is irreversible.

3.5.5 Reproducibility

These experiments were run to check reproducibility of the experimental procedure. Three batches of adsorption experiments were performed at two metal concentrations (1.78 x10^{-5} M [Cd] and 3.39 x 10^{-5} M [Co]); and a goethite surface area of 75 m^2/g The first two batches of experiments utilized identical batches of reagents and goethite but were run on different days, whereas the third batch utilized a different batch of goethite. The closeness of the results between the three batches curves indicates very good reproducibility as shown in Figures 3.4 and 3.5. The representative data format used to calculate the metals sorbed on goethite and the statistical presentation are depicted in Table 3.3. The average standard deviations for percent of adsorption for the three runs from triplicate measurements are 1.72, 1.80 and 2.42.

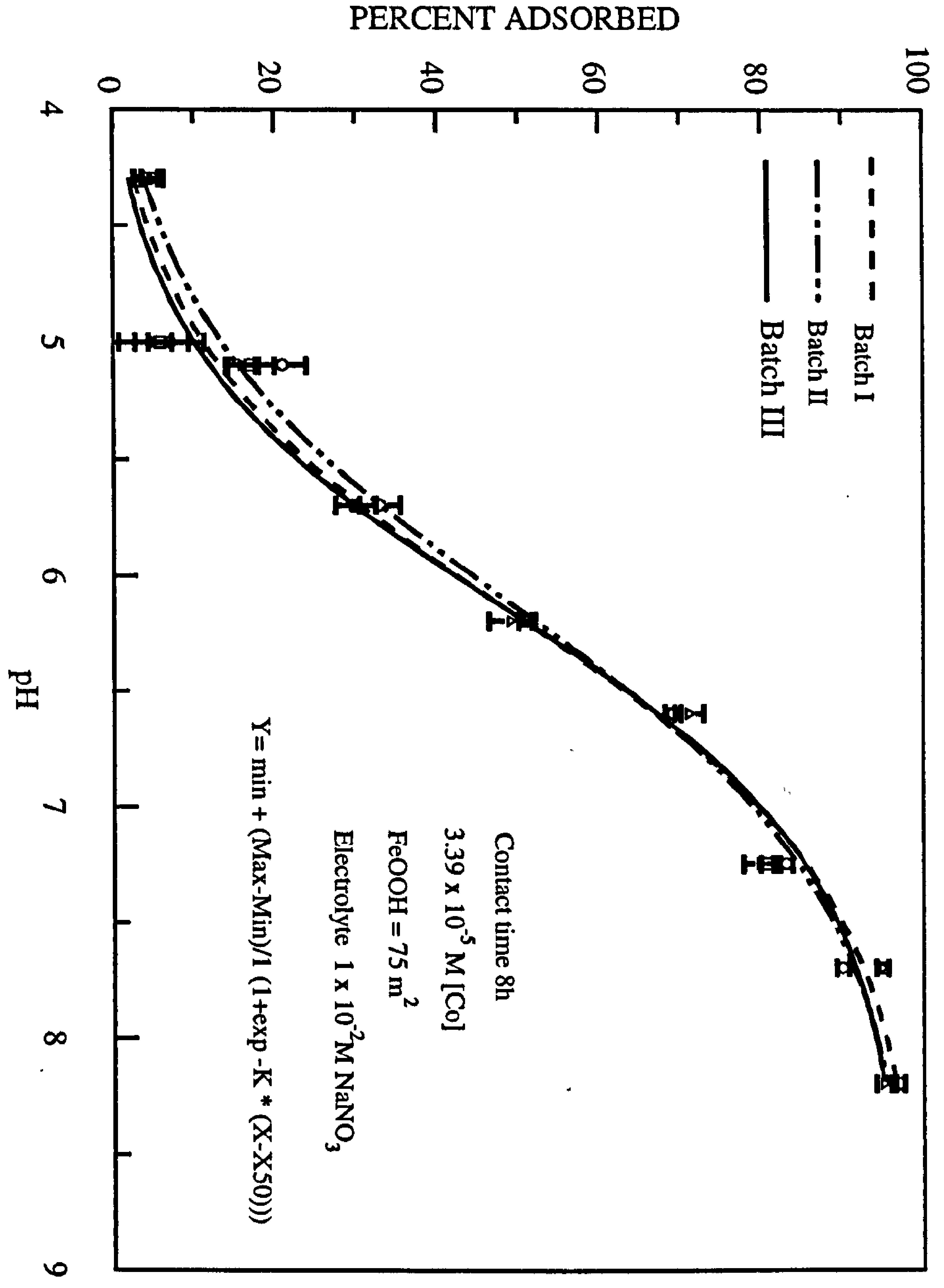


Fig 3.4 Co adsorption reproducibility as a function of pH

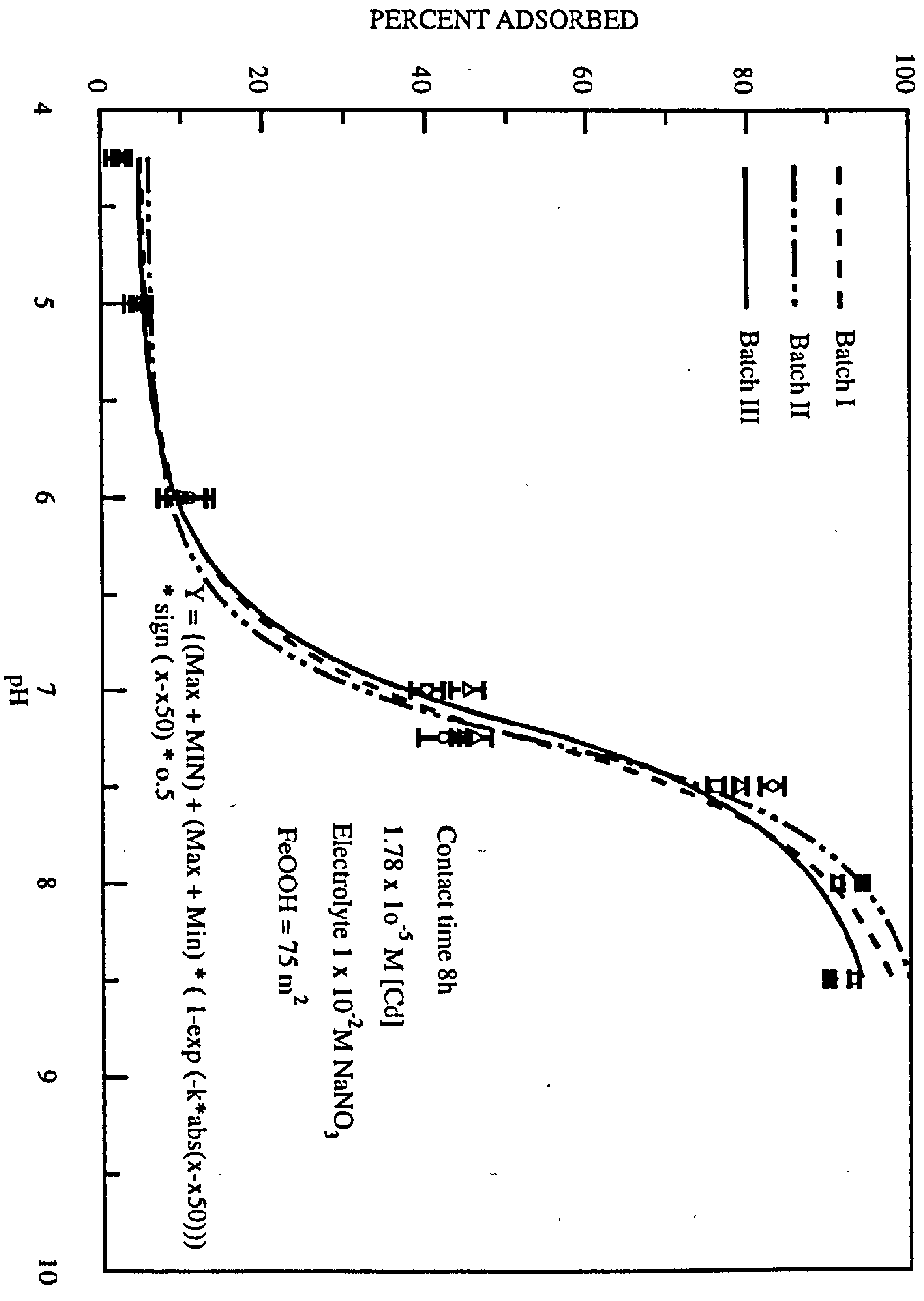


Fig 3.5 Cd adsorption reproducibility as a function of pH

Table 3.3 Replicate analysis statistical data for Figure 3-4

RUN I					
	Replicate (mg/l)				
pH	1	2	3	MEAN	S.D
4.30	1.95	1.90	1.90	1.92	0.02
5.00	1.90	1.85	1.80	1.85	0.04
5.30	1.75	1.70	1.60	1.68	0.06
5.70	1.45	1.35	1.40	1.40	0.04
6.20	1.00	0.95	0.85	0.93	0.06
6.60	0.65	0.60	0.60	0.62	0.02
7.25	0.40	0.40	0.35	0.38	0.02
7.70	0.15	0.10	0.10	0.12	0.02
8.20	0.10	0.10	0.08	0.09	0.01
RUN II					
	Replicate (mg/l)				
pH	1	2	3	MEAN	S.D
4.30	1.94	1.90	1.90	1.91	0.02
5.00	1.95	1.90	1.85	1.90	0.04
5.30	1.75	1.65	1.65	1.68	0.05
5.70	1.45	1.35	1.40	1.40	0.04
6.20	1.00	0.95	0.95	0.97	0.02
6.60	0.60	0.55	0.55	0.57	0.02
7.25	0.40	0.30	0.37	0.36	0.04
7.70	0.20	0.20	0.10	0.17	0.05
8.20	0.15	0.05	0.10	0.10	0.04
RUN III					
	Replicate (mg/l)				
pH	1	2	3	MEAN	S.D
4.30	1.95	1.94	1.93	1.94	0.01
5.00	1.90	1.90	1.80	1.87	0.05
5.10	1.70	1.60	1.66	1.65	0.04
5.70	1.45	1.40	1.30	1.38	0.06
6.20	1.10	1.00	0.85	0.98	0.10
6.60	0.60	0.60	0.45	0.55	0.07
7.25	0.45	0.40	0.40	0.42	0.02
7.70	0.20	0.20	0.10	0.17	0.05
8.20	0.15	0.10	0.07	0.11	0.03

RUN I											
	Replicate										
	1			2			3				
pH	(mg/l)	E %	A%	(mg/l)	E %	A%	(mg/l)	E %	A%	Mean	S.D.
4.30	1.95	97.50	2.50	1.90	95.00	5.00	1.90	95.00	5.00	4.17	1.18
5.00	1.90	95.00	5.00	1.85	92.50	7.50	1.80	90.00	10.00	7.50	2.04
5.30	1.75	87.50	12.50	1.70	85.00	15.00	1.60	80.00	20.00	15.83	3.12
5.70	1.45	72.50	27.50	1.35	67.50	32.50	1.40	70.00	30.00	30.00	2.04
6.20	1.00	50.00	50.00	0.95	47.50	52.50	0.85	42.50	57.50	53.33	3.12
6.60	0.65	32.50	67.50	0.60	30.00	70.00	0.60	30.00	70.00	69.17	1.18
7.25	0.40	20.00	80.00	0.40	20.00	80.00	0.35	17.50	82.50	80.83	1.18
7.70	0.15	7.50	92.50	0.10	5.00	95.00	0.10	5.00	95.00	94.17	1.18
8.20	0.10	5.00	95.00	0.10	5.00	95.00	0.08	4.00	96.00	95.33	0.47

RUN II											
	Replicate										
	1			2			3				
pH	(mg/l)	E %	A%	(mg/l)	E %	A%	(mg/l)	E %	A%	Mean	S.D.
4.30	1.94	97.00	3.00	1.90	95.00	5.00	1.90	95.00	5.00	4.33	0.94
5.00	1.95	97.50	2.50	1.90	95.00	5.00	1.85	92.50	7.50	5.00	2.04
5.30	1.75	87.50	12.50	1.65	82.50	17.50	1.65	82.50	17.50	15.83	2.36
5.70	1.45	72.50	27.50	1.35	67.50	32.50	1.40	70.00	30.00	30.00	2.04
6.20	1.00	50.00	50.00	0.95	47.50	52.50	0.95	47.50	52.50	51.67	1.18
6.60	0.60	30.00	70.00	0.55	27.50	72.50	0.55	27.50	72.50	71.67	1.18
7.25	0.40	20.00	80.00	0.30	15.00	85.00	0.37	18.50	81.50	82.17	2.10
7.70	0.20	10.00	90.00	0.20	10.00	90.00	0.10	5.00	95.00	91.67	2.36
8.20	0.15	7.50	92.50	0.05	2.50	97.50	0.10	5.00	95.00	95.00	2.04

RUN III											
	Replicate										
	1			2			3				
pH	(mg/l)	E %	A%	(mg/l)	E %	A%	(mg/l)	E %	A%	Mean	S.D.
4.30	1.95	97.50	2.50	1.94	97.00	3.00	1.93	96.50	3.50	3.00	0.41
5.00	1.90	95.00	5.00	1.90	95.00	5.00	1.80	90.00	10.00	6.67	2.36
5.30	1.70	85.00	15.00	1.60	80.00	20.00	1.66	83.00	17.00	17.33	2.05
5.70	1.45	72.50	27.50	1.40	70.00	30.00	1.30	65.00	35.00	30.83	3.12
6.20	1.10	55.00	45.00	1.00	50.00	50.00	0.85	42.50	57.50	50.83	5.14
6.60	0.60	30.00	70.00	0.60	30.00	70.00	0.45	22.50	77.50	72.50	3.54
7.25	0.45	22.50	77.50	0.40	20.00	80.00	0.40	20.00	80.00	79.17	1.18
7.70	0.20	10.00	90.00	0.20	10.00	90.00	0.10	5.00	95.00	91.67	2.36
8.20	0.15	7.50	92.50	0.10	5.00	95.00	0.07	3.50	96.50	94.67	1.65

	Adsorbed (mg/l)			% adsorbed			S.D		
pH	1	2	3	1	2	3	1	2	3
4.30	0.08	0.09	0.06	4.17	4.33	3.00	1.18	0.94	0.41
5.00	0.15	0.10	0.13	7.50	5.00	6.67	2.04	2.04	2.36
5.30	0.32	0.32	0.35	15.83	15.83	17.33	3.12	2.36	2.05
5.70	0.60	0.60	0.62	30.00	30.00	30.83	2.04	2.04	3.12
6.20	1.07	1.03	1.02	53.33	51.67	50.83	3.12	1.18	5.14
6.60	1.38	1.43	1.45	69.17	71.67	72.50	1.18	1.18	3.54
7.25	1.62	1.64	1.58	80.83	82.17	79.17	1.18	2.10	1.18
7.70	1.88	1.83	1.83	94.17	91.67	91.67	1.18	2.36	2.36
8.20	1.91	1.90	1.89	95.33	95.00	94.67	0.47	2.04	1.65

3.6 Results and discussion

3.6.1 Effect of metal concentration

Adsorption occurs in a narrow pH range between pH 6.5 and 7.5. In this narrow pH range a sharp increase in metal adsorption commonly known as the adsorption edge is observed. Figures 3.6 -3.17 present the result of adsorption of cadmium and cobalt and the respective K_ds. The effects of pH and initial cadmium and cobalt concentrations on the adsorption of the metals on to goethite, goethite coated on sand and goethite pellets are presented. The surface area obtained for goethite by the BET method is used in which a suspension of 1g of goethite in 1 litre of solution is assumed to be equivalent to 1g of goethite surface area. The pH range moves to higher pH as the initial adsorbate concentration is increased. An increase in metal concentrations, requires a higher pH to achieve the same fractional adsorption as that at a lower cadmium or cobalt concentrations.

The strongly pH-dependent adsorption of Cd and Co on goethite is characterized by an increase in the amount of metal adsorbed at a narrow pH range at constant goethite -metal solution ratio for all three types of preparations. The curves for the colloidal goethite and goethite-coated sand as shown in Figures 3.6, 3.8, 3.14 and 3.16 have a sigmoidal shape and shift to a higher pH as the initial metal concentration of the solution increases. Goethite pellets showed a different pattern as shown in Figures 3.10 and 3.12, which is mainly due to reduced interparticle pore sizes due to granulation. Goethite pellets were also unable to withstand agitation during the whole contact time. This is mainly because of the binding material used but could also be due to the low compaction strength and low drying temperature. Increasing the drying temperature would alter the surface property of the goethite which will directly affect its sorption capacity.

Although the adsorbing capacity of goethite-coated sand is lower than that of the goethite suspension it has a similar sorption curve and was able to withstand agitation during the sorption reaction. The physical and chemical characteristics of goethite-coated sand observed in this experiment make them acceptable for use in column reactors.

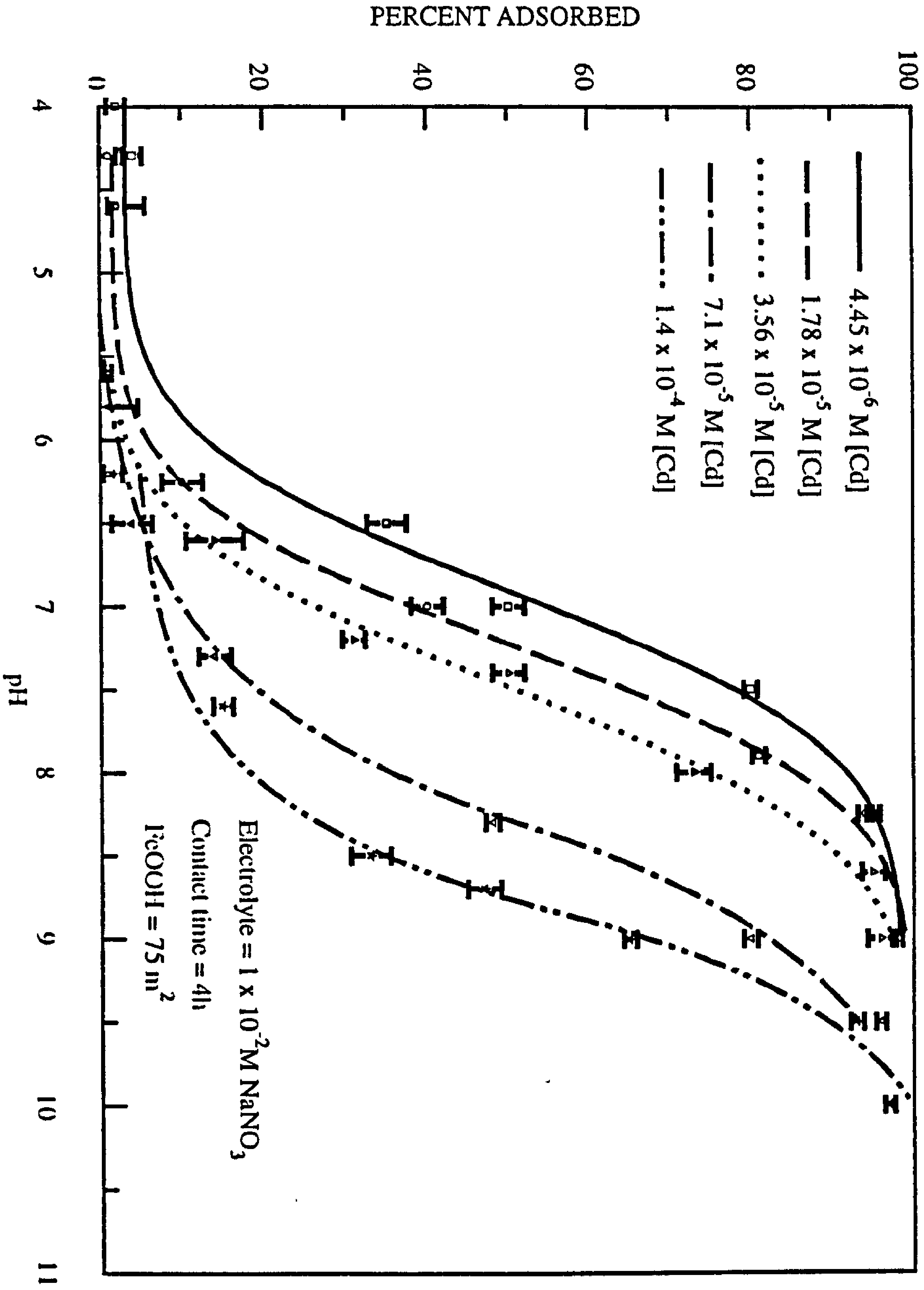


Fig 3.6 Cd adsorption as a function of pH and Cd concentration

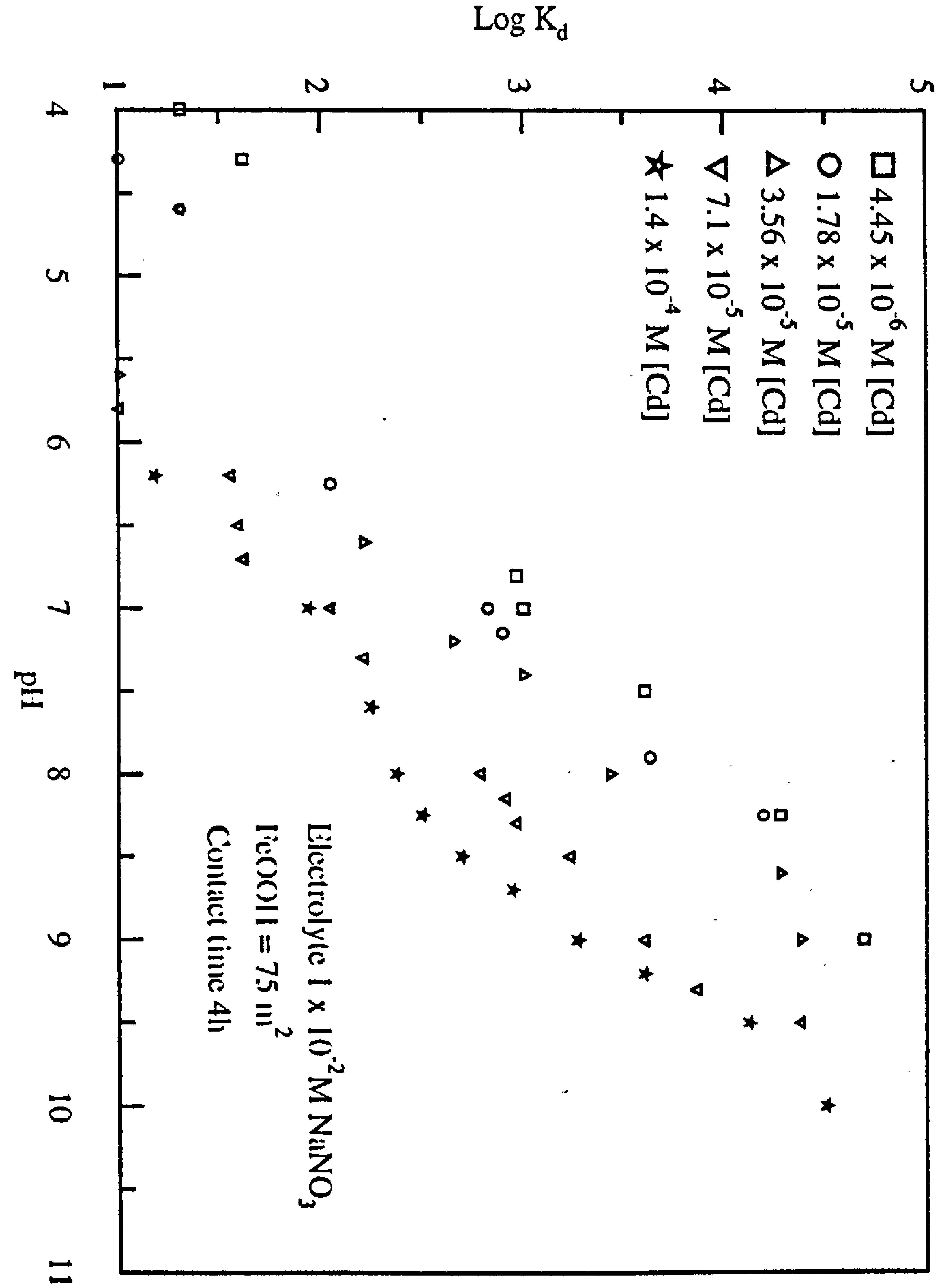


Fig 3.7 K_d of Cd adsorption as a function of pH and Cd concentration

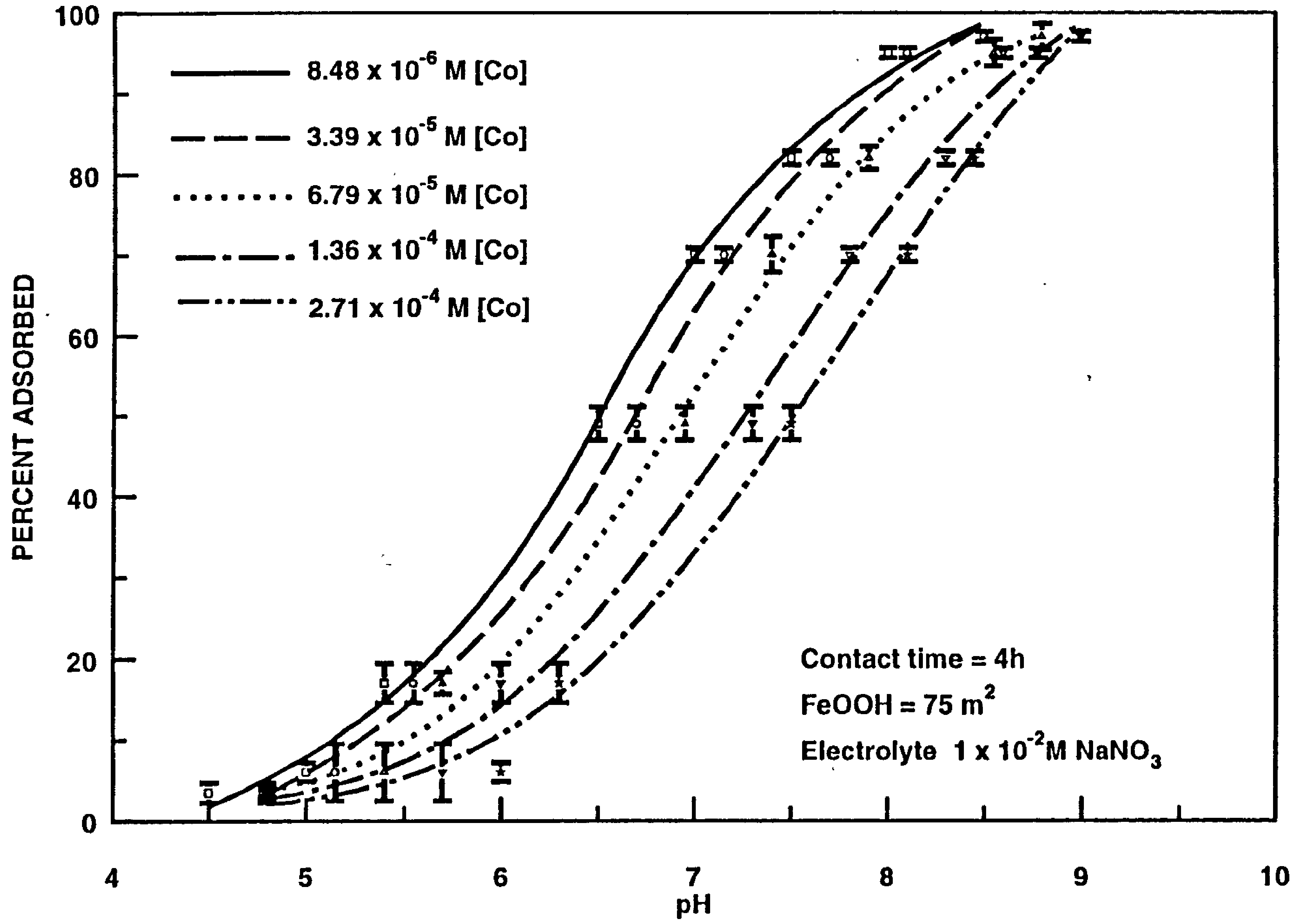


Fig 3.8 Co adsorption as a function of pH and Co concentration

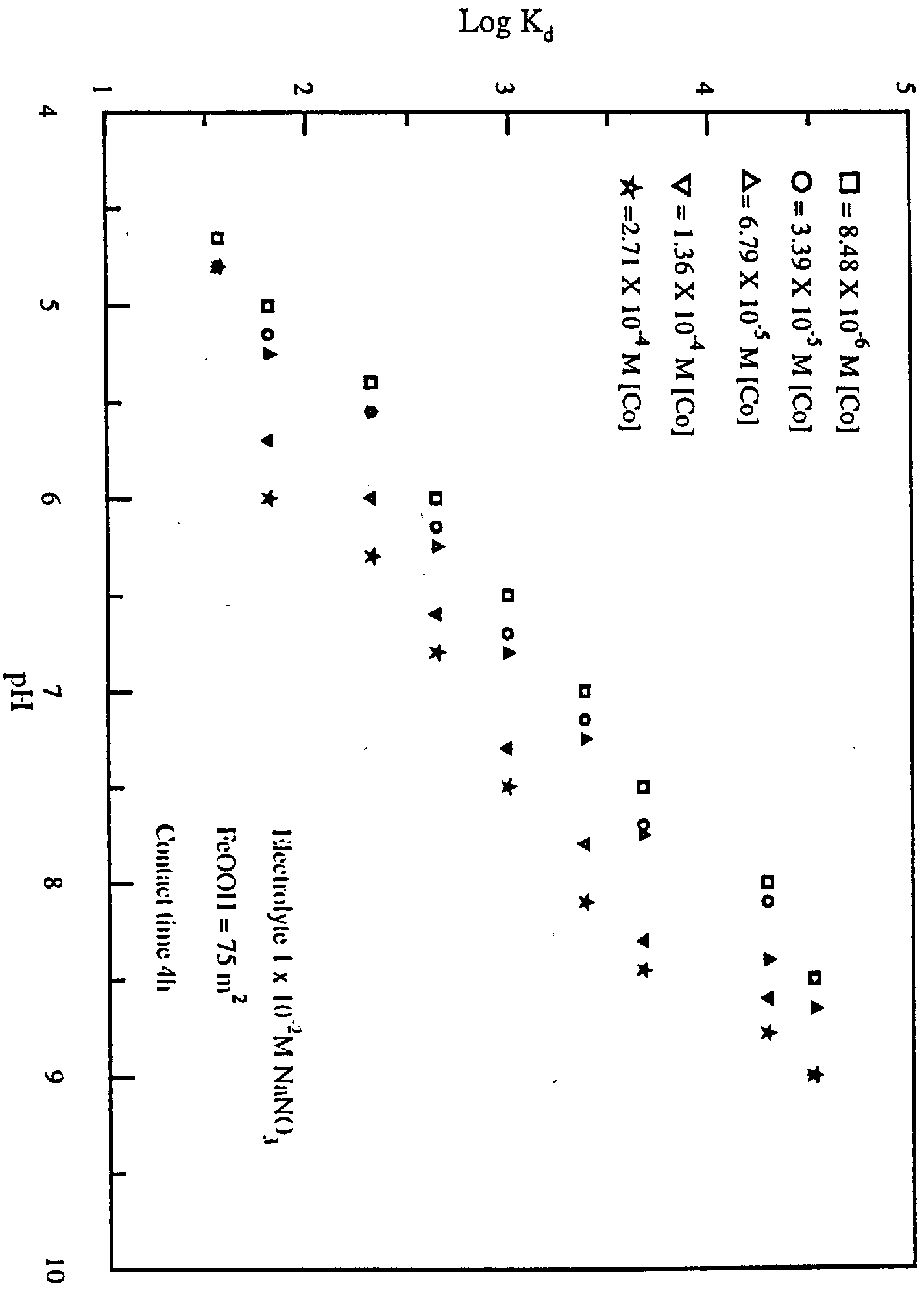
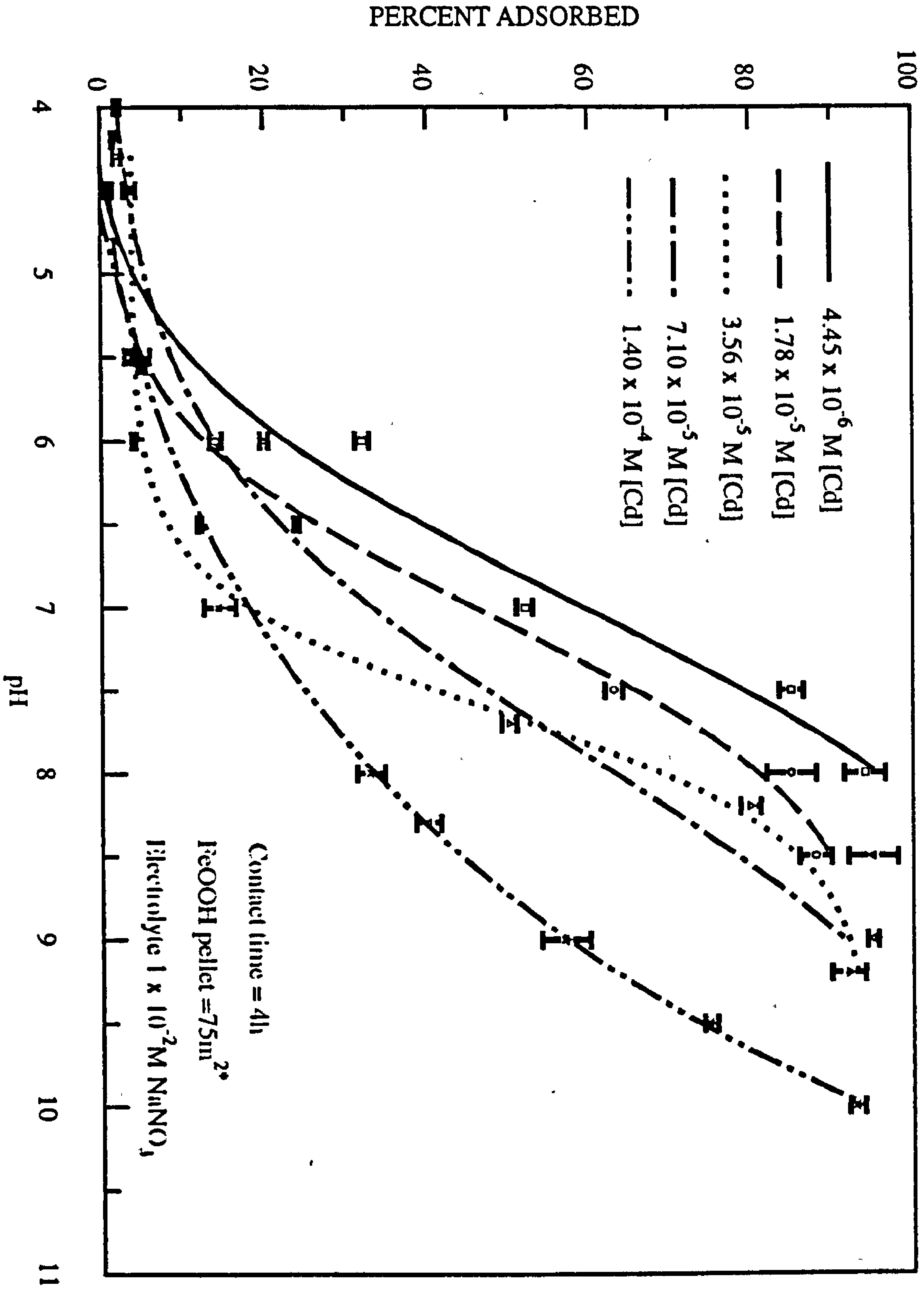
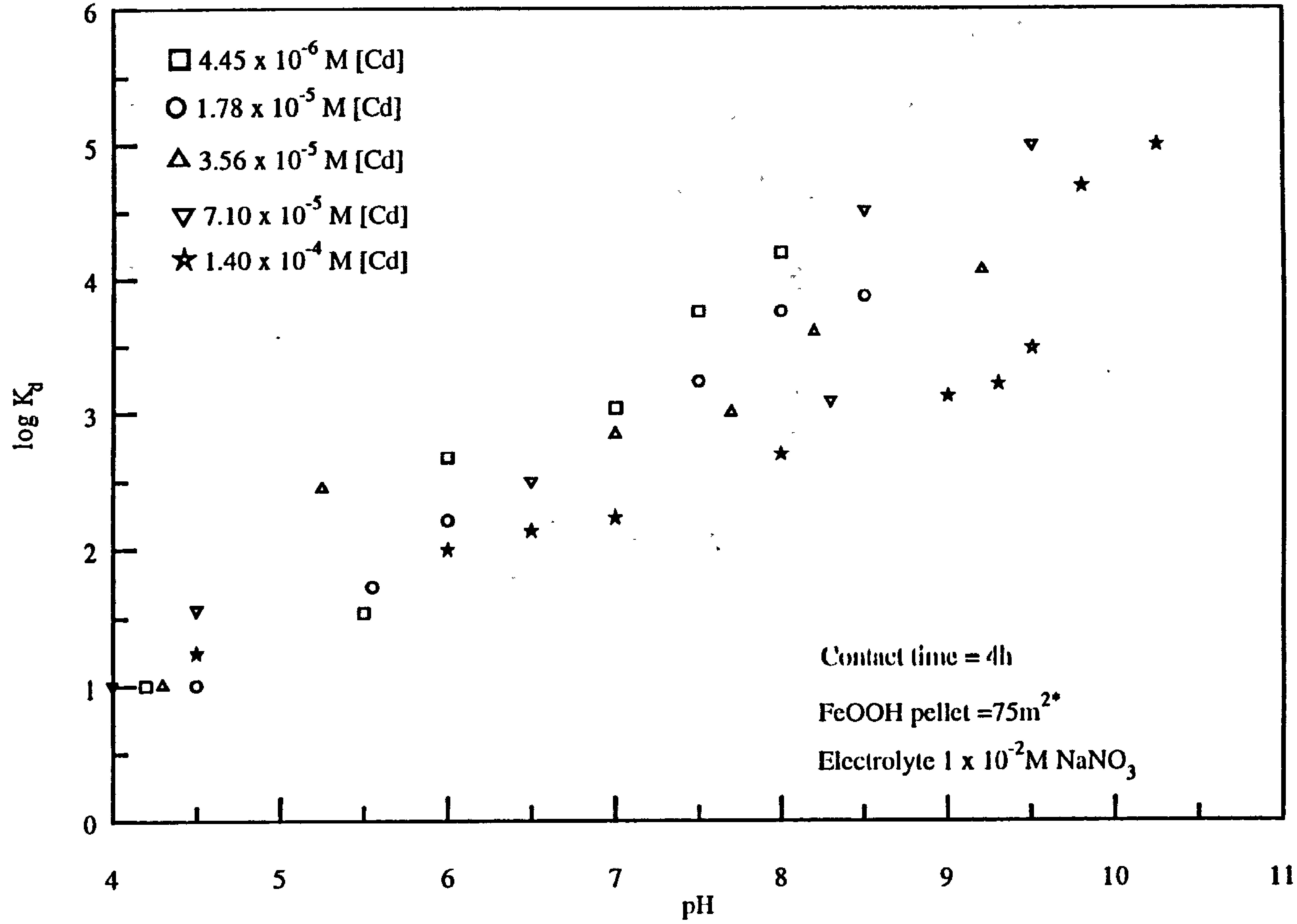


Fig 3.9 K_d of Co adsorption as a function of pH and Co concentration



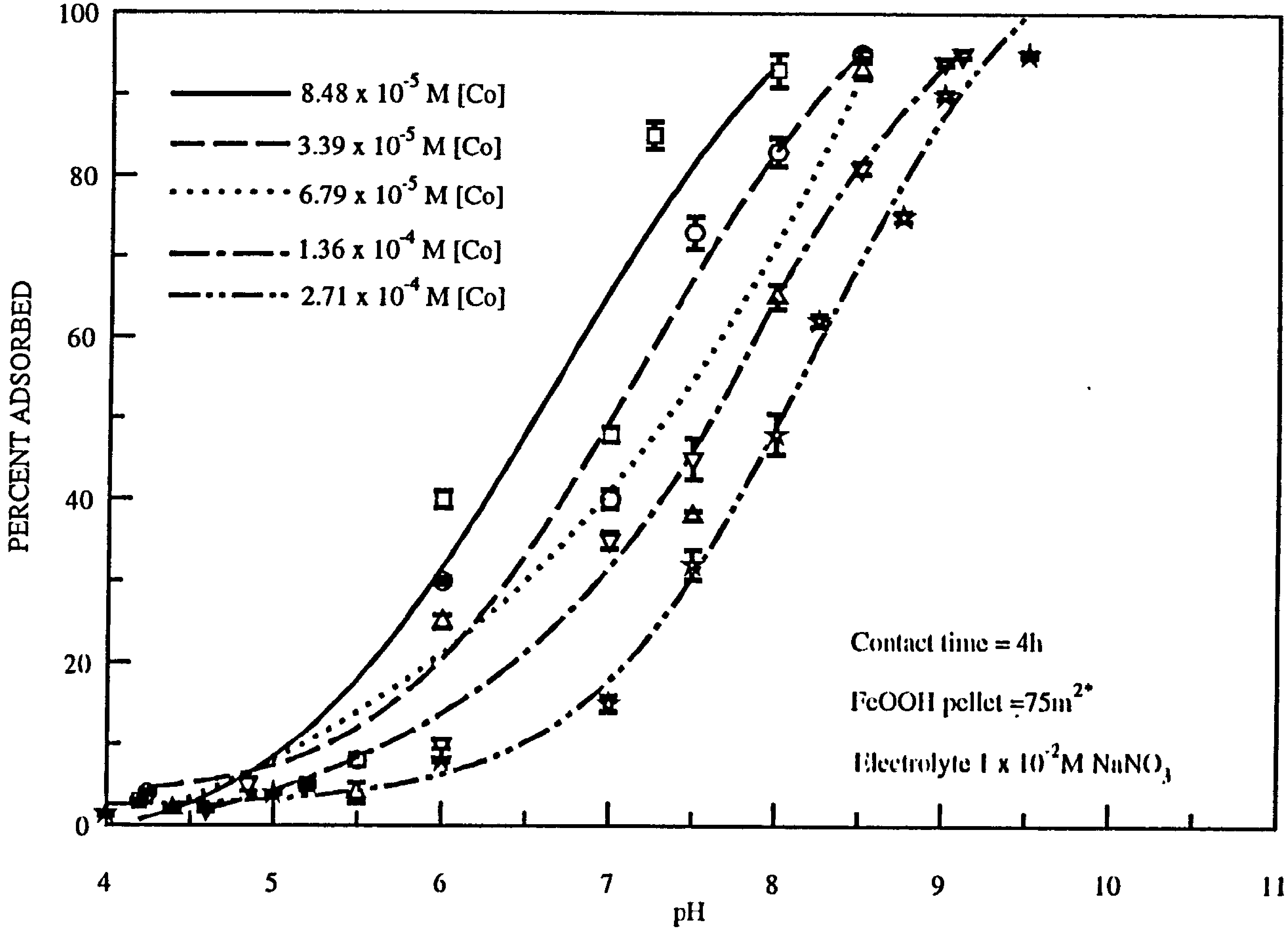
* This is the equivalent amount of goethite to give 75m^2 which is about 1.8g in 100ml

Fig 3.10 Cd adsorption as a function of pH and Cd concentration



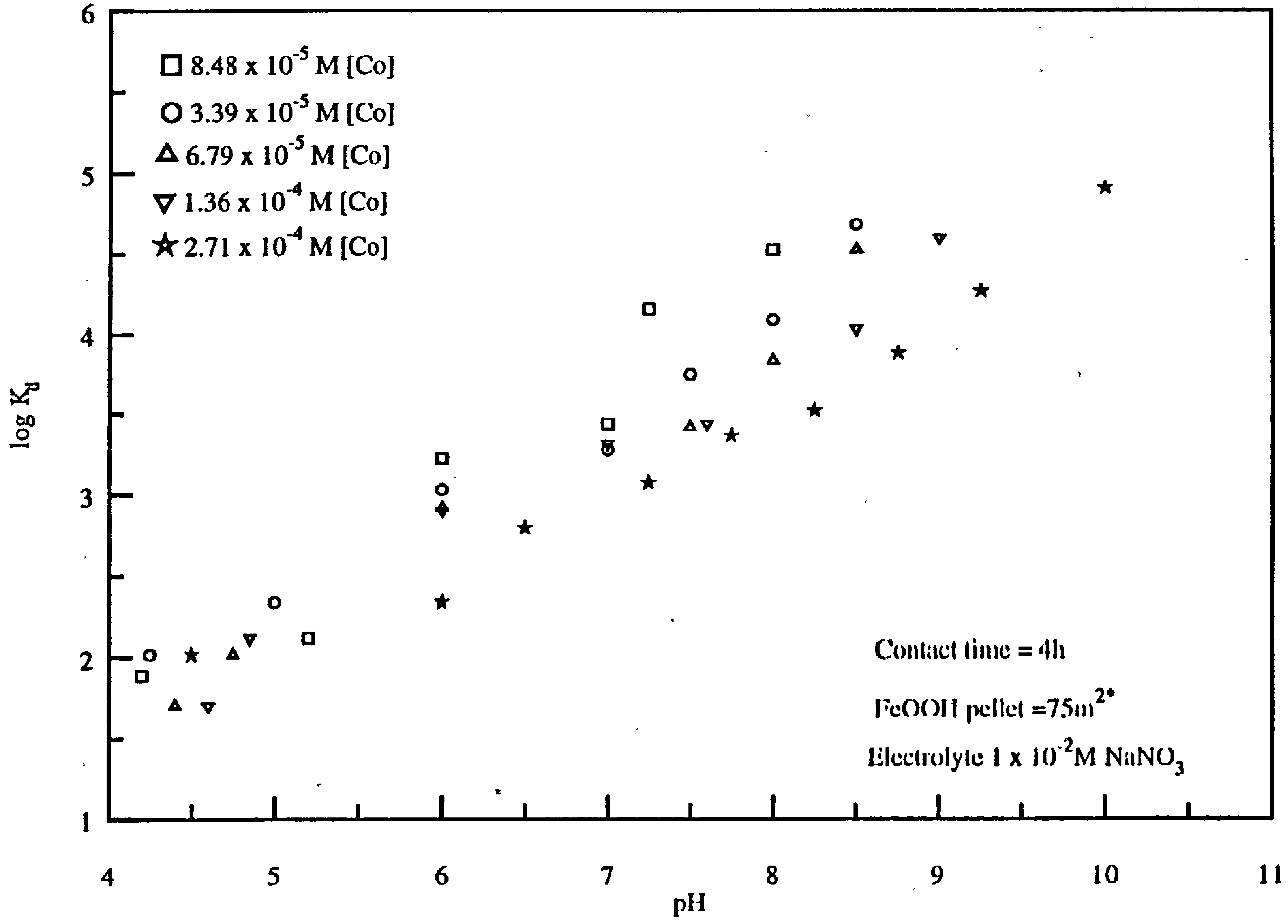
*This is the equivalent amount of goethite to give 75m^2 which is about 1.875 g in 100ml

Fig 3.11 K_d Cd adsorption as a function of pH and Cd concentration



* This is the equivalent amount of pellets to give 75m^2 which is 1.875g in 100ml

Fig 3.12 Co adsorption as a function of pH and Co concentration



* This is the equivalent of goethite to give $75m^2$ which is 1.875 g in 100ml

Fig 3.13 K_d Co adsorption as a function of pH and Co concentration

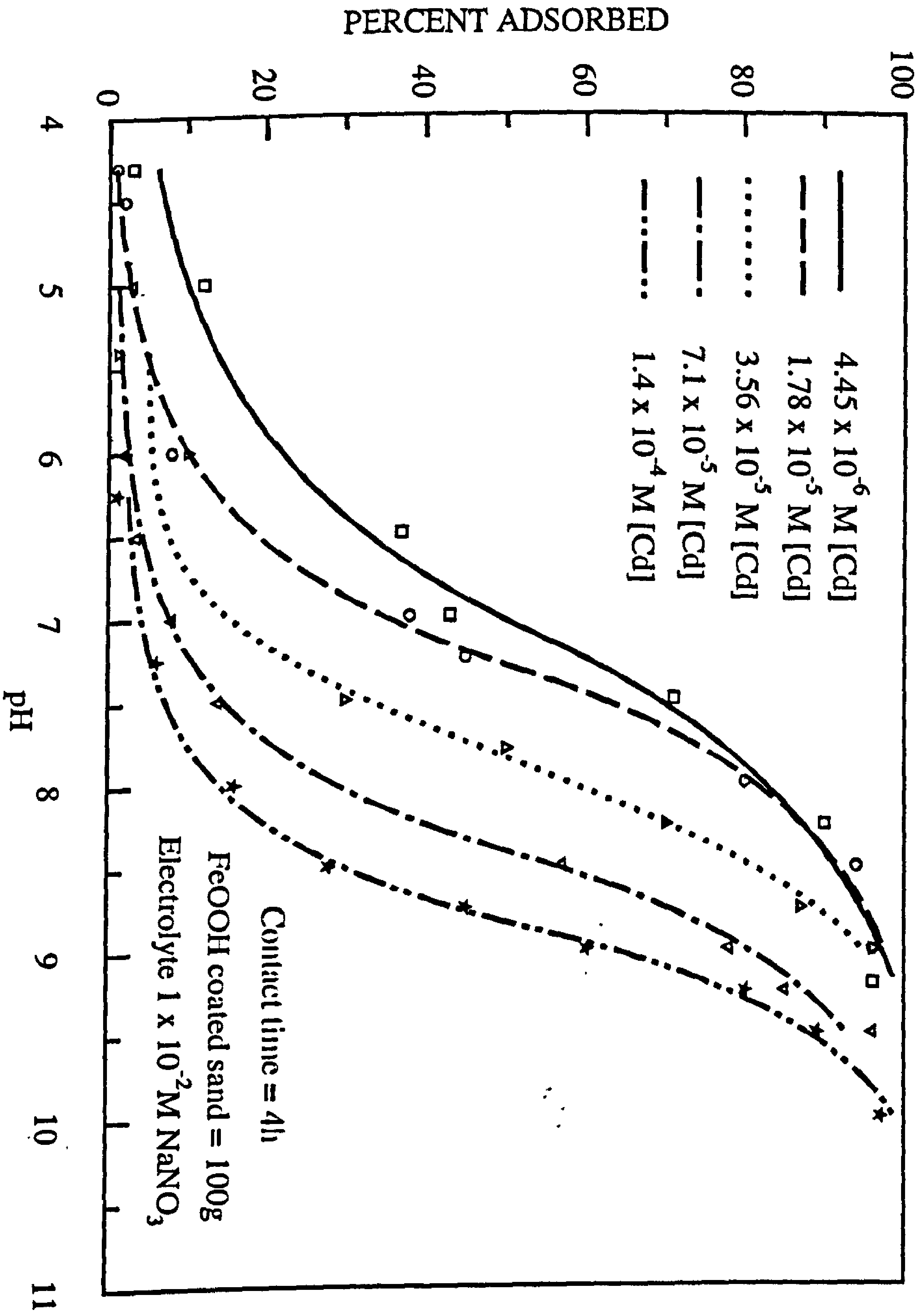


Fig 3.14 Cd adsorption as a function of pH and Cd concentration

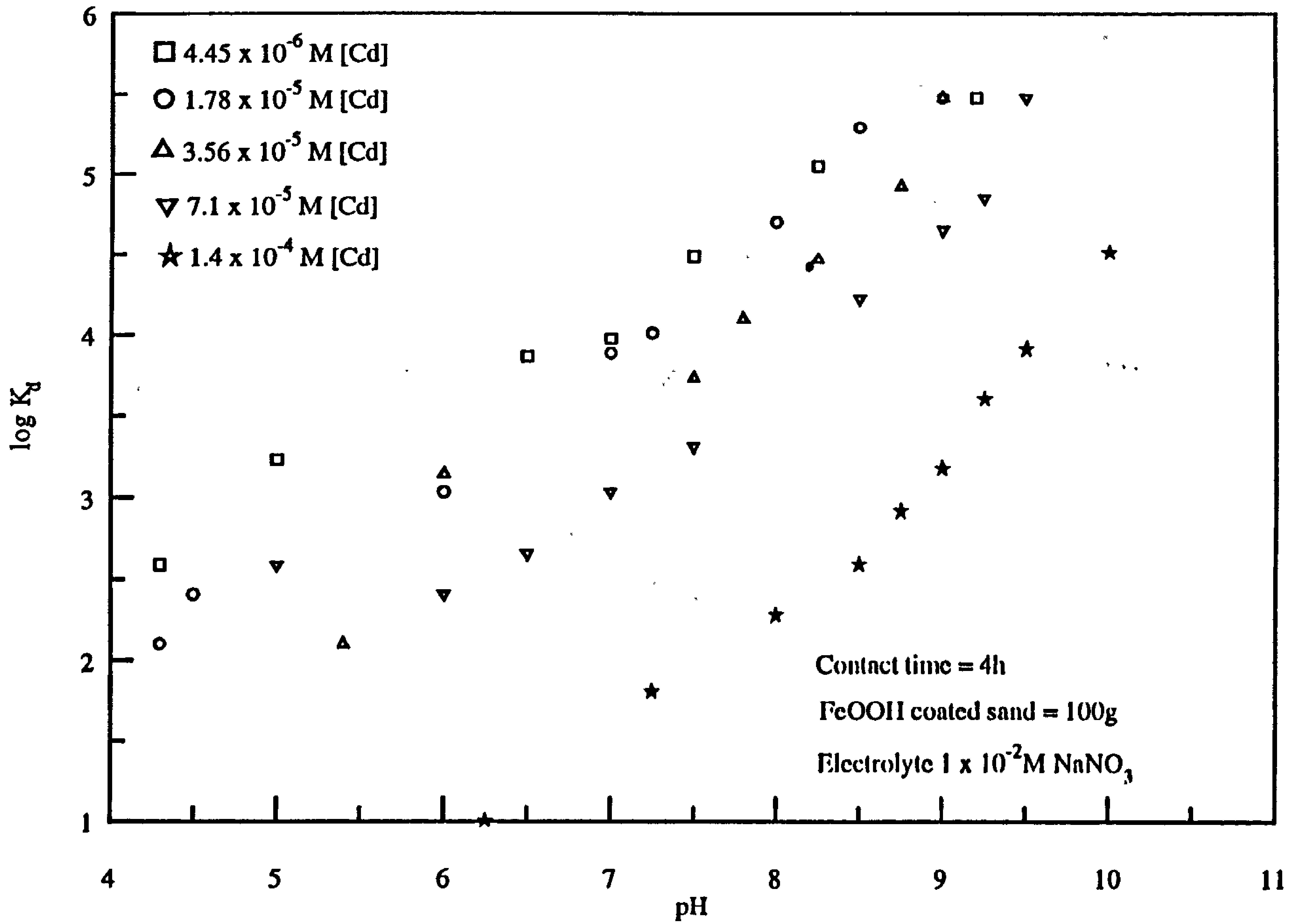


Fig 3.15 K_d Cd adsorption as a function of pH and Cd concentration

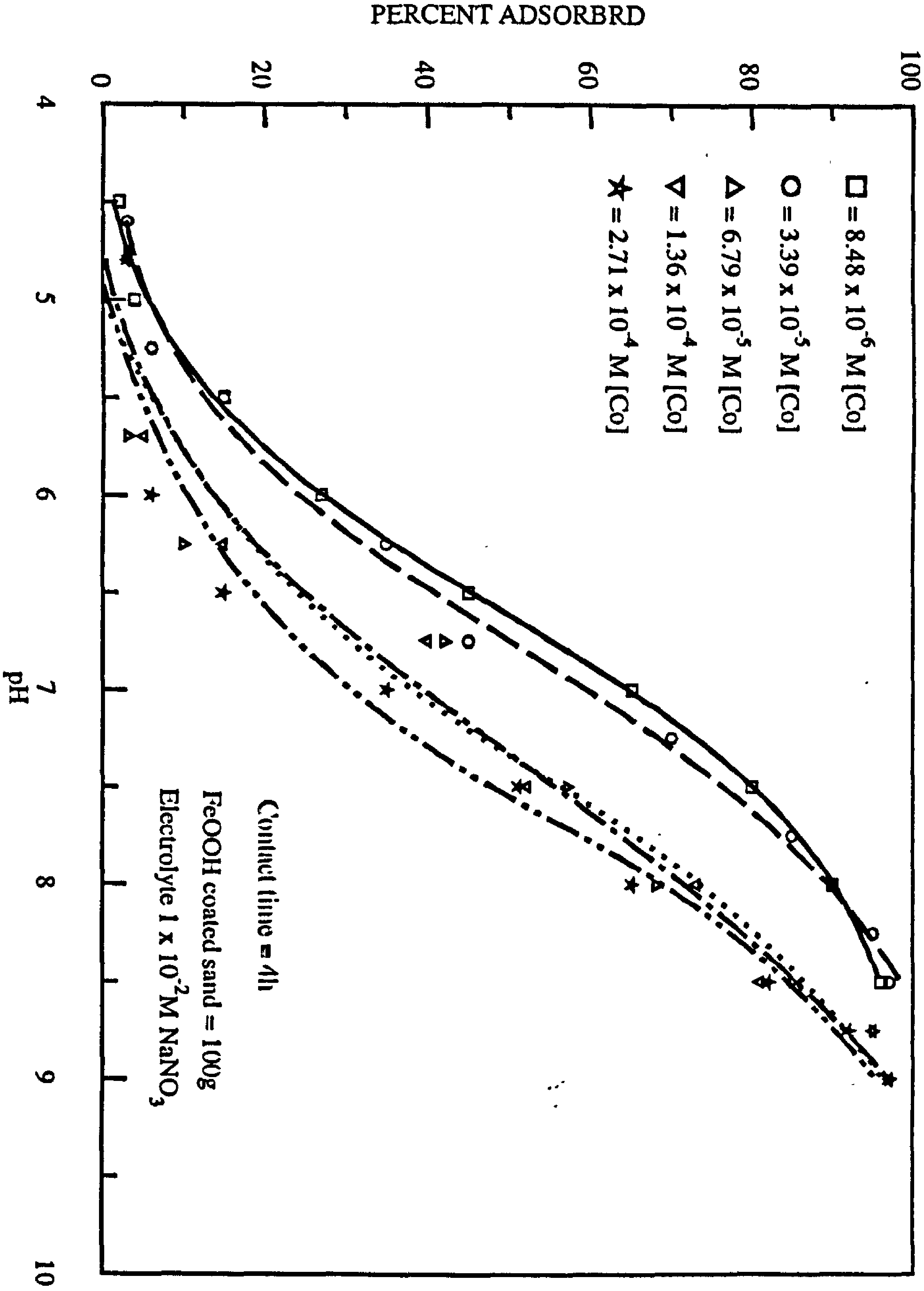


Fig 3.16 Co adsorption as a function of pH and Co concentration

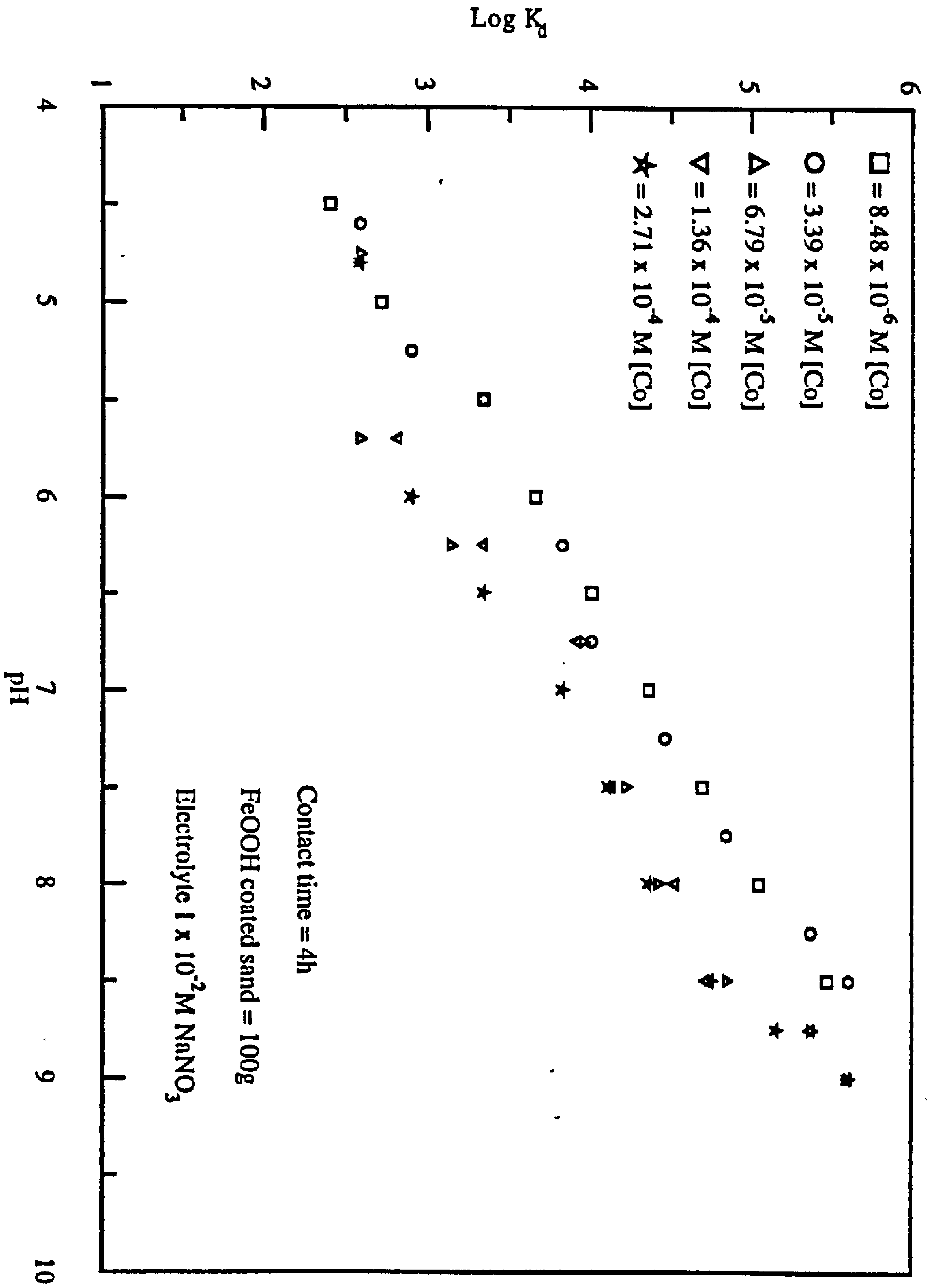


Fig 3.17 K_d of Co adsorption as a function of pH and Co concentration

At a constant pH relative adsorption decreases with increasing initial metal concentration indicating gradual saturation of binding sites. The adsorption curves of the two metals examined are similar in slope and can therefore be compared by their pH at 50% adsorption values (pH_{50}), pH at which fifty percent of the sorbate is adsorbed. The increased pH_{50} values with increasing initial metal concentrations are summarized in Figure 3.18 The decrease in pH_{50} at low concentrations of metals in solution is limited by a value below which the fractional adsorption of metals becomes independent of initial concentration.

The percentages of metal ions adsorbed at different pH values and their relative position on the curves with respect to pH is related to the hydrolysability of the metal ion in solution. Thus the pH values at which 50% of the added amount has been adsorbed from a given initial solution concentration level can be correlated with their respective first hydrolysis constants in solution (pK_i). The hydrolysis constants are the negative logarthims of the acidic dissociation constant for the general proton reactions.

The pH_{50} values of Cd and Co as shown in Table 3.4 are related to the pK_i. The pK_i values for Co and Cd are 8.9 and 9.2 respectively. The hydrolytic properties of the two metals affect adsorption on to goethite surfaces. It is clear that the lower pK value of Co corresponds to lower pH_{50} values, and thus characterizes a higher adsorption affinity of Co for goethite. The higher pK , values of Cd and the corresponding higher pH_{50} values of cadmium indicate the lower affinity of the metals for goethite. Adsorption must be controlled to an extent by hydrolytic reactions of the metal on the oxide surfaces. However, variations in contact time and temperature can cause significant changes in the metal's affinity for goethite.

Cadmium		Cobalt	
Con. (M)	pH_{50}	Con. (M)	pH_{50}
4.45×10^{-6}	6.90	8.48×10^{-6}	6.50
1.78×10^{-5}	7.32	3.39×10^{-5}	6.70
3.66×10^{-5}	7.50	6.79×10^{-5}	6.95
7.10×10^{-5}	8.27	1.36×10^{-4}	7.30
1.41×10^{-4}	8.72	2.71×10^{-4}	7.50

Table 3.4 Cd and Co concentration and their corresponding pH_{50} at constant goethite concentration

3.6.2 Effect of Contact times

The adsorption curves of Cd and Co are shown in Figures 3.19 and 3.20 for an initial metal concentration of 1.78×10^{-5} M [Cd] and 3.39×10^{-5} M [Co]. The curve shifted to lower pH as contact time increases. With increasing contact time from 4 - 120 h at room temperature the adsorbed amounts of Co at pH 6.7 increased from 50 to 78% and shows an increase of 28%. The corresponding increases in the Cd adsorption are 33%. This shows that at higher pH and longer contact times more Cd is adsorbed than Co, but at the lower pH more Co is adsorbed. Nevertheless, it does not change the general affinity ranking of the two metals. There is similarity in the effects of contact time and temperature which indicate that both parameters act in the same way and seem compatible.

The continuous increase in the amount adsorbed with prolonged contact time is reflected by a decrease in pH_{50} as a function of time. Differences in the rates of reaction of the metals lead to differences in the measured relative affinities of the metals for goethite. At the contact times of 4 - 120h the pH_{50} value is highest for Cd. The general adsorption affinity for goethite is Co >Cd.

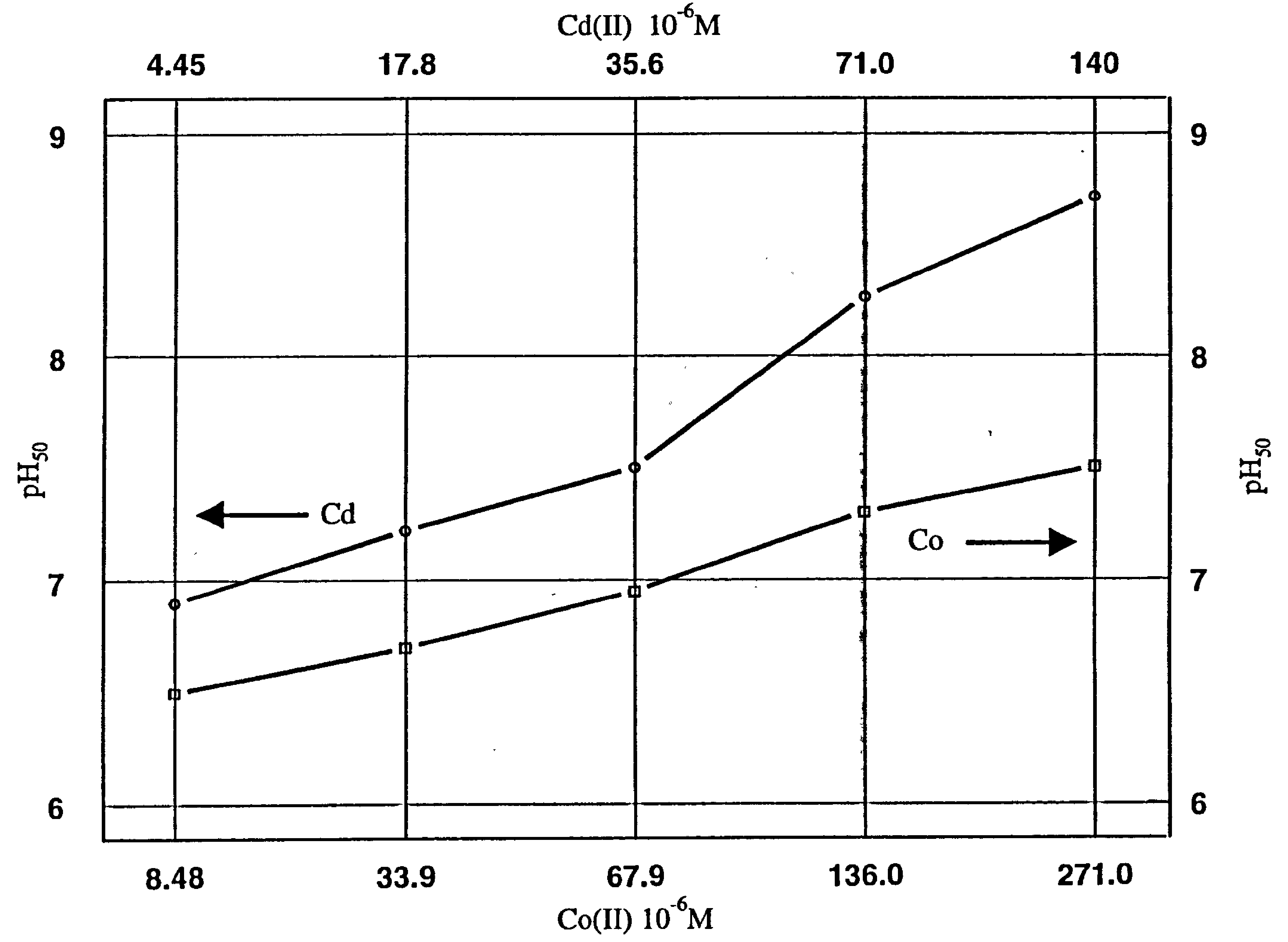


Fig 3.18 Cd and Co adsorption at pH_{50} at diffrent concentration onto goethite dispersion

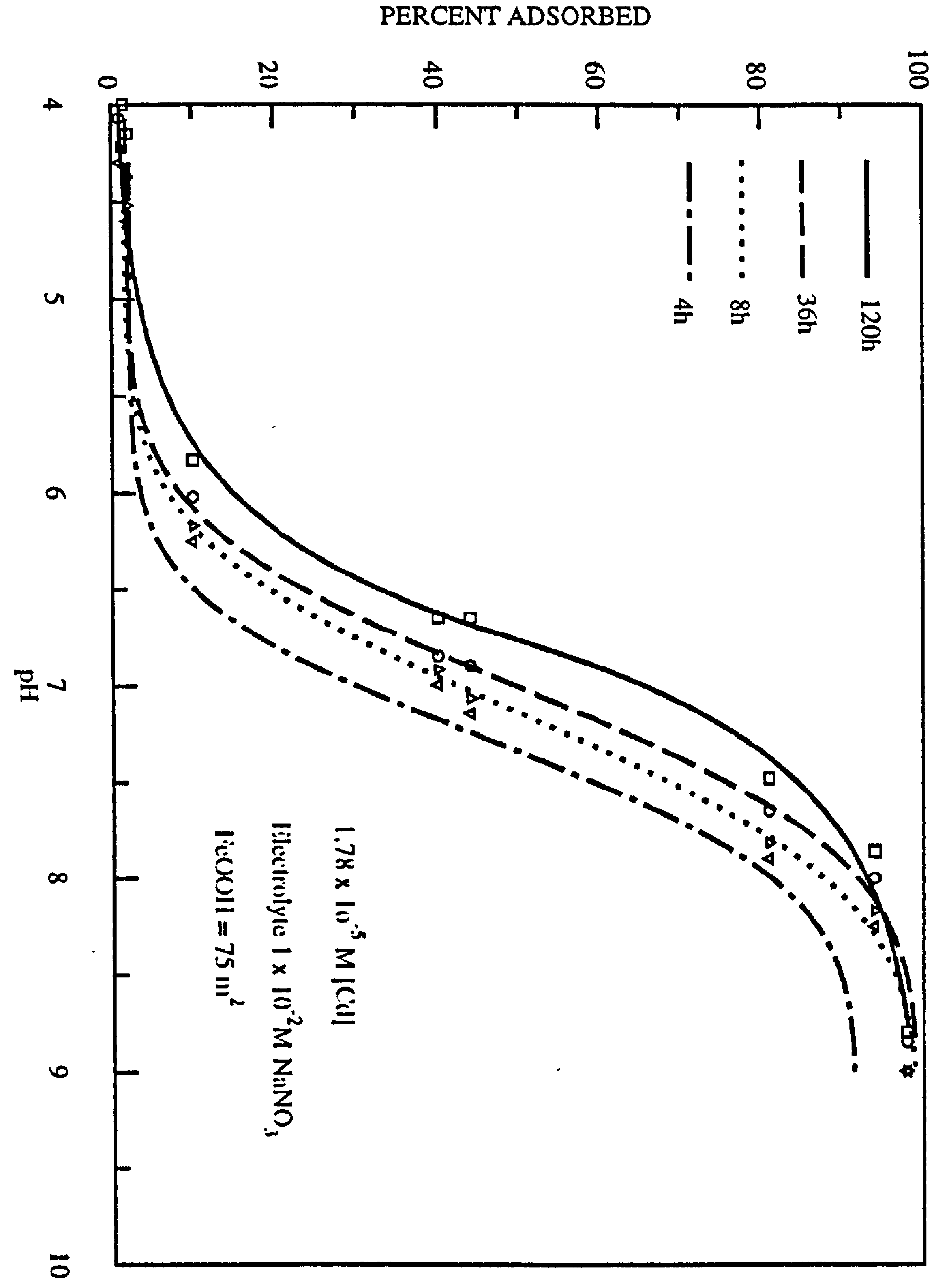


Fig 3.19 Cd adsorption as a function of pH and reaction time

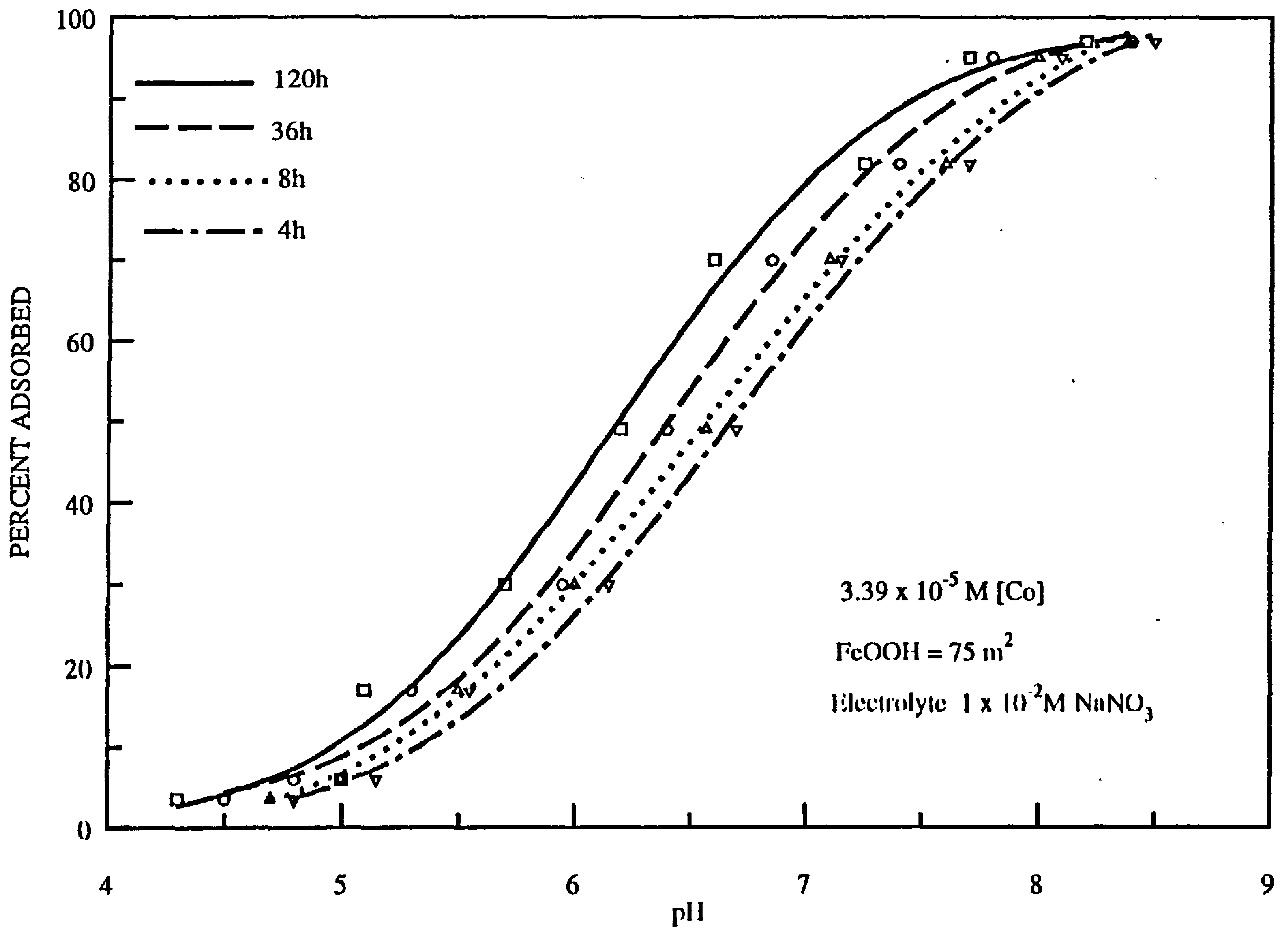


Fig 3.20 Co adsorption as a function of pH reaction time

3.6.3 Effect of temperature

The adsorption of Cd and Co was studied for an initial metal concentration of 1.78×10^{-5} M [Cd] and 3.39×10^{-5} M [Co]. Four temperature ranges were studied (12, 24, 35, and 45°C) at the given initial cadmium and cobalt concentrations for a contact time of 4 hours. The results are shown in Figures 3.21 & 3.22 and show that the adsorption edge is shifted to lower pH values as the temperature is increased. Figure 3.21 shows that for initial cadmium concentrations of 1.78×10^{-5} M, at any pH in the range from pH 6 to 9 more cadmium is adsorbed from solution at higher temperatures. The same figure also shows that at pH 6.5, the percent cadmium adsorbed rises from 10 % at 12 °C to 35% at 45 °C. At pH 7.0, the percent cadmium adsorbed increases from 30% at 12 °C to 58 % at 45 °C.

Table 3.5 shows the pH_{50} data in relation to temperature. The pH given at each concentration and temperature is that required for 50% adsorption of the initial cadmium and cobalt concentration. Both temperature and contact time are seen to have a marked effect on adsorption. Higher temperatures and longer contact times cause a decrease in $pH_{50\%ads}$. The effect of temperature is shown in Table 3.5, which indicates that the pH required to adsorb 50% of the cobalt decreases by 0.65 pH unit over the temperature range from 12 to 45 °C.

The continuous increase in the amount adsorbed with prolonged contact time and increasing temperature is reflected by a decrease of pH_{50}. The steepness of the slopes for the relationships between pH_{50} values and temperature indicates a rising preference of goethite for Co relative to Cd with increasing temperatures. At 12°C the pH_{50} values for Co and Cd are high and drop as temperature rises. The sequence in the affinity for goethite remains as Co > Cd even when considering the combination of contact time and temperature. The differences between the pH_{50} values at different contact times have increased for both metals with the increase in contact time and temperatures.

Cadmium 1.78×10^{-5} M		Cobalt 3.39×10^{-5} M	
Temp. (°C)	pH_{50}	Temp. (°C)	pH_{50}
12	7.90	12	6.85
24	7.25	25	6.70
35	6.90	35	6.30
45	6.80	45	6.20

Table 3.5 Variation in pH_{50} with constant initial metal concentration and varying temperature

3.6.4 Effect of oxide concentration

The adsorption of cadmium and cobalt at the three surfaces of the oxide were studied at constant temperature and contact time. Figures 3.23 - 3.26 show adsorption curves and their respective K_d, with the range of surface area studied (40, 75, 300 m^2/l) at constant metal concentration the percentage of cations adsorbed decreases with a decrease in surface area. At low surface area, the number of binding sites per cation is relatively low and the cation has to compete with other cations for the available binding sites. As a result, the percentage of cations adsorbed decreases. However, as the surface area is increased at constant metal concentrations the number of binding sites is sufficient for cations not to have to compete for available sites.

Figures 3.23 and 3.25 show the effect of the goethite surface area on the adsorption edge at a cadmium and cobalt concentration of 1.78×10^{-5} M [Cd] and 3.39×10^{-5} M [Co]. The adsorption edge has moved to a lower pH with an increase in the goethite surface area. At constant pH with an increase in surface area, more goethite is present in the suspension to remove cations. As a result, the percentage of cations adsorbed increases, which results in the shift of an adsorption edge to a lower pH with an almost fourfold increase in the surface area, the adsorption edge moved by more than half a pH unit.

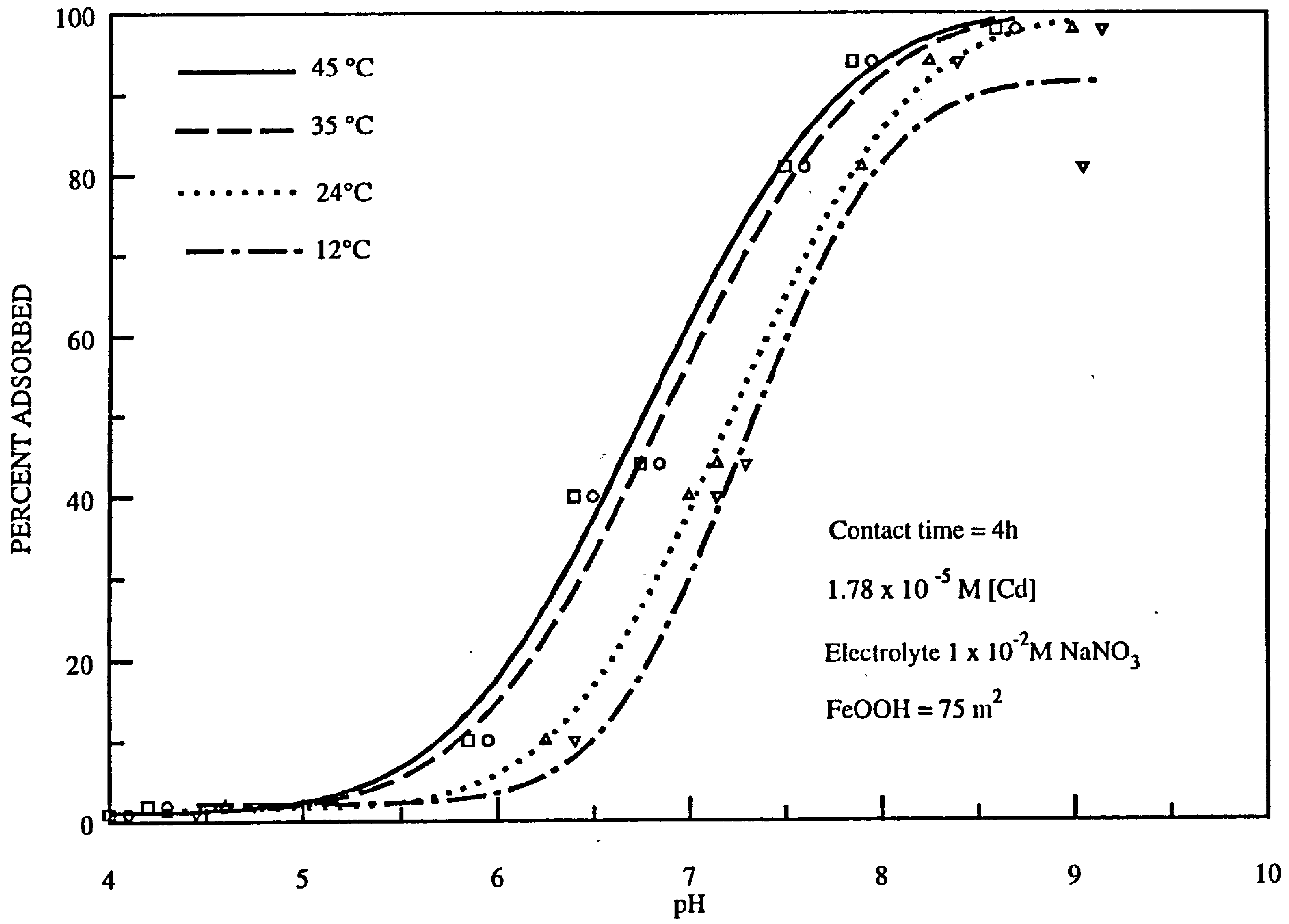


Fig 3.21 Cd adsorption as a function of pH and temperature

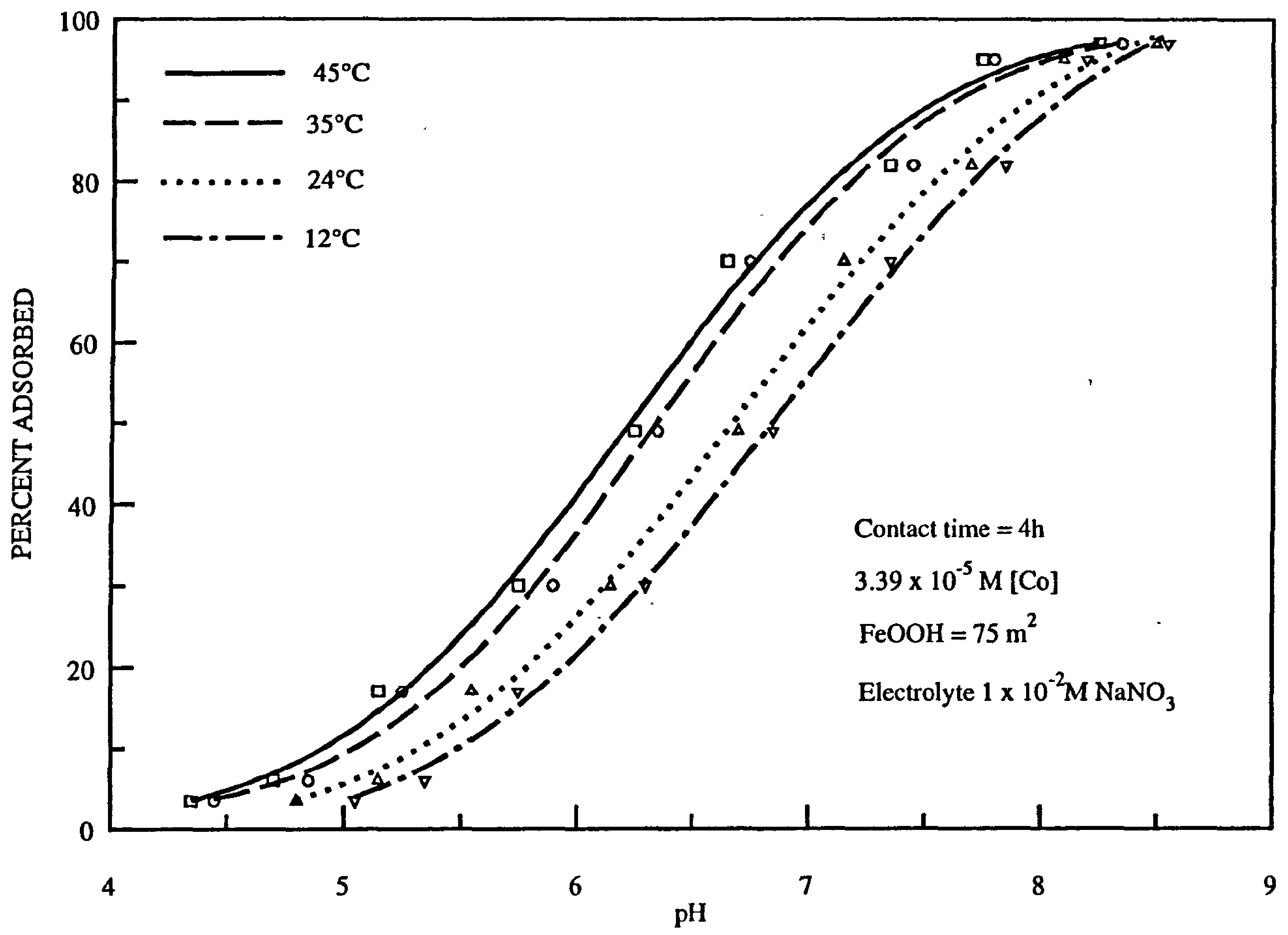


Fig 3.22 Co adsorption as a function of pH and temperature

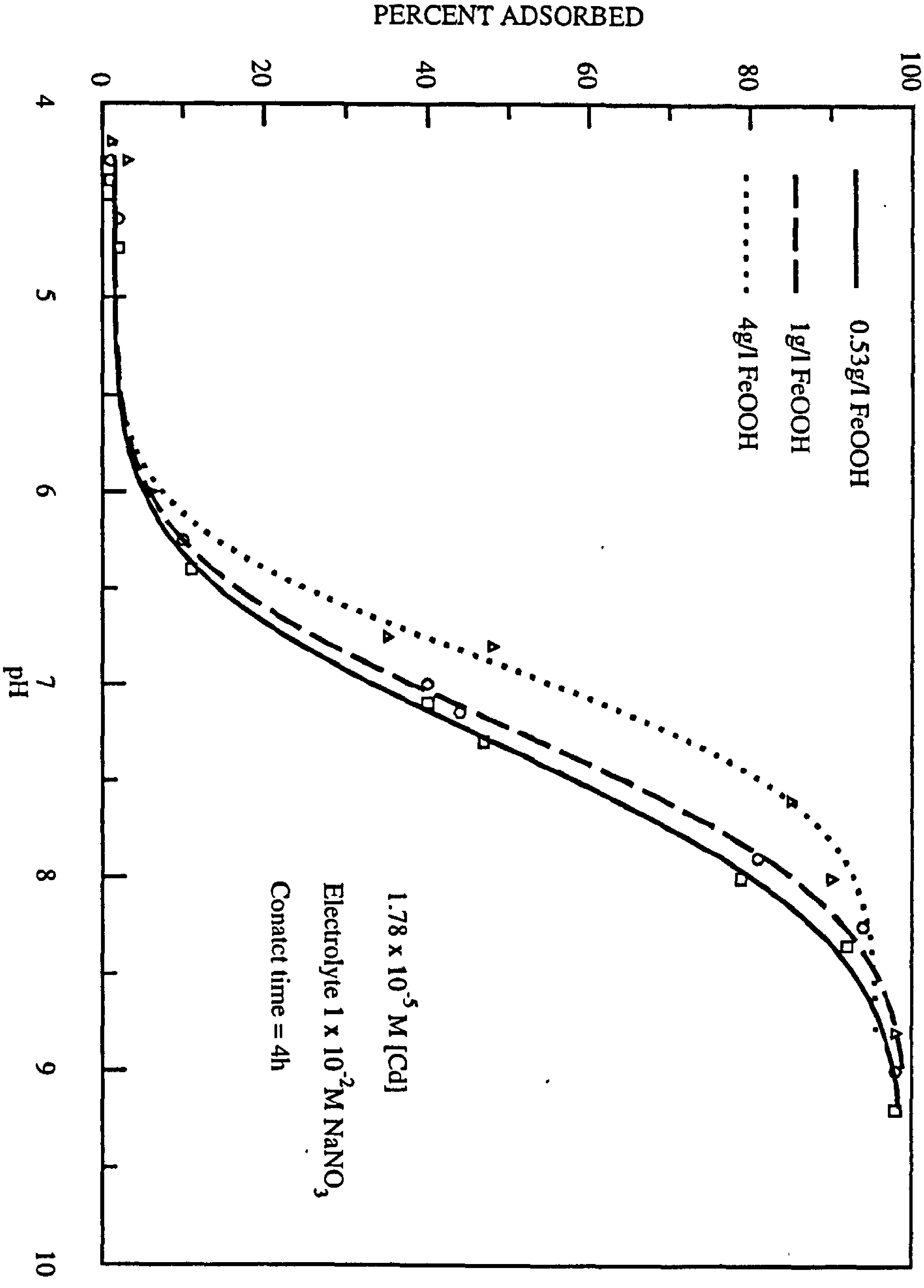


Fig 3.23 Cd adsorption as a function of FeOOH concentration

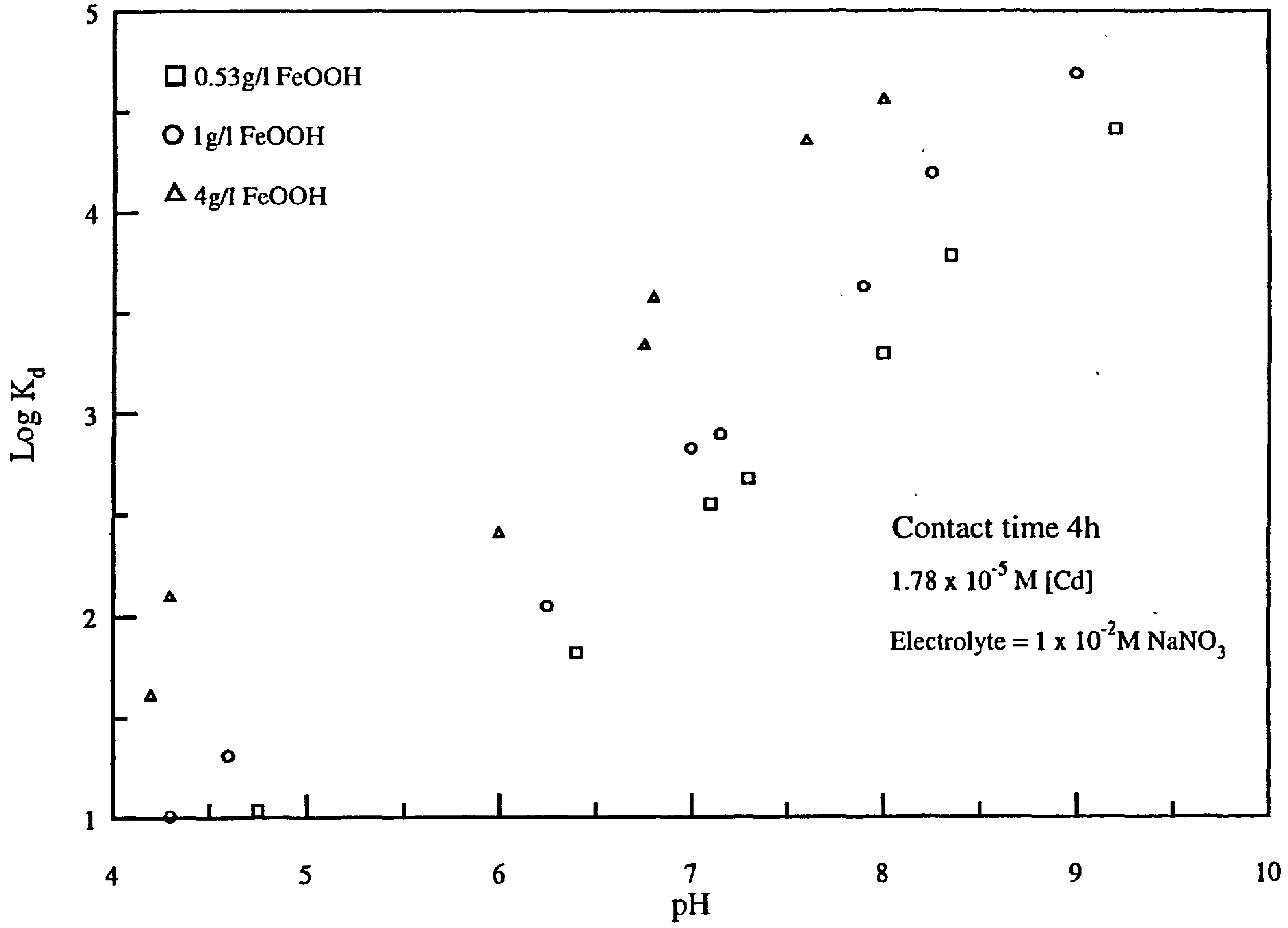


Fig 3.24 K_d of Cd adsorption as a function of FeOOH concentraion

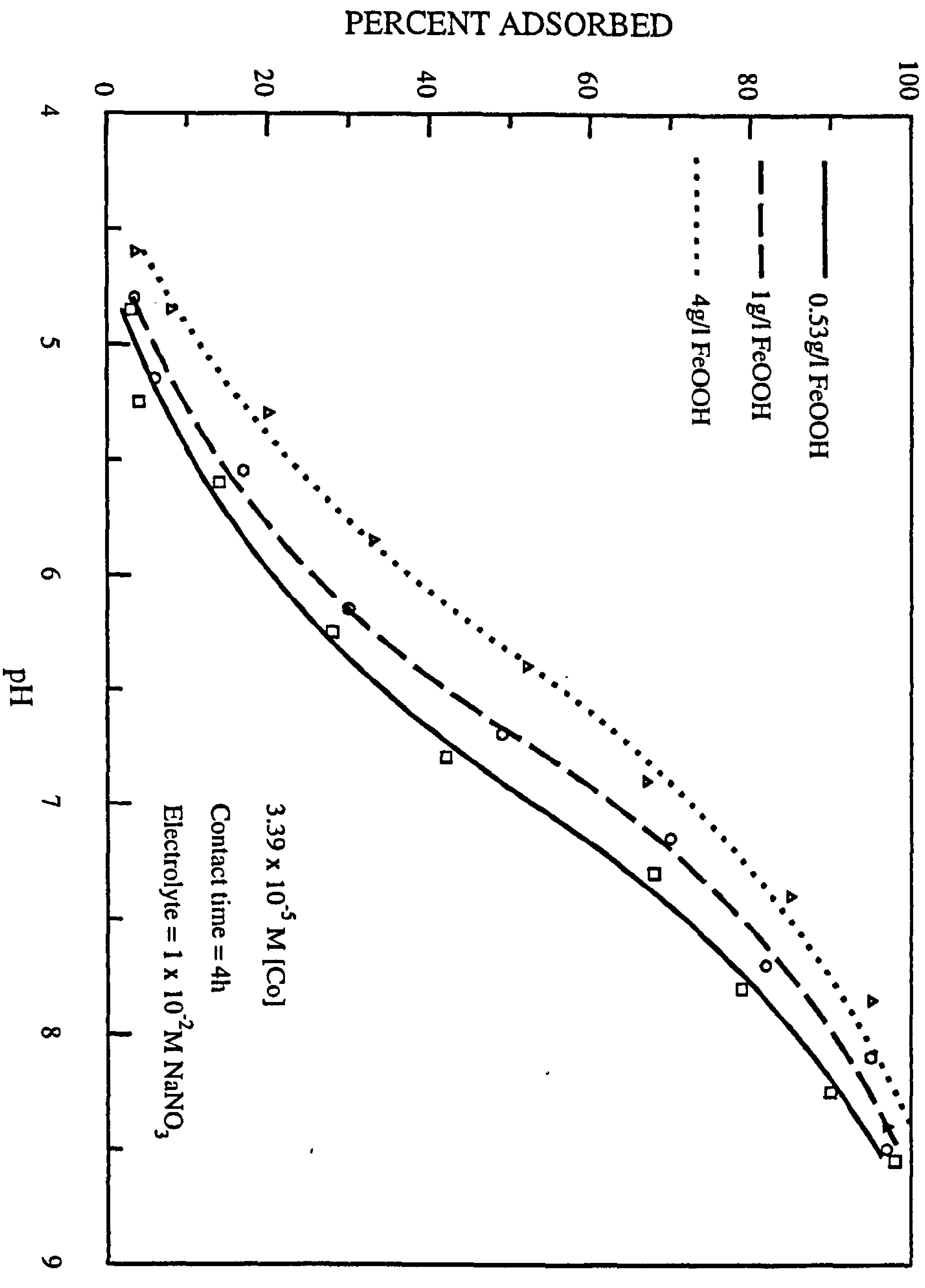


Fig 3.25 Co adsorption as a function of FeOOH concentration

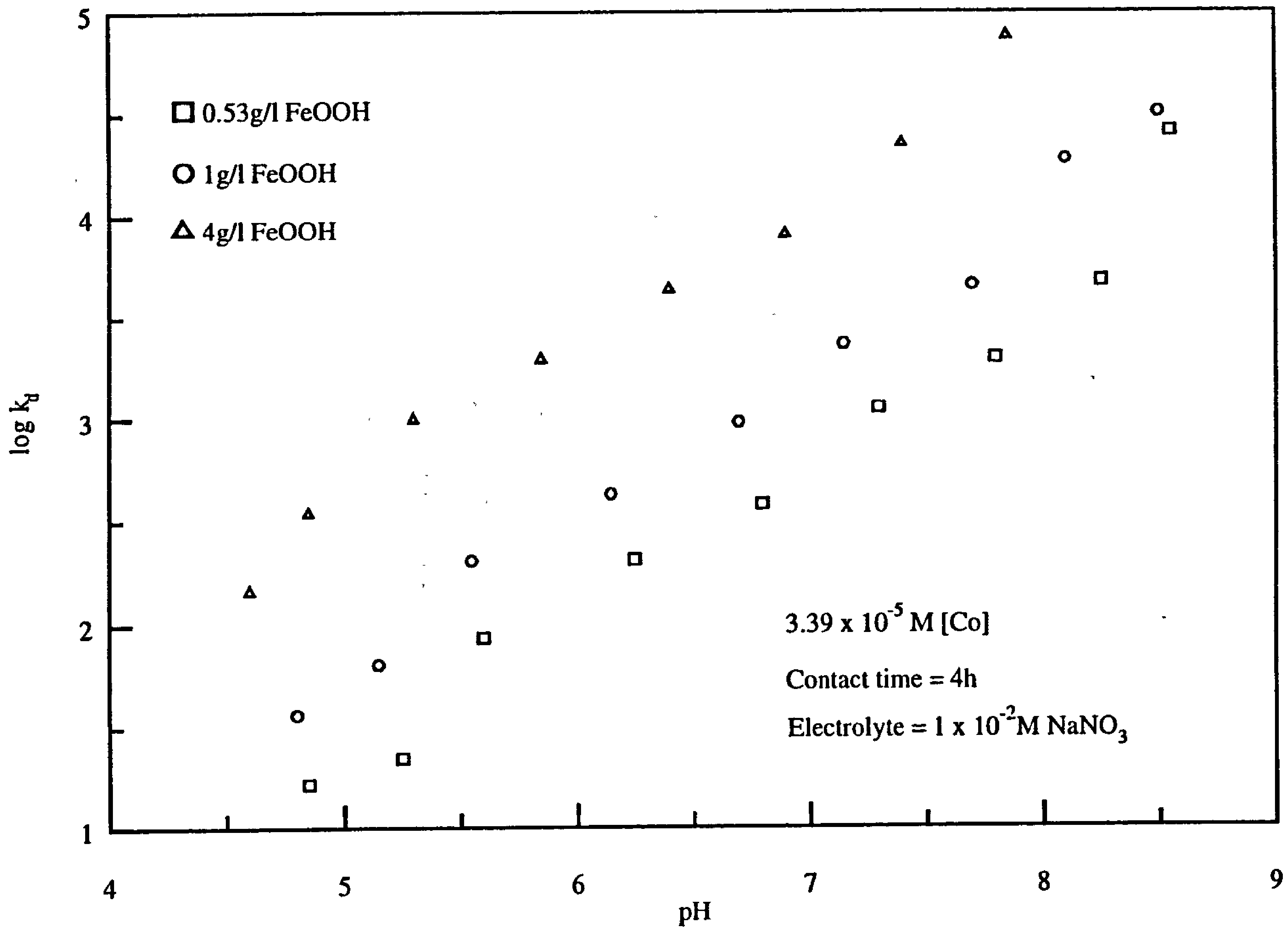


Fig 3.26 K_d Co adsorption as a function of FeOOH concentration

3.6.5 Effect of electrolyte concentrations

The effect of electrolyte concentrations on the adsorption capacity of goethite at constant metal concentration as a function of pH was studied. An increase in concentration from 0.001 M to 0.1 M $NaNO_3$ does not affect the adsorption of cobalt or cadmium as shown in Figures 3.27 & 3.28. This is not unusual, considering that nitrate does not significantly complex with cadmium and cobalt , and sodium and nitrate do not strongly interact with the goethite surface.

3.6.6 Effect of electrolyte composition

The effect of anion type on the adsorption capacity of goethite was also studied as a function of pH at constant metal concentration. Adsorption of cadmium (II) and cobalt (II) from an initial solution concentration of 1.78 x 10^{-5} M [Cd] and 3.39 x 10^{-5} M [Co] as a function of pH in the presence of nitrate or chloride (10^{-2} M NaNO3 or NaCI) shows that there is little difference in the rate of adsorption in the presence of nitrate or chloride as shown in Figures 3.29 and 3.30 The relative effect of anion type is observable at low pH values as more is adsorbed in the presence of chloride but the overall effect is not sufficient to draw a distinction between the two. The observed difference at low concentration and pH may be due to a low surface-promoted hydrolysis. In, general there is no change that resulted in any change in the order of affinity of goethite for metals.

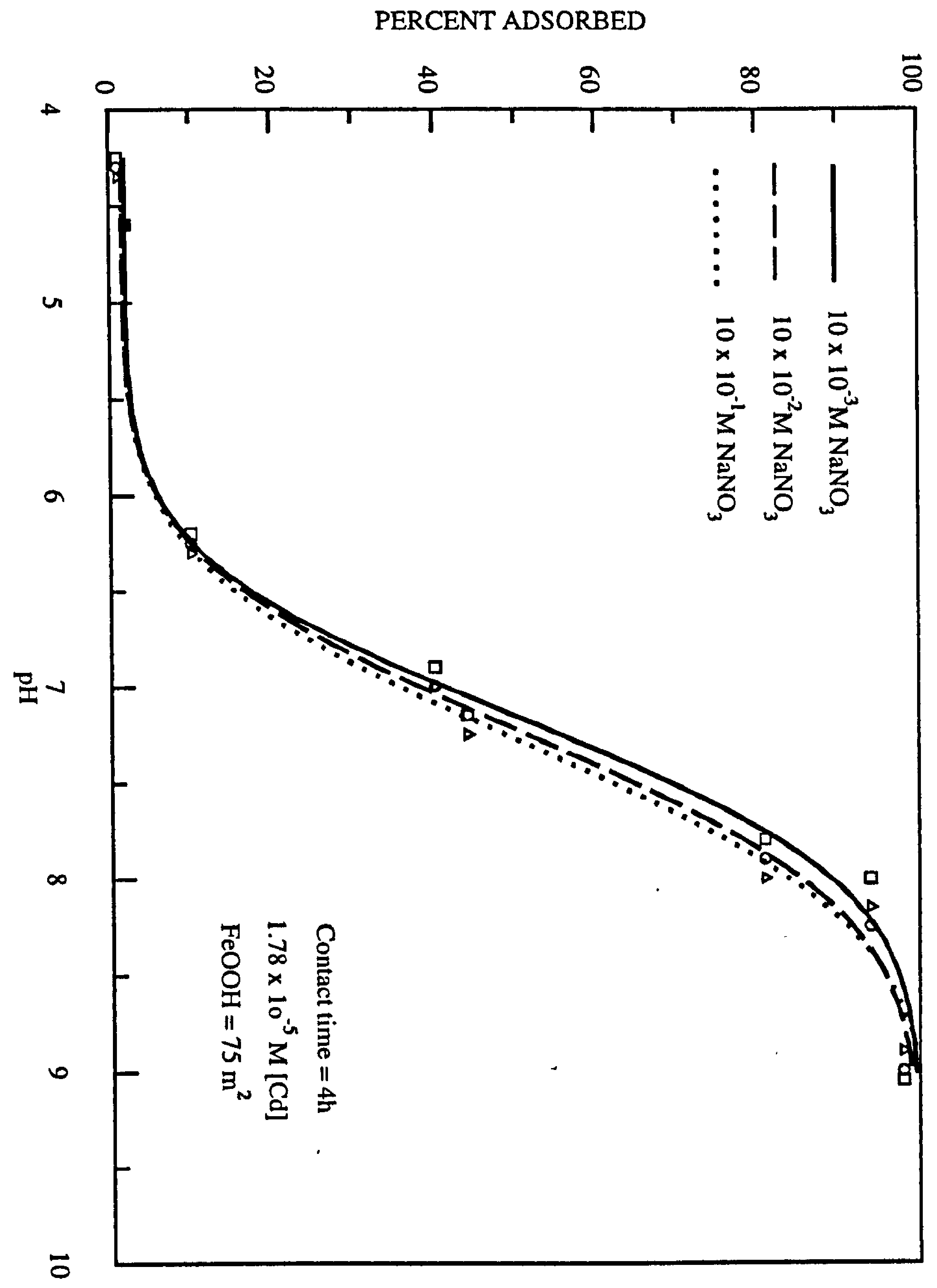


Fig 3.27 Cd adsorption as a function of pH and electrolyte concentration

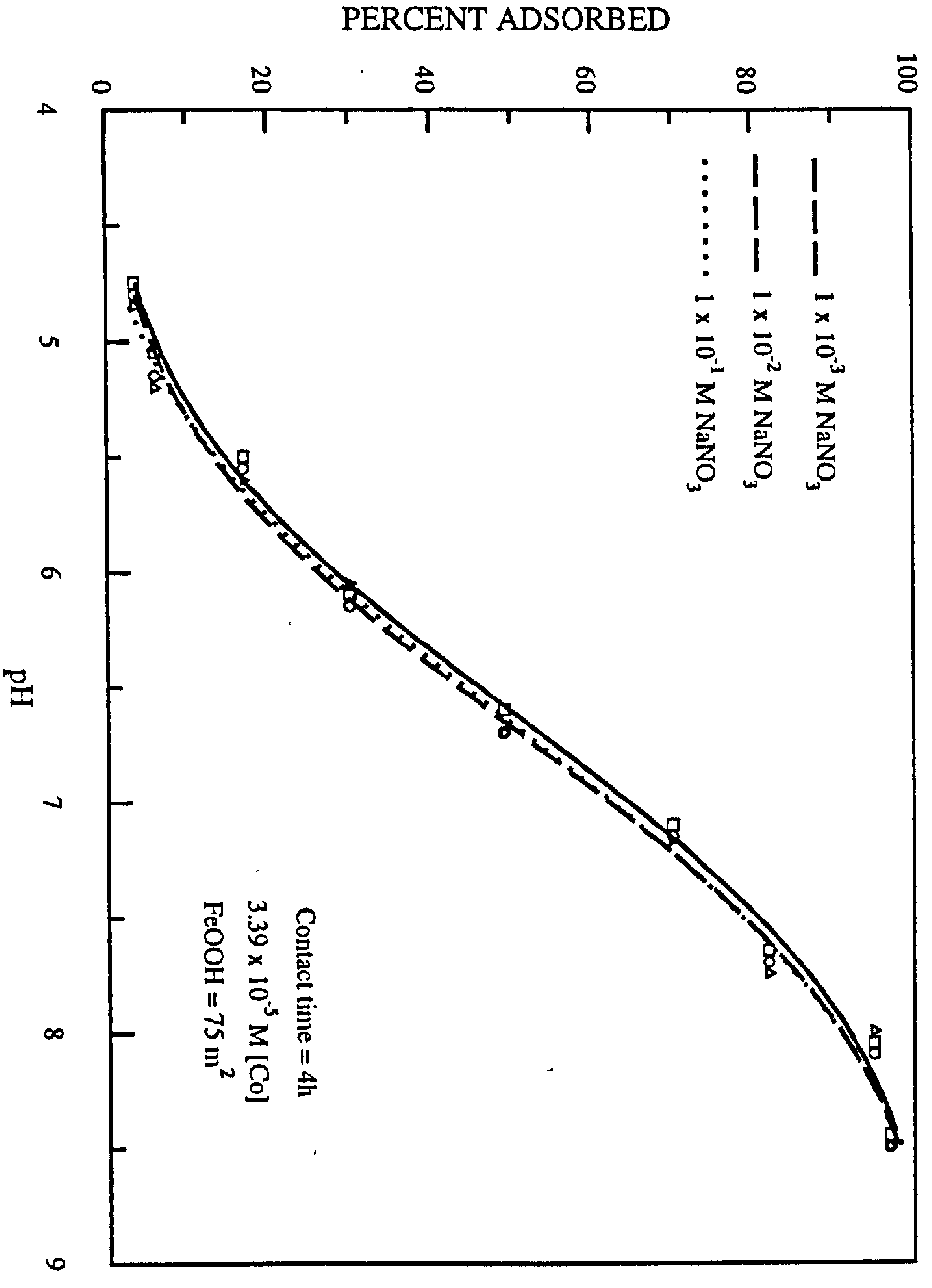


Fig 3.28 Co adsorption as a function of pH and electrolyte concentration

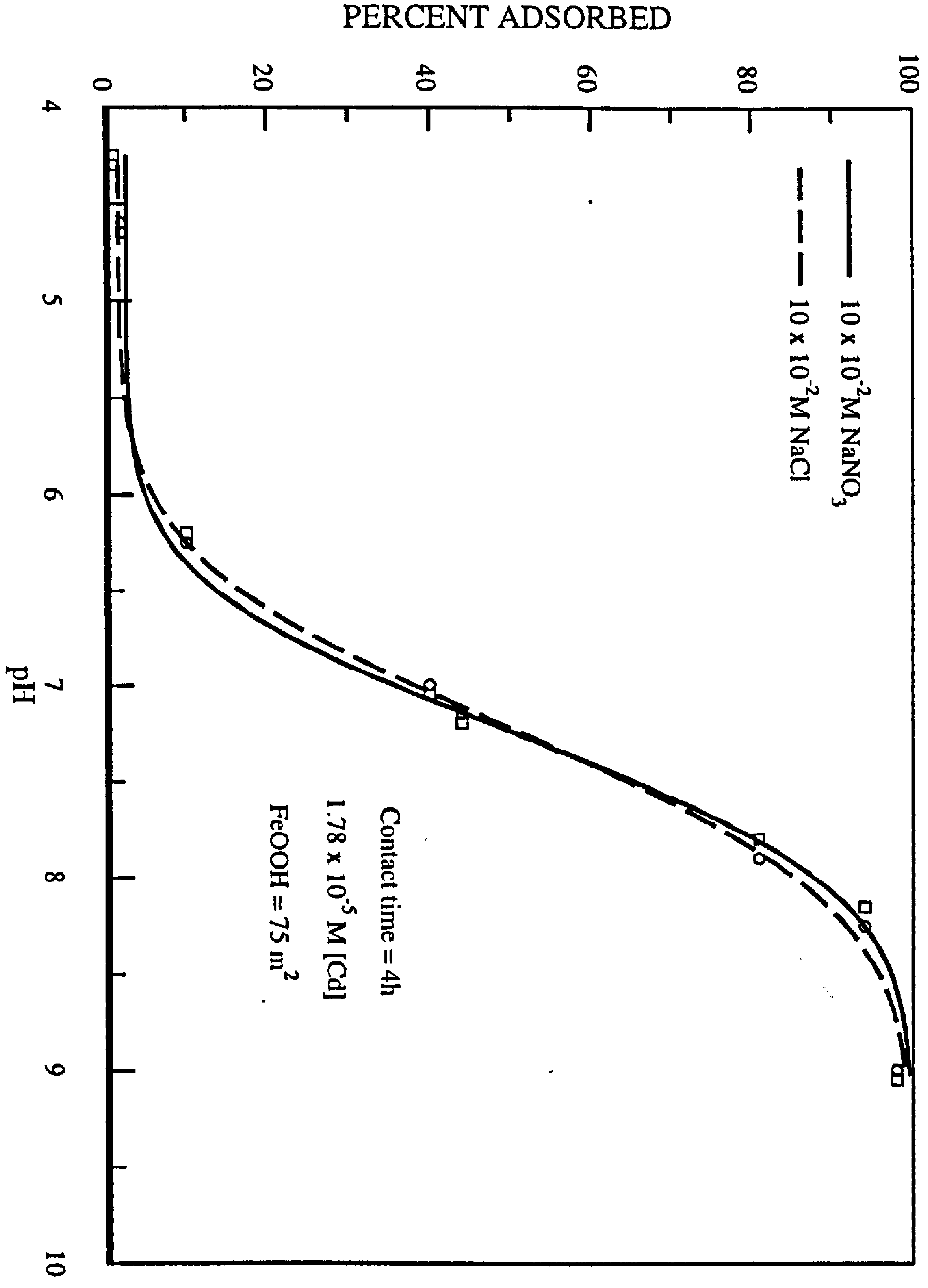


Fig 3.29 Cd adsorption as a function of pH and electrolyte compostion

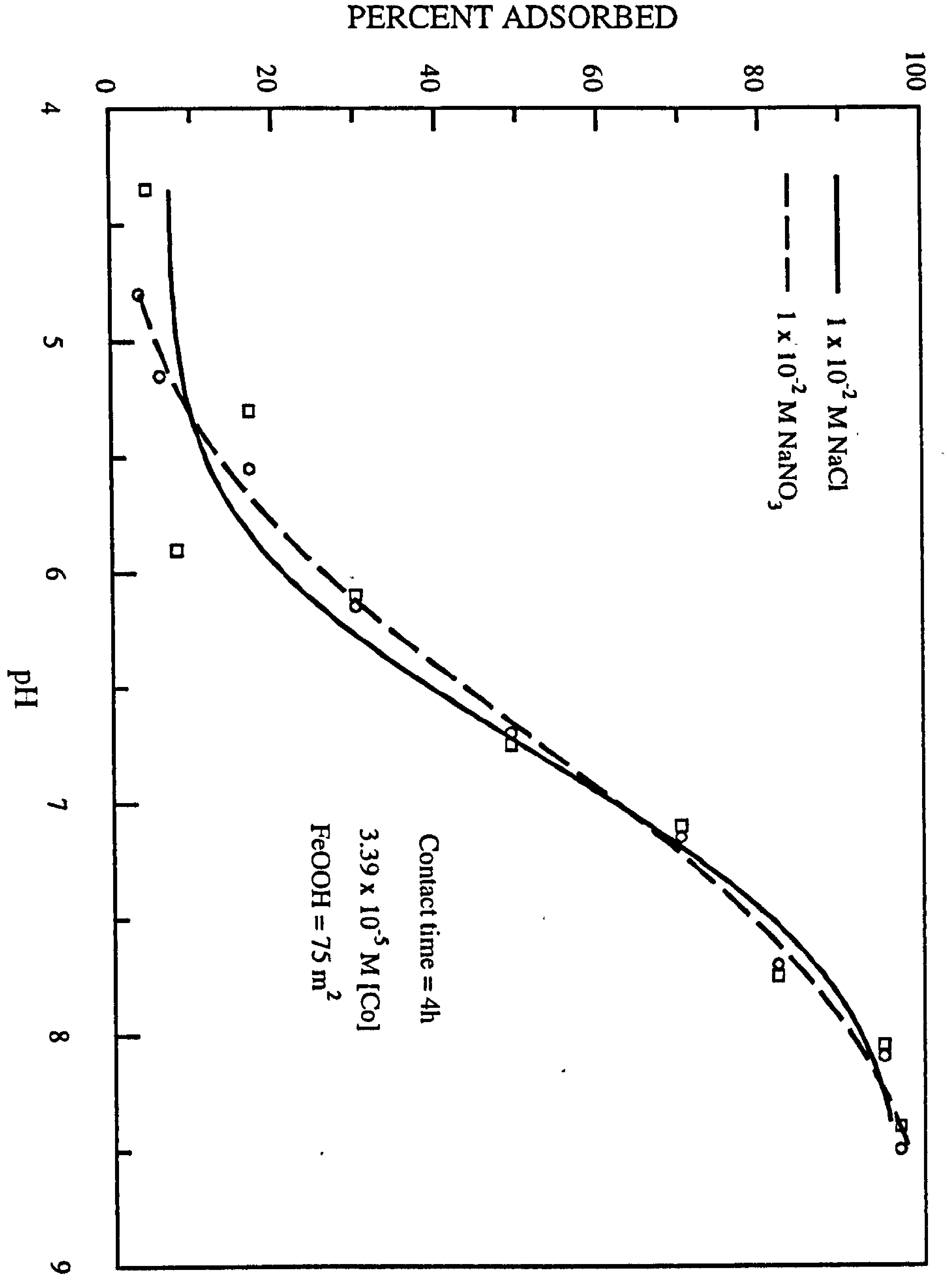


Fig 3.30 Co adsorption as a function of pH and electrolyte compostion

3.6.7 Coefficient of distribution in the system studied

The mobility of the metals in the soil-water system can be characterized by a distribution coefficient, which may be defined as the ratio of the amount of metal adsorbed onto the solid phase to the amount of metal in the aqueous phase at equilibrium. Distribution coefficients act as indicators of the mobility of the metal in the aqueous medium. A high distribution coefficient value indicates that most of the metal is retained by the adsorbent due to sorption processes. The higher the distribution coefficient, the lower the ability of the metal to stay in the solution and vice versa.

The distribution coefficient, K_d for an aqueous system may be defined by the following equation: [20-21]

$$K_d\ (ml/g) = [SO\text{-}M]/[M^{2+}] \tag{3.14}$$

where

SO-M is moles of cations adsorbed per gram of goethite, and M^{2+} is the equilibrium cation concentration in moles per millilitre.

K_d may also be calculated from experimental data by using the following equation: to present the data on logarthmic scale.

$$K_d\ (ml/g) = 1000*\%M_{ad}/[(100 - \%M_{ad})S] \tag{3.15}$$

where

$\%M_{ad}$ is percentage of cadmium or cobalt adsorbed by goethite

S is goethite concentration in suspension in grams per 1 litre.

1000 is used to convert g/l to ml/g

Equation 3.14 has been used to calculate the distribution coefficients of several sets of data, and the results are shown in Figures 3.7, 3.9, 3.11, 3.13, 3.15, 3.17, 3.24 and 3.26.

K_d become larger with higher pH and ranged from 10 to 55,000 ml/g over the pH range studied, depending on the pH, goethite concentration, and cation concentration but are independent of electrolyte concentration. Lower K_d means little cation is bound to the goethite, which leaves most of the metal in the solution where it is available for other reactions. This means it is available to be transported with aqueous solution in the natural environment. Cd and Co will be more mobile in acidic media rather than neutral or alkaline media. Although an increase in surface area has a significant effect on the adsorption edge, it does not affect the magnitude of distribution coefficients. This is because, K_d by definition is the ratio of metals concentration in the solid phase to that in the solution at equilibrium. At constant pH and constant cation concentration, as the amount of goethite increases, cation distribution in solid and a solution phase is adjusted so that the $[\%M_{ad}/S]$ term in equation 3.15 remains constant.

The distribution coefficient does not change with the decrease in goethite surface area at constant pH and constant cation concentration, as long as the suspension is supersaturated with goethite. Also, a tenfold decrease in the ionic strength of the medium is seen not to affect the distribution coefficients.

3.7 Conclusions

The adsorption of cadmium and cobalt onto goethite has been studied as part of a programme designed to understand (i) the interactions between metal containing species and soil components and (ii) metal transfer in soils. The factors that could influence adsorption are metal concentration, oxide concentration, pH, temperature, contact time, electrolyte composition and electrolyte concentration. Of these only contact time, pH, and temperature are found to play a major role in the metal goethite interactions at constant metal concentration and goethite surface area.

The adsorption edge depends on the cation concentration at a low goethite surface area but is independent of the cation concentrations at a high goethite surface area. A fourfold increase in the goethite surface area shifts the adsorption edge to a lower pH by less than half a pH unit. It should be noted that for every mole of cadmium and cobalt adsorbed two hydrogen ions are released and this should result in the lowering of pH. An increase in both temperature and contact time leads to a significant increase in adsorption of both cobalt and cadmium on goethite. Goethite concentration also has an effect but is less significant than those due to temperature and contact time. A decrease in electrolyte concentration of the metal transport medium does not affect the adsorption edge. The distribution coefficients of metal adsorption/metal transportation increase sharply with an increase in pH and more cadmium and cobalt are retained by goethite around neutral pH than at a lower pH. Although the soil-water environment is complex with a multitude of variables, the experimental results show that the main factors affecting the adsorption process are pH, contact time and temperature

The occurrence of hydrous oxides in soils means that oxide minerals can exert chemical activity which is large in comparsion to their relative concentration. Goethite coated on sand was studied in this work to model the effects of the deposition of highly surface active oxides particle on inert materials such as silica sand. Soils contain hydroxide phases which result from weathering of primary mineral in the form of fine partticulates. The small particle size taken with the surface activity due to hydroxide groups encourages their deposition on inert material. If this happens the hydroxide surface area in contact with the soil-aqueous system should be considerably increased and should result in greater uptake of metals per unit mass of hydrous oxides in comparsion with the situation for aggregated particles.

The results of the present work show that goethite coated on sand does in fact behave in a similar manner to colloidal goethite and more efficiently than pelleted goethite in the uptake of cadmium and cobalt. The pH dependence of the coating reaction of goethite on silica sand suggests that the mechanism of adhesion is electrostatic attraction. Goethite coated silica is also an ideal material for use in column reactors for metal extraction in industrial effluent clean-up applications.

The work described in this chapter highlights the type of information that is expected in consideration of soil remediation and metal transport in soils. Particularly it highlight the need to understand the effects of the quantity and surface area and activity of materials such as goethite because of the possiblity that they will dominate the extraction of metal species from the soil-aqueous system.

3.8 References

1 Jenne, E. A.,(1968) Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides, Adv. in Chem. 73, 337-387.

2 Quirk, J. P., and. Posner, A.M.(1975), Trace element adsorption by soil minerals, In:. Nicholas, D.J.I. and. Egan, A.R. (eds), Trace Elements in Soil-Plant-Animal Systems: 95-107 Academic Press, New York.

3 Dudley, L M.,. Mclean, J. E. Slms, R.C. and Jurlnak, J.J. (1988) Sorption of copper and cadmium from the water of copper concentrations at a high goethite surface soluble fraction of an acid mine waste by two calcareous soils: Soil Sci., 145, 207-214.

4 Tiller,K.G., Gerth,J. & Bruemmer,G. (1984) The sorption of Cd , Ni, and Zn by soil clay fractions :procedure for partition of bound forms and their interpretation . Geoderma, 34,1-16

5 Kinnburgh, D.G. Jackson, M.L. & Syers, J. K. (1976), Adsorption of alkaline earth , transition and heavy metals cations by hydrous oxide gels. Soil Sci. Soc. of Amer. J., 46, 56-61

6 James, R. O., Healy, T. W. (1972). Adsorption of hydrolysable metal ions at the oxide-water interface. J. Colloid Interface Sci.,40, 42-52

7 Tiller,K.G., Gerth, J. & Bruemmer,G. (1984) The relative affinity of Cd , Ni, and Zn for different soil clay fractions . Geoderma, 34,17-35.

8 Tewari, P. H., Lee, W. (1975), Adsorption of Co (II) at the oxide water interface, J. Colloid Interface Sci. 52, 77-88.

9 Forbes,E.A., Posner, A.M., and Quirk, J.P. (1976) The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite. J. soil sci. , 27, 154 - 166

10 Bowell, R.J., (1994), Sorption of arsenic by iron oxides and oxyhydroxides in soils, Applied Geochemistry, 9, 279-286.

11 Balistrieri, L.S. and Murray, J.W. (1982) The adsorption of Cu, Pb, Zn and Cd on goethite from major ion seawater. Geochim Cosmochim Acta, 46, 1253-1265

12 Padmanabham M (1983) Comparative study of the adsorption desorption behaviour of copper(ll), zinc(ll), cobalt(ll) and lead(ll) at the goethite solution interface. Aust. J. Soil Res 21, 515-525

13 Kinniburgh, D.G.& Jackson, M.L. (1982) Concentration and pH dependence of calcium and zinc adsorption by iron hydroxide gels , Soil Sci. Soc. of Amer. J., 40, 796 - 799

14 Westall, J.C. (1986), Reactions at the oxide-solution interface: chemical and electrostatic models. Am. Chem. Soc. Symposium ser., V, 323, 54-78.

15 Benjamin, M. M. and Leckie I.O. (1981) Multiple-site adsorption of Cd, Cu, Zn and Pb on amorphous iron oxyhydroxide. J Colloid Interface Sci 79, 209- 221

16 Grimme, H. (1968). Die adsorption von Mn Co Cu and Zn durch Goethit aus Verdllnnten Losungen Z. Pflonzenernoehr. Bodenkd, 121, 58-65.

17 Barrow, N.J. (1986) Testing a mechanistic model: the effect of time and temperature on the reaction of zinc with a soil. Journal of soil science , 37, 277-286.

18 Tamura, H.; Matijevic, E.; Meites, L. J. (1983)Adsorption of Co^{2+} ions on spherical magnetite, Colloid Interface Sci. 92, 303-314.

19 Honeyman, B.D. and Leckie, J.O., (1956) Macroscopic partioning coefficients for metal ion adsorption . Am. Chem. Soc. Symposium ser., V, 323, 162-190.

20 Anderson, P.R . and Christensen, T. H. (1988) Distribution coefficients of Cd, Co, Ni, and Zn in soils. J Soil Sci., 39, 15-22

21 Konner, Z.S., (1992) Adsorption of copper on to goethite in aqueous systems, Environ. Geol. Water Sci. , 20 (3), 205 -212.

22 Davis, J.A., and Leekie, J.O., (1978) Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. Environmental sci. Technology, 12, 1309-1315

23 Davis,J.A., and Hayes, K.F., (1986), Geochemical processes at mineral surfaces. An overview Am. Chem. Soc. Symposium ser., V. 323, 2-18

24 Davis, J.A., James, R.O., and Leckie, J.O., (1978) Surface ionization and complexation at the oxide-water interface. I Jour. colloid interface sci., 63, 480-499.

25 Schwertmann, U. and Taylor, R.M. (1989). Iron oxides, In: Dixon, J.B. (eds), Minerals in soil environments 379-437. Soil Science Society of America, Madsion.

26 Schwertmann, U., & Cornell, R.M., (1991), Iron oxides in the laboratory prepartaion and characterization, VCH, Weinheim.

27 Nakai, M., and Yoshinaga, N. (1980), Fibrous goethite in some soils from Japan and Scotland. Geoderma, 24, 143 -158.

28 Fordham, A.W. , Merry, S. and Norrish, K. (1985), Occurrence of microcrystalline goethite in an unusual fibrous form, Geoderma, 34, 135 -148.

29 Atkinson, R. J., .Posner, A . M., and Quirk, J.P (1967) Adsorption of potential-determining ions at the ferric oxide - aqueous electrolyte interface: J. Phys.

Chem., 71, 550-558

30 Forbes, E.A., Posner, A. M., Alan, M., and Quirk, J.P., (1974) The specific adsorption of inorganic Hg(II) species and Co(III) complex ions on goethite. J. Colloid interface sci., 49, 403- 409.

31 Wangen, L.E., Stallings, E.A. , Walker, R.D. (1982) The transport of contaminants from energy process waste leachate through subsurface soils and soil components. Laboratory experiments. Rept La-9406-MS, Los Alamos Natl Lab., Los Almos.

32 Allen, A. P. (1987) Iron ore pelletisation, Euro. patent appli. No. EP 0 225 171 A3

33 Jha, M. C., Blandon, A.E.; Hepworth, M.T. (1986), Durable zinc ferrite sorbent pellets for hot gas desulfirization, US patent No 4732888

34 Theis, T.L., Iyer, R., and Ellis, S.K., (1992), Evaluating a new granular iron oxide for removing lead from drinking water, Journal AWWA, 101-105.

35 Lyklema, J (1987) Electrical double layers on oxides:disparate observations and unifying principles, Chemistry and Industry, 2 November, 741-747.

36 Hunter, J. H. (1981) Zeta Potential in Colloid Science Principles and Applications, Acadamic press, London.

37 Parks, G.A., and DeBruyn, P.L.(1962), The zero point of charge of oxides, J. Phys. chem., 66, 967-983

38 Parks, G.A, (1965), The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. Chem. Rev., 65, 177 - 198

39 Parks, G.A, (1965), Aqueous surface chemistry of oxides and complex oxide minerals : isoelectric point and zero point of charge, Adv. chem. ser.,67, 121-160.

40 Lewandowski, G.A., and Linford,H.B., (1972), Filtration of ferric hydroxide , J. Environ. sci. Techn., 6, 169 -172.

41 International Centre for Diffraction Data - JCPDS (1979), Powder diffraction file 29-713, JCPDS.

42 Borggaard, O.K., (1987), Effect of granulation of soil samples and minerals on measurements of specific surface area by nitrogen adsorption. Geoderma, 28, 147 -149

43 Gregg, R.G., & Langford, J.F., (1977) Study of the effect of compaction on the surface area and porosity of six powders by measurement of nitrogen adsorption isotherms. J.Chem. Soc. Faraday Trans., I , 747-759

4.0 UPTAKE OF CADMIUM AND COBALT ON TO BIRNESSITE

4.1 Introduction

Soil is the main source of many dietary micronutrients for plants, animals and humans and is also a point source for toxic metals. Increasing our understanding of the natural control process as exhibited by iron and manganese oxides and hydroxides is important. The importance stems from the continuous endeavour to refine our understanding of natural processes towards pollution control.

There are at least twenty naturally-occurring manganese oxide varieties containing tetravalent, trivalent and divalent manganese [1]. The oxides can be present as coatings, particles, colloid-size aggregates or micro nodules. Birnessite and lithophorite are the most commonly identified forms; others include hollandite, todorokite, pyrolusite, psilomelane, cryptomelane and amorphous oxyhydroxides [2-4].

Manganese oxides and hydroxides play a major role in the control of metal ions in soil-water system and control the mobility of the labile fraction of heavy metals present in soils, sediments and waters. Previous workers [5-9] have reported Mn oxides and hydroxides to be considerably better scavengers for heavy metals than iron oxides. Manganese oxides in soils and sediments have a strong uptake affinity for Co and Cu resulting in relatively high concentrations of these trace metals in the soil hydrous manganese oxides. These metals are important, both to plants and animals [10 - 13]. Taylor and Mackenzie[10] have shown that a range of soils in Australia retain about 80% of the Co contained in or associated with hydrous manganese oxides. The manganese-oxide-hydroxide phases can also control the mobility of toxic metals such as Cd and Pb into the food chain. There are many instances of cadmium contamination of soil and water that have been shown to result from anthropogenic processes. The best example of a natural system that was unable to control the availability of cadmium and consequently resulted in deaths is the "Itai-Itai" catastrophe at the Jintsu valley in Japan. Cadmium pollution in rice fields from effluents of an abandoned lead-zinc mine, produced rice containing about 3ppm of Cd. The consumption of this over a period of several years led to the illness called "Itai-Itai", ("it hurts" in Japanese), which has afflicted many local inhabitants [14 - 15].

Due to their high exchange capacities for metals, hydrous manganese oxides have been in use to measure low concentrations of radioactive metals in the ocean and in analytical chemistry to concentrate trace metals from dilute aqueous solutions [16 - 17].

Marine ferro-manganese nodules are rich deposits of metals such as Ni, Cu, Co, Pb, and there is an on-going desire to mine these deposits. Thus, one can see the diversified use of manganese oxides and hydroxide.

The importance of hydrous manganese oxides and their diverse uses is being recognised in many fields; reports describing the mechanisms by which they sorb heavy metal ions are not consistent. This is partly due to complexity of manganese soil minerals and incomplete characterization of some of the more abundant oxides[18]. The aim of the work described in this chapter is to study the fundamentals of metal ion sorption kinetics of birnessite, $Na_4Mn_{14}O_{27}.9H_2O$, in the ecosystems. Birnessite is an important and active component of soils [10-12], water [19-21] and ocean [22 - 24]. The variables considered in the study are pH, temperature, metal concentration, oxide concentration, electrolyte concentration and contact time. Co and Cd are chosen for the sorption studies. because cobalt is an essential metal, and cadmium is toxic at even relatively low concentrations. Refining our understanding of Cd control and enhancing Co availability in the soil-water system is important.

The manganese content of soils averages about 850µg/g and ranges from 100 to 4000µg/g. In soil solutions manganese levels of 0.02-2 µg/g are reported while levels in river water average at 0.012 µg/g with ranges of 0.0002 - 0.13 µg/g. Igneous rocks contain an average of 950µg/g Mn, shales contain 850µg/g while sandstone and limestone contain 50 and 1100µg/g respectively [21]. The geochemical ratio for Fe and Mn in the earth's lithosphere is approximately 60:1.

Manganese oxides and hydroxides besides showing a scavenging capacity are also important constituents of soil because manganese is an essential element required for the nutrition of plants and animals. The availability of manganese in the soil-water system is controlled by the oxidation-reduction behaviour of the manganese species present. An alkaline pH with oxidizing conditions can reduce the availability to the extent that it leads to a deficiency of available Mn. On the other hand reducing conditions combined with acid pH may increase the availability to such an extent that it reaches toxic levels.

Mackenzie [22] described how the mineralogy of manganese is complicated by the number of oxides and hydroxides formed, with substitution of Mn^{2+}, Mn^{3+} and Mn^{4+} widely observed. The substitution changes the average Mn-O bond lengths, consequently leading to an alteration in the unit cell. These changes are accompanied by the substitution of some O^{2-} by OH^- to maintain electroneutrality. Most of the stable and metastable compositions fall in the concentration range MnO-MnO_2.

The characterisation of manganese oxides and hydroxides is further complicated by a lack of consistency in nomenclature and by a lack of understanding of structures of the phases. Furthermore there are still uncertainties about whether certain forms, such as birnessite, are distinct mineral species, or variants of existing forms [23-24]

Birnessite refers to a group of oxides, some of which have been known as manganous manganite, 7Å-manganite, Mn(III)manganate(IV), manganous(II) manganate (IV), and NaMn(II, III) manganate(IV). Although the detailed structure has not been determined, a structure has been proposed by Giovanoli et. al. [25], which is similar to that of chalcophanite ($Zn_2Mn_6O_{14}.6H_2O$) [26,27]. The proposed structure consists of layers of edge-shared [MnO_6] octahedra separated by about 7 Å along the *c axis*, with H_2O and OH molecules occupying the interlayer region by analogy with chalcophanite. However in $Na_4Mn_{14}O_{27}.9H_2O$ it is assumed that one in six octahedral sites in the layer of linked [MnO_6] octahedral sheet is unoccupied, compared with one in seven for chalcophanite. Mn^{2+} and Mn^{3+} lie above and below each octahedral vacancy as shown in Figure 4.1. The low valence Mn ions are coordinated to oxygens in both the octahedral MnO_6 sheet and the water sheet. This arrangement repeats about every 7.0 Å along the *c-axis.*

Birnessite is one of the most common manganese oxides that occurs in soils generally in a nonstoichiometric colloidal form. Its composition is derived from samples of natural occurrence collected from Birness, Aberdeenshire, Scotland as reported by Jones and Miline[28].

The compositions of three synthetic members of birnessite have been given as:

$Na_4Mn_{14}O_{27}.9H_2O$

$Mn_7O_{13}. 5H_2O$

$Mn_7O_{12}. 6H_2O$

The sodium birnessite is closer in composition to that identified by Jones and Miline [28-30]. Although the originally reported birnessite is in a Fluvioglacial deposit the subsequent studies have identified birnessite in terrestrial deposits [31] and desert varnish [32].

Taylor et.al. [33] and Chukhrov and Gorshkov [34] have identified birnessite in soil concretions in Australia and the Soviet Union respectively. The relative solubility of birnessite under waterlogged or extremely acid conditions can be a major factor in the high availability of Mn in these environments. This is the cause of Mn toxicity to many plants [35].

The high uptake capacity of birnessite for heavy metals makes it an important soil mineral oxide from the pollution abatement perspective and also in controlling the availability of some vital trace elements. It has, for example, been reported that the availability of cobalt to plants is controlled mostly by the amount of manganese in the soil[36]. It is therefore important that the chemistry, structure, surface properties and the derivatives of natural birnessite are well understood.

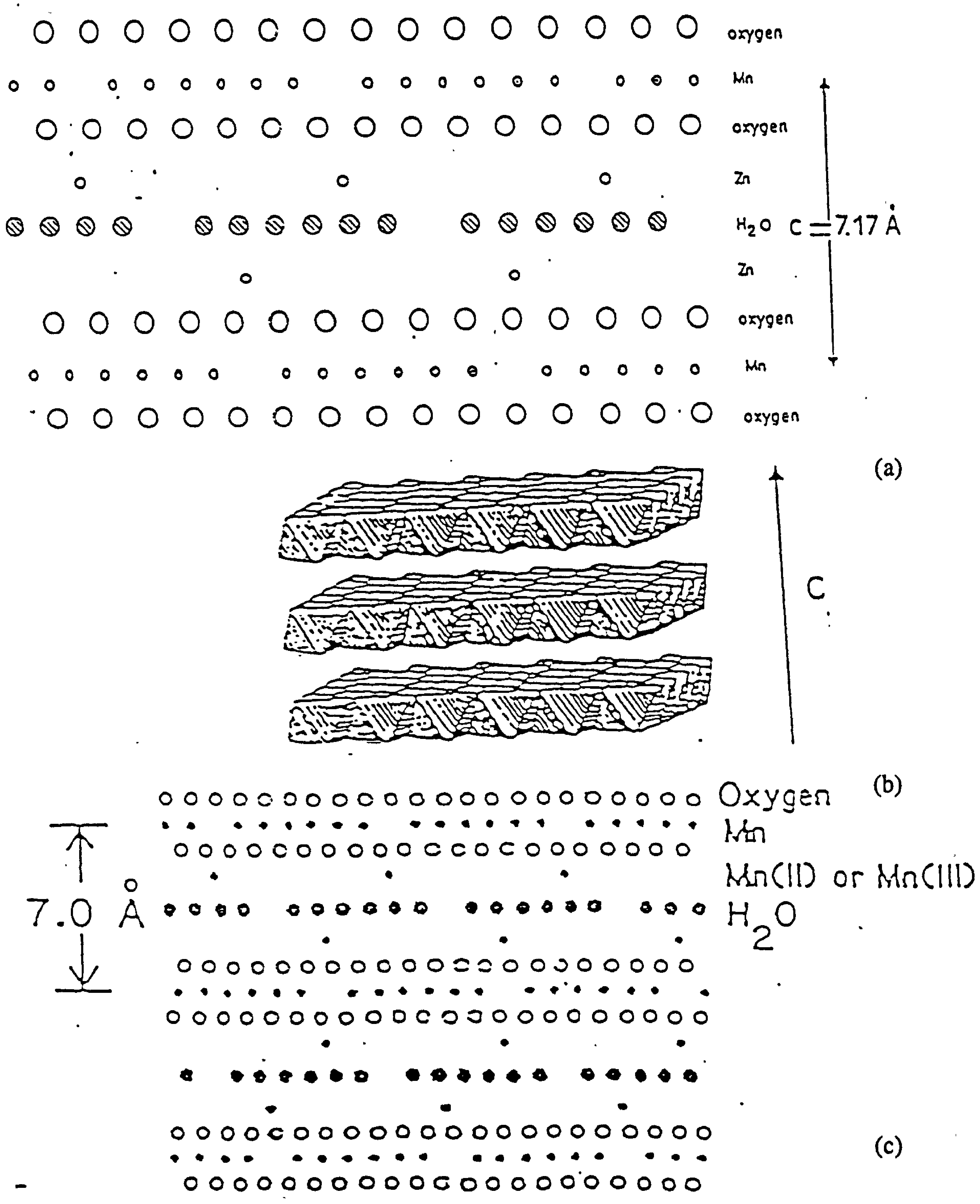


Figure 4.1 (a) Layered structure of chalcophanite (b) Schematic lamellar structure of birnessite (c) Layered structure of birnessite [25,35]

4.2 Materials and Methods

4.2.1 Reagents and labware

All reagents used in this study were of an analytical grade. Reagents used as a source of manganese, cobalt, cadmium and the background electrolyte were as follows: cadmium nitrate tetrahydrate ($CdN_2O_6.4H_2O$) assay >99% and cobaltous nitrate hexahydrate ($CoN_2O_6.6H_2O$), assay >99 percent), both were supplied by Fluka. Sodium nitrate, as pellets (99.6 percent), was supplied by Fisons, Loughborough, England. Manganous (II) chloride tetrahydrate $MnCl_2.4H_2O$ Analar (minimum assay =99%), was supplied by BDH, Poole, England. A 4 M sodium hydroxide solution and a 1M nitric acid solution convol supplied by BDH were used. Potassium chloride (KCl minimum assay 99.5 %) was supplied by BDH. Cadmium and cobalt standard solution, (1000 ppm spectrosol), suitable for atomic adsorption spectroscopy were also supplied by BDH. The water used in this study was doubly deionized water processed by the Milli-Q system.

Cadmium and cobalt stock solutions of 100 ppm were prepared by diluting concentrated cadmium and cobalt solutions (1000 ppm). The solutions were also prepared from their respective nitrate salts by dissolving them in a minimum amount of concentrated nitric acid and then diluting them with the required amount of deionized water. The standard solutions and those prepared from nitrates were analysed by atomic absorption spectroscopy and the value is 2.5% higher than the spectrosol standard solution value.

All glassware and plasticware was cleaned by overnight immersion in acid. Containers used to contain Cd or Co solutions and birnessite ($Na_4Mn_{14}O_{27}.9H_2O$) were soaked in a 10% nitric acid bath and rinsed repeatedly with deionised water. Soaking baths were changed every two days.

4.2.2 Adsorption into reaction vessel walls

The possible uptake of metal species on to reaction bottle walls was checked in the following manner. An adsorbate of lowest concentration studied was added to the container (3.39×10^{-5}M [Co] and 1.78×10^{-5}M [Cd]). The pH was adjusted to 4 for both Cd and Co and the mixture was allowed to equilibrate for a time equal to the duration of the uptake experiments. The solution was then poured out of the container which was rinsed and the metal concentration determined to assess any metal loss. Finally a known volume of acid and deionised water was added to the container to desorb any Cd or Co from the container walls prior to analysis by AAS. The results from both sets of analyses showed that metal adsorption on the container walls was negligible.

4.2.3. Preparation of birnessite

Birnessite was prepared by controlled dehydration of buserite [NaMn oxide hydrate- 10Å = (Na, Mn)$Mn_3O_7.nH_2O$] according to the method of Stahli [38] as described by Giovanoli and Brutsch [25,37] and reported by Golden et al. [35]. Buserite is considered to have a layer structure similar to birnessite, with the layers of edge-shared MnO_6 octahedra about 10Å apart. It is named after the late W. Buser who discovered it in deep sea ferromanganese nodules in 1959.

A solution of 55g of NaOH in 250 ml H_2O is added to 200ml of 0.5M $MnCl_2.4H_2O$ at room temperature into a 2L plastic measuring cylinder. The mixture forms $Mn(OH)_2$ suspensions through which oxygen is bubbled through a G-1 glass frit at rate of 3 litres/min for six hours. After six hours of oxygenation the black precipitate formed is washed by repeated centrifugation and decantation with doubly deionised water until the supernatant liquid is free of chloride. It is important to ensure that during this process the precipitate remains moist. The precipitate is finally filtered off, vaccum dried and stored. Buserite dehydrates to form birnessite during the vacuum drying process.

4.3 Characterization of birnessite

4.3.1 Chemical analysis

The following procedure was used to determine total manganese, Mn^{2+}, Mn^{3+} and Mn^{4+} [39 - 42]. For total manganese an accurately weighed birnessite sample (about 0.5g) was dissolved in 25-30 ml of concentrated HCl at 80-90°C. The solution was evaporated to dryness in a hot water bath, and the residue redissolved in slightly acidified warm water and made up to 100 ml in a volumetric flask. An aliquot was removed and the total manganese extracted by titration against 0.05 M EDTA at pH 10 in the presence of 5 ml of 20% triethanloamine [39].

Mn^{2+} was estimated by leaching an accurately weighed sample of birnessite (about 0.5g) with 3M $(NH_4)_2SO_4$ solution at 90°C using a liquid-solid ratio of 20:1. The leached solution was filtered off the residue rinsed and the filtrate and washings made up to 100ml in a volumetric flask. Manganese was estimated in an aliquot by the standard bismuthate method [39-40].

Since the Mn^{3+} component of the manganese oxide is thermodynamically unstable it will disproportionation to Mn^{2+} and Mn^{4+} in strong acid medium as shown below [39].

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+$$

An accurately weighed sample of a birnessite (about 0.5g) was leached in 6M HNO_3 at 90°C using a liquid:solid ratio of 10:1. The leached solution was filtered, the residue was thoroughly washed with acidified water and the filtrate and rinsings made up to 100ml in a volumetric flask. Manganese was estimated in aliquots by the standard bismuthate method [40-41].

The Mn^{4+} content of the sample was determined by sodium oxalate method in 2 M H_2SO_4 medium. The differences between the total Mn and Mn^{4+} correspond to the experimentally determined value for Mn^{3+} [39,42]. The sodium concentration is determined using atomic absorption specctroscopy and total H_2O was obtained by TGA. The results are shown in Table 4.1.

Constituents	%
Mn(IV)	38.10
Mn(III)	13.57
Mn(II)	0.13
Total Mn	51.73
Na	6.93
Total H_2O	13.20

Table 4.1 Chemical analysis of birnessite

In a separate analysis total manganese was determined using an atomic absorption spectrophotometer. An accurately weighed sample of birnessite (about 0.5g) was dissolved in hydrochloric acid and made up to 100ml with deionised water in a volumetric flask. The AAS analysis gave 54% total manganese.

4.3.2 Zero Point of Charge (PZC)

The measurement of zero point of charge(ZPC) of $Na_4Mn_{14}O_{27}.9H_2O$ in aqueous solution was obtained using two independent methods: potentiometric titration for the measurement of adsorption density of the potential determining ions, measurement of electrophoretic mobility.

4.3.2.1 Potentiometric titration

When a particle is immersed in a fluid, the interface becomes electrically charged. Some common charging mechanisms include loss of ions from the crystal lattice of the solid and ionisation of surface groups. These processes lead to the development of surface charges. It is generally assumed that H^+ and OH^- ions play a potential determining role in the oxide/solution double layer [43-44].

Although PZC values of manganese dioxides have been determined using potentiometric titrations [45-49], there are problems associated with slow equilibrium, large blank correction and steepness of the titration curves particularly at high pH values. Extrapolation was generally necessary to obtain an intersection point of titration curves.

2×10^{-5} M suspensions of $Na_4Mn_{14}O_{27}.9H_2O$ in 1×10^{-3}M KCl, 1×10^{-2}M KCl, and 1×10^{-1}M KCl were used. The suspension was mixed with a teflon coated magnetic stirring bar driven by a magnetic stirring unit under a nitrogen atmosphere. After addition of 1×10^{-1}M HCl or 1×10^{1} M KOH, the pH was measured at intervals until it become constant to about ±0.05 (after about 4hours). The amount of H^+ released or abstracted by the solid was computed by comparison with the blank titration curve of the supporting electrolyte. Three curves were obtained by potentiometric titration and they are non-intersecting as shown in Figure 4.2.

4.3.2.2. Electrophoresis

Electrophoresis is used to determine the point of zero charge. When $Na_4Mn_{14}O_{27}.9H_2O$ is dispersed in an electrolyte, ionisation causes the particles to acquire a surface charge. This development of charge induces oppositely charged ions of the electrolyte to migrate to the $Na_4Mn_{14}O_{27}.9H_2O$ surface, creating an electrical double layer as shown in Figure 4.3.

The attractive forces between the $Na_4Mn_{14}O_{27}.9H_2O$ and the counter ions of the electrolyte decay as the distance from the $Na_4Mn_{14}O_{27}.9H_2O$ surface increases and eventually reach zero in the bulk electrolyte solution. Individual birnessite particles and their most closely associated counterions move together through the bulk electrolyte solution. The potential at the boundary of each particle ion and the surrounding electrolyte is the zeta potential.

When an electrical field was applied across the suspension, the surface charged $Na_4Mn_{14}O_{27}.9H_2O$ particles are attracted towards the electrode of opposite charge and move accordingly. Nevertheless, the particles do not drift on their own, they also carry a thin layer of ions and solvent around them. The surface separating the stationary medium from the moving particle and its bound ion and solvent is called the surface of hydrodynamic shear. The potential at this surface, zeta potential, determines the speed of the particle in the electric field. Surfaces of shear normally enclose a few molecules of a solvent, so it is only few angstroms from the true particle surface.

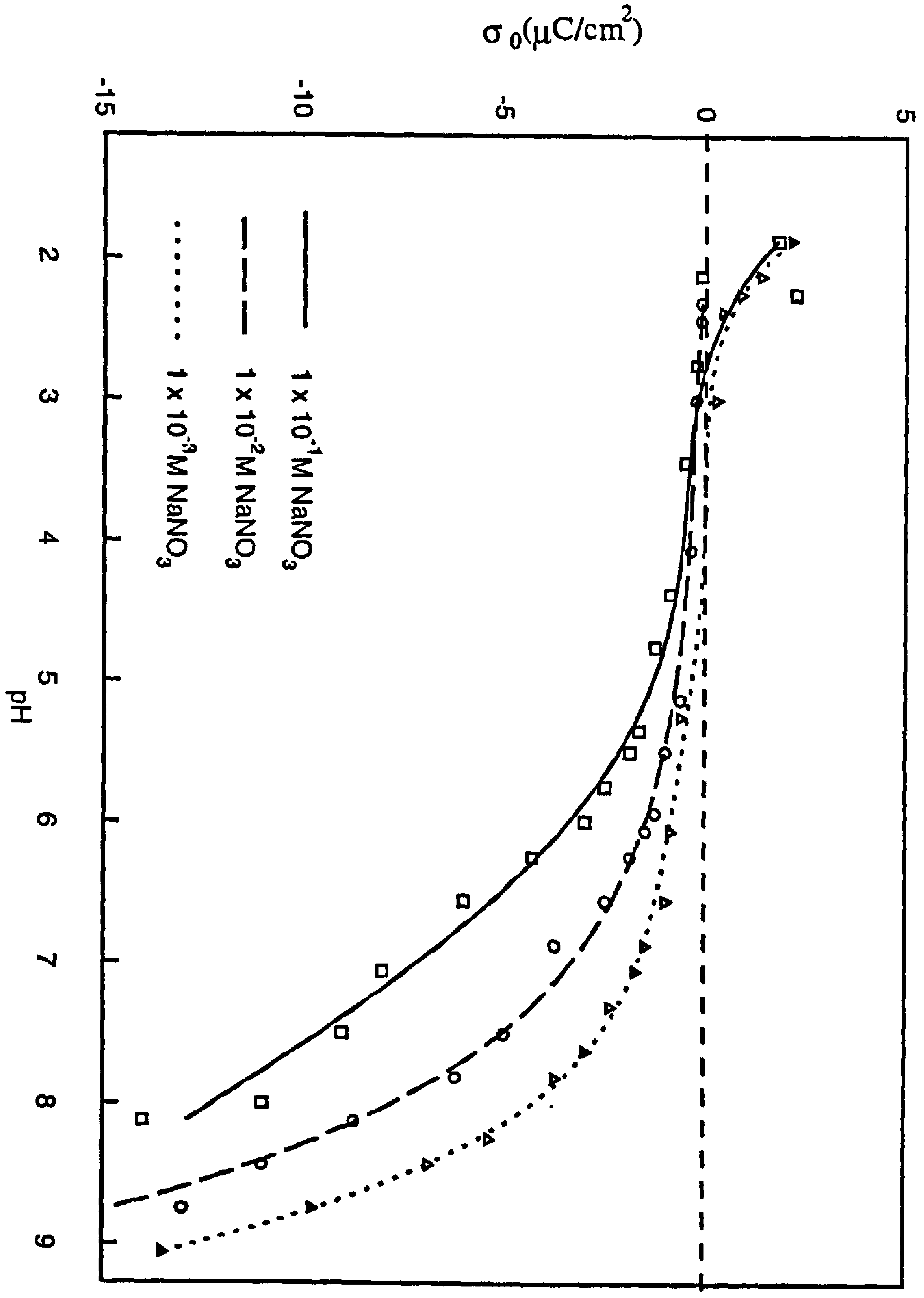


Fig 4.2 Surface charge density as a function of pH for $Na_4Mn_{14}O_{27}.9H_2O$

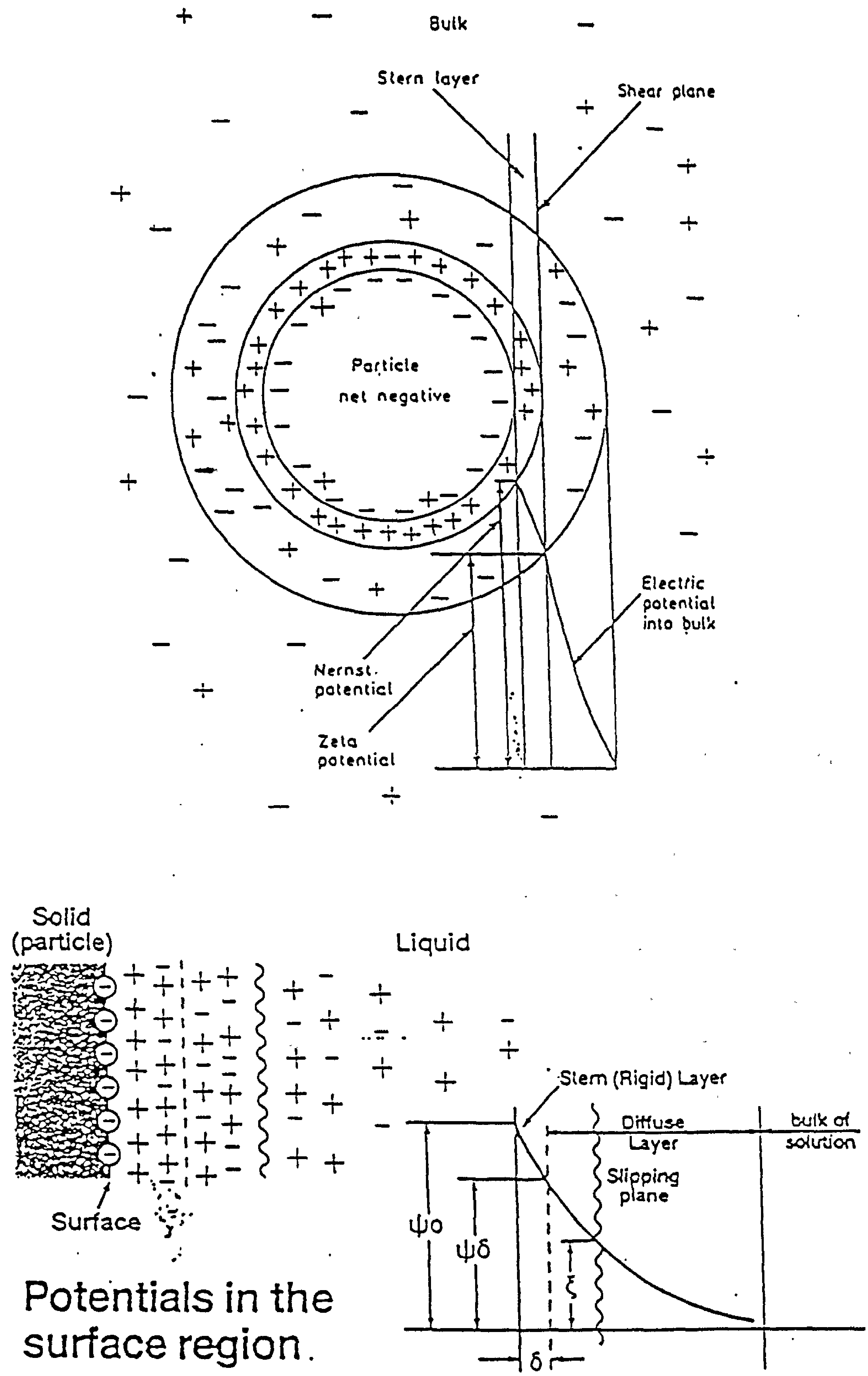


Figure 4.3 The colloidal model of double layer [43]

The velocity at which the particles move through the electrolyte under the influence of the electric field is known as their electrophoretic mobility [47-48].

Zeta potential can be determined by measuring the drift velocity of the particle in an electrical field of known strength. The common instrumental method now available is based on scattering light off the moving particles and measuring the resultant Doppler shift. Impurity in the sample has an effect on surface charge, and consequently on its zeta potential value. Similarly, the effect that an influx of H^+ and OH^- ions has on the surface charge makes the zeta potential of the sample pH dependent.

The pH at which the sample exhibits a zeta potential of zero value is called the isoelectric point (IEP). This is obtained by measuring the zeta potential values over a pH range. The value can sometimes be obtained from direct reading but if this is not possible, the results can be plotted on a graph and the point at which a curve crosses the abscissa is taken as IEP

The zeta potential of birnessite was measured using the electrophoresis method as follows. A 1×10^{-5} M suspension of $Na_4Mn_{14}O_{27}.9H_2O$ sample was prepared using 10^{-3} M KCl as the electrolyte. 25 ml of this sample suspension was transferred to a beaker and the pH of the solution adjusted to the desired level using 1×10^{-1} M HCl or 1×10^{-2} M KOH solutions. The beaker was placed in a sonic bath for one minute after which period the pH of the solution was rechecked to ensure that it had not been affected by the dispersion of the birnessite. The sample cell of a zetasizer III was flushed with 1×10^{-3}M KCl and the sample solution injected. The zeta potential of the sample was recorded by the zetasizer III with the average of five readings. The procedure was repeated at different pH and IEP was determined as 2.9 from the graph as shown in Figure 4.4

4.3.3 X-ray analysis

The X-ray diffraction patterns reveal that sodium birnessite is crystalline with a strong first and second order basal plane reflections at 7.14 Å, and 3.57 Å respectively. These results are close to the X-ray diffraction patterns reported in the literature [50] which consist of

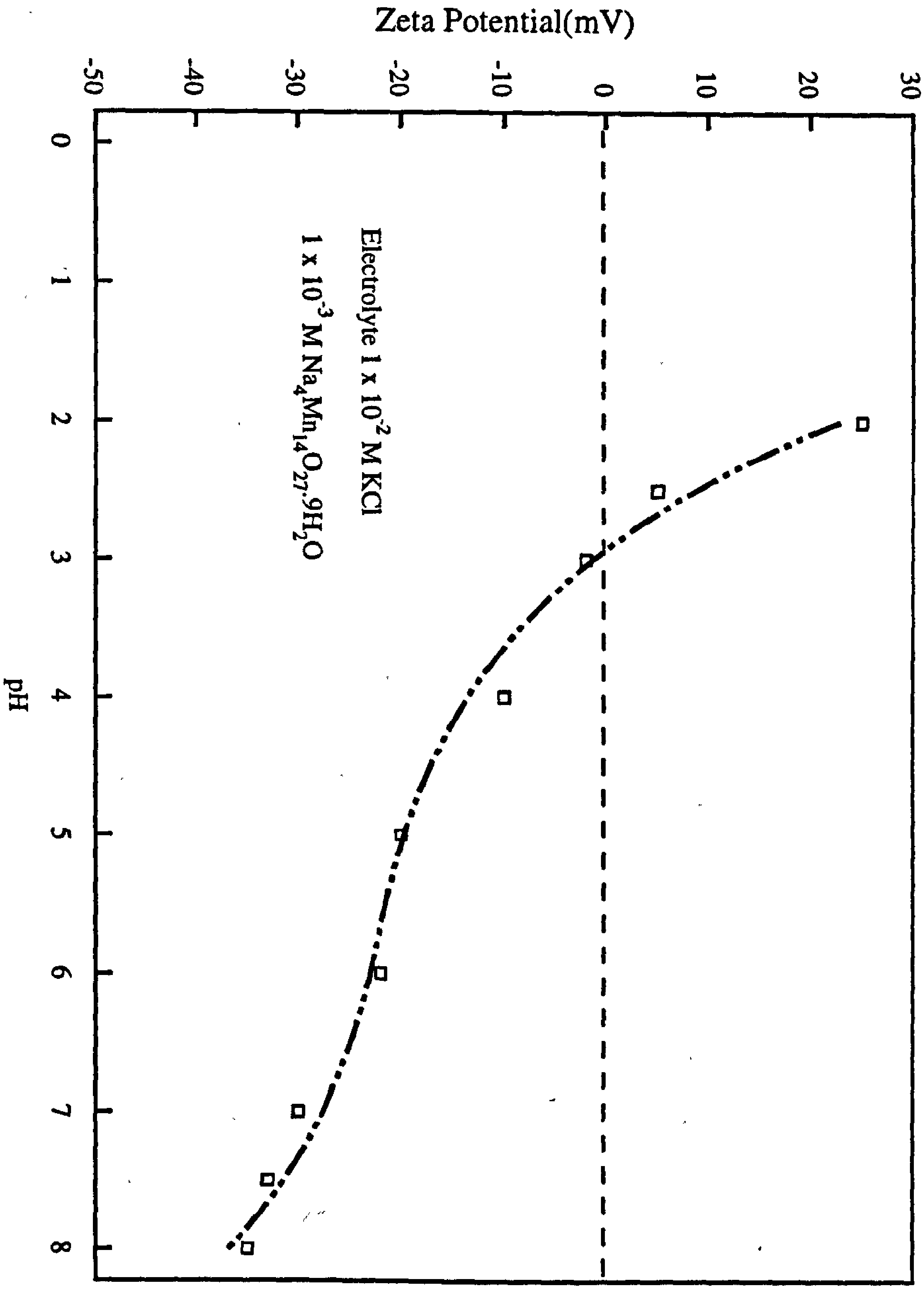


Fig 4.4 Zeta potential measurements of $Na_{14}O_{27}.9H_2O$

four major lines corresponding to spacings near to 7.15 Å, 3.57Å, 2.52 Å, and 2.43Å. The lines near 7.14 Å and 3.57Å are reported to be the basal spacings resulting from the separation of the sheets of MnO_6 octahedra of about 7.0 Å. The lines at 2.43Å, and 1.42Å are common to many Mn(IV) oxide phases, and arise from layers of close packed O atoms containing edge-shared MnO_6 octahedra.

Standard		Sample	
dÅ	**Intensity**	**dÅ**	**Intensity**
7.14	100	7.155	100
3.57	27	3.57	41
2.56	1	2.572	1
2.52	14	2.521	15
2.48	2	2.487	3
2.43	13	2.431	17
2.32	2	2.325	2
2.26	2	2.263	2
2.22	5	2.222	5
2.15	7	2.154	9
1.87	3	1.87	5
1.82	4	1.827	5
1.79	1	1.787	2
1.64	2	1.639	3
1.53	2	1.535	2
1.48	5	1.477	6
1.45	3	1.446	4
1.42	3	1.426	2

Table 4.2 XRD results as compared to results from XRD data file [50]

4.3.4 Scanning Electron Microscopy

This is another useful technique which enables external crystal dimensions and crystal morphology to be measured directly. It is also useful for indicating the presence of amorphous material or traces of iron oxides not detectable by XRD. Scanning electron micrographs were obtained using a Jeol JXA 840A electron probe microanalyser. The micrographs are shown Figure 4.5 and the crystal consists of very thin platelets about 2 μm diameter.

4.3.5 Surface area

The uptake of metals onto soil oxides and hydroxides can be reflected in the surface area and uptake affinity at constant solid composition at varying initial metal concentrations. An adsorbent can have high affinity for a metal, but the amount adsorbed per gram of the oxide may be smaller because the surface area is small and vice versa. Uptake affinity is governed by the chemical nature of the oxide, whereas surface area is a combination of both the physical and chemical nature of the oxide.

Several methods can be used for surface area determination. The widely used methods are based on the physical adsorption of gases, liquids, and various compounds to the particle surfaces. Other methods are negative adsorption, measurement of thermal effects and particle size determination by microscopic method. In this work the Birnessite surface area was determined by the N_2 - BET method [51] which gave 95 m^2/g for the birnessite surface area.

4.3.6 Thermogravimetry analysis

A sample is continuously heated at a constant rate of 10°C min^{-1} for thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TG curves for birnessite sample were obtained using a Stanton Redcroft STA-780 series thermo-balance linked to a BBC SE 460 chart recorder. The analysis conditions were:

Sample weight	15 mg
Gas	Nitrogen
Flow rate	25ml min^{-1}
Temperature	20 - 600° C
Heating rate	10° C min^{-1}
Crucible type	Aluminium

Birnessite mass loss measured from each TG curve was 1.8 and 11.6 % for adsorbed water and crystalline water respectively. The curves are in Figure 4.6

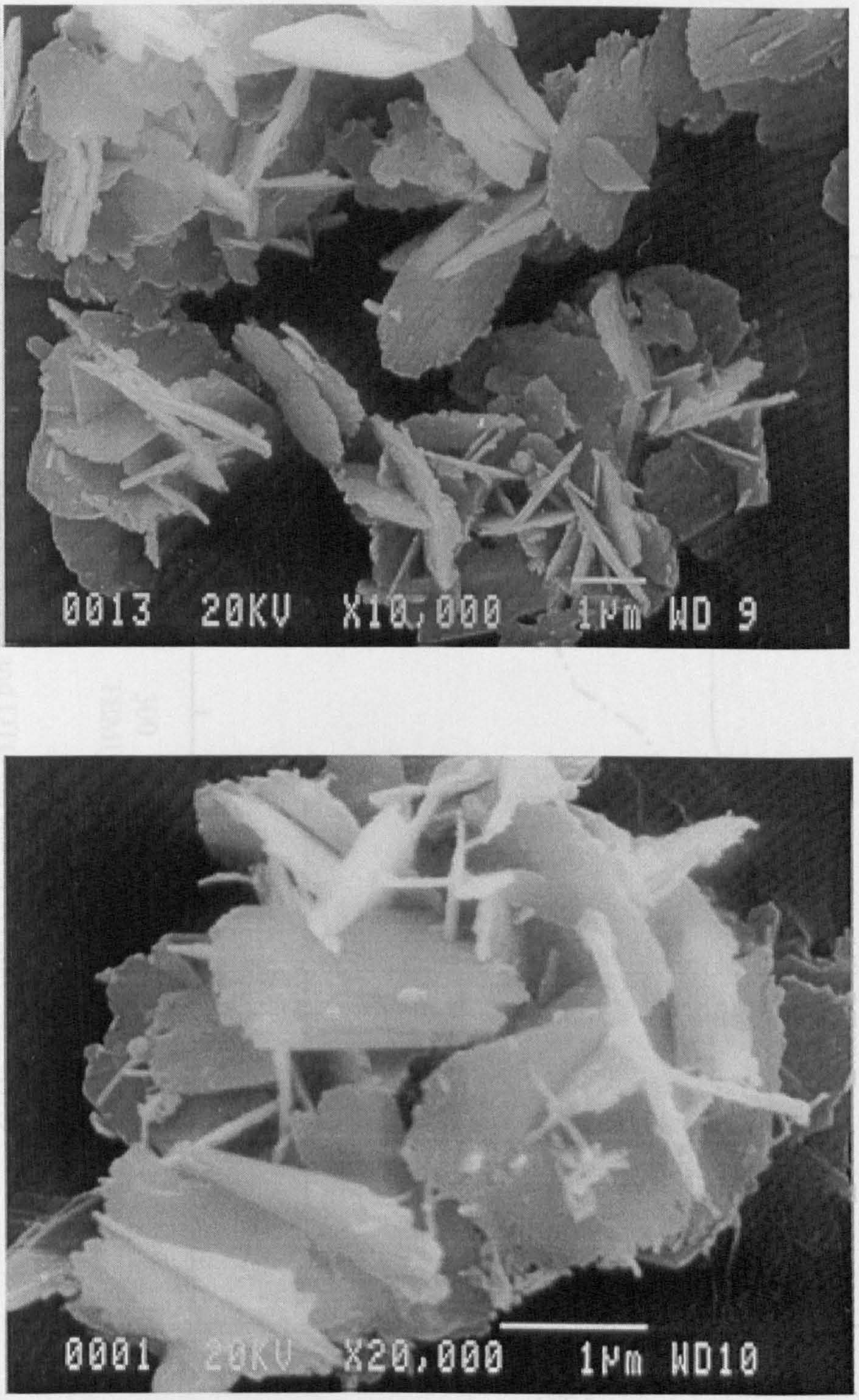


Figure 4.5 Scanning micrographs of birnessite at different magnification

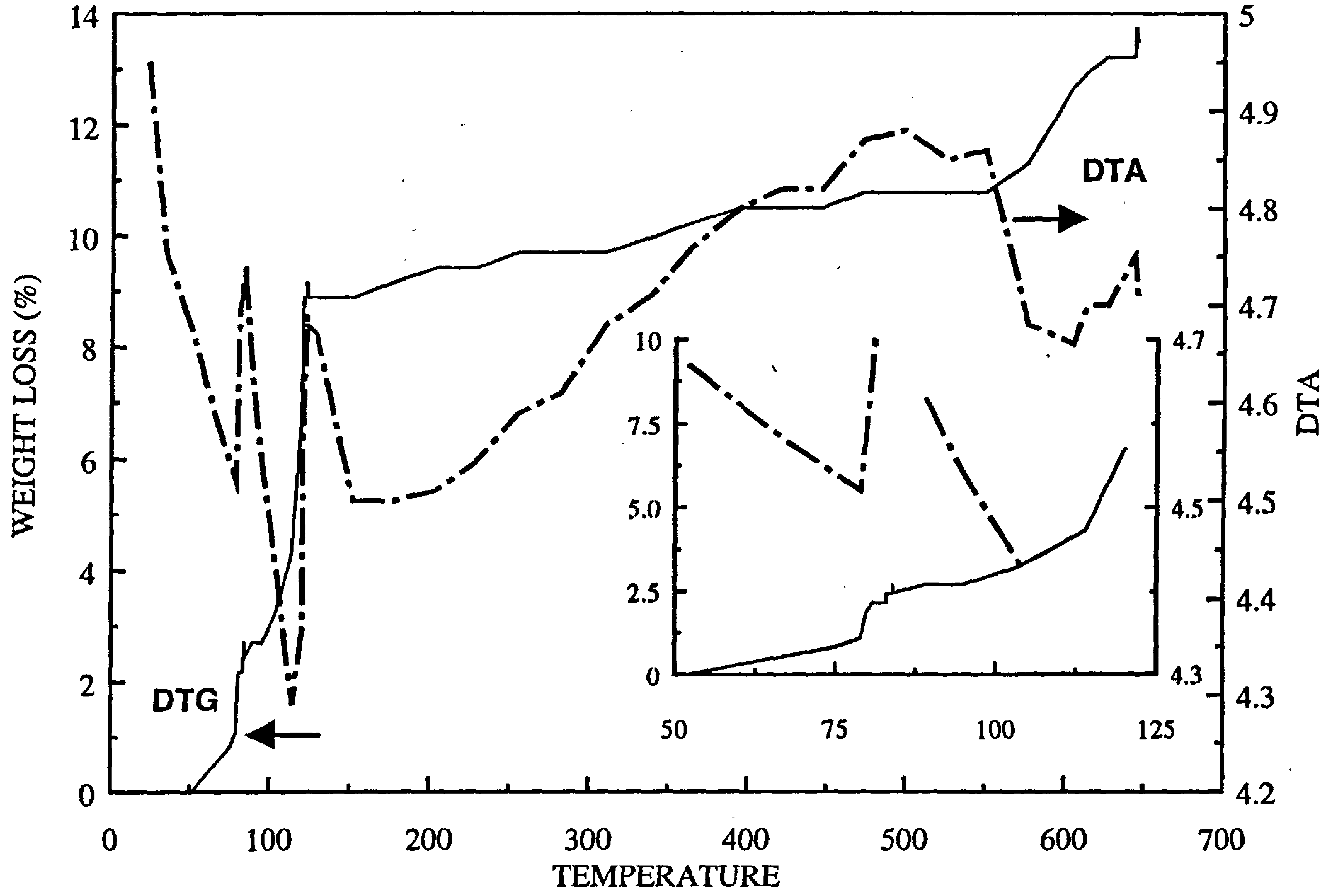


Figure 4.6 DTA and DTG curves for $Na_4Mn_{14}O_{27}.9H_2O$

4.4 Uptake of cadmium or cobalt onto birnessite

4.4.1 Uptake mechanism

The surface active soil oxides found in the natural environment vary widely in their geochemical properties and surface chemistry. Hydrated suspensions of iron and manganese oxides are known to show high uptake capacity for cations and anions. The hydrolysis of metal is generally assumed to be responsible for the increase in the uptake of metals onto oxide surfaces with increasing pH. The three main mechanisn of uptake are surface hydrolysis, ion exchange and oxidation of the metals and structural substitution for Mn [52-53].

The uptake of Cd and Co on to birnessite in general can be explained by a mechanism involving first hydrolysis of metal ions in the solution, and then subsequent uptake of a hydrolysed product.

The three uptake processes for cadmium-cobalt uptake in the birnessite-water system may be attributed to: ion exchange, binding on the oxide surface and migration into a crystal lattice as shown in Figure 4.7.

Adsorption is the separation of the metal species from solution accompanied by its concentration at the oxide surface. The three principal types of adsorption, depending on the nature of the forces involved are (1) physical adsorption (2) chemical adsorption (chemisorption) and (3) ion exchange

Ion exchange refers to the exchange between the counter ions balancing the surface charge on the dispersion and the ions in the solution. Positively charged cations in solution are attracted to the negatively charged edges and surfaces of the oxide particles. If the cations do not form covalent bonds with the surface, only a weak association is formed between the adsorbed ion and the oxide particle. Because of the weak association, the adsorbed ions are easily exchanged by other cations. The drop in pH in the negative surface charges on the oxide is indication of ion exchange

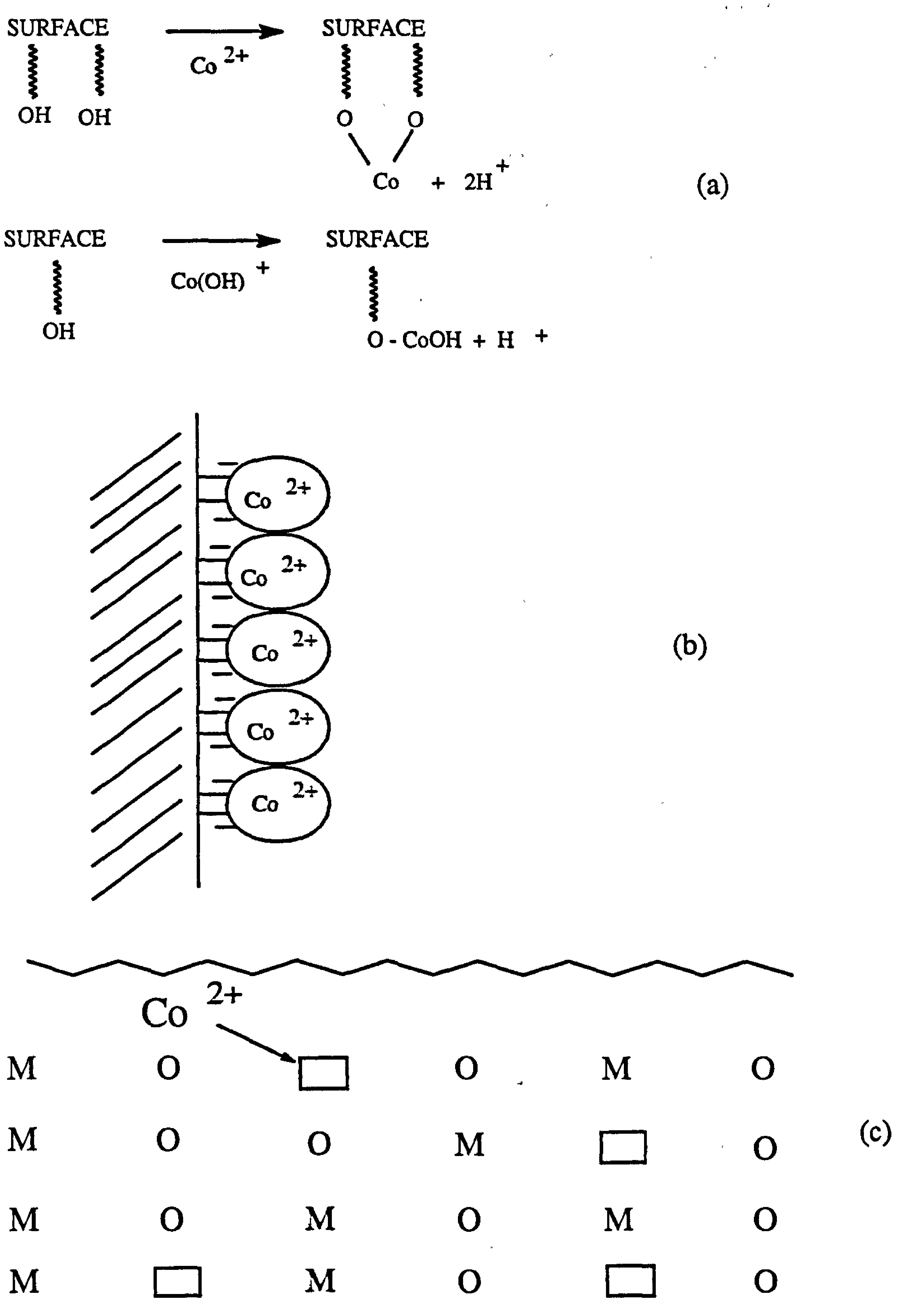


Figure 4.7 Schematic representation of hydrated oxides uptake mechanism (a) ion exchange (b) adsorption (c) migration into lattice vacancy [53]

In the lattice of the oxide there are cation vacancies into which cations can migrate as shown in Figure 4.7(c). The relative migration rates depend on the ionic diameters and the pH conditions. With increasing pH the affinity of the oxide surface is increased up to the point where the formation of anionic hydroxo complexes of the metals inhibits the access to the surface. With increasing effective ionic radii at coordination area the migration rate decreases in the order Cd^{2+}(0.97pm) > Co^{2+} (0.745pm). In the bulk of the solid these ions can migrate to lattice sites and remain fixed in the lattice. This process is irreversible and causes the metals to become immobilized and unavailable with time

The ion uptake also occurs in the interfacial region that includes adsorption and surface precipitation at pH values significantly below the bulk precipitation. The uptake of metal species above PZC on the negatively charged surface of the oxide is facilitated due to the attraction between the oxide surface and the metal ions in the solution. Accordingly, when ions are adsorbed in a solid-liquid interface, the solvation sheath about the ions must be removed. The energy requirement for the displacement of the water layer may be quite large. A major contribution to the solvation energy is made by the dielectric constant of the solid. The dielectric constant is the property of the gel-like amorphous layer in the solid-liquid interface and the value may be quite different from that obtained experimentally on a single crystal or powder. Solvation energy is high when the solid has a low dielectric constant therefore both specific and columbic attractions of ions to the surface are opposed. Metal ion uptake in such instances will be observed when the pH increases. A pH increase should be enough so that the solvation energy decreases in response to an increased hydrolysis and the coulombic attraction increases owing to the increased negative energy on the surface. In contrast, the solvation energy is low if the solid has a high dielectric constant in the solid-liquid interface. Consequently significant uptake can occur even when the surface charge on the solid is nearly zero.

4.4.2 Establishing uptake rate parameters

Preliminary runs were carried out to determine the effect of pH as a major experimental parameter. Two samples with duplicates weighing 50 mg of $Na_4Mn_{14}O_{27}.9H_2O$ were dispersed in 25 ml of 1 x 10^{-2} M $NaNO_3$ background electrolyte solution. The samples were adjusted to 6 and 8 pH values.The dispersion was left for seven days during these period the pH of the suspension dropped continuously. The pH was adjusted to the original pH with 1 x10^{-1}M NaOH. When a constant pH was observed 25 ml of 1.36 x10^{-4} M [Co] and 7.1 x 10^{-5} M [Cd] solution was added to the the duplicate dispersions. Samples were taken at 15, 45, 90, 360 minutes, then at 12, 36 and 72 hours contact times. Both batches show a drop of pH. A drop of one pH value is measured in 18 hours; then another 0.2 pH unit drift occurred during the remaining time for pH 8 batch. The final pH (pH 6 batch), after 72 hours, for the cobalt and cadmium are 5.00 and 5.20 respectively with 30% cobalt and 22% cadmium uptake. For the pH 8 batch uptake percentage is 52 and 45 for cadmium and cobalt respectively.

The role of contact time was studied using 25 ml of 50 mg sodium birnessite suspensions plus 25 ml cobalt or cadmium solution in 1x 10^{-2}M $NaNO_3$ which was stirred for 6 hours while the pH was continuously checked and adjusted. After six hours the sample was centrifuged and filtered, and cobalt or cadmium concentrations were determined. Two additional sets of samples were subjected to 8 and 12 hours contact time prior to metal content analysis. An apparent change in cobalt and cadmium uptake was observed in extended contact time and 10 hours was taken as the optimum contact time. Consequently an uptake period of 10 hours was adopted and during this time the pH was checked and adjusted every hour.

The reversibility of uptake process was also studied. Uptake of cadmium onto $Na_4Mn_{14}O_{27}.9H_2O$ at pH 4 was reversed within an error of 1.5%. when the pH was raised to 8 and brought back to 4 once again after 5 hours. Similar tests were performed for cobalt at pH 3 and 7, and the results show the extent of irreversibility of cobalt uptake.

4.4.3 Experimental procedure

Cobalt and cadmium uptake measurements on to birnessite were carried out on a series of samples with six variable factors: pH, metal concentration, sorbent concentration, contact time, supporting electrolyte concentration, and temperature being studied independently. Partitioning measurements between birnessite and the solution were determined with atomic absorption spectrophotometry.

The following procedure was used in all experiments. A weighed sample of birnessite ($Na_4Mn_{14}O_{27}.9H_2O$) was added to 25 ml of 1 x 10^{-2} M $NaNO_3$ supporting electrolyte and allowed to rehydrate and disperse overnight.

Before the addition of the adsorbate, the pH of birnessite ($Na_4Mn_{14}O_{27}.9H_2O$) slurry was adjusted, by appropriate addition of 1 x 10^{-1} M NaOH or 1 x 10^{-1} M HNO_3 solution slowly to the mixture, to the pH were added; pH values of the $Na_4Mn_{14}O_{27}.9H_2O$ with the sorbate were adjusted to values ranging from 2.5 to 8. As both adsorbates are cations, the starting pH is in the acid range. To the rehydrated suspension 25 ml of predetermined concentration of cobalt or cadmium solution in 1x 10^{-2} M $NaNO_3$ is added.

The suspension was agitated continuously on an end- to- end shaker at 250 throws min^{-1} for the required time at room temperature. During this period the pH of the suspension was adjusted periodically. The suspension was then centrifuged for fifteen minutes, and the supernatant solution was filtered off through a 0.45μ membrane filter. The clear supernatant solution was then analysed for Cd or Co by atomic absorption spectroscopy. A minmum of six data pairs average were used to define the uptake edge.

The cobalt and cadmium initial concentrations used were 3.39 x 10^{-5} , 6.79 x 10^{-5}, 1.36 x 10^{-5} and 2.7 x 10^{-4} M [Co], and 1.78 x 10^{-5}, 3.56 x 10^{-5}, 7.10 x 10^{-5} and 1.4 x 10^{-4} M [Cd]. Other experimental parameters were varied according to experimental requirements. The metal-containing solution was prepared by diluting a fresh stock solution for each batch to the required concentration. Stock solutions were prepared by diluting a concentrated cadmium or cobalt solution of 1000 μg ml^{-1} to 100 μg ml^{-1}

4.5 Results and discussion

4.5.1 Effect of pH

The uptake of cadmium or cobalt onto $Na_4Mn_{14}O_{27}.9H_2O$ increases with increasing pH as shown in Figures 4.8-4.9. The percentage cadmium or cobalt adsorbed on $Na_4Mn_{14}O_{27}.9H_2O$ increases between pH 4 and 6 for the first three concentrations. At pH values higher than 6 the percentage uptake reaches its peak and levels off. The largest rate of increase of uptake is in the pH range 4 - 6 which is the typical soil pH range

Metal oxides in aqueous solution carry a surface charge that is dependent on the pH of the solution. The point of zero charge value is the point where the surface charge of the sodium birnessite should not change. It is expected to be positively charged at pH below PZC and negatively charged above the PZC. In this experiment the pH of PZC of $Na_4Mn_{14}O_{27}.9H_2O$ determined experimentally is 2.9 using electrophoresis. Accordingly, cation uptake should be favourable at pH values greater than pH 2.9 while anions should be preferentially adsorbed at relatively higher rates at pH values below 2.9. At pH below PZC there is an electrostatic repulsion between Co^{2+} and Cd^{2+} ions and the positively charged surface of $Na_4Mn_{14}O_{27}.9H_2O$. A very low adsorption of both cations below PZC as observed in Figures 4.8-4.9 suggests that ion exchange may be taking place. At a pH above PZC, counter-ion type adsorption in the diffuse double layer of an interface is expected and an increase in pH will result in cations replacing hydrogen ions from oxide surface sites giving rise to a nonspecific adsorption reaction.

4.5.2 Effect of metal ion concentration

The variation in the uptake percentage of cadmium and cobalt onto $Na_4Mn_{14}O_{27}.9H_2O$ as a function of metal concentration is shown in Figures 4.8 and 4.9. Both figures show that with increasing concentration higher pH values are required to allow adsorption of comparable amounts. The uptake at lower metal concentrations should be governed by simple sorption processes, whereas at higher concentrations it will be lower than the maximum possible because of the saturation of the sorption sites.

4.5.3 Effect of Temperature

The uptake of cobalt and cadmium on to $Na_4Mn_{14}O_{27}.9H_2O$ was studied at 15,25 and 60°C. The effect was studied at electrolyte concentration of 1×10^{-2} M $NaNO_3$ at the same initial metal concentration 3.56×10^{-5}, 6.79×10^{-5} for cadmium and cobalt respectively. Both metals uptake have shown an increase with increasing temperature as shown in Figures 4.10 and 4.11. Both metals react similarly to the reduction in temperature which is manifested in a pH increase.

It is difficult to ascribe a particular trend to temperature, but caution is required in interpreting the results as temperature change can affect several factors simultaneously. For example an increase in temperature can affect an increase in the rates of uptake, hydrolysis and recrystallization. An increase in temperature can also change the dissociation constant of water and may alter the potential of the reference electrodes.

4.5.4 Effect of electrolyte concentration

The effect of electrolyte concentration on the adsorption of cobalt or cadmium by $Na_4Mn_{14}O_{27}.9H_2O$ was studied by varying the electrolyte concentration from 10^{-1} to 10^{-3} M $NaNO_3$ at the same initial metal concentration 3.56×10^{-5} and 6.79×10^{-5} for cadmium and cobalt respectively. The results in Figures 4.12 and 4.13 show that uptake for both metals decreases with increasing electrolyte concentration.

As the strength of the electrolyte is increased, the electrical double layer about the particles becomes compressed; in turn, the increased electrical field and solvation energy result in a decrease in the uptake of the metal ions. Accordingly, there is a relatively small effect on the solvation energy, by increasing the electrolyte concentration of the solution.

4.5.5 Effect of surface area

The uptake of cadmium and cobalt at three surface areas was studied at constant temperature, contact time and metal concentrations. Figures 4.14 and 4.15 show that with the range of surface area studied (50, 95, 285 m^2/l) at cadmium and cobalt concentration of 3.56×10^{-5} M [Cd] and 6.79×10^{-5} M [Co]. The uptake edge has moved

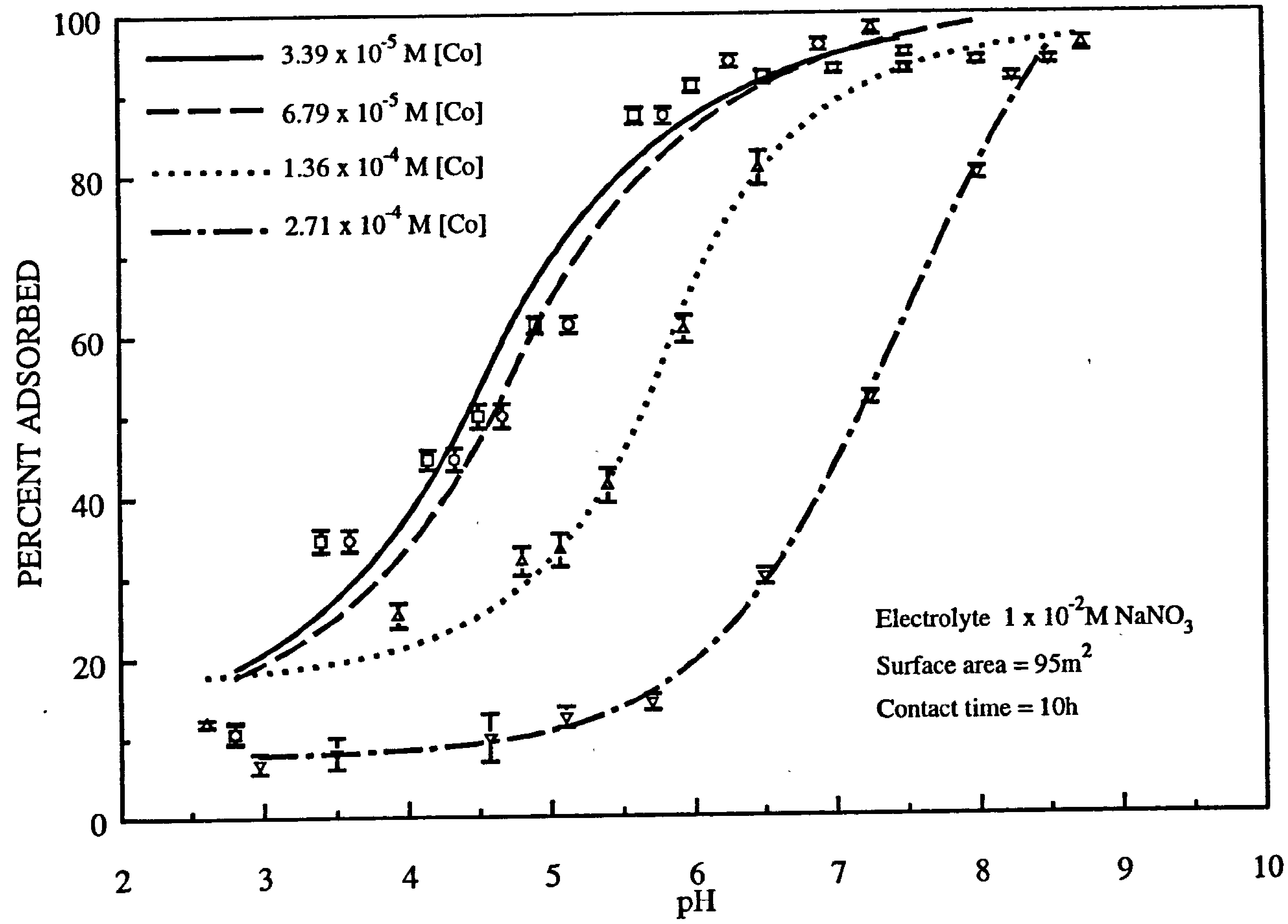


Fig 4.8 Co adsorption as a function of pH and Co concentration

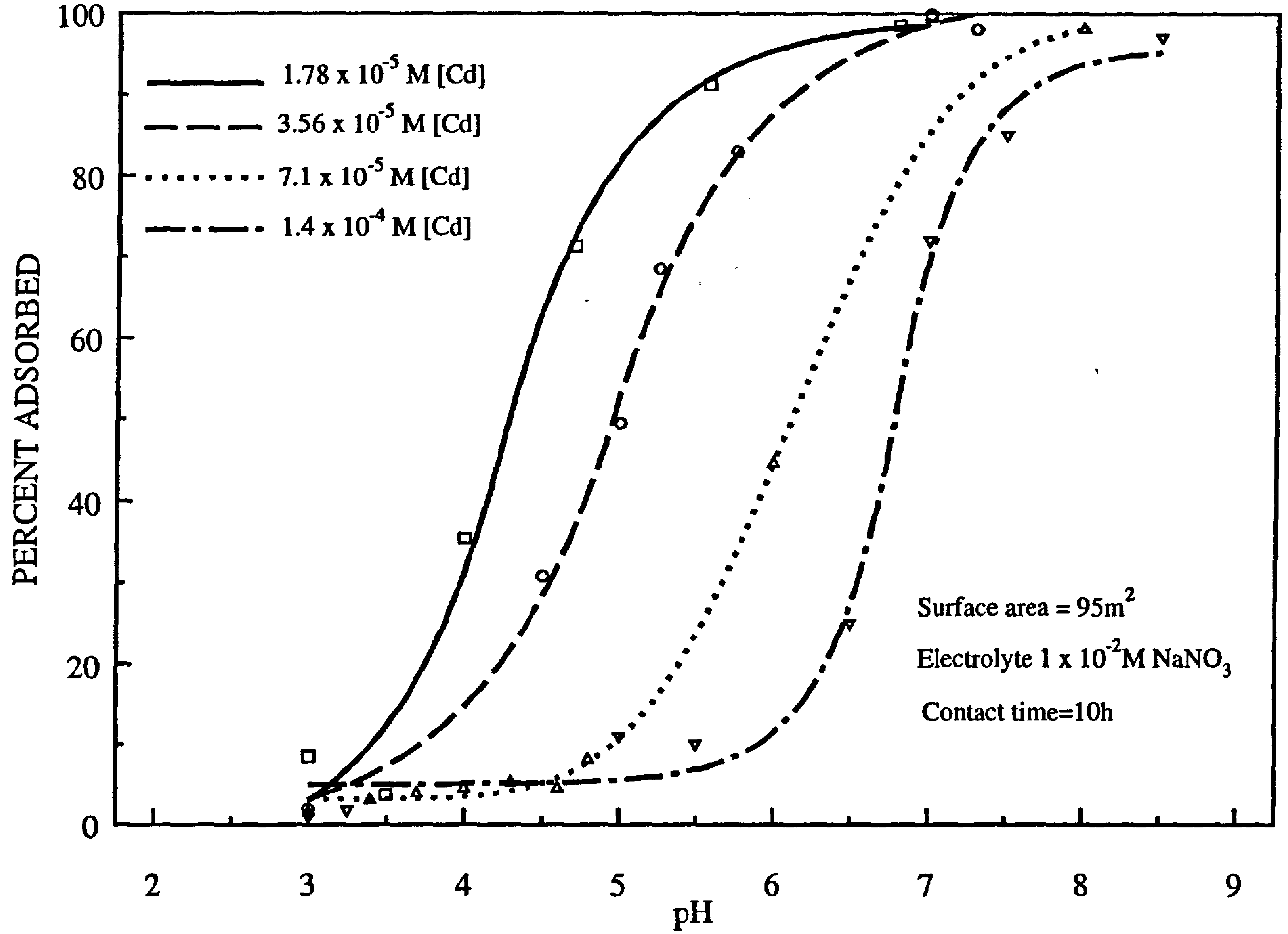


Fig 4.9 Cd adsorption as a function of pH and Cd concentration

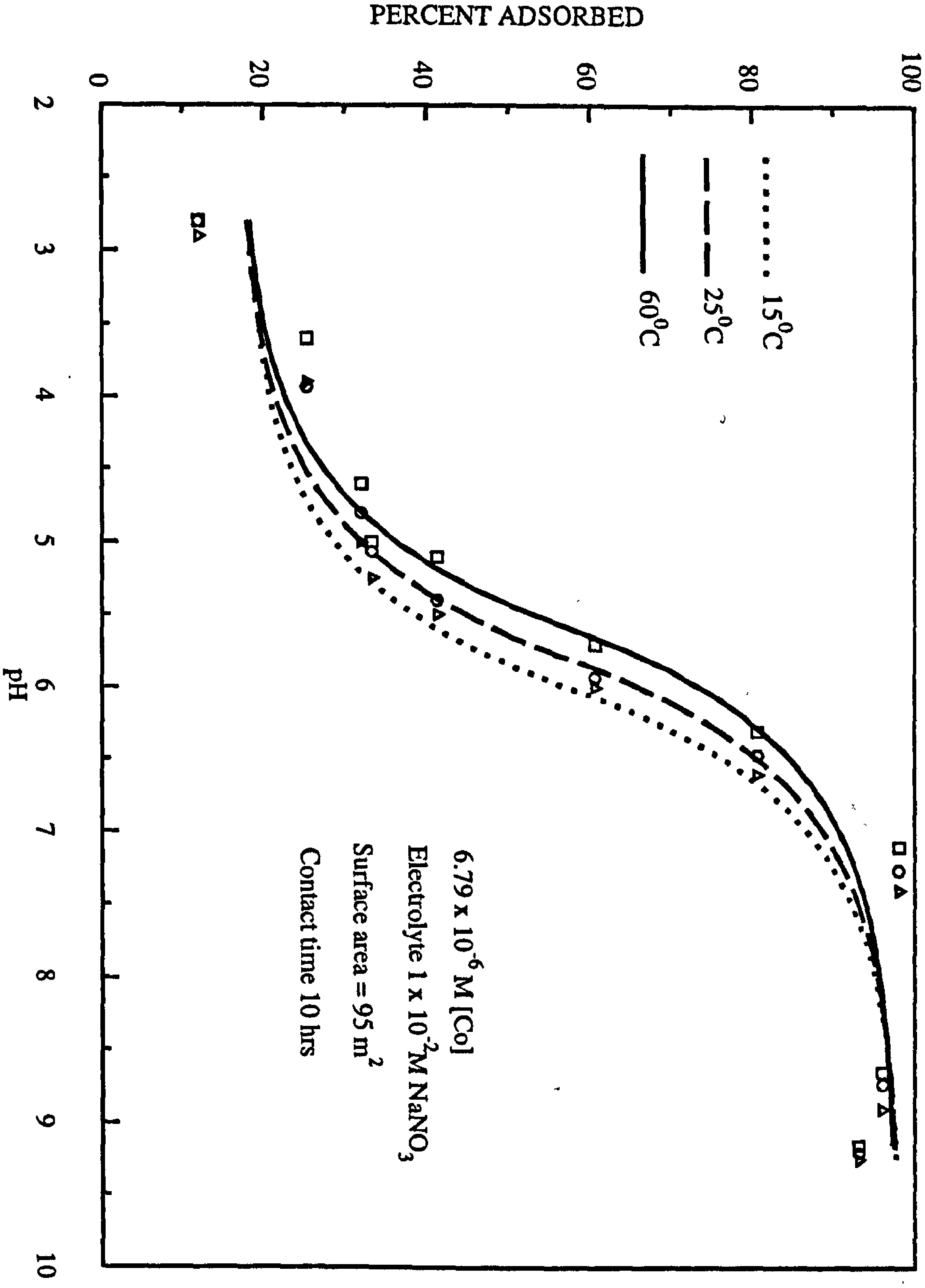


Fig 4.10 Co adsorption as a function of pH and temperature

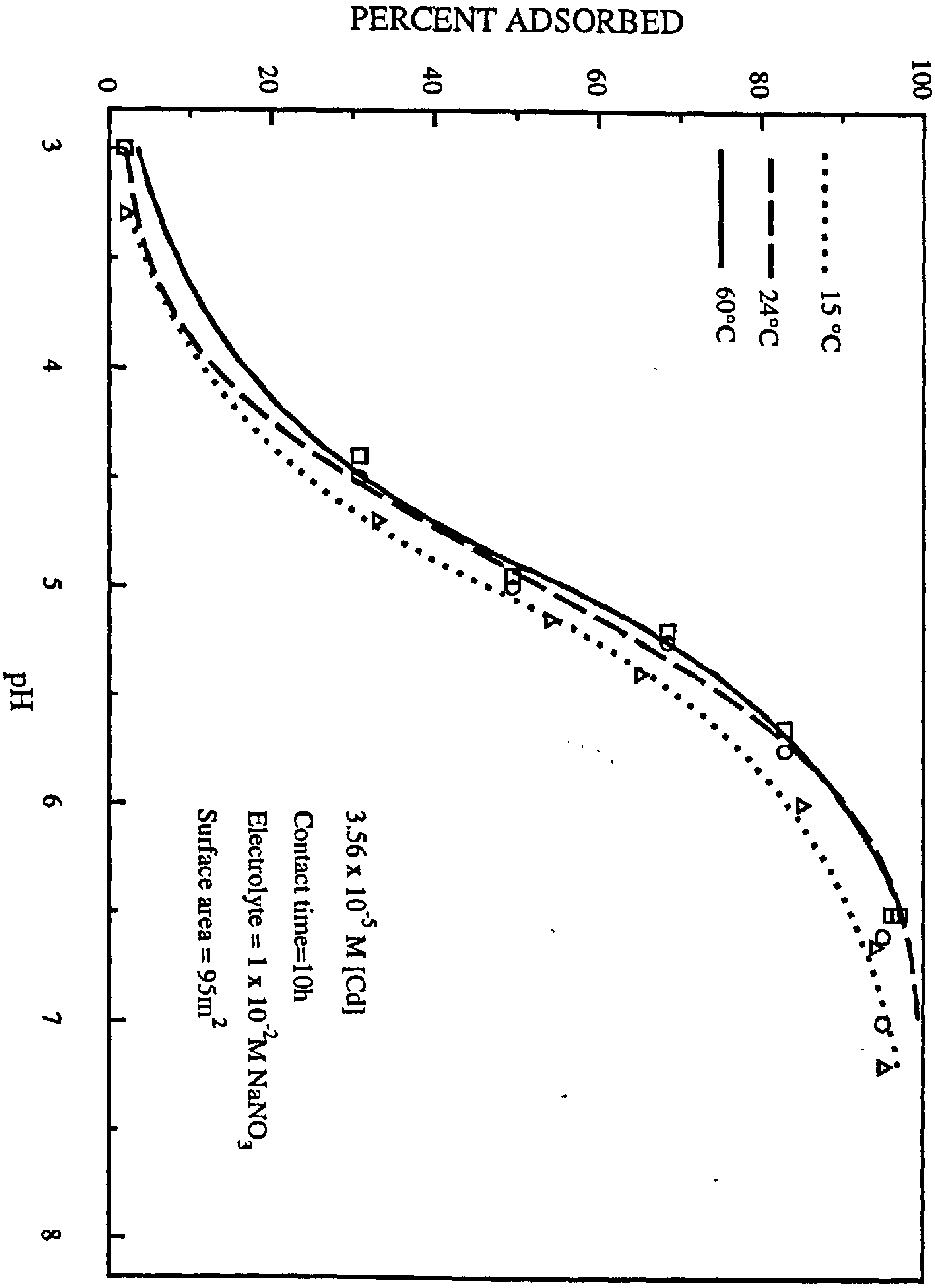


Fig 4.11 Cd adsorption as a function of pH and temperature

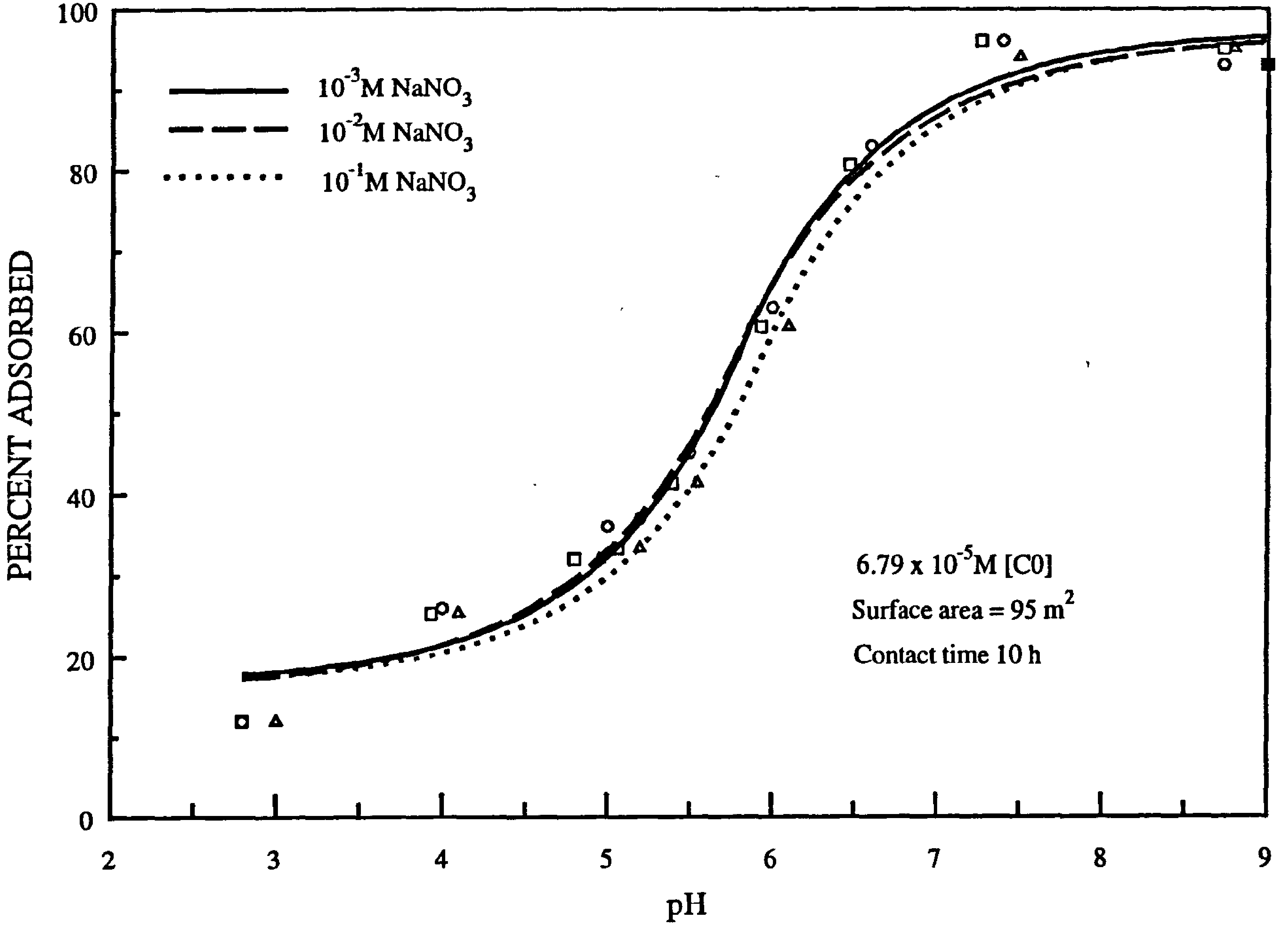


Fig 4.12 Co adsorption as a function of pH and electrolyte concentration

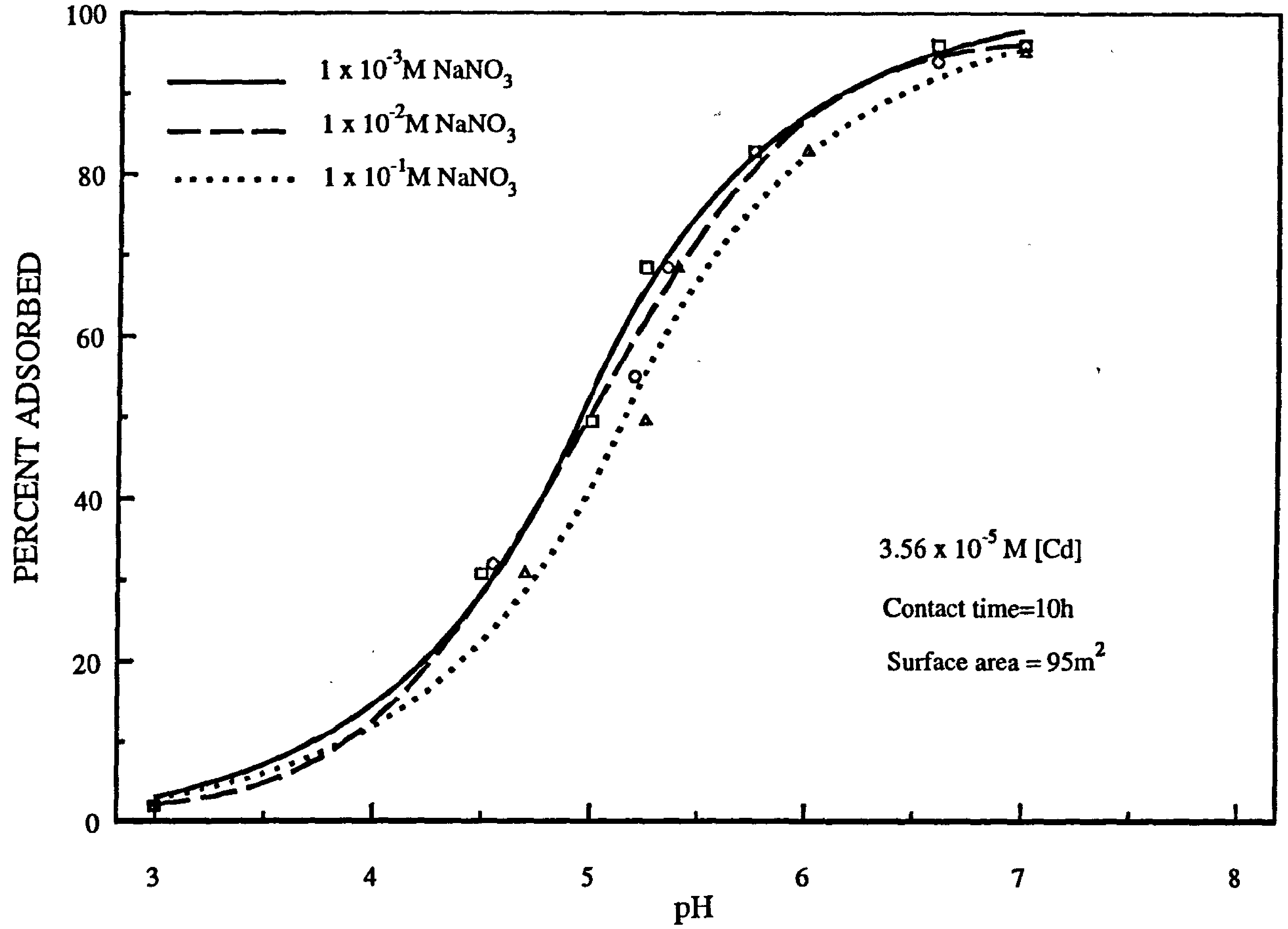


Fig 4.13 Cd adsorption as a function of supporting electrolyte concentration

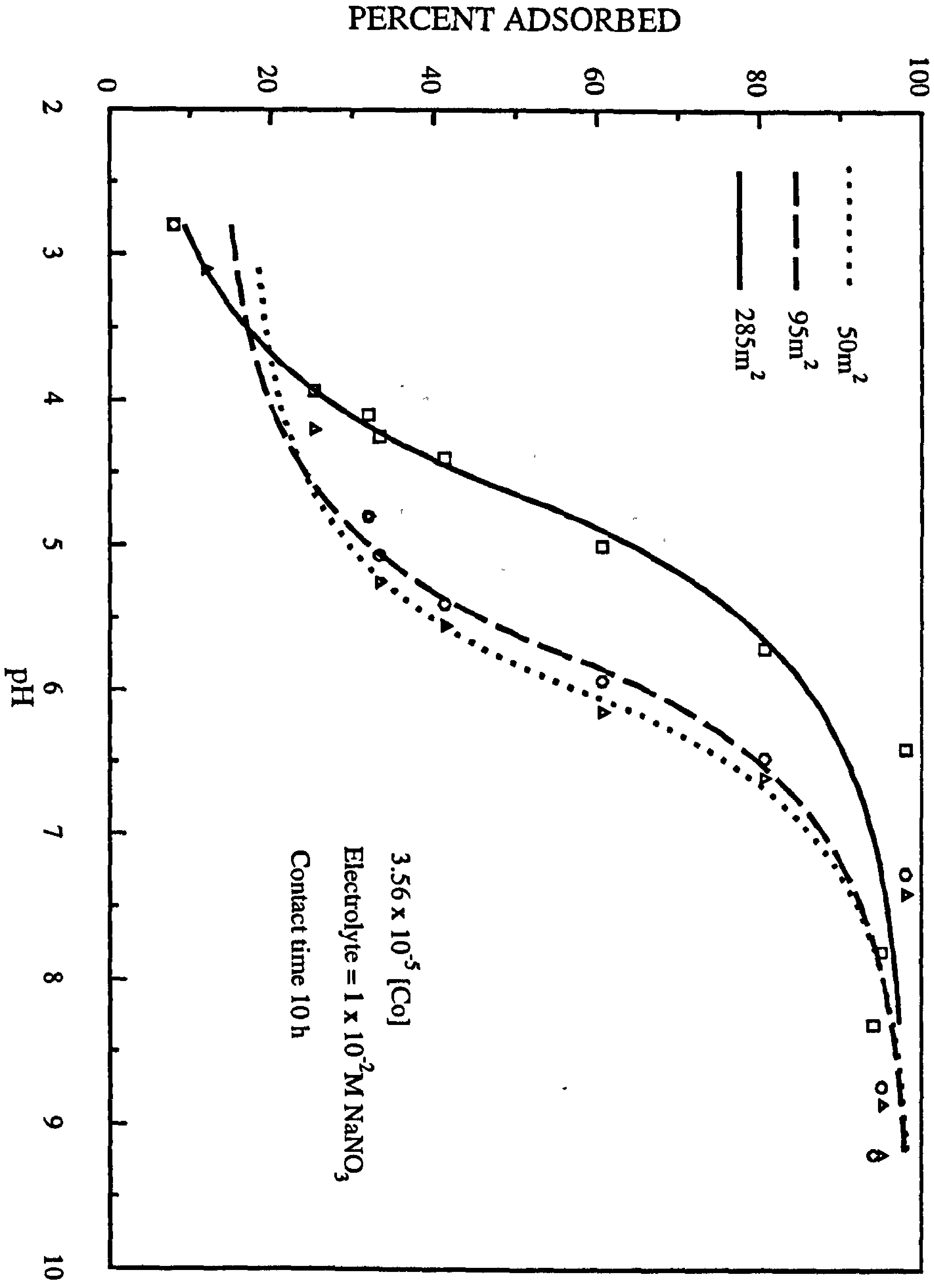


Fig 4.14 Co adsorption as a function of surface area

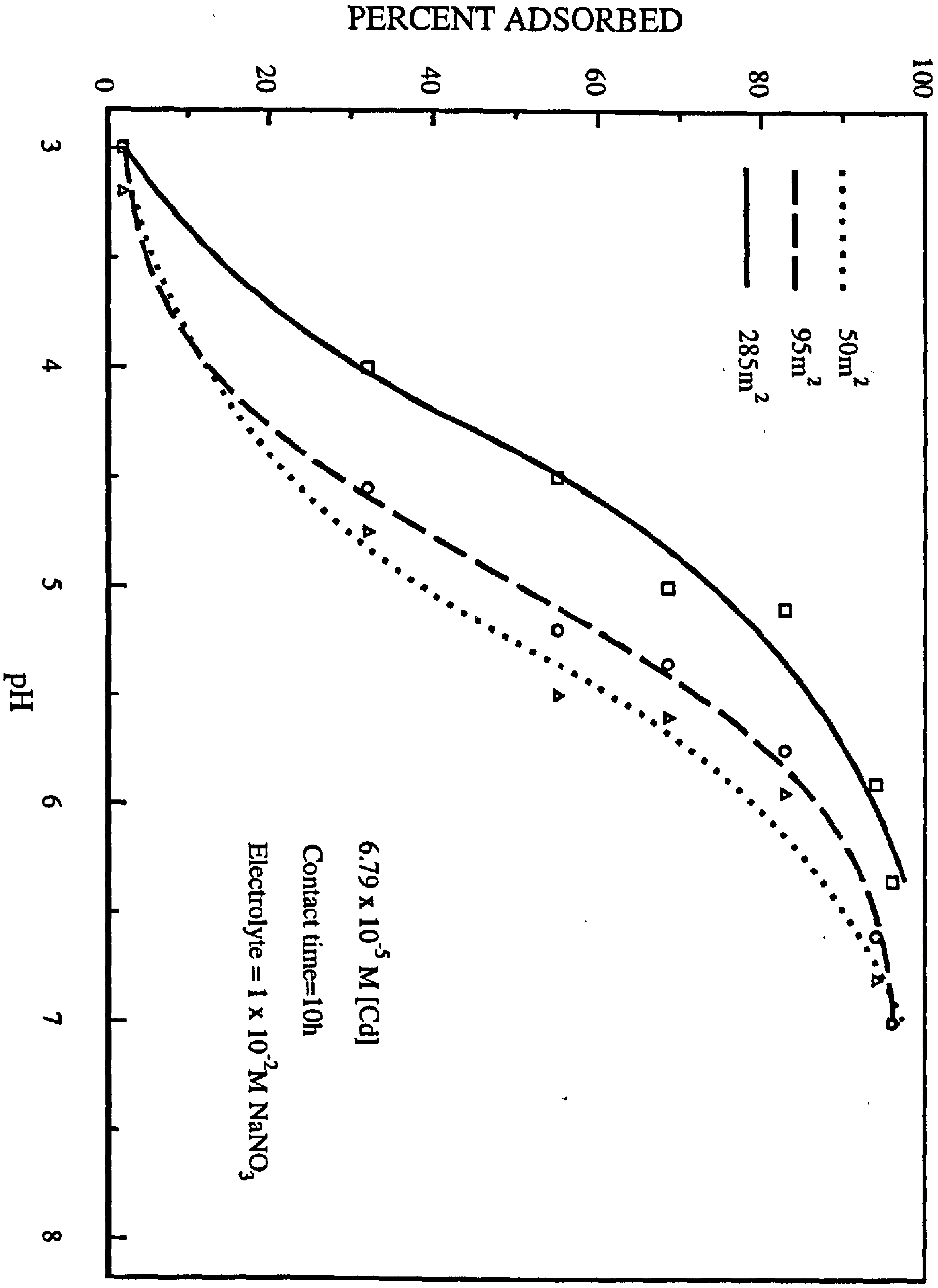


Fig 4.15 Cd adsorption as a function pH and surface area

to a lower pH with an increase in the birnessite surface area. the percentage of cations adsorbed decreases with a decrease in surface area and vice versa. The general explanation is, that at a low surface area the number of binding sites and exchangeable ions per cations is relatively low and cations have to compete with other cations for the available binding sites. As a result, the percentage of cations adsorbed decreases. However, as the surface area is increased at constant metal concentrations the number of binding sites is sufficiently large so that cations do not have to compete for available sites.

At constant pH with an increase in surface area, more birnessite is present in the suspension to remove the metals. As a result, the percentage of the metals adsorbed increases, which results in the shift of an uptake edge to a lower pH. A three- fold increase in the surface area results in a decrease in pH of one unit. There is not such a significant pH increase for a half reduction in the surface area. Uptake of both cadmium and cobalt showed a tendency to increase with the surface area. Surface area of the birnessite is therefore, as expected, a major factor that determines the effectiveness of cadmium and cobalt uptake at a given pH.

4.5.6 Effects of contact time

The uptake curves of Cd and Co are shown in Figures 4.16 and 4.17 for an initial metal concentration of 3.56 x 10^{-5} M [Cd] and 6.79 x10^{-5} M [Co]. The curve shifts to lower pH as contact time increases. With increasing contact time from 10-120 h at room temperature the amounts of Co adsorbed at pH 4 increase from 15 to 30%. The corresponding increase in the Cd uptake is 12%.

The reduced uptake at longer contact time, especially as observed with Co, can be indicative of processes other than a surface exchange contact that may include oxidation of $[Co]^{2+}$ to $[Co]^{3+}$ and substitution of $[Co]^{3+}$ for structural manganese. It was difficult to attain equilibrium at constant pH in these experiments, and it was necessary to continuously adjust the pH throughout the contact time. This pH drop is an indication of ion exchange.

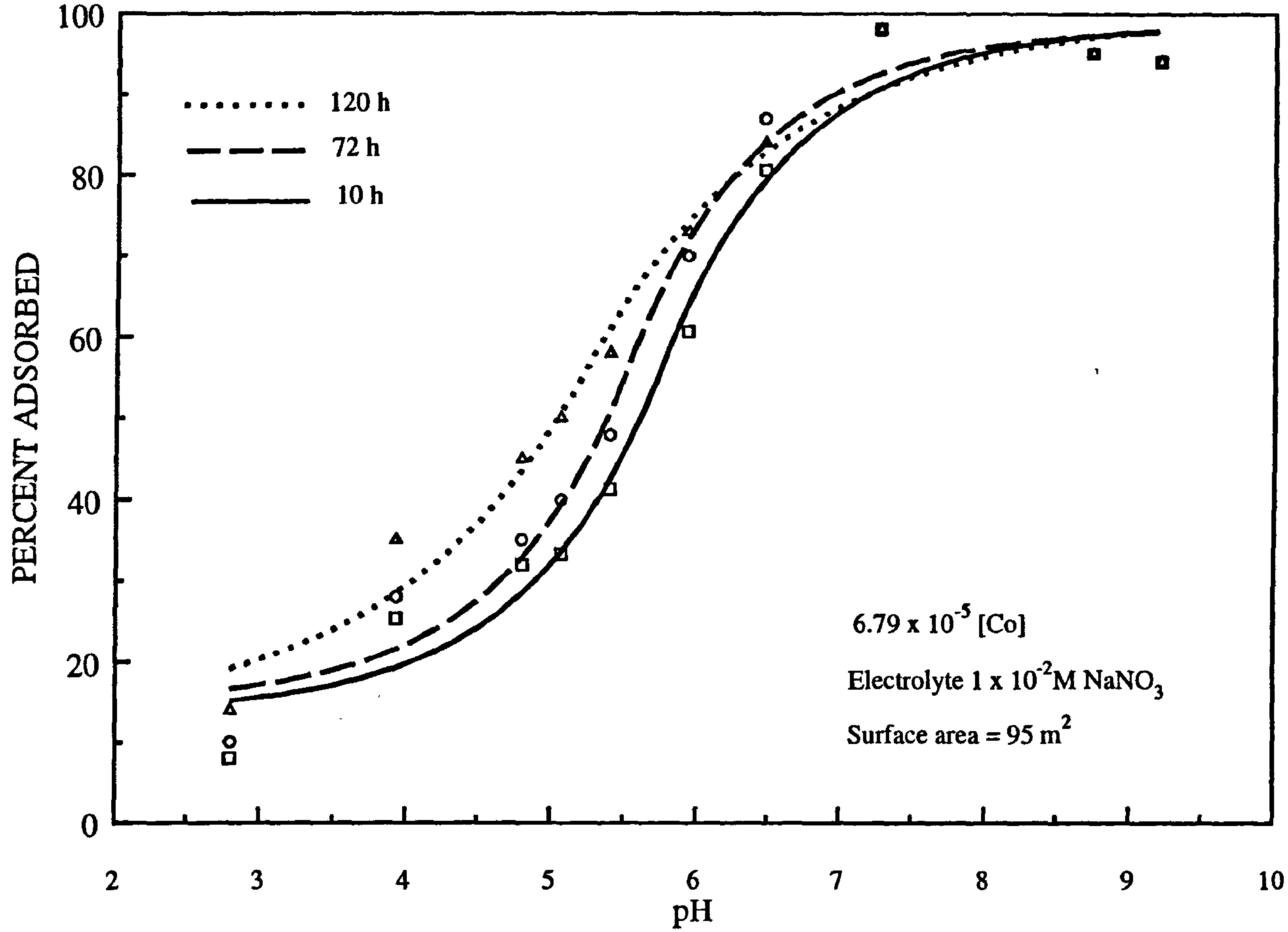


Fig 4.16 Co adsorption as a function of pH and reaction time

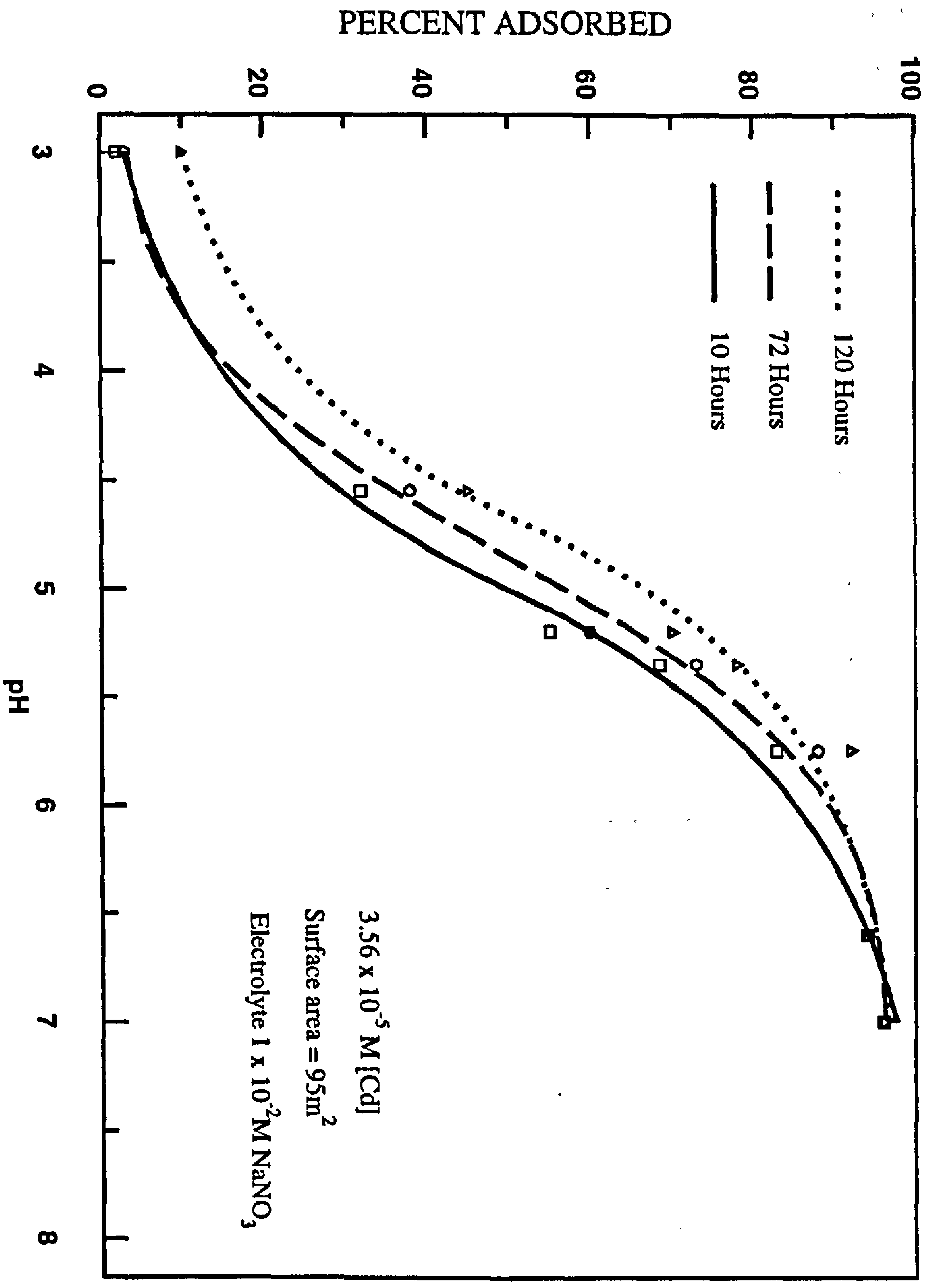


Fig 4.17 Cd adsorption as a function of pH and reaction time

4.6 Conclusions

Results of the sorption experiments of cadmium and cobalt on to synthetic birnessite $(Na_4Mn_{14}O_{27}).9H_2O$ is presented; birnessite is among the manganese oxides widely available in soil which have a relatively high surface area. The experiment was performed under both acid and alkaline conditions to enable extrapolation to a real environment.

The prepared oxide was characterised by measurement of surface area, surface charge density, crystal dimension and morphology, and an evaluation of its composition. The characterisation data confirmed that the product was birnessite $(Na_4Mn_{14}O_{27}).9H_2O$.

The uptake of cadmium and cobalt was measured as a function of pH, metal concentration and oxide concentration, electrolyte concentration, contact time and temperature. The uptake occurs in a pH range both above and below PZC (3.0-8.0), indicating various types of sorption mechanisms. The sorption curves are sigmoidal. The uptake capacity increases with increasing pH with a peak at about 6.4. With increasing concentration of metals, higher pH values are required to sorb comparable amounts. The uptake of both metals has showed an increase with increasing temperature, but also a decrease with increasing electrolyte concentration. The uptake edge has moved to a lower pH with an increase in the birnessite surface area and contact time. Thus, pH, oxide concentration and contact time and temperature are the major factors for the retention of both cobalt and cadmium on to birnessite.

The capacity of birnessite to retain and release both contaminants and nutrients are controlled by the physico-chemical properties of the oxide, the properties of the contaminant and environmental factors such as temperature and electrolyte. The retention is the result of processes such as sorption and migration into the crystal lattice. The rates at which these reactions occur together with the physical characteristics of birnessite control the concentrations of the contaminants and nutrients in the soil-water system. Contaminants retained maybe released or transported into other environmental media. The form and rate of release are controlled by the properties of both the contaminants and the medium as well as the environmental conditions and by the management of land.

The transport and fate of contaminants in soil oxide-water system as exemplified by birnessite can illustrate the retention ability of birnessite. Birnessite is prevalent in soils and sediments, and the pH range of uptake indicates that it can be the most important heavy metal scavenger in the natural environment where the pH range is between 5 and 7. Thus birnessite can serve as a sink for contaminants in the adverse impact of both human activities and natural phenomena on the soil-water environment. This can be a contamination of soil and groundwater by heavy metals associated with industrial and commercial operations, waste disposal facilities, agricultural production flooding, and volcanic activity.

The knowledge of contaminant partitioning and mobility in the soil-water environment is required to address environmental problems, as shown in this work. It is needed to evaluate the probability of contamination associated with accidental release that can be bioavailable and will also reach the aquifer and contaminate groundwater. Such knowledge is also valuable to develop and evaluate methods for remediation of contaminated soils. Above all knowledge of contaminant interaction, transport and fate is necessary to design pollution prevention strategies.

4.7 References

1 Huebner, J.S., (1976) The Manganese oxides - a bibliographic commentary. In : Rumble, D. (ed), Oxide Minerals, Min. Soc. Am.

2 Taylor, R. M., and Mackenzie, R.M., and Norrish, K. (1964) The Mineralogy and chemistry of manganese minerals in some Australian soil, Australian soils Aust. J. soil Res., 2, 235 - 248

3 Cerar, D.A., Cormick, R.K. and Barnes, H.L. (1980) Geochemistry of manganese: An overview. In: Varentsov, I.M. & Graselly, G. (eds.) Geology and geochemistry of Manganese, Vol. I, Hungarian Academy of sciences, Budapest.

4 Jenne, E. A.,(1968) Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides, Advances in Chemistry 73, 337-387,

5 Chao, T.T, and Theobald, P.K., (1976) The significance of secondary iron and manganese oxides in the geochemical exploration. Econ. Geol., 71, 1560 - 1569

6 Means, J.L., Crerar, D.A., Borcsik, M.P., and Duguid, J.O. (1978) Adsorption of Co and selected actinodes by Mn and Fe oxides in soils and sediments. Geochim. Cosmochim. Acta. 42, 1763 - 1773

7 Murray, D.J., Healy, T.W., and Fuerstenau, D.W., (1968), The adsorption of aqueous metal on colloidal hydrous manganese oxide, Advances in chemistry series, 79, 74 - 81.

8 Zasoski, R.J. and Burau, R.G. (1988) Sorption and sorptive interaction of cadmium and zinc on hydrous manganese oxide. Soil Sci. Soc. Am. J. 52, 81 -87.

9 Tewari, P.H., Campbell, A.B., and Lee, w. (1972) Adsorption of Co^{2+} by oxides from aqueous solution, Can. J. Chem. 50, 1642-1648

10 Taylor, R. M., and Mackenzie, R.M. (1966) The association of trace elements with manganese minerals in Australian soils. Aust. J. soil Res., 4,29 - 39.

11 Taylor, R. M., and Mackenzie, R.M., and Norrish, K. (1964) The Mineralogy and chemistry of manganese minerals in Australian soils . Aust. J. soil Res., 2, 235 - 248

12 Taylor, R.M. (1968) The association of Mn and Co in soils--further observations J. Soil Sc., 19, 77 - 80

13 Mackenzie, R. M., (1970) The reaction of Co with manganese dioxide minerals. Aust. J. Soil Res. 8, 97 - 106

14 Kobayehi, J., (1972), Relation between the Itai-Itai disease and pollution of river water by cadmium from a mine. Adv. Water Pollu. Res. Proc., 5th int. conf. San Francisco and Hawaii, I-25, 1-7

15 Friberg, L., Piscator, M., Norberg, C., (1971), Cadmium in the environment., Chemical Rubber Company, Cleveland.

16 Yamagata, N., and Iwashima, K., (1963) Monitoring of sea water for important radioisotopes released by nuclear reactors. Nature, 200, 52-53

17 Fukai, R., Huynh-Ngoe, and Vas, D., (1966) Determination of trace amount of cobalt in sea water after enrichment with solid manganese oxide, Nature, 211, 726-727

18 Mackenzie, R.M. (1989), Manganese oxides and hydroxides: in minerals in the soil environments, 2nd ed., J.B. Dixon and S. B. Weed, eds. , Soil Science society of America, Madison, Wisconsin.

19 Posselt, H.S., Andeson, F.J., Weber, W.J. (1968), Cation sorption on colloidal hydrous manganese dioxide. Environ. Sci. Technol. 2, 1087-1093

20 Posselt, H.S., Reidies, A. H., Weber, W.J. (1968), Coagulatioation of colloidal hydrous manganese dioxide, J. Amer. Water Works Assoc., 60, 48 - 68

21 Slavek, J., and Pickering, W.F. (1985), Chemical leaching of metal ions sorbed on hydrous manganese oxides, Chemical Geology, 51, 213 -223

22 Burns, R. G. (1976).The Uptake of Cobalt into Ferromanganese Nodules, Soils, and Synthetic Manganese(IV) Oxides, Geochim. Cosmochim. Acta 40, 95-102

23 Hammond, A.L. (1974) Manganese nodules (I) mineral resources in the deep sea bed. Science, 183, 502 - 503.

24 Usui, A. (1979), Nickel and copper accumulations as essential elements in 10Å manganite of deep - sea manganese nodules. Nature 279, 411-413

25 Bowen, H.J.M., (1966), Trace elements in biochemistry. Academic press, New York

26 Buser, W. Graf, P., and Feitknecht W., (1954) Beitrag zur Kenntnis der Mangan(II) -manganite und des δ-MnO_2. Helv. Chim. Acta 37, 2322-2333.

27 Bricker, O.P., (1965) Some stability relations in the system Mn-O_2-H_2O and one

atmosphere total pressure. Am. Mineral. 50, 1296-1354.

28 Giovanoli, R., E. Staehli, and W. Feitknecht. (1970) Ueber oxidhydroxide des vierwertigen Mangans mit Schichtengitter. 2. Mangan(lll)-manganat(lV). Helv. Chim. Acta 53, 453 - 464.

29 Burns, R.G. and Burns, V.M. (1977) The mineralogy and crystal chemistry of deep sea manganese nodules , a polymetallic resource of the twenty first century. Phil. Trans. R. Soc. Lond. (A), 283 - 301

30 Wadsley, A.D. (1955) The crystal structure of chalcophanite, $ZnMn_3O_7.3H_2O$, Acta Crystallogr.,8, 165 - 172

31 Jones, L.H.P., and A.A. Milne, (1956), Birnessite, a new manganese oxide mineral from Aberdeenshire, Scotland. Mineral. Mag. 31, 283-288.

32 Giovanoli, R., E. Staehli, and W. Feitknecht. (1970) Uber Oxidhydroxide desvierwert gen Mangans mit Schichtengitter1. Natriummangn(ll,lll)-manganat(lV). Helv. Chim., 53, 209 - 220

33 Giovanoli, R., H. Buehler, and K. Sokolowska.(1973) Synthetic lithiophorite: Electron microscopy and x-ray diffraction. J. Microscopie. 18, 271-284.

34 Brown, F.H., Pabst, A., and Sawyer, D.L. (1971) Birnessite on colemanite at boron, california. Am. Mineral. 57, 284 - 287

35 Potter, R.M., and Rossman, G.R. (1979) The manganese and iron oxide mineralogy of desert varnish. Chem. Geol., 25, 79 - 94

36 Golden, D.C., Dixon, J.B., and Chen, C.C., (1986) Ion exchange, thermal transformations, and oxidizing properties of birnessite, 34 , (5), 511 -520

37 Adams, S.N., Honeysett, J.L., Tiller, K.G., and Norish, K., (1969) Factors controlling the increase of cobalt in plants following the addition of cobalt fertilzer. Aust. J. Soil Res., 7, 29 - 42

38 stahli, E., (1968) Uber Manganates (IV) mit schichten-struktur, Ph. D. Thesis, University of Bern, Switezerland

39 Parida, K.M., Kanungo, S.B., and Sant, B.R. (1981), Studies on MnO_2 - I. Chemical compostion, microstructure and other characteristics of some synthetic MnO_2 of various crystalline modifications. Electrochimica Acta, 26, 435 - 443.

40 Vogel, A.I., (1961), Quanitative inorganic chemical analysis, Longmans, London

41 Kolthoff, I.M., and Sandell, E.B. (1952) Text book of inorganic quanitative chemistry, 3rd ed, Macmillan, New York.

42 Murray, J.W.,Balistreieri. L.S., and Paul, B. (1984), The oxidation state of manganese in marine sediments and ferromanganese nodules, Geochemica et Cosmochimica Acta, 48, 1237-1247

43 Gray, M.J., Malati, M.A., and Rophael, M.W. (1978) The point of zero charge of manganese oxides., J. Electroanal. Chem., 89, 135 - 140

44 Morgan, J.J., and Stumm, W. (1964) colloid-chemical properties of manganese dioxide, Journal of colloid science, 19, 347 - 359

45 Yopps, J.A. and Fuerstenau, D.W., (1966) Effect of crystal structure on the surface properties of a series of manganese oxide , J. colloid Interface, 21, 435 - 444

46 McKenzie, R.M., (1981), The surface charge on manganese dioxides. Aust. J. Soil Res. 19, 41- 50

47 Shaw, D.J., (1969) Electrophoresis, Butterorth press, London

48 Shaw, D.J., (1992) Introduction to colloid and surface cheimstry, Butterorth press, London

49 Wiese,G. R., James,R.O. and Healy,T.W. (1971), Discreteness of Charge and Solution Effects in Cation Adsorption at the Oxide/Water Interface, Disc. Faraday Soc. 52, 302-311

50 International Centre for Diffraction Data -JCPDS (1992) Powder diffraction file 43-1456, JCPDS.

51 Brunauer, S., Emmett, P.H., and Teller, E. (1938) Adsorption of gases in multimolecular layers , J. Am. Chem. Soc, 60, 309 -319

52 Gadde, R.R., and Laitine, H.A., (1974) Studies of heavy metal adsorption by hydrous iron and manganese oxides. Anal. Chem. 46, 2022-2026.

53 Donaldson, J.D., Clark, S.J., & Grimes, S.M,.(1988) Cobalt in electronic technology-the monograph series, The Cobalt Development Institute, London.

5.0 ADSORPTION OF DISSOLVED AND PARTICULATE SPECIES ON TO MAGNETITE AND ITS SOLUBILITY IN AQUEOUS MEDIA

5.1 INTRODUCTION

Magnetite, a primary iron oxide formed in a variety of crystalline rocks, occurs from trace to moderate quantities in soils. It is present as an accessory mineral in many soils, and sometimes makes up a significant portion of the ferromanganese mineral constituents of soils. This is specially true for young soils influenced by basic igneous rocks. Magnetite (Fe_3O_4) and ilmenite ($FeTiO_3$) comprise approximately 2% of the Earth's crust. Magnetite is also an important ore of iron [1]. The name magnetite is said to be derived from the district of Magnesia, near Macedonia. There is, however, a fable that it was named after a shepherd, Magnes, whose ironbound staff and shoes with iron nails stuck to the ground in which magnetite is present [2].

There is a widespread presence of ultra fine grained magnetite in soils as observed from the magnetic properties of the soil even where there is no detrital input of magnetite [3-4]. It is frequently encountered with maghemite (γ-Fe_2O_3) in the top layer of soil horizons [5-6]. Magnetite in the soil is a product of the soil formation process which includes the weathering of ferromagnesian igneous rocks. Maher & Taylor [3] reported the occurrence of pure fine grained magnetite in soils from parts of a United Kingdom that have no apparent external source of magnetite. They considered magnetite as a product of *in situ* inorganic origin. However, Schwertmann & Taylor [7] reported that magnetite has not been found as a newly formed mineral in soils and regard the mechanism of formation as lithogenic rather than pedogenic. Lithogenic magnetite is a common mineral in the coarse, heavy mineral fractions of soils, where as pedogenic magnetite is attributed both to an abiotic and biotic processes. The magnetic properties of soil profiles are characterised by a maximum magnetic susceptibility in the top of the soil, which also suggests pedogenic formation of magnetite [7-8].

In addition to inorganic processes, biomineralization results in magnetite formation in soil and aquatic environments. It is a "biologically induced" mineralisation process that results in the minerals having a crystal, habit similar to those produced by precipitation from inorganic solutions [8]. Magnetotactic bacteria are among the biota that play a significant role in the production of bacterial magnetite [9-11]. The process is characterised by bulk extracellular and/or intracellular mineral formation, without the elaboration of organic matrices. Magnetotactic bacteria contain intracellular chains of single magnetite crystals which are bound to the membrane. It has been suggested that a ferric oxide bearing compound may be the precursor of magnetite crystals [12]. Recent studies also indicate another source in anaerobic environments [13] in which an organism denoted as GS-15, produces ultra fine magnetite. GS-15 is not magnetotactic, but reduces amorphous ferric oxide to extracellular magnetite during the reduction of ferric iron as the terminal electron acceptor for oxidation of organic matter. Sakaguchi et. al. [11] isolated another anaerobic bacterium in aquatic environments where the source of magnetite is attributed to sulphate-reducing bacteria denoted as RS-1. These bacteria are also capable of extracellular iron sulphide precipitation. The process takes place in a zone between the levels at which nitrate and iron reduction occurs. In sediment, this is at a depth where a sulphate-reducing habitat is available. It should be noted that there is little information on the stability of magnetite in near-surface environments.

The objective of the work described in this chapter is to prepare (1) magnetic particles of iron oxides, (2) mixed magnetic oxides by the substitution of iron with other oxides and transition metal cations and (3) magnetite precipitated on inert materials. The adsorption capacity and solubility of the magnetite, and mixed magnetite in the aqueous media under varying physico-chemical conditions analogous to soil mechanisms are studied. The results provide an insight into the behaviour of magnetite in soils and into the use of magnetite and mixed magnetite oxides in environmental pollution prevention and control.

5.2 Magnetite in water and effluent treatment

5.2.1 Magnetite

Magnetite is one of the most commonly occurring iron (II) - iron (III) oxides and has the formula Fe_3O_4. It crystallizes in the cubic system and belongs to the spinel group of minerals. Spinels form a large class of compounds whose structure is related to that of the mineral spinel itself, $MgAl_2O_4$. The general formula for a spinel is AB_2O_4 where A is divalent ion such as Mg^{2+}, Fe^{2+}, Zn^{2+}, Mn^{2+} etc. in a tetrahedral site and B is a trivalent ion such as Fe^{3+}, Al^{3+}, Cr^{3+}, Mn^{3+}, Ti^{3+} in an octahedral site. Most transition metal ions show an octahedral site preference and will have the ion with the highest octahedral site preference in the B site [14]. $Mn^{2+}Mn_2^{3+}O_4$ for example is a normal spinel $Mn_{tet}^{2+}Mn_{2oct}^{3+}O_4$ with the 3+ ions in the B site. In the case of iron, however, Fe^{3+} has a zero octahedral site preference and that for Fe^{2+} is higher. For this reason half of the B sites in Fe_2O_3 are occupied by Fe^{2+} and the tetrahedral site is occupied by Fe^{3+} giving an inverse spinel $Fe^{3+}_{tet}\,Fe^{2+}_{oct}\,Fe^{3+}_{oct}O_4$ [15]. The unit cell of the spinel structure is formed by 32 oxide ions and 24 positive cations. In the cubic form (face-centred) the layers of oxygen atoms alternate with layers of iron atoms. The material has high electrical conductivity because of the distribution of Fe^{2+} and Fe^{3+} ions in the unit cell permits continuous interchange of electrons between Fe^{2+} and Fe^{3+} ions in the lattice by inter-valence charge transfer mechanisms [16-17].

Magnetite has a density of 5.2g/cc, and a hardness of 7.5- 8 on Mohs scale. The saturation magnetisation of magnetite, M_{sat} is 4.78 x 10^5 A/m; its initial permeability (single crystal) μ, is about 100 and the Curie temperature, θ_c, is about 585°C. Other strongly magnetic materials include maghemite (γ-Fe_2O_3), ferrites, pyrrhotite (FeS) iron, nickel, cobalt, wüstite (FeO) and ferrosilicon. None of these possesses any obvious advantage over magnetite in terms of magnetite properties compared with availability and cost[14].

Magnetite is an important component of numerous catalytic and magnetic systems in industry. In its industrial applications is widely used to overcome separation difficulties associated with adsorbents. It can be magnetically removed from solution or isolated from nonmagnetic solids. Magnetite has been used in precipitation/adsorption/coagulation treatment schemes to treat potable water and industrial effluent [18-24].

As magnetism and some magnetic characteristics of magnetite are important, the fundamentals of magnetism are described here.

5.2.2 The Magnetic Field

Most magnetic effects arise from the electrons in a material. The electrons can give rise to magnetism in two ways; by revolving around the nucleus of the atom and by their angular momentum about their own axis. This latter effect is termed spin. In both cases the electron charge can be thought of as moving round in a closed path and so acting as a current loop. In a magnetic field a couple is exerted on the current loop. A measure of this is the magnetic moment. The effect is of the same kind as that experienced by a current carrying coil in a magnetic field [14]

Magnetic substances have two regions called poles. One pole is north or positive, and the other is south or negative. Depending on polarity the poles either repel or attract one another. Coulomb established that the attractive or repulsive forces operating between the poles can be expressed as [25-26]:

$$F_x = Km_1m_2 r_o/r^2 \qquad (5.1)$$

where

F_x is the force in the direction x

m_1 and m_2 the pole strengths

r_0 a unit vector directed along the distance r between the poles

K is proportionality constant

The proportionality constant permits a definition of pole strength; K = 1 when two like poles of unit strength 1cm apart repel each other with a force of 1 dyne.

The magnetic field H_x may be defined as the force one pole exerts on a unit positive pole;

$$H_x = mr_{x0}/r^2 \qquad (5.2)$$

For a current circulating in a closed loop, the magnetic moment m is defined as the product of the current I (A) and the enclosed area A(m^2)

$$m_x = IA_x\,(Am^2) \tag{5.3}$$

If the molecular magnetic moments combine to give composite behaviour, magnetic phenomena are demonstrated on a macroscopic scale. Magnetization M then can be defined as the magnetic moment per unit volume of the magnetic substance which may arise due to the action of a background magnetic field strength H on the material present in the sphere of the influence of such a field. Magnetic induction (or magnetic flux density) B then can be defined as:

$$B_x = \mu_0(H_x + M_x) = \mu H_x \tag{5.4}$$

where

μ_0 is permeability free space, it is unitless and is taken as unity

μ is the permeability of the material present

B_x is expressed in Gauss and M_x and H_x in Oersteds. The term Gauss is often used to refer to both B_x and H_x. In SI units M_x and H_x are given in Am^{-1} and B_x in Tesla (Weber m^{-2})

Equation (5.4) relates the total magnetic flux density B_x at any point in space to the sum of the flux density in free space plus that conveyed by the magnetised substance. The intensity of magnetization of many substances is proportional to the intensity of the applied background field

$$M_x = XH_x \tag{5.5}$$

Where

X is a dimensionless, quantity called magnetic susceptibility.

Various substances may then be categorised according to the manner in which the magnetic field intensity causes magnetization. Depending on the susceptibility X, materials are called paramagnetic when X is positive ($B_x > H_x$ in the presence of the material), diamagnetic when X is negative and $B_x < H_x$ due to the negative M_x value and ferro (ferri) magnetic which are highly magnetic and show non linearity in the relation between H_x and M_x values. In simple terms, ferromagnetic and para substances are attracted to the magnetic field while diamagnetic substances are repelled. In everyday terms these correspond to strongly magnetic, weakly magnetic, and nonmagnetic magnetic materials respectively. The main difference between ferro and para magnetism is that ferromagnetism is a group effect while the paramagnetism is an atomic or molecular effect. The three types of magnetism, and their natural occurrence are summarized below

5.2.2.1 Ferromagnetism

The origin and nature of ferromagnetism have been the subject of a number of theoretical studies and it is thought that the existence of ferromagnetism requires the presence of a permanent atomic magnetic moment [26]. This moment is supplied solely by the electron spins, the orbital contribution being completely quenched. Such spin magnetic moments at the crystalline lattice sites interact in a strong exchange force to yield positive interaction between neighbouring spins. Ferromagnetism arises when the interaction between adjacent atoms or ions is strong enough to hold the electronic moments parallel to each other in spite of thermal agitation. Such spontaneous magnetisation occurs below the temperature refered to as the Curie point where the thermal energy is not high enough to randomise the spin interactions. Above the Curie point ferromagnetic substances become normal paramagnetic. Another important characteristic of ferromagnetic materials is that they can posses a bulk permanent magnetization, which depends on the alignment of the microscopic magnetic domains. A domain is a region in which the crystalline magnetic moments are all aligned, the interior of ferromagnetic materials is divided into number of such domains, each of which is spontaneously magnetized. The bulk permanent magnetic moment is then a result of the orientation of the respective domain regions. Ferromagnetic materials display hysteresis. When removed from a magnetic field the density does not generally return to zero. The materials remain magnetic. This is an effect of the domain structure. Ferromagnetic materials can be grouped into "hard" magnetic materials which retain their magnetism and "soft" magnetic materials which do not. "Hard" magnetic materials are used in permanent magnets; and "soft" magnetic materials are used in electromagnets, transformers and motors.[27-29].

The effectiveness of the magnetic interaction and consequent separation of the particles from the solution depends mainly on the magnetic characteristics of the particles, background magnetic field strength and also on the collision frequency. Examples of ferromagnetic materials are cobalt, magnetite and maghemite.

5.2.2.2 Paramagnetism

Paramagnetism results from the independent behaviour of unpaired electron spins in an external magnetic field. The size of the magnetic field induced in a paramagnetic substance by an external magnetic field is proportional to the number of unpaired electrons and to certain details of the electronic structure of the sample, to the strength of the applied field, and to the temperature. The induced field reinforces the applied field. Typical paramagnetic materials include salts of many transition metals. Paramagnetic particles are attracted to the region of highest magnetic field. The force on the particle is proportional both to the strength of the magnetic field and to that of the field gradient. Usually individual molecules cannot be manipulated using magnetic forces because thermal effects in the solution overwhelm the weak magnetic effects. Paramagnetic particles are magnetically responsive at room temperature, and show a range of microscopic effects in external magnetic fields which can be used in separation processes.

5.2.2.3 Diamagnetism

In diamagnetic materials the atoms possess zero magnetic moment and are, for all practical purposes, not influenced by magnetic fields. Diamagnetism represents the magnetic field induced in all matter by an externally applied magnetic field, and is considered classically in terms of changes in the circulation of a paired electron caused by this. The induced field of diamagnetic materials opposes the applied magnetic field. Diamagnetic substances are weakly repelled from regions of high magnetic fields. Diamagnetic materials are commonly regarded as magnetically unresponsive, and paramagnetic and ferromagnetic effects, if present, ordinarily overwhelm diamagnetic effects. Examples of diamagnetic materials are quartz and water.

5.2.3 Magnetic-based treatment processes

Magnetite in its industrial application is widely used to overcome separation difficulties associated with other adsorbents. It can be magnetically removed from solution or isolated from nonmagnetic solids. Therefore a magnetite-based process potentially offers advantages of both magnetic separation and oxide adsorbent and reuse. Natural and synthetic magnetites are used in water or wastewater treatment processes [18-24]. Synthetic magnetite preparation permits control of surface properties and particle size.

A patent by Urbain and Stemen[24] in 1941 was the first to propose the use of magnetite in water clarification to accelerate sedimentation. Magnets placed at the base of settlers were supposed to increase the settling rate of the flocs. Subsequent work described the use of magnetite and other magnetic particles for water purification generally used in conjunction with inorganic coagulants or organic flocculants [30-33]. The industrial applications of magnetite, which include potable water and effluent treatment, metal recovery and concentrating biological species have been reviewed in several works [18,34-35]. The three major magnetic-based solution treatment processes are: High Gradient Magnetic Separation (HGMS), the Sirofloc and Rotating Drum Separation.

5.2.3.1 High Gradient Magnetic Separation - HGMS

The high gradient magnetic separation system is based on the attachment of pollutants from aqueous media on to magnetic material (e.g. magnetite) and a subsequent magnetic separation of magnetite-pollutant coagulates. After the separation, the magnetite is recovered and reused [36]. The original high gradient magnetic filtration was based on the Kolm type separator [30-31] In this process magnetically susceptible particles are collected on steel wool or an expanded metal matrix. The background magnetic field magnetises the matrix and produces a strong magnetic gradient that is converged on the matrix fibre strands. In 1973 De Latour [18] described the use of the HGMS technique in the water and wastewater treatment process. Reduction of the amount of various water contaminants such as coloured species, organic colloids, bacteria and phosphate is possible via their attachment onto magnetite particles. A primary coagulant, like alum, may be used to coagulate and bind the impurities with magnetite. The advantages of the HGMS method are claimed to be its simplicity and very high filtration rates.

Heavy metal removal from industrial effluent using HGMS was also described by Okamoto [34], the process is based on heavy metal interactions with the magnetic oxide precipitates. The process involves the addition of ferrous salt to the wastewater which is then neutralized, oxidised and the magnetic co-preciptate (ferrite $M_x Fe_{3-x} O_4$) is removed by HGM filtration. HGMS has also been used in concentrating algae [35] with magnetite in conjunction with ferric chloride. Higher removal rates were observed for small residence times, low magnetic field strengths and reduced coagulant doses. It was also reported that the removal rate was strongly dependent on the size of the magnetite particles.

5.2.3.2 Sirofloc Process

The Sirofloc process was developed by the Commonwealth Scientific and Industrial Research Organization (CSIRO), in Australia. The chemistry of the process and the engineering developments were presented in a series of published papers and a patent [32, 36-39]. The process uses magnetite with particle size 1 - 10 μ treated with 0.1 M NaOH solution. The treated magnetite was reported to produce better coagulation-adsorption characteristics. The magnetite is recycled and chemically regenerated as an adsorbent with 0.1 M NaOH solution which releases the attached impurities. This process produces an alkaline effluent which needs to be handled separately. There is similarity between Sirofloc with HGMS, especially with the recently reported Smit Nymegen Water Treatment Systems (MWS) from The Netherlands [40].

5.2.3.3 Rotating drum magnetic separators

These separators are widely used in the machine tool and mining industries and are especially useful for the continuous separation of ferromagnetic support particles from a liquid stream. Most operate at field strengths below 5 kilo gauss. The claimed advantage of this process over HGMS is that the equipment is much cheaper and operates at much higher concentrations of solids. However, if total removal of trace quantities of ferromagnetic is required, then the HGMS is preferable[41].

The fact that magnetite has been used for industrial separation processes suggests that its behaviour as an adsorbent of inorganic and organic materials in soil will be similar. The purpose of the study described in this chapter is to demonstrate the ability of magnetite to act as an adsorber and to draw inferences from the results in terms of transport behaviour in soils.

5.3 Materials and Methods

5.3.1 Reagents and labware

Most reagents used in this study were of analytical reagent grade. Reagents used in the preparation of magnetite and for subsequent adsorption and dissolution tests were as follows: ferrous sulphate ($FeSO_4.7H_2O$) assay 99.5%; ferric chloride hexahydrate ($FeCl_3.6H_2O$) assay 99%; ferrous chloride ($FeCl_2.4H_2O$) assay 99%; sodium hydroxide (NaOH) as pellets assay 99.0%; potassium nitrate (KNO_3), assay 99%; ammonia solution, about 35%; sulphuric acid (H_2SO_4) assay 90-91%; stannic chloride ($SnCl_4.5H_2O$) assay 97.5%, GPR; Aluminium sulphate [$Al_2(SO_4)_3.16H_2O$] assay 54-59% as Al_2 SO_4 GPR; titanium dioxide (TiO_2) assay 98% GPR ; silica colloidal powder (SiO_2); cobaltous chloride ($CoCl_2.6H_2O$) assay 99.0%; potassium chloroplatinate (K_2PtCl_6) assay, 99.5; hydrochloric acid (HCl) assay 47%; potassium chloride (KCl) assay 99.5 %; orthophosphoric acid (H_3PO_4) assay 99%; ferroin, cerium (IV) sulphate solution ($Ce(SO_4)_2.4H_2O$ were supplied by BDH, Poole, England hydrazine sulfate ($NH_2NH_2.H_2SO_4$) assay $\geq$ 99%; hexamethylenetetramine ($C_6H_{12}N_4$), ferric sulphate hydrate (Fe_2 SO_4 $)_{3\,aq}$, assay $\geq$ 99% were supplied by Fluka. Iron standard solution (1000 mg\l) 'spectrosol' suitable for atomic absorption spectroscopy was also supplied by BDH, Poole, England. The water used in this study was doubly deionized water processed by the Milli-Q system. Iron stock solutions of 100 ppm were prepared by diluting a concentrated iron solution (1000 ppm).

All glassware and plasticware were cleaned by overnight immersion in acid. Containers used for equilibrium reactions were soaked in 10% nitric acid bath and rinsed repeatedly with deionised water. Soaking baths were changed every other day.

5.3.2 Preparation of Magnetite.

The magnetite used in this study was prepared by different methods. The method used to produce magnetite and magnetic materials are summarised in Table 5.1 with details following. Three types of material were prepared. The first series consisted of magnetic phases containing iron(II)/ iron(III) oxides prepared using $FeSO_4.7H_2O$, $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ as starting material. The second series consist of materials prepared in which a portion of the iron was replaced by tin(IV) or aluminium(III). The third series consists of materials prepared as magnetite deposited on inert materials using titanium dioxide (anatase) and silica powder.

All products were separated from their mother liquor by centrifugation. Portions were washed with water and dried in an oven at different temperatures. Other portions were washed with ethanol and dried in air at ambient temperature or in a vacuum oven at 40°C.

Table 5.1 Summary of preparation methods used

Method	Process
A	Addition of ammonia at 65°C to a solution containing iron (II) and iron (III) chloride
B	Addition of KOH/KNO_3 solution to iron(II) sulphate solution at 90°C with oxygen excluded
C	Addition of iron (II) sulphate solution to boiling KOH/KNO_3
D	Addition of iron (II) and iron (III) chloride solution to an ammonia solution
E	This method is similar to method B except that it incorporates Sn and Al into the magnetite structure. This was achieved by replacing part of iron (II) sulphate by dissolving their respective sulphate salts with the ferrous sulphate
F	Deposition of magnetic iron oxides on an inert titanium dioxide and silica support

Method A

This method is a modification of the methods reported by Flygare and Larssson [42], and Molday and Mackenzie [43]. A 100ml solution containing 3.2g $FeCl_2.4H_2O$ and 7.55g $FeCl_3.6H_2O$ was heated to 65°C and 100ml of 7.5% NH_4 OH added in four portions. Continuous vigorous stirring at 7000 rev min^{-1} with an overhead motor stirrer of diameter 20mm was maintained during the ammonia addition and then continued for 15 minutes. The black precipitate was centrifuged at 7500 rpm for 30 minutes and the settled particles washed with doubly deionised water three times and finally twice with acetone and dried at 40°C in the oven.

Method B

This method is based on the precipitation of a ferrous hydroxide alone with no ferric iron present in any form. This procedure makes it necessary to oxidize at least two-thirds of the iron to the ferric form during and after precipitation.

The method is based on David and Welch [44] and Sidhu et. al. [45 - 46]. $FeSO_4.7H_2O$ (100g) was dissolved in 700 ml deionised water previously flushed with N_2 to expel dissolved oxygen. The solution was boiled and KNO_3 (8.08g) and KOH (56.1 g) dissolved in 300ml doubly deionised water were added dropwise over a period of forty-five minutes while N_2 was continuously bubbled through the boiling suspension. After complete addition of the alkaline mixture, the suspension was boiled for an additional period of 20 minutes. During the reaction, the mixture was stirred continuously using a magnetic stirrer. The suspension was then allowed to cool with the reaction flask sitting on a permanent magnet. The resulting black precipitate was centrifuged several times and washed with deionised water until free of sulphate and then followed by three washing with acetone. Finally the sample was dried in a vacuum oven at 40°C for 36 hours.

Method C

This method is based on the procedure set out by Lefort [47]. A solution containing 1M ferrous sulphate and 2M ferric sulphate was poured into a boiling solution of sodium hydroxide which must be present in excess. The precipate was then cooled, centrifuged and washed until the filtrate showed no alkali reaction and dried under a vacuum at 40°C. It is noted here that the proportion of the Fe^{2+} to Fe^{3+} ions present prior to the synthesis was 1:2 as required in magnetite

Method D

This procedure is adopted from Massart [48]. An aqueous solution of 40 ml containing 1M $FeCl_2.4H_2O$ and 10 ml of 2M $FeCl_3.6H_2O$ was added to 500ml of 0.7M ammonia solution. The precipitate was isolated from the solution by centrifugation and magnetic decantation, and washed with distilled water and acetone. The product was then dried in a vacuum oven.

Method E

This is based on method **B**, and the objective was the incorporation of Sn(IV) and Al (III) into the magnetite structure. This was achieved by dissolving the required amount of their respective chloride and sulphate salts with ferrous sulphate in predetermined proportions to give 5, 10, 15, 25, 50% substitution of iron. The washing and drying of the products were identical to that of method **B**

Method F

This method was again based on method **B**, and the objective was deposition of magnetite on inert particles. Titanium dioxide and silica powder amounting to 10, 15, 25 and 50% of the ferrous sulphate was slurried with the iron(II) sulphate solution prior to addition of KOH/KNO_3 to the slurry.

5.3.3 Characterisation

The materials produced using the six methods are shown in Tables 5.2-5.6. The magnetite samples were analysed for both iron(II) and iron(total), by titration and atomic absorption spectroscopy, while the aluminium, tin, titanium dioxide and silica substituted magnetic substances have been analysed for iron (II). Selected magnetite samples were also studied by thermal analysis, X-ray diffraction, scanning electron microscope and surface area measurement to establish additional characteristics of the products.

5.3.3.1 Chemical analysis

The following procedure has been adapted from that described in Vogel [49] and was used to determine iron(II), iron (III) and total Fe. In addition total Fe was determined with atomic absorption spectroscopy. Ferrous and total Fe was determined by titration with cerium sulphate and Fe^{3+} was calculated from the difference between total Fe and Fe^{2+}.

1 REAGENTS

1.1 Standard 0.1N cerium sulphate solution.

1.2 Ferroin indicator solution

1.3 1M sulphuric acid solution

1.4 Concentrated hydrochloric acid

1.5 Aluminum foil

1.6 Concentrated phosphoric acid

2 PREPARATION OF SAMPLE SOLUTION

2.1 Weigh accurately 0.6 - 0.8 g sample into a 100cm³ beaker

2.2 Dissolve the sample in concentrated hydrochloric acid using gentle heat if necessary (20cm³ is usually sufficient)

2.3 Transfer the solution quantitively to a 100cm³ standard flask and make up to the mark with deionised water.

3 DETERMINATION OF IRON (II)

3.1 Pipette a 20cm³ aliquot of solution 2.3 into a 250cm³ conical flask

3.2 Dilute to 100cm³ with 1M sulphuric acid solution.

3.3 Add 2 drops Ferroin indicator solution

3.4 Mix well

3.5 Titrate with 0.1N ceric sulphate solution till the colour changes from orange to a green yellow

3.6 Perform the determination in duplicate

3.7 Determine the blank value using 80 cm³ 1M sulphuric acid and 2 drops of indicator solution.

4 DETERMINATION OF TOTAL IRON

4.1 Pipette a $20cm^3$ aliquot of solution 2.3 into a $250cm^3$ conical flask

4.2 Add $75cm^3$ 1M sulphuric acid solution.

4.3 Add $20cm^3$ conc hydrochloric acid

4.4 Heat this solution to boiling

4.5 Remove from the source of heat

4.6 Add 0.4g aluminium foil cut into small pieces. (A vigorous reaction will ensue with the evolution of hydrogen)

4.7 When the reaction is complete, cool the flask and contents quickly.

4.8 Add $10cm^3$ conc. phosphoric acid and mix well

4.9 Add two drops of Ferroin indicator solution. Titrate as in 3.5

5 CALCULATIONS

$$\%Fe^{2-} = \frac{(T_1 - T_2) \times 2.7925}{W}$$

Where:

T_1 = Volume of 0.1N ceric sulphate solution used in titration

T_2 = Volume of 0.1N ceric sulphate solution required for the blank

W = Weight of a sample taken (g)

$$\%Fe_{total} = \frac{(T_3 - T_2) \times 2.7925}{W}$$

Where :

T_3 = Volume of 0.1N ceric sulphate solution used in titration

$$\therefore \%Fe^{3+} = \%Fe_{total} - \%Fe^{2+}$$

Table 5.2 Chemical composition of samples prepared using methods **A & D**

Sample Number	Fe (II) (%)	Total Fe (%)	Fe(III): Fe(II)	Washing & drying
A1	2.6	70	26:1	water & oven 110°C
D1	7	66.4	8.5:1	ethanol & vacuum oven 40°C

Table 5.3 Chemical composition of samples prepared using method **B**

Sample Number	Fe (II) (%)	Total Fe (%)	Fe(III):Fe(II)	Washing & drying
B1	21.7	72.9	2.3:1	ethanol & ambient air
B2	21.9	72.8	2.3:1	ethanol & vacuum oven
B3	21.4	72.6	2.4:1	ethanol & vacuum oven
B4	21.8	73.5	2.4:1	water & vacuum oven
B5	21.0	74.0	2.5:1	water & ambient
B6	19.1	72.6	2.8:1	ethanol & vaccum oven
B7	18.4	70.7	2.8:1	water & vaccum oven
B8	11.5	51.1	3.4:1	ethanol & vaccum oven

Table 5.4 Chemical composition of samples prepared using method **C**

Sample Number	Fe (II) (%)	Total Fe (%)	Fe(III): Fe(II)	Washing & drying
C1	16.6	71.4	3.3:1	ethanol &vaccum oven
C2	16.2	72.7	3.5:1	ethanol & vaccum oven
C3	15.3	69.8	3.6:1	ethanol & vaccum oven
C4	13	70.4	4.4:1	water & oven 110°C
C5	9.0	71.5	6.9:1	water & oven 110°C
C6	7.7	74.2	8.5:1	water & oven 110°C

Table 5.5 Chemical composition of samples prepared using method E

Sample Number	% Fe replacement in the preparation	Fe(II) %	Washing & drying
E1(Sn IV)	10	23	ethanol & ambient
E2(Sn IV)	25	8.4	ethanol & ambient
E3 (Sn IV)	50	6.2	ethanol & ambient
E4 (Sn IV)	5	21.6	ethanol & ambient
E5 (Sn IV)	10	22.3	ethanol & ambient
E6 (Sn IV)	15	8	ethanol & ambient
E7 (Sn IV)	25	6.7	ethanol & ambient
E8 (Sn IV)	50	5.1	ethanol & ambient
E9 (Al II)	10	15.7	ethanol & ambient
E10 (Al II)	25	5.4	ethanol & ambient
E11 (Al II)	50	7.1	ethanol & ambient

Table 5.6 Chemical composition of samples prepared using method **F**

Sample Number	**% Fe replacement in the preparation**	**% Fe(II)**	**Washing & drying**
F1 (TiO_2)	10	18.6	ethanol & ambient
F2 (TiO_2)	25	15.4	ethanol & ambient
F3 (TiO_2)	50	10.4	ethanol & ambient
F4(TiO_2)	25	16.13	ethanol & ambient
F5 (TiO_2)[a]	25	16.70	ethanol & ambient
F6 (SiO_2)	10	8	ethanol & ambient
F7 (SiO_2)	15	5	ethanol & ambient
F8(SiO_2)[a]	25	1.97	ethanol & ambient
F9 (SiO_2)	25	1.23	ethanol & ambient
F10 (SiO_2)	10	9.46	ethanol & ambient

[a] washed with 0.1M HCL

As shown in Tables 5.2-5.6 for all products prepared using various methods, method B produces a material closest to the theoretical ratio. Further refinements of the method were made but attempts to obtain an ideal ratio by varying the amount of the oxidising agent (KNO_3) as shown in Table 5.7 were unsuccessful.

Table 5.7 Effect of KNO_3 concentration on the product quality

Product Number	Wt. KNO_3(g)	%Fe (II)	Fe(III):Fe(II)
B9	0.5	7.5	8.5:1
B9.1		-	-
B9.2		5.5	-
B9.3		0.3	-
B10	1.0	13.0	4.6:1
B10.1		11.5	-
B10.2		10.4	-
B10.3		0.5	-
B11	2.0	22.6	4.4:1
B11.1		18.2	-
B11.2		18.2	-
B11.3		0.2	-
B12	3.0	22.1	3.5:1
B12.1		18.0	-
B12.2		18.1	-
B12.3		0.7	-
B13	5.0	20.8	2.7:1
B13.1		14.4	-
B13.2		17.8	-
B13.3		0.4	-
B14	8.0	21.5	2.3:1
B14.1		18.2	-
B14.2		18.2	-
B14.3		0.2	-

B9-14	products washed with ethanol and dried at ambient temperature
.1	products washed with 0.1M HCl
.2	products washed with 0.05M HCl
.3	products washed with ethanol and heated at 200°C for three hours

The products were then selected for further study on the basis of their magnetic properties. Preparation methods **A** & **D** gave very poor products and did not merit further preparation and study. Method **C** produced a better magnetic product but trials of the product did not indicate better adsorption and solubility properties.

Method **B** appears to give the best product among the six methods and also gave a reproducible product. Varying methods of drying the product have been tested. The highest Fe (II) content was achieved by washing samples with ethanol and drying the product in a vacuum oven at 40°C or in air at ambient temperature. The best sample prepared (B2) has the following composition:

	Stoichiometric composition	**Sample Composition**
Total Fe (%)	72.4	72.8
Fe (II)	24.1	21.9
Fe (III): Fe(II)	2:1	2.3:1

Method **E** products with 10% Sn (IV) and Al (III) were better when compared with methods other than **B** and **F**.

Method **F** products prepared on 25% silica are yellowish brown and not magnetic whereas that deposited on 10% silica was slightly magnetic but did not merit further investigation. 25% titanium dioxide was better in Fe(II) composition but the product as a whole is poorly magnetic; subsequent trial of the products for adsorption capacity did not show appreciable adsorption property.

5.3.3.2 Point of Zero Charge (PZC)

All solids including magnetite exhibit a charged surface in aqueous suspension. At any given pH the surface is made up of different numbers of positive, neutral and negative charged sites. As the pH is increased, the negative charge on the surface of the magnetite increases.

Thus, the net charge on the magnetite can be measured in terms of zeta potential; at low pH it is positive and at high pH it is negative. At a certain pH the number of positive and negative surface groups are equal and that point is called the point of zero charge (PZC). The pH where the zeta potential is zero is the isoelectric point (IEP). If specific adsorption of other ions from solution occurs, the PZC is equal to the isoelectric point (IEP), which is a point of zero zeta potential [50-52]. The zeta potential and IEP are determined by a number of methods which can be categorised as electrokinetic techniques including microelectrophoresis and streaming potential.

The zeta potential of magnetite (B2) was measured using an electrophoresis method as follows. A 3 x 10^{-4} g magnetite was dispersed in 40ml of 1x 10 M KCl used as an electrolyte. 10 ml of the dispersion was transferred to a beaker and the pH of the solution adjusted to the desired level using 1x 10^{-1} M HCl or 1 x 10^{-2} M KOH solutions. The beaker was placed in a sonic bath for two minutes after which period the pH of the solution was rechecked to ensure that it had not been affected by the sonication process. The sample cell of a Zetasizer III was flushed with 1 x 10^{-3} M KCl and 2.0 ml of the sonicated sample was injected into the sample cell. The zeta potential of the sample was recorded by the Zetasizer III with the average of five readings. The procedure was repeated at different pH and IEP was determined as 6.5 from the graph as shown in Figure 5.1.

5.3.3.3 X-ray analysis

X-ray powder diffraction is an essential tool for the identification of the product and in determining its degree of purity. Additional information such as crystal size and disorder, structural parameters, degree of isomorphous substitution and surface area can also be obtained.

The magnetite sample produced with method B2 was characterised by X-ray diffraction (XRD) using CuKα 1.5406 Å radiation and a Philips PW 1050 x-ray diffractometer automated and computer contolled by Sietronics software. The sample was scanned in the range 10 - 100° 2θ. An X-ray powder diffraction pattern showed the main peaks at

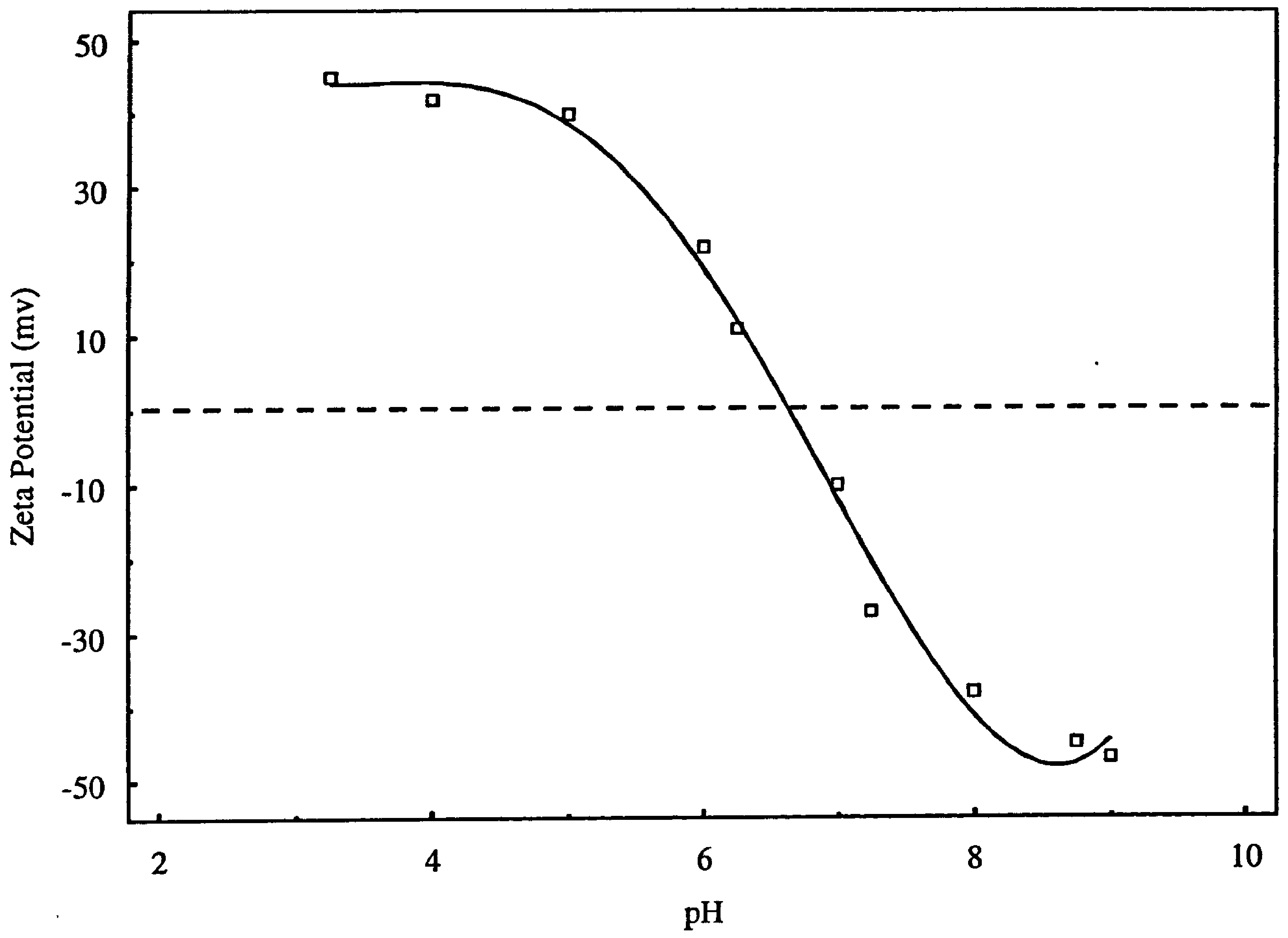


Figure 5.1 Zeta potential as a function of pH for magnetite suspensions

4.844, 2.965 and 2.529 Å, which compared to the literature values [53] of 4.852, 2.967, and 2.532 Å confirmed that the sample was magnetite

Table 5.8 XRD results as compared to results from XRD data file [53]

Sample		Standard	
dÅ	**Intensity (I/I_0)**	**dÅ**	**Intensity (I/I_0)**
4.844	7	4.852	8
2.965	31	2.967	30
2.529	100	2.532	100
2.423	7	2.4243	8
2.096	24	2.096	20
1.712	9	1.7146	10
1.614	31	1.6158	30
1.483	39	1.4845	40
1.326	3	1.3277	4
1.279	8	1.2807	10
1.265	3	1.2659	4
1.211	3	1.2119	2
1.121	3	1.1221	4
1.092	10	1.0930	12
1.049	4	1.0496	6

5.3.3.4 Scanning electron Microscopy (SEM)

The SEM is used to study the surface, or the near-surface structure of the material. This technique enables crystal dimensions and also crystal morphology to be measured directly. Scanning electron micrographs were obtained using a Jeol 100 JXA 840A electron probe micro analyser and are shown in Figures 5.2; they consist of spherical particles with an approximate diameter of 100nm.

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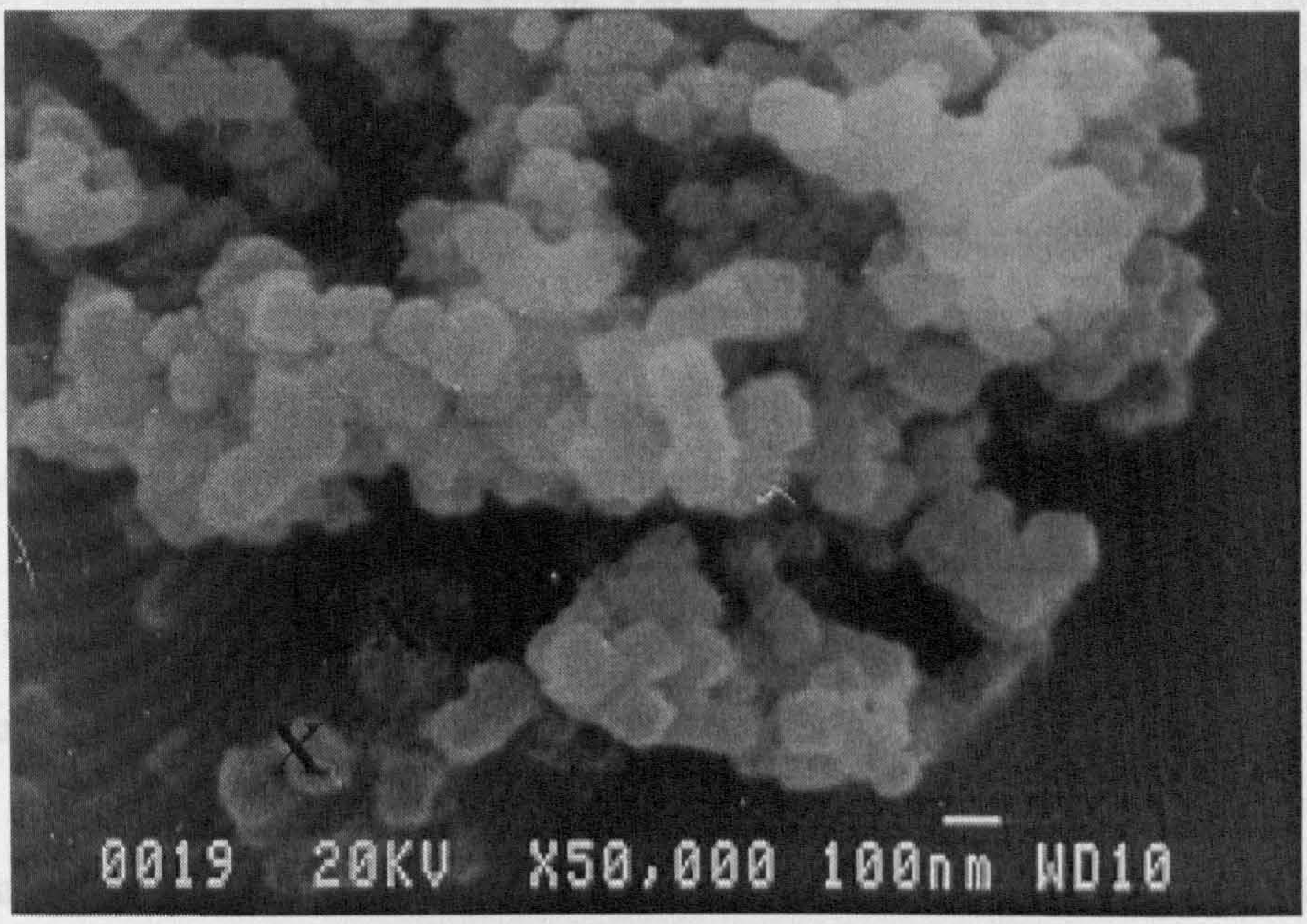

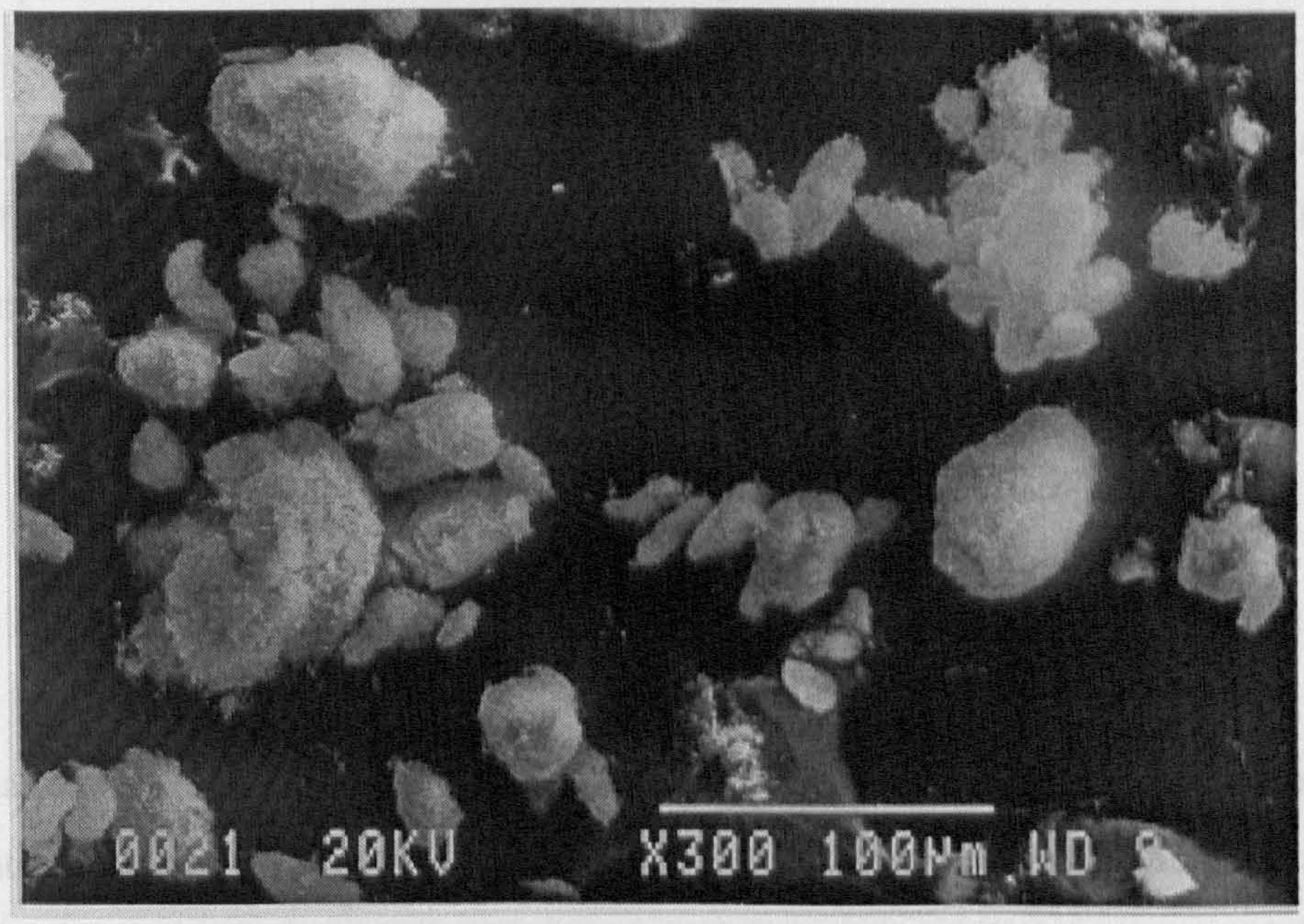

Figure 5.2 SEM of magnetic at (B1) various magnification

5.3.3.5 Surface area

The most widely used method for determining the surface area of iron oxides is the Brunauer-Emmett- Teller (BET) method. The area determination is based on the fact that, if a gas is brought in contact with a powdered solid at a temperature near the condensation temperature of the gas, part of the gas is physically adsorbed on the surface of the solid. Sample B2 was outgassed overnight at 70°C to remove physically adsorbed water which would otherwise interfere with the surface area determination and surface area measurements were carried out using Micromeritics A S A P 2000 instrument. The average result obtained was 4 m^2/ g. The duplicate results are 4.1 ± 0.0650 and 3.95 ± 0.0635.

5.3.3.6 Thermogravimetry analysis (TGA)

This is another technique that provides information about the adsorbed and structural water present in the sample and also about phase-specific changes and transformations. A sample is continuously heated at a constant rate (2-10°C min^{-1}) and its weight loss is measured as a function of temperature using a balance. This provides quantitative information on weight change processes and enables the stoichiometry of a reaction to be followed.

TG curves for magnetite samples were obtained in triplicate using a Stanton Redcroft STA-780 series thermo-balance linked to a BBC SE 460 chart recorder. The analysis conditions were:

Sample weight	15 mg
Gas	Nitrogen
Flow rate	25 ml min^{-1}
Temperature	20 - 600° C
Heating rate	10° C min^{-1}
Crucible type	Aluminium

The Magnetite samples mass loss was measured from each TG curve and averages for the triplicate samples were 3 and 6.2 % for adsorbed water and crystalline water respectively. The instrument is calibrated for temperature accuracy and weight accuracey using magnetic alloy wires and calcium oxalate respectively. The accuracy for temperature is ±2°C and 0.5% for weight.

5.4 Adsorption of organic colloids and coloured species onto magnetite

The purpose of this chapter is to model the behaviour of magnetite in soil and to estimate the potential of magnetite as a sorbent in pollutant clean-up processes of coloured species and organic colloids. Magnetite-based adsorption process for the removal of simulated coloured and turbid water was used with different magnetic products produced using various methods. A magnetite based process potentially offers advantages of both magnetic separation and adsorption when compared with other iron oxides like goethite ; such processes will also occur at magnetite soil -water system boundaries

Sources of colour species in water may include natural metallic ions, humic and fulvic acids from humus and peat materials, plankton, dissolved plant components, and industrial wastes. Turbidity in water is caused by the presence of suspended matter such as clay, silt, finely divided organic and inorganic matter, plankton, and other microscopic organisms. Turbidity also increases the apparent but not the true colour of water and the particles are generally in the size ranges from 1 to 50 μm. The inorganic and organic materials which are sources of turbidity may have both an aesthetic effect and a health risk. The risk is mainly from toxic metals leached from soil components into the water body.

Humic substances are divided in two: humic acids that precipitate below pH 2 and fulvic acids that are soluble at lower pH. In most non-coloured waters the fulvic acid is the major portion, making up an average about 90% of the humic substances or 45% of the total dissolved organic carbon (DOC) present. DOC is naturally occurring and comprises humate and fulvate anions. It varies enormously in level depending on the source of the water and the geology of the area. The level of DOC in rivers and lake waters is usually more than that in sea water, groundwater and rain water. River and lake water contain 2-10 mg/l whereas the latter three waters contain generally less than 1mg/l

Humic substances are yellow to brown in colour, and have elemental composition:
$C \approx 45.5\%$, $H \approx 4.5\%$, $O = 35\text{-}40\%$, $N = 1\text{-}2\%$, S and $P < 1\%$. This can be assumed to be an unsaturated organic substance containing some conjugated chromophores with

approximate average empirical formula C_2H_2O. Humic substances are highly substituted with oxygen-containing functional groups and these are responsible for many of their dominant properties such as water solubility, acidity, metal complexing capacity, surface activity and adsorption to particle surfaces. The major functional groups in the humic acids are carboxyl, phenol, hydroxyl, carbonyl, ether and ester. The actual process involved in the formation of humic substances is not well understood, though it is a known fact that they result from the microbial degradation of plant organic matter such as lignin, cellulose and polypeptides. In addition polymerization, condensation and oxidation reactions may occur modifying the degradation products. Aquatic humic substances may be derived from leaching of terrestrial plant and soil organic matter. Soil organic matter may be generated by bacterial action on phytoplankton. The difference between aquatic humic substances and soil humic substances may be due to differential leaching of soil organic compounds. The inherent difference in the source of organic matter may be due to ultraviolet radiation induced oxidation and polymerization. [54-56].

5.4.1 Adsorption experiments

Batch and continuous adsorption experiments, with magnetite and simulated organic colloids and coloured species were carried out to study the ability of magnetite to adsorb coloured species and organic colloids.The magnetite samples were demagnetised and crushed using a mortar and pestle, and size fractioned with a sieve. The three average particle sizes used were approximately, 38-45, 63-75 and $\geq$ 100µ. All samples were washed with dilute HNO_3 and rinsed several times with deionised water to clean the surface. All adsorption experiments were conducted in 1×10^{-3} M $NaNO_3$. Organic colloidal and coloured species stock solutions were prepared using the standard method [57]. Coloured species result from the presence of natural metallic ions, humic substances, plankton and effluent, and colloidal protein is caused by suspended material, organic and inorganic colloids, soluble organic compounds, and plankton [55,57].

Aliquots of demagnetised and sized magnetite samples were sonicated in 5ml deionised water for thirty seconds. The sonicated sample was transferred to 200 ml centrifuge tubes and adjusted to the required volume with simulated stock solution. The pH was then adjusted to the desired pH with 0.1 M sulphuric acid or 0.1 M sodium hydroxide solutions. After adjusting the pH, the mixture was sonicated for another thirty seconds and shaken with the mechanical shaker for twenty minutes. After the completion of the equilibration reaction the mixture was placed on a permanent magnet having a magnetic field strength of 500 Gauss. The magnetic field accelerates flocculation and separation of magnetic particles from solution. The separation process is continued by decanting the solution into another container and then recentrifuging and decanting it. Finally the solution was filtered through 0.45 μ cellulose acetate filters. The filtered solution was measured for turbidity or colour using a turbidimeter and spectrophotometer respectively.

Preparation stock platinum-cobalt solution

Dissolve 1.245g potassium chloroplatinate (K_2PtCl_6) and 1g cobalt chloride ($CoCl_2.6H_2O$) 100 ml concentrated hydrochloric acid and a small amount of water in , then making up the mixture to 1000ml. This stock standard has a colour of 500 units. Comparison solutions are prepared from the stock solution. The colour of a sample can be determined by filling a matched Nessler tube to the 50 ml mark with sample and matching the colour against those of platinum-cobalt standard solutions or by using a spectrophotometer.

Preparation of stock turbidity suspension

A qualitative method in which the concentration of suspended matter in a liquid is determined by the measurement of light absorption is called Nephelometric analysis and the unit is Nephelometric turbidity unit (NTU).

The preparation procedure is as follows:

1 Solution A -- Dissolve 1.0g hydrazine sulphate, $(NH_2)_2.H_2SO_4$, in distilled water and dilute to 100ml in a volumetric flask.

2 Solution B -- Dissolve 10.00 g hexamethylenetetramine, $(CH_2)_6N_4$, in distilled water and dilute to 100 mL in a volumetric flask.

3 In 100-ml volumetric flask, mix 5.0 mL solution A and 5.0 mL solution **B**. Let stand for

24 hours at room temperature (25 ± °C), dilute to mark and mix. The turbidity of this suspension is 400 NTU

4 Dilute 10.00 ml stock turbidity suspension to 100 ml with turbidity-free water. The turbidity of this suspension is defined as 40 NTU

5.5 Dissolution of magnetite

There is little published on the solubility of magnetite in neutral and alkali environment at ambient conditions [15,48]. Most of the detailed work refers to the nuclear industry [58-63]. As far as iron is concerned , humans suffer no harmful effects from drinking water containing iron. Excess iron is found in soft ground water areas. Iron is an essential element and is very unlikely to cause a threat to health at concentrations occasionally recorded in water supplies. On the other hand sectors such as food and beverage, and pharmaceuticals have a requirement for low iron in the water as certain production process are affected by raised iron concentration. Iron is soluble in the ferrous state (Fe^{2+}) and is oxidized in the presence of air to the ferric state (Fe^{3+}) forming colloidal precipitates.Magnetite usually dissolves faster than pure Fe^{3+} oxides due both to its Fe^{2+} content.

Iron is so ubiquitous that some will find its way into nearly all water supplies. The taste threshold is about 300μg/l although it varies considerably between individuals. The EC Drinking Water Directive sets a maximum allowable concentration (MAC) value of 200μg/l [64].

In this study the solubility of synthetic magnetite was determined under acid and alkali conditions at room temperature. The effect of particle size was also investigated. Dissolution tests were conducted on magnetite over a pH range between 2 and 10 using a similar procedure as described in 5.4.1 above ; the supernatant solution was acidified with nitric acid, and analysed for total Fe using AAS.

5.6 Results and discussion

5.6.1 Adsorption of colour species and colloidal proteins onto magnetite

The results of colour species and organic colloids removal experiments are shown in Figures 5.3 - 5.8. Colour species and colloidal protein are most effectively reduced in acid pH and the adsorption decreases with increasing alkalinity. Although there are variations in removal rate depending on pH, magnetic dose and magnetite particle size. The results can be explained in terms of the surface properties of magnetite.

The interactions of magnetite and colloids in the aqueous system is an interfacial phenomenon. Particles in suspension are usually charged. For magnetite the charge arises from ionisation of surface groups that tend to have hydroxylated surfaces that ionize with increasing pH. The surface charge is balanced by ions of opposite charge that concentrate close to the surface. Hydroxo complexes of metals are adsorbed onto the magnetite surface and change its characteristics. Both physical and chemical forces are involved in the interaction.

Colloids are stabilized in the aqueous system by the electrostatic repulsion of particles that possess negative charges. The charge removal requires the neutralization of their charges to coagulate the particles and to encourage them to collide with each other to form flocs. The role of magnetite in this instance is to destabilize colloidal suspension by neutralisation or reduction of negative surface charge. This leads to coagulation and eventually to flocculation and finally the flocs are made to settle quickly with the help of a permanent magnet.

5.6.1.1 Effect of a magnetite dose

The increase in a magnetite dose increases the removal of colour species and organic colloids at the lowest contact time studied (30 minutes) as shown in Figures 5.3 and 5.4 This is mainly due the availability of larger surface area for the adsorption mechanism

5.6.1.2.Effect of contact time

Colour species removal for the system was more effectively achieved for a contact time of 30 minutes and for organic colloids at the contact time of 120 minutes, as shown in Figures 5.5 and 5.6 respectively. The longer contact time may be attributed to the dissociation of magnetite that in turn increases the apparent colour of the solution.

5.6.1.3 Effect of particle size

The smaller particle size (38-45µ) showed better removal capacity both for colour species and organic colloids as shown in Figures 5.7 and 5.8. This can be attributed to the increased surface area available for adsorption.

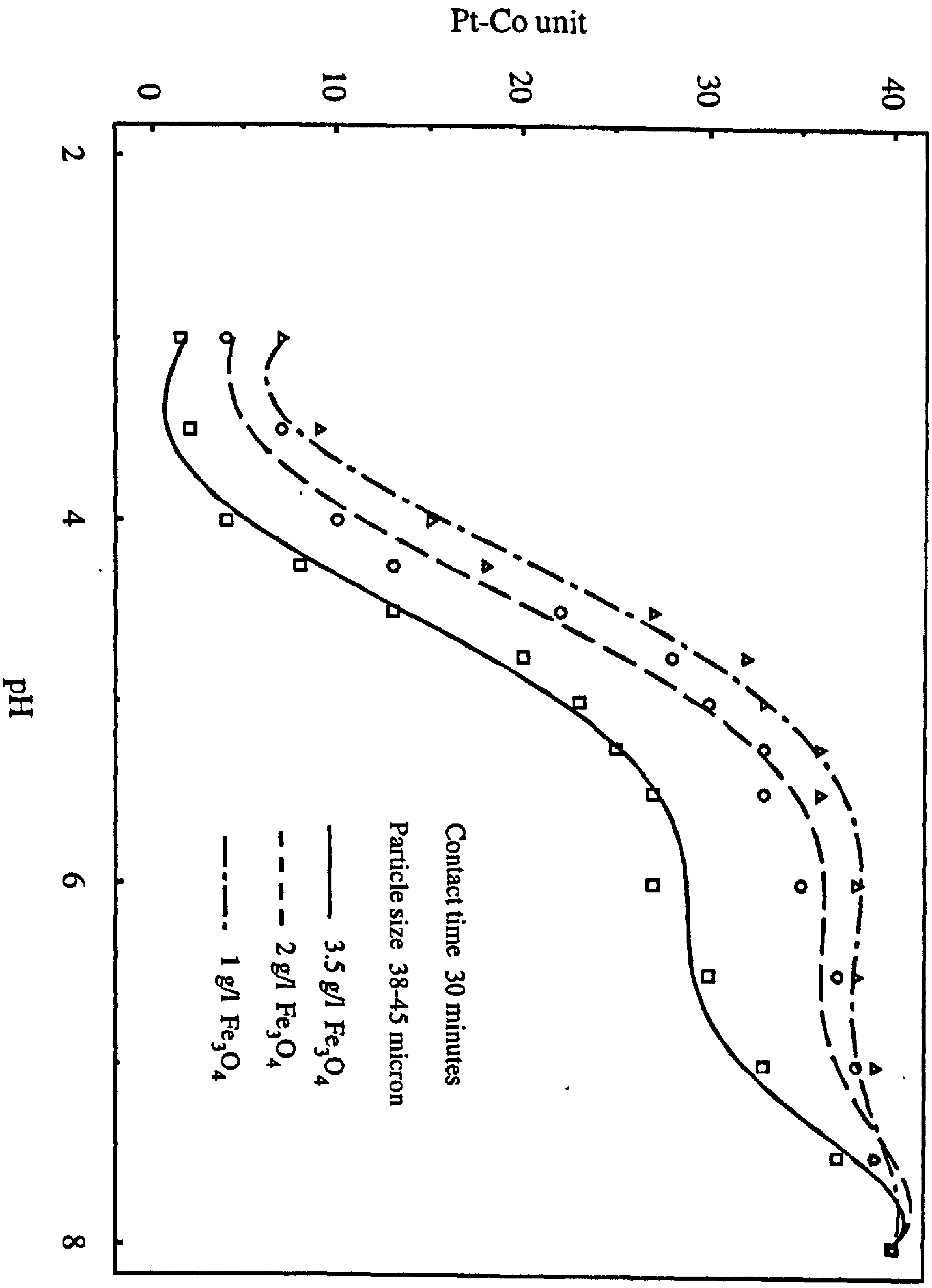

Figure 5.3 Colour species adsorption as a function of pH and magnetite dose

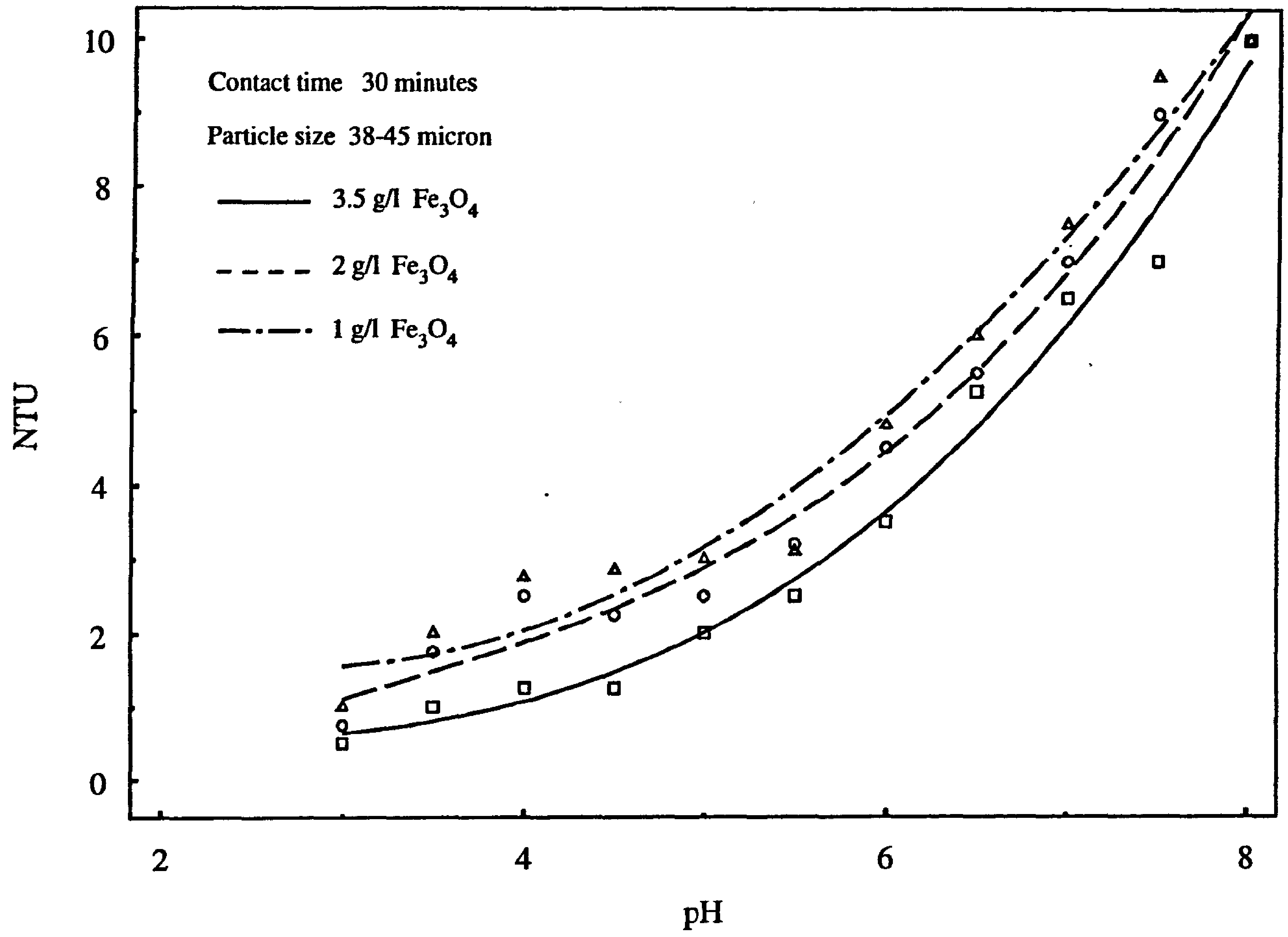

Figure 5.4 Colloidal protein adsorption as a function of pH and magnetite dose

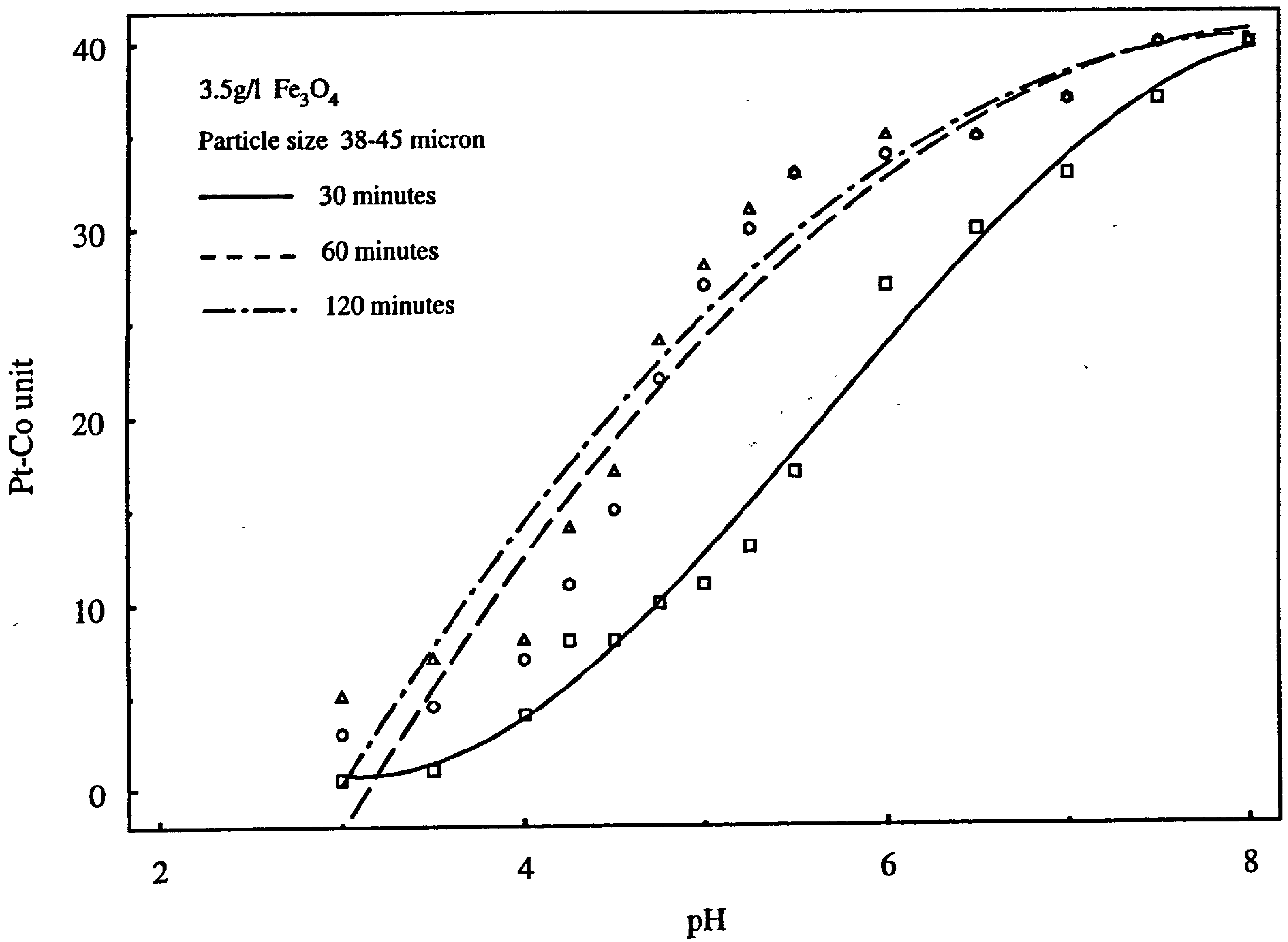

Figure 5.5 Colour species adsorption as a function of pH and contact time

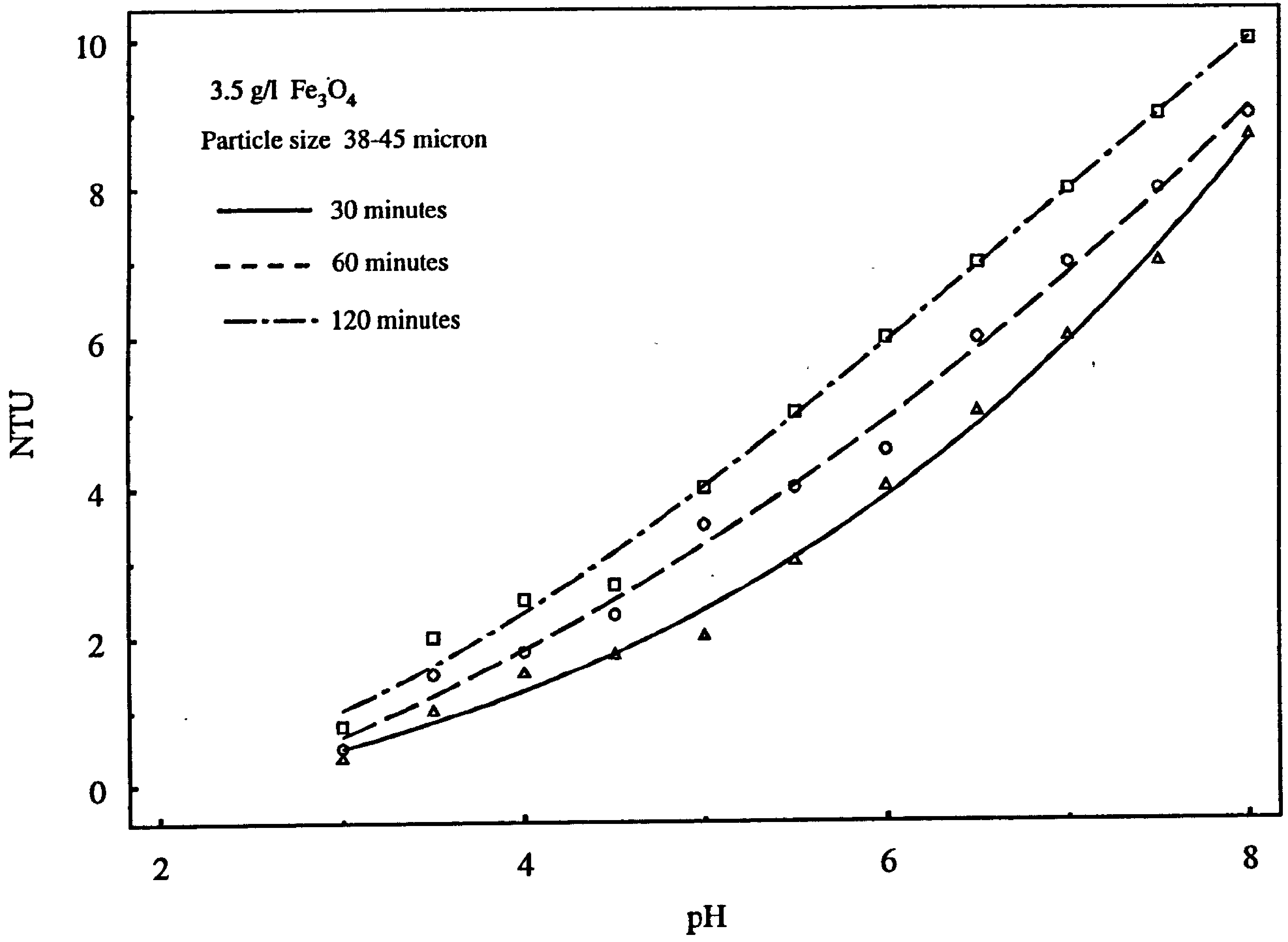

Figure 5.6 Colloidal protein removal as a function of pH and contact time

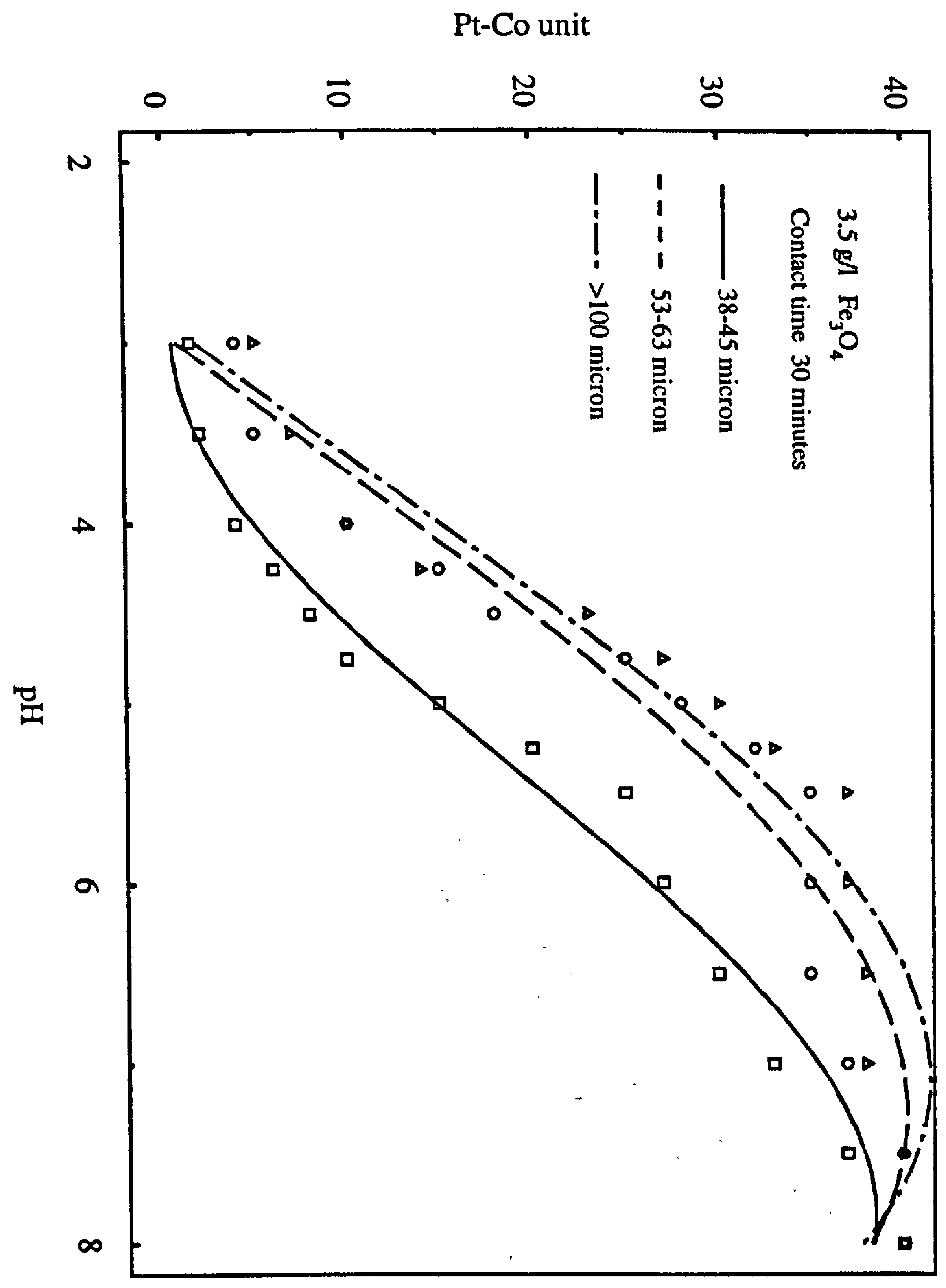

Figure 5.7 Colour species adsorption as a function of pH and particle size

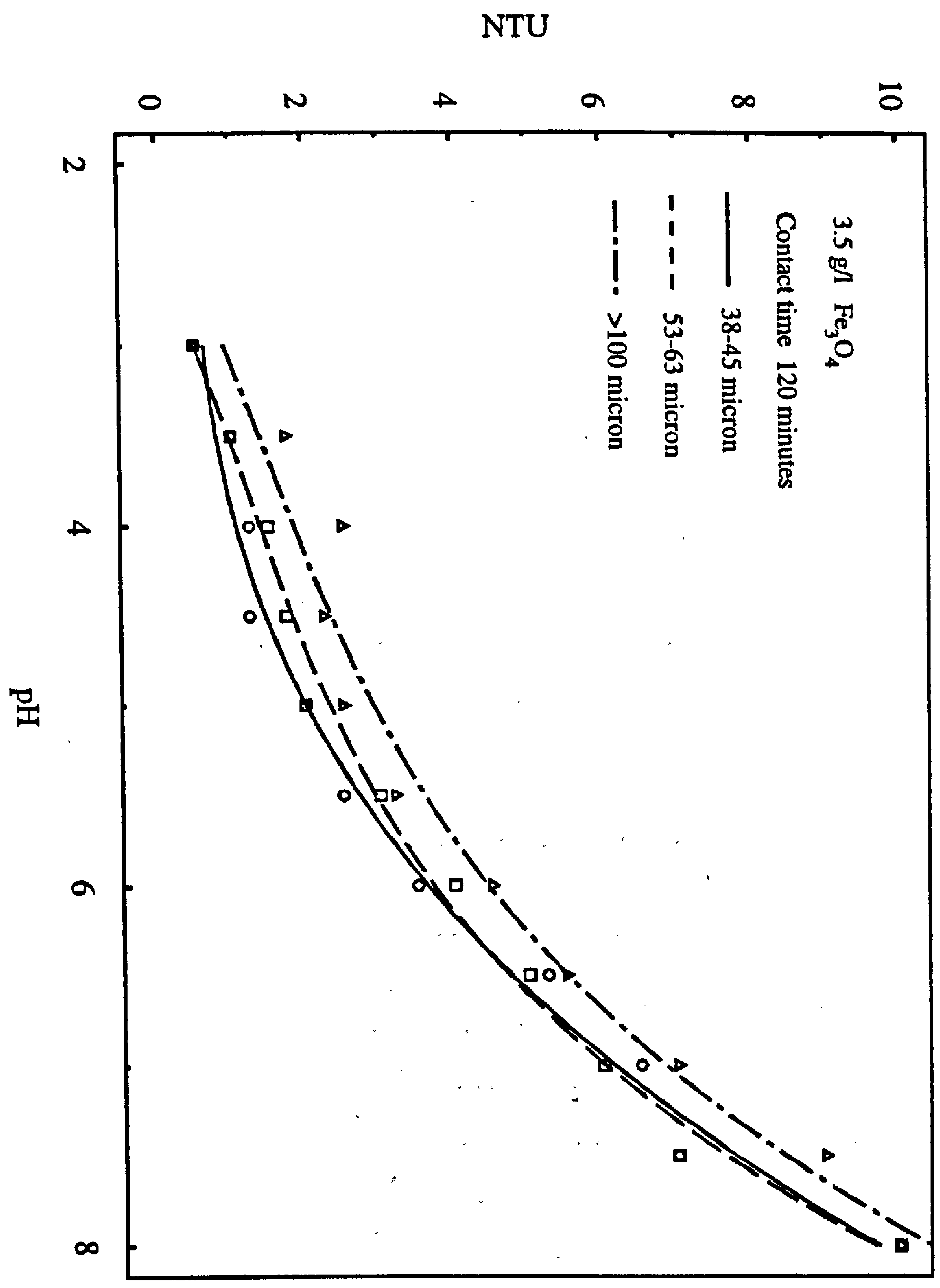

Figure 5.8 Colloidal protein removal as a function of pH and particle size

5.6.2 Dissolution of magnetite

If magnetite is to be used as an extractant in industries to adsorb coloured species and organic colloids from effluent, the solubility of the magnetite will also be a contributing factor.

The results of dissolution experiments of magnetic materials prepared in this work are given in Tables 5.9 - 5.13 and Figures 5.9- 5.11. These dissolution studies were carried out in an electrolyte containing 0.01 M $NaNO_3$ at pH 5 and magnetite dose of 1g /l. The particle size of the magnetite is greater than 100 μ.

Table 5.9 Dissolution of magnetite particles produced via methods A & D

Sample Number	Total Fe (%)	Fe dissolved (μg/ml)
A1	70	2.7
D1	66.4	1.2

Table 5.10 Dissolution of magnetite particles produced via method B

Sample Number	Total Fe (%)	Fe dissolved (μg/ml)
B1	72.9	0.2
B2	72.8	0.3
B3	72.6	0.4
B4	73.5	0.6
B5	74.0	0.4
B6	72.6	0.6
B7	70.7	0.7
B8	51.1	0.6

Table 5.11 Dissolution of magnetite particles produced via method C

Sample Number	Total Fe (%)	Fe dissolved (µg/ml)
C1	71.4	3.4
C2	72.7	4.5
C3	69.8	5.4
C4	70.4	6.9
C5	71.5	3.9
C6	74.2	5.8

Table 5.12 Dissolution of magnetite particles produced via method E

Sample Number	Fe(II)	Fe (µg/ml)
E1(Sn IV)	23.0	1.4
E2(Sn IV)	8.4	1.7
E3 (Sn IV)	6.2	ND
E4 (Sn IV)	21.6	0.54
E5 (Sn IV)	22.3	0.37
E6 (Sn IV)	8.0	0.57
E7 (Sn IV)	6.7	0.59
E8 (Sn IV)	5.1	0.34
E9 (Al II)	15.7	2.0
E10 (Al II)	5.4	5.0
E11 (Al II)	7.1	1.2

Table 5.13 Dissolution of magnetite particles produced via method F

Sample Number	Fe(II)	Total Fe (μg/ml)
F1 (TiO_2)	18.6	0.48
F2 (TiO_2)	15.4	0.46
F3 (TiO_2)	10.4	0.35
F4(TiO_2)washed with 0.1M	16.13	0.24
F5 (TiO_2)	16.70	0.22
F6 (SiO_2)	8	ND
F7 (SiO_2)	5	ND
F8(SiO_2) washed with 0.1M HCl	1.97	ND
F9(SiO_2)	1.23	ND
F10(SiO_2)	9.46	ND

The products that are least soluble are B1, B2 and the products from method E (substitution of Sn (IV) and Al (III)) and method F (deposited on TiO_2 and SiO_2). Although methods E and F have shown low solubility values, the results were not reproducible and there were also problems in washing the material as it was difficult to separate the TiO_2. Aluminium substituted products gave dull brownish washing and tinged black material on continuous washing. The products deposited on silica were not magnetic and were not analysed because they were difficult to wash.

The second series of dissolution experiment was conducted on product B1, which showed the best chemical and physical characteristics of all the samples prepared. The results are shown in Figures 5.9- 5.11

Dissolution of magnetite particles was significant, below pH 3, and above pH 8. The general trend is an increase in total Fe concentration with time. The results also showed that dissolution of relatively smaller particles (38-45 μ) in alkali is high when compared with the other two sizes (66-73 & >100 μ). Where the values of iron in aqueous solution are small and below the atomic absorption detection limit of 0.3 μg/ml samples were concentrated with standard iron solution to be able to determine the concentration with atomic absorption spectroscopy

5.6.2.1. Effect of a magnetite dose

The magnetite dose effect as shown in Figure 5.9 indicates that an increase in the amount of magnetite present does not result in the proportionate amount of dissolved iron, instead it is the lowest dose (1g/l) which showed higher dissolution value when compared with the other two magnetite doses (2g/l and 3.5 g/l).

5.6.2.2 Effect of contact time

The dissolution of magnetite having a particle size 38-45μ and 1g/l magnetite dose increases with longer contact time. It is very significant in the acid side, below pH 4 . There is also relatively an increased dissolution in the alkali side. The concentration of total Fe species at various pH values and contact times are shown in Figure 5.10 and the concentration of total Fe in the pH region below 4 is generally higher. Although the highest Fe concentration is observed at pH 2 there is also elevated concentration of iron at pH 10. Dissolution in acid medium depends on the pH and contact time, and the concentration of total Fe increases with pH and contact time. The results suggest that the dissolution increases in acidic and some alkali conditions, and dissolution overall is more affected with time.

5.6.2.3 Effect of particle size

The effect of particle size is shown in Figure 5.11. Three distinct pH regions with different patterns of behaviour are observed in Figure 5.11. The first is below pH 4 where the highest dissolution is observed and the second is between pH 4 and 8 where a minimum dissolution in the system is observed. The third region is that which occurs above pH 8 where an increase in dissolution is observed when compared with region two.

The observations made in the dissolution of magnetite due to the effects of magnetite dose, reaction time and particle size can be explained in relation to the aqueous solution chemistry of Fe(II) /Fe(III) and their hydrolysis products at 25°C and various pH values.

The three distinct pH regions include: (1) acidic environment, $pH < 4$, where, magnetite dissolves readily. The concentration of Fe produced per unit time increases as pH and particle size decreases: (2) between pH 4 and 8, the values of Fe were determined to be $\leq 0.1 \mu g/ml$ and it is assumed that the Fe (II) hydrolysis products should be the predominant species, Fe (III) being much less soluble ($K_{so} = 10^{-38}$) for $Fe(OH)_{3(s)}$ compared with K_{so} $10^{-14.5}$ for $Fe(OH)_{2(s)}$ [65]; (3) alkali, $pH > 8$, where the appearance of iron in solution can only be attributed to $Fe(II)_{(aq)}$ species until at very high pH where the Fe(II) and Fe(III) precipitation edges come together. Thus, unlike the acid region where the magnetite surface may be depleted of Fe(II) and Fe(III) stoichiometrically, the alkaline region (pH 10-11) corresponds to preferential Fe(II) release and enrichment of the surface in Fe(III) [64-66]

Iron is usually present in the ferric state (Fe^{3+}), and its salts are readily hydrolysed to insoluble forms ; in anoxic conditions ferrous (Fe^{2+}) ions are formed and many of its compounds are soluble, such as those formed from the ions Fe^{2+}, $Fe (OH)^{+}$, $[Fe (OH)_3]^{+}$. Ferric iron slowly hydrolyses to form insoluble hydrated iron oxide, which forms particles of colloidal size. These particles are important in controlling the concentration of organic and inorganic substances because of their absorptive capacity.

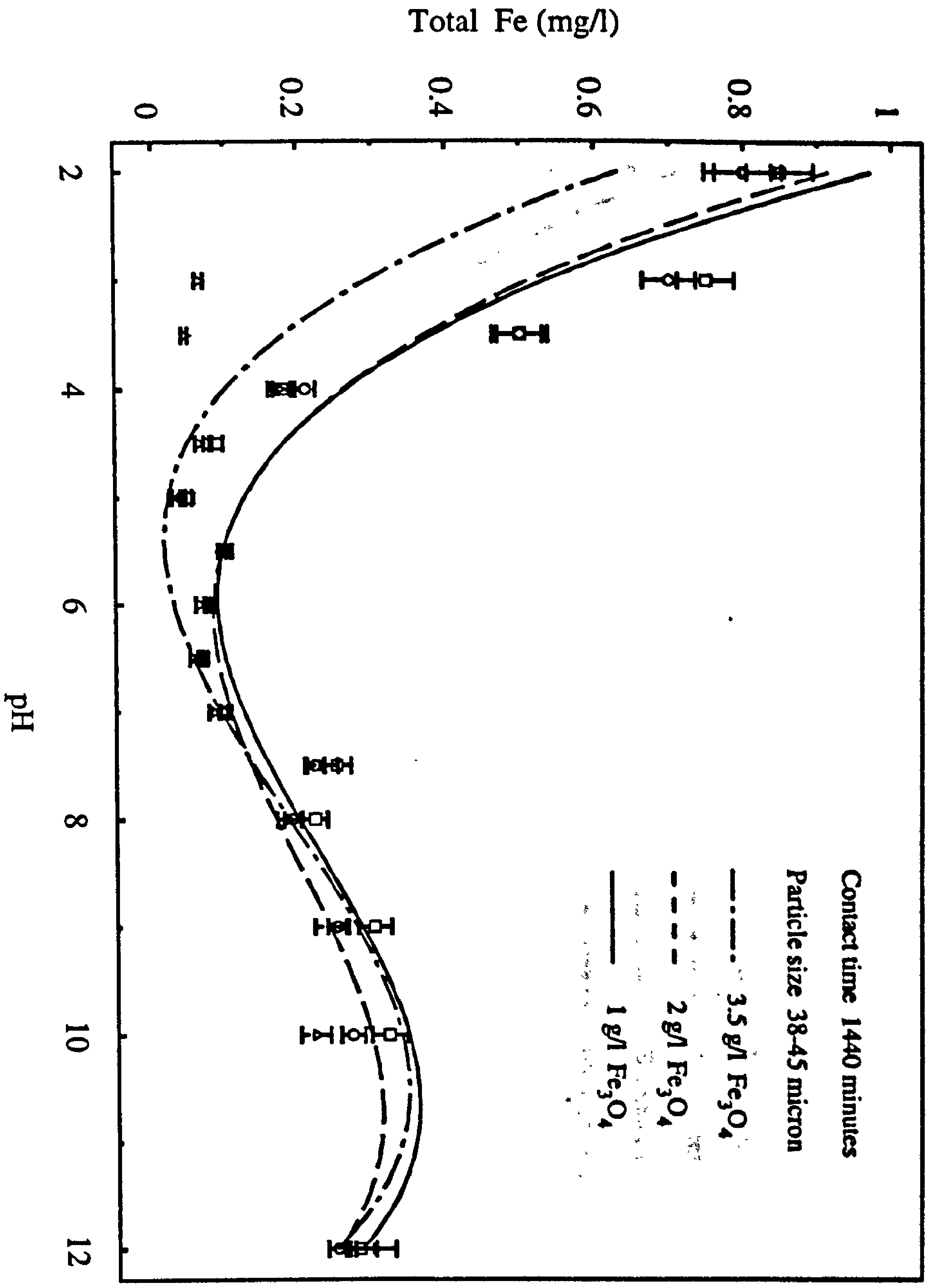

Figure 5.9 Dissolution of magnetite as a function of pH and magnetite dose

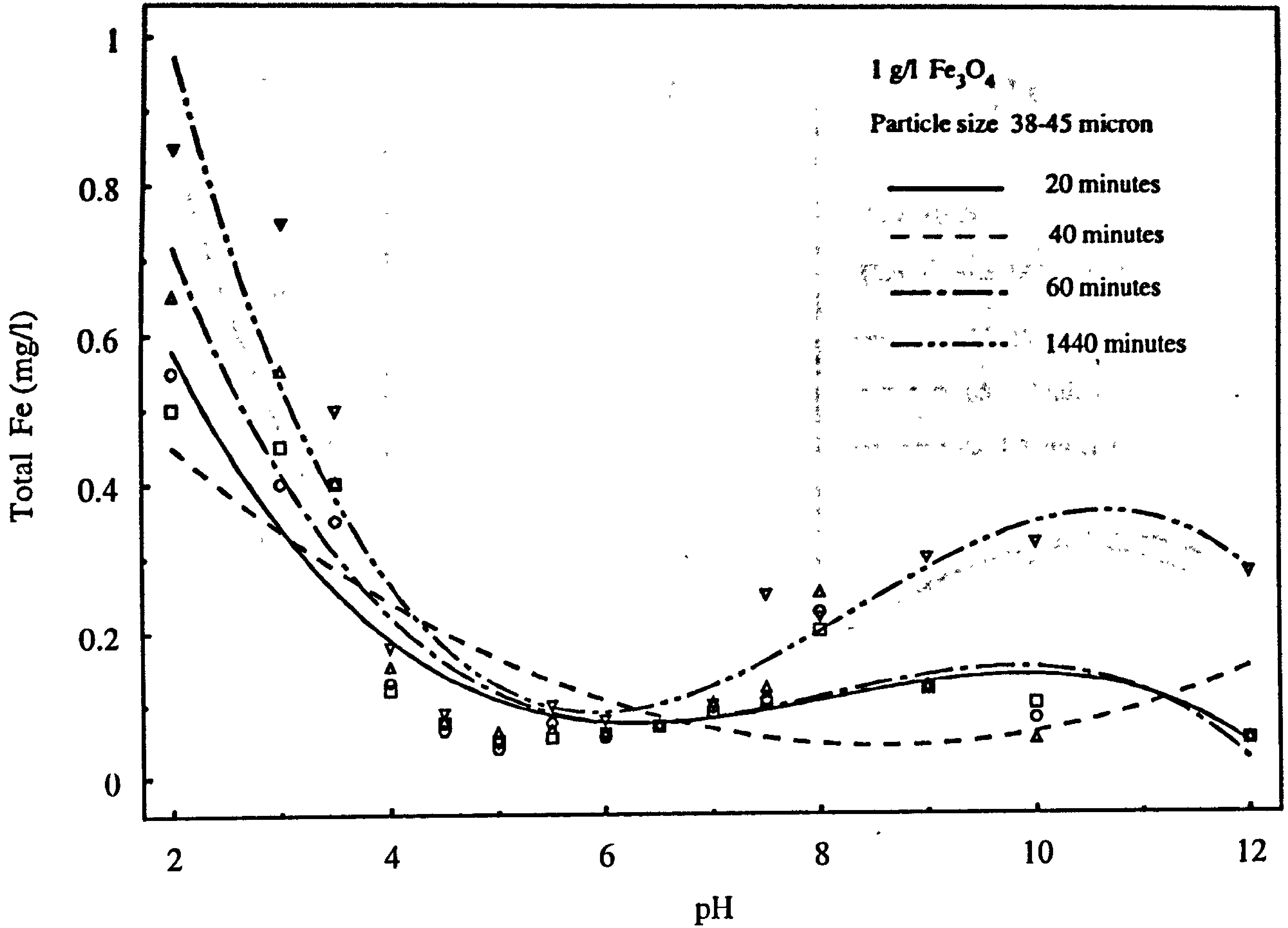

Figure 5. 10 Dissolution of magnetite as a function of pH and time

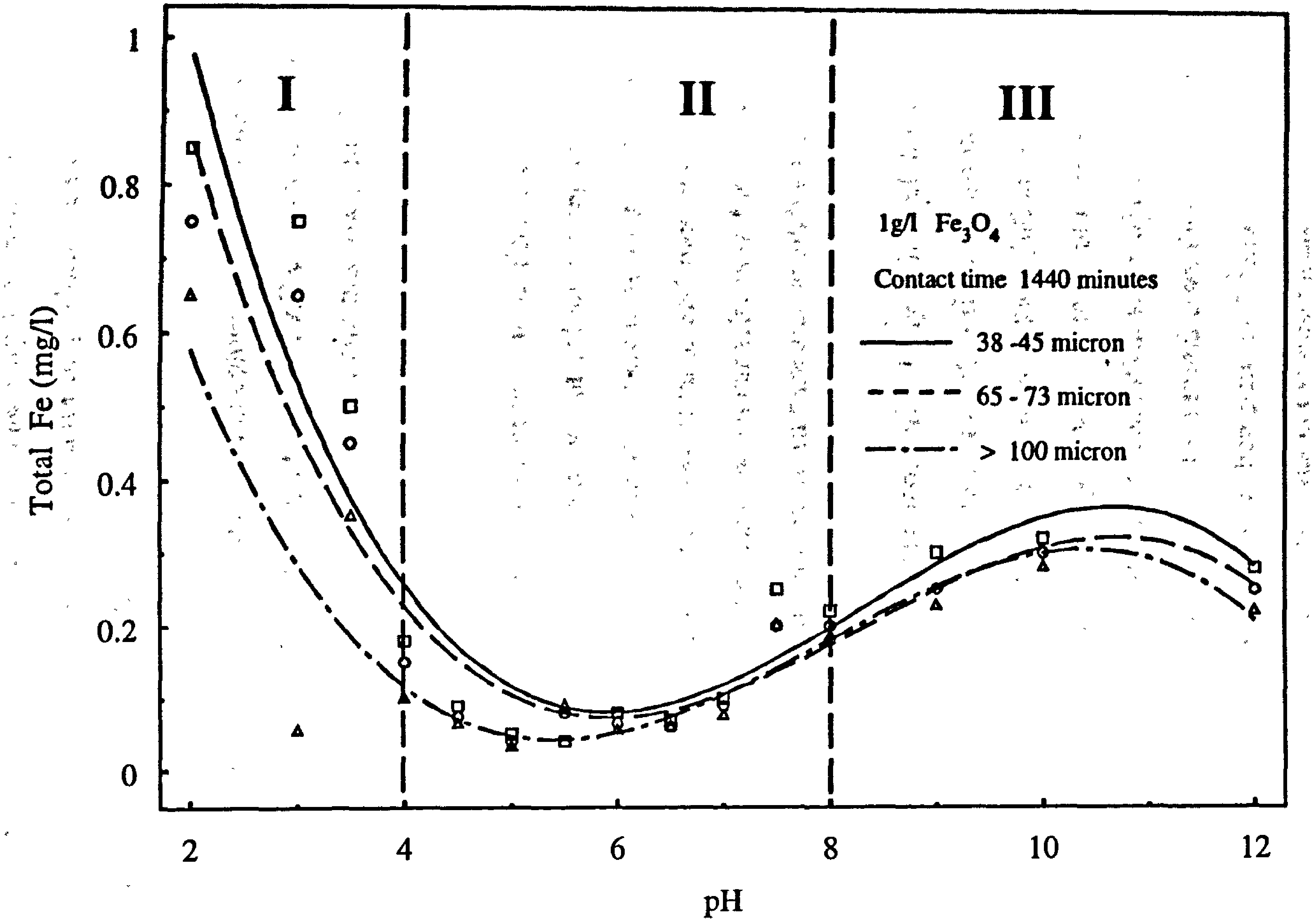

Figure 5.11 Dissolution of magnetite as a function of pH and particle size

5.5 Conclusions

Magnetite can adsorb coloured species and colloids. This is mainly due to the reaction that takes place at magnetite-solution interfaces. The sorption from aqueous systems is followed by magnetic separation, which helps in forming flocs to ease separation, using the magnetic properties of magnetite.

This is consistent with adsorption of negative ions in coloured solutions and of negatively charged colloids on to positively charged magnetite whose PZC was 6.5. It has favourable surface characteristics, depending on its particle size, and has low solubility around the PZC.

The factors that affect adsorption are: magnetite dose, contact time and particle size. The increase in a magnetite dose increases the removal of colour species and turbidity at the lowest contact time studied. The Fe^{3+} hydrolyses slowly to form insoluble hydrated iron oxides, which are important in removing most organic and inorganic substances. The smaller particle size (38-45μ) showed better removal capacity both for colour species and colloids. This can be attributed to the increased surface area available for adsorption.

Coloured species and colloids removal were more effectively achieved for a contact time of 30 and 120 minutes respectively. The longer contact time led to the dissolution of magnetite that in turn may increase the apparent colour of the solution. An increase in the amount of magnetite does not result in a proportionate increase of dissolved iron, instead it is the lowest dose (1g/l) which showed higher dissolution value when compared with the other two magnetite doses (2g/l and 3.5g/l). The minimum solublity is observed around the PZC. Magnetite usually dissolves faster than pure Fe^{3+} oxides due both to its Fe^{2+} content As magnetite is amphoteric, it dissolves in the acid media to form cationic hydro species and in basic media to form anionic hydroxo species. Hence solublity rises as the pH moves away in either direction from the PZC. Three distinct pH regions of magnetite dissolution were observed The first is below pH 4 where the highest dissolution is observed and the second is between pH 4 and 8 with a minimum dissolution, and third that occurs above pH 8 where an increase in dissolution is observed when compared with region two. Thus the use of magnetite for separation purposes at high and low pH would be restricted by its solublity at high and low pH.

Implications for soil transport are, that negative species in soil aqueous systems, both negative ions and particles, will be strongly adsorbed by magnetite in typical soil pH regions. These adsorptions will of course affect the rate of transport of such species from surface to aquifer and will determine the type of physical and chemical methods that would have to be used in any remediation process designed to remove the contaminants. The relatively high abundance of magnetite in the earth's crust and soil can serve as an important natural adsorbent for pollutants disposed on land.

5.6 References

1 Ronov, A.B., and Yaroshevsky, A.A. (1969) Chemical compostion of the earth crust, In:Hart, P.J. (ed) The Earth's crust and upper mantle, 37-57, Amer. Geophys. Union, Washington, DC.

2 Rowley, E.B. (1994) Magnetite. In: Consdine, D. M. (ed) , 1948, Van Nostrand's Scientific Encyclopdia, Van Nostrand, New York.

3 Maher, B.A. & Taylor, R.M. (1983), Formation of ultrafine magnetite in soils. Nature, 336, 368-370.

4 Maher, B.A., (1986), Characterisation of soils by mineral magnetic measurements , Phys. Earth planet inter., 42, 76 - 92.

5 Mullins, C.E., (1977) Magnetic susceptiblity of the soil and its significance in soil science, J. Soil Sci., 28, 223 - 246.

6 Fine, P., Singer, M.J., La ven, R., Verosub, K. & Southard, R.J. (1989) Role of pedogenesis in distribution of magnetic susceptiblity in two California chronosequences, Geoderma, 44, 287 - 306.

7 Schwertmann, U. & Taylor, R.M. (1989) Iron oxides , In: Dixon, J.B. & Weed, S .(ed). Minerals in soil environment, 145 - 180, Soil Sci. Soc. Am., Madsion

8 Lowenstam, H.A., (1981) Minerals formed by organisms, Science , 211, 1126 - 1131.

9 Mann,S., Moench. T.T. & Williams, R.J. P. (1984) A high resolution electron microscopic investigation of bacterial magnetite : Implications for crystal growth, Proc. R. Soc. Lon., B221, 385 -393.

10 Moskowitz, B.M., Frankel, B.B. & Bazylinski, D.A., (1993), Rock magnetic criteria for the detection of biogenic magnetite. Earth and planetry science letters,120,283 - 300.

11 Sakaguchi, T.,Burgess, J.G. & Matsunaga, T., (1993), Magnetite formation by a sulfate reducing bacterium, Nature, 365, 47 -49.

12 Frankel, R.B., Blakemore, R.P., & Wolfe, R.S., (1979) Magnetite in freshwater magnetotactic bacteria.Science, 4387, 1355 - 1356.

13 Lovely, D.R., Stoltz, J.F., Nord, G.L. & Phillips, E.J.P., (1987) Anaerobic production of magnetite by dissimilatory iron-reducing microorganisms, Nature, 330, 252 - 254.

14 Parsonage, P (1991) A review of the physical, magnetic and surface properties of magnetite relevant to the sirofloc process of water treatment, Warren Spring Laboratory , Stevenage.

15 Lindsley, D.H., (1976) The crystal chemistry and structure of oxide minerals as exemplified by Fe-Ti oxides. In : Rumble, D.(ed), Oxides minerals , L 1-84, Min. Soc. Am., Washington D.C.

16 West, A.R. (1985) Solid state chemistry and its applications, Wiley, Chichester.

17 Wells, A.F, (1982) Structural inorganic chemistry, Claredon , Oxford.

18 De Latour, C., (1973), Magnetic separation in water pollution control, IEEE Transactions on Magnetics, Mag-9, 315 - 316.

19 Terashima, Y.,Ozaki, H., & Seikene, M., (1986) Removal of dissolved heavy metals by chemical coagulation, Magnetic seeding and high gradient magnetic filtration. Water Res. 20, 537 - 545.

20 Bolto, B.A., & Spurling, T.H., (1991), Water purification with magnetic particles, Environmental Monitoring and Assessment, 19, 139 -143.

21 Moffat, G., Williams,R.A., Webb., C., & Stirling, R., (1994), Selective separations in environmental and industrial processes using magnetic carrier technology, Mineral engineering, 7, 1039 - 1056.

22 Choi, S., Calmano, W., Forstner, U., (1994) Studies for the separation of heavy metals from wastewater with freshly preciptated magnetite, Acta Hydrochimia et Hydrobiologica, 22, 254 -260.

23 Selwood, P.W., (1975) Chemosorption and magnetization, Acadamic press, London.

24 Urbain, O.M. and Stemen, W.R. (1941) Water purification,U. S. Patent No.2,232,294.

25 Jakubovics, J.P., (1994) Magnetism and magnetic materials, Institute of metal, London.

26 Craik, D (1995) Magnetism principles and applications, Wiley, Chichester.

27 Morrish, A.H., (1965) The Physical Principles of magnetism, Wile y, London.

28 Selwood, P.W., (1956) Magnetochemistry 2nd ed.., Interscience, New York.

29 Bozorth, R.M., (1951) Ferromagnetism, van Nostrand, New York.

30 Oberteuffer, J.A., (1973), High graident magnetic separation, IEEE Transactions on Magnetics, Mag-9, 303 - 306.

31 Kolm, H., Oberteuffer & Kelland, D. (1975), High gradient magnetic separtaion, Sci. Am., 233, 46 - 54.

32 Weiss, D.E., Kolarik,L.O., Priestly, A.J., Andeson, N.J., (1981) Water clarification, U. S. Patent, 4,279,756.

33 De Latour, C..(1976), Process removing dissolved phosphorus from water magnetically,.U.S. Patent No 3,983,033.

34 Okamoto, S., (1974) , Iron hydroxides as magnetic scavengers, IEEE Transactions on magnetics, 10, 923-926

35 Yadidia, R., Abeliovich, A. & Belfort, G., (1977), Algae removal by high graident magnetic filteration, Environmental Sci. & Tech, 11, 913- 916

36 Kolarik, L.O., (1980) Chemistry of the Sirofloc process, Chemistry in Australia, 47, 234 - 240.

37 Kolarik, L.O.,(1983), Colour and turbidity removal with reusable magnetite particles -IV: alkali activated magnetite - A new solid reusable coagulant adsorbent, Water research, 17, 141 - 147.

38 Dixon, D.R., & Kolarik, L.O., (1984) Magnetic microparticles for treatment of natural waters and waste waters, Studies in Environmental science, 23, 179-191

39 Anderson, N.J., Bolto, B.A.,Blessing, N.V., Kolarik, L.O., Priesley, A.J., & Raper, W. C.J., (1983) Colour and turbidity removal with reusable magnetite particles-VI, Pilot plant operation. Water research, 17,1235-1243

40 van Velsen, A.F.M., van der Vos, G., Boersma, R. & de Reuver, J.L. (1991) High gradient magneticseparation technique for waste water treatment, Wat.Sci.Tech.,24, 195-203

41 Munro, P.A., Dunnil,P., Lilly,M.D, (1981), Casein hydrolysis in stirred tank reactors using chymotrypsin immobilised on magnetic supports, Biotechnol. Bioeng. 23, 677-689

42 Flygare, S., & Larson, P.O., (1987), Steroid transformation using magnetically immoblized mycobacterium sp. Enzyme Microb Technology, 9, 494 - 499

43 Molday, R.S., & Mackenzie, D., (1982) Immunospecfic ferromagnetic iron-dextran reagents in the labelling and magnetic separation of cells, J. Immunol. Methods, 52, 353

- 367.

44 David, I., & Welch,A.J.E., (1956), The oxidation of magnetite and related spinels :constitution of gamma ferric oxide , Trans. Faraday soc., 52, 1642 - 1650

45 Sidhu, P.S., Gilkes,R.J., & Posner, M.A., (1977) Mechanism of the low temprature oxidation of synthetic magnetites J. inorg. nucl. chem., 19, 1953 - 1958

46 Sidhu, P.S., Gilkes,R.J., & Posner, M.A., (1978) The synthesis and some properties of Co, Ni,Zn, Cu, Mn and Cd substituted magnetite, J. inorg. nucl. chem., 40, 429 - 435

47 Lefort, J., (1852) Mémoir sur les oxydes ferroso-ferriques et leurs combinaisons salines, Compt. rend. acad., 34, 488-496 ; Lefort, J., (1869) Mémoir sur l'oxyde de fer magnétique et ses combinaisons salines, Compt. rend. acad., 69, 179-180.

48 Massart, R., (1981), Preparation of aqueous magnetic liquids in alkaline and acidic media . IEEE transactions on magnetics , 17, (2), 1247 -1248

49 Jeffery, G.H. (1989), Vogel's textbook of quanitative chemical analysis, 5th edition, Longman scientific and technical, Harlow

50 Ahmed, S.M., (1966) Studies in the dissocation of oxide surfaces at the liquid-solid interface,Canada. J. Chem., 44, 1663-1670

51 Parks, G.A, (1965), The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. Chem. Rev., 65, 177 - 198

52 Parks, G.A, (1965), Aqueous surface chemistry of oxides and complex oxide minerals isoelectric point and zero point of charge, Adv. chem. ser. ,67, 121-160.

53 International Centre for Diffraction Data - JCPDS (1973), Powder diffraction file 23-1046, JCPDS.

54 Malcom, R.L., (1985) Humic substances in rivers and streams, In:Aiken, D.M, Wershaw, R L, and MacCarthy, P., (eds) Humic substances in Soil, Sediment and water, 181-210, Wiley-Interscience, New York.

55 Beckett, R., (1990) The surface chemistry of Humic substances in Aquatic Systems, In: Beckett, R., (ed) Surface and Colloid Chemistry in natural waters and Water Treatment, 3 - 20. Plenum press, London.

56 Harvey, G. R., Boran, D. A., Chesal, L.A., and Tokar, J.M. (1985) The structure of marine fulvic and humic acids. Mar. Chem.12,119-132

57 American Public Health Association (1985) Standard methods for the examination of water and waste water, 16th ed. American Public Health Association, Boston

58 Bohnsack, G. (1987), The solublity of magnetite in water and aqueous solutions of acid and alkali. Hemisphere, Washington, D.C.

59 Ven cataramani, B.. Venkatewariu, K. S. and Shankar, J., (1978) Sorption properties of oxides, J. Coll. and Interf. Sci. 7, 187- 194

60 Tremaine, P.R., and Leblanc, J.C.,(1980) The solubility of magnetite and the hydrolysis and oxidation of Fe^{2+} in water to 300°C. J. of Solution Chem. 9 , 415-442

61 Balakrishnan, P.V., (1977), A radiochemical technique for the study of dissolution of corrosion products in high-temperature water. The Canadian J. of Chem. Engineering 55, 357-360.

62 Sweeton, F. H. , and Baes, C. F. Jr., (1970) The solubility of magnetite and hydrolysis of ferrous ion in aqueous solutions at elevatecd temperatures. J. Chem. Thermodynamics 2, 479-500.

63 Zarembo, V. I., Kritiskii, Slobodov, A.A., & Puchkov, L.V (1988), Solublity of magnetite in the coolant of an atomic power station equiped with a boiling water reactor, Soviet Atomic Energy, 1988, 65, 587-593

64 Gray, N.F. (1994), Drinking water quality: problems and solutions, John Wiley Chichester.

65 Snoeyink, V.L. & Jenkins, D (1980) Water chemistry , John Wiley, New York.

66 Dojlido, J.R. & Best, G.A. (1993), Chemistry of water and water pollution. Ellis Horwood, New York.

6.0 SUMMARY AND CONCLUSIONS

Iron and manganese oxides are among the major components of the soil that play important roles in soil-water systems. Their significance in a soil-water system can be attributed to the reactions that take place at phase boundaries, mainly at soil-water interfaces with additional reactions at soil-atmosphere and atmosphere-hydrosphere boundaries. The reactions at these interfaces affect the distribution of both contaminants and nutrients among the components of soil-water systems and also their transformations and mobility. The chemical and surface-chemical reactions at the soil-water interface are the main controlling factors of the system.

This work has attempted to illustrate the significance of soil-solid components in contaminant and nutrient retention and transport as exemplified by the behaviour of iron and manganese oxides. It has shown the need for a detailed understanding of the uptake of potential contaminants and retention of nutrients by soil-water systems. The chemical and physical properties of synthetic iron and manganese oxides in the oxide-solution system where the variables are known and under control have been used to understand and formulate a simplified model that can assist the interpretation of observed facts in soil contamination. Model systems of this type have an advantage in that the experimental and analytical conditions are generally better controlled than in field investigations but care should be taken to ensure that they do not differ significantly from those obtained under field conditions. Although relating the results between model and real systems is not always easy, model systems do offer insights into those circumstances where chemical reactions are not sufficiently well understood and where the descriptive data of the real systems are not sufficiently accurate or specific.

Sorption processes are simulated using synthetic iron and manganese oxides *viz.* goethite (α-FeOOH), birnessite ($Na_4Mn_{14}O_{27}$).$9H_2O$) and magnetite (Fe_3O_4) analogous to soil oxides. Studies were also made on mixed metal oxides containing iron, titanium, aluminium and inert materials like silica sand and on goethite pellets.

The prepared oxides used to simulate a soil-water environment were characterised by various techniques *viz.* scanning electron microscopy, x-ray diffraction, surface area measurement, chemical analysis, and thermogravimetric analysis. Their electrokinetic behaviour was also investigated to determine the electrochemical properties at the soil-water interface.

The sorption of cobalt and cadmium from aqueous solutions on to goethite, and birnessite was measured as a function of pH; cadmium and cobalt concentration; oxide concentration; electrolyte concentration; electrolyte composition, contact time and contact temperature.

The adsorption edge pH (6.5 -7.5) of cadmium and cobalt on goethite depends on the cation concentration at a low surface area but is independent of the cation concentrations at a high surface area. A fourfold increase in the goethite surface area shifts the adsorption edge to a lower pH. It should be noted that for every mole of cadmium and cobalt adsorbed, two hydrogen ions are released and this should result in the lowering of pH. An increase in both in temperature and contact time leads to a significant increase in adsorption of both cobalt and cadmium on goethite. Goethite concentration also has an effect but is less significant than those due to temperature and contact time. A decrease in electrolyte concentration of the metal transport medium does not affect the adsorption edge. The distribution coefficients of metal adsorption/metal transportation increase sharply with an increase in pH and more cadmium and cobalt are retained by goethite around neutral pH than at a lower pH. The experimental results show that the main factors affecting the sorption process are pH, contact time and temperature and the adsorption edge is around PZC (7.2).

Goethite coated on sand has shown the potential for industrial use, although the adsorption capacity of both goethite coated sand and a goethite pellet is less than that of the colloidal form, their industrial potential is greater.

Because in goethite the maximum sorption is around the PZC there can be no electrostatic driver of the process, this means that the attractive or repulsive forces between the surface and positive ions can not be important and that the cation-exchange process must be predominant.

$$\sim\sim O{-}H + 1/2\,M^{2+} \longrightarrow M/2^{+} + H^{+}$$

The uptake of cobalt and cadmium on birnessite occurs in a pH range (3.0 - 8.0) with sigmoidal shaped curves of percent uptake against pH. Birnessite uptake capacity increases with increasing pH with a peak at about 6.4. With increasing concentration of both metals higher pH values are required to sorb comparable amounts. The uptake of both metals shows an increase with increasing temperature, and a decrease with increasing electrolyte concentration. The uptake edge is moved to a lower pH with an increase in the birnessite surface area or contact time. Thus, pH, oxide concentration, temperature and contact time are the major factors for high retention of both cobalt and cadmium on to birenessite. The major uptake of cobalt or cadmium on to birnessite occurs when the surface carries a negative charge, PZC 2.9, indicating that under these conditions, the metals will be adsorbed on the birnessite surface.

In birnessite since the sorption occur above the PZC, three reactions become possible:

(1) the attraction of negative surface for the positive ions
(2) ion-exchange with hydroxide surface group
(3) ion exchange with the sodium form of the surface

$$\sim\sim O{\cdots}Na + 1/2\,M^{2+} \longrightarrow O{-}M/2 + Na^{+}$$

However, in view of the results obtained with goethite it seems more likely that the processes (2) and (3) above are more important.

Birnessite is available in soils and sediments at the pH 4-7. Based on the results of uptake experiments its potential as a heavy metal scavenger in the natural environment is evident, and can also limit the availability of nutrients. Therefore birnessite plays a major role both in limiting the availability of trace metals like cobalt and toxic metals like cadmium.

Magnetite can adsorb coloured species and dispersed organic colloids via reactions that take place at magnetite-solution interfaces. The sorption from aqueous systems can then be followed by magnetic separation which helps in forming flocs resulting in the separation of the adsorbed species with the magnetite in the magnetic field.

For both negative coloured ionic species and dispersed negatively charged organic colloids the decrease in pH has significant effect. This is consistent with adsorption of negative ions and of negatively charged colloids on to positively charged magnetite at a pH below the PZC at 6.5, where the surface charge is positive.

The factors that affect adsorption are: magnetite dose, contact time and particle size. The increase in a magnetite dose increases the removal of colour species and dispersed organic colloids at the lowest contact time studied. The Fe^{3+} in the magnetite hydrolyses slowly to form insoluble hydrated iron oxides, which is important in removing most organic and inorganic substances. Smaller particle size samples (38-45μ) show a better removal capacity for both colour ions and colloids. This can be attributed to the increased surface area available for adsorption.

The minimum solubility of magnetite is observed around the PZC. As magnetite is amphoteric, it dissolves in the acid media to form hydrated cationic species and in basic media to form anionic hydroxo species. Hence solubility rises as the pH moves away in either direction from the PZC. Three distinct pH regions of a magnetite dissolution were observed The first is below pH 4 where the highest dissolution is observed and the second is between pH 4 and 8 with a minimum dissolution, and third that occurs above pH 8 where an increase in the dissolution is observed when compared with region two. Thus the use of magnetite for separation purposes at high and low pH would be restricted by its solubility at high and low pH. The relatively high abundance of magnetite in the earth crust and soil means that it must serve as an important natural adsorbent for pollutants disposed on land.

The studies carried out in this work indicate the type of information required before soil management and remediation protocols can be developed. It is clear that much future work needs to be carried out on: (1) reversibility of the sorption of metal ions; (2) the competition between contaminants for the sorption sites; (3) the speciation of metal containing sorbates and their migration into the lattice of oxide; (4) the effect of mixtures of Mn and Fe oxides on sorption; (5) the behaviour of coatings formed on other soil materials such as clay.

The current knowledge of soil contamination management was reviewed to highlight the unique difficulties of the problem and the need for the development of integrated approach. Soil contamination is a complex problem, starting with the very definition of what level and type of contamination is acceptable or unacceptable. Although soil pollution is a major environmental concern, it is probably the least understood source of pollution in terms of both transport of contaminants and remediation. The current knowledge of soil processes and the situation in remediation techniques and legislation highlights the need for continued endeavour.

APPENDIX

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Review

Contaminated and Polluted Land: A General Review of Decontamination Management and Control

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Abstract: Although land pollution is a major environmental concern it is probably the least understood source of pollution in terms of both transport of toxins and remediation. This paper deals with the current situation in legislation and land pollution remediation and highlights future requirements.

Key words: contaminated land, remediation technique, remediation cost, pollution prevention.

1 INTRODUCTION

Although there has been concern about land pollution since the onset of industrialization, this has been largely the interest of a relatively limited number of people. Consequently until recently land has not been seen as an environmental sector deserving protection to the same extent as air or water; but now it is recognized that land pollution cannot continue unabated. This recognition has risen because of incidents of contamination, scarcity of usable land and increased general concern about the effect of industrial activity on the environment.

Concern about land pollution increased in the 1960s when the writing of two famous activists came to public attention. Rachel Carson's prophetic book, *Silent Spring*, exposed the use of toxic chemicals and their effect on the environment;[1] Galbraith also showed how the ever-increasing demands of our society are a burden on the environment.[2] Concern intensified in the 1970s during an upsurge of anxiety following the discovery in some spectacular cases of serious damage caused mostly by old landfills and abandoned contaminated sites. Because a large number of these sites exist, and in response to increasing public pressure, the problem has now received much more governmental attention in many developed market economies. As a result, policies are under development at both national and international level with the intention of protecting the soil environment from further contamination. In a number of industrialized nations legislation is either in force or proposed, which aims to investigate, remediate and protect land. Internationally, soil pollution and soil protection have attracted the attention of a number of intergovernmental organizations including the Food and Agriculture Organization (FAO), the United Nations Environmental Programme (UNEP), the International Organization for Standardization (ISO), the International Society of Soil Science (ISSS), the Organization for Economic Co-operation and Development (OECD) and the North Atlantic Treaty Organization (NATO). Furthermore, much progress has been made in the last fifteen years in the development of effective investigative methods and remediation techniques for contaminated land but much remains to be done to optimise decontamination processes at both research and operational levels. All these measures and developments show how contaminated land is currently an area of much activity in scientific, technical and legislative spheres.

In a review of this length it is not possible to consider all aspects of polluted and contaminated land in detail. For this reason we have focused on what we consider to be the key areas, viz. a lack of detailed knowledge of the

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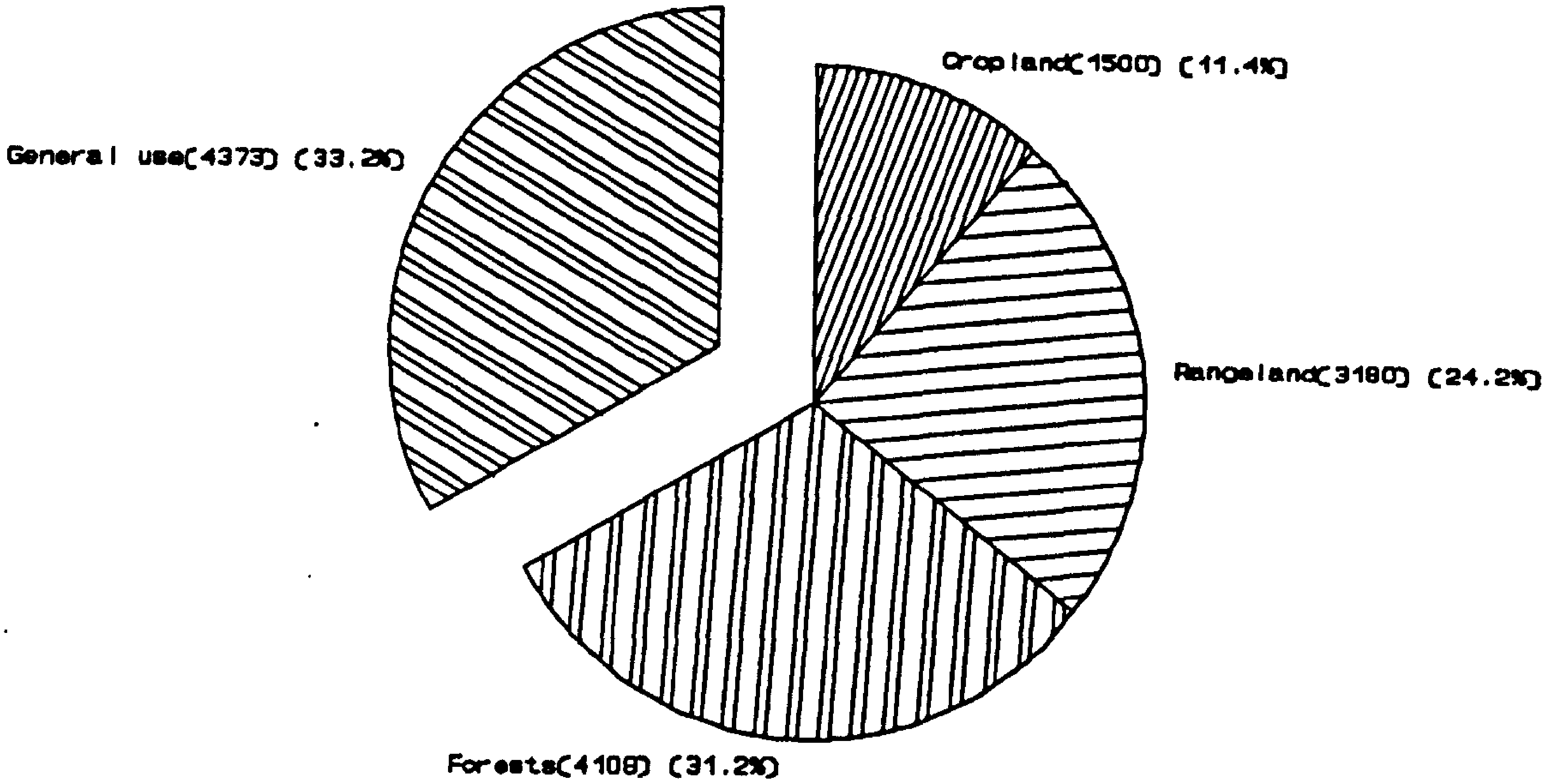

Fig. 1. Land use classification of Earth (million hectares and percentages).

exact nature of the polluting species and their transport in soil legislation and remediation techniques.

In dealing with regulations concerning contaminated and polluted land, we have highlighted the content of these regulations without reference to the economic costs of the tasks required by them in various countries. In many instances, the cost of achieving a 'near natural' situation for land usage would be excessive and this clearly raises the issue of the important difference between a potential hazard and a real risk.

2 LAND CONTAMINATION

The total land area on Earth is estimated to be about 14 477 million hectares, of which 13 251 million hectares is ice-free. Land use patterns are mainly determined by the interactions between climate, geography, geology, human and economic processes. The Food and Agriculture Organization has categorized land use into four categories: arable and permanent cropland, permanent pasture (rangelands), forests and land for general use including unused land in urban areas, and waste and barren land. The latter encompasses about one-third of the earth's land surface, 4373 million hectares, of which more then 3000 million hectares is suspected to be exposed to chemicals[3] (Fig. 1). Even though all categories are open to pollution and consequently hazardous to humans, animals, plants and buildings, attention has been focused on land categorized under general use because this represents the more direct risk to humans and hence receives greater publicity in the case of incidents.

Contaminated land results from a wide range of human activities including industrial discharge processes and disposal of waste. It is also recognized that apart from human activities, natural phenomena such as flooding, landslides, volcanic eruption and mineralization will upset the local balance of contaminants in the soil environment. In spite of a long history of contamination, contaminated land management is a relatively new field and there are many differences in understanding and tackling the problem between institutions and countries. This is evident from different definitions of the term 'contaminated land'.

The definition of what constitutes 'contaminated' land in different countries illustrates the different emphasis placed on the problem. In the United States, Germany and The Netherlands contaminated land is considered as a serious threat to human health and the environment. On the other hand in Canada and the United Kingdom the problem is addressed only within the context of the intended future use of the land.[4]

In nature there are broadly three levels that are important in considering the effects of any potentially toxic species in soil, viz. background levels, tolerable levels and harmful polluting levels. Attempts have been made to assess the ranges of concentration applicable to these levels and to use these data to produce trigger values for action (see Section 3.2). For the purposes of this review we have defined contaminated land as that containing tolerable levels of potentially toxic species, and polluted land as that containing harmful levels of toxic species.

There are, however, problems even in deciding on background levels of, for example, heavy metals in the soil. Total analytical heavy metal content would include both metal species available to biota and the metal fixed in minerals which would, under normal circumstances, not be available to plant and animal species. It is therefore important in deciding the background level of heavy metals that the data quoted are for available species, essentially those soluble in dilute acids such as acetic, hydrochloric and sulphuric, and not total heavy metal concentrations.

In the United Kingdom three definitions currently exist which portray different views. The Royal Commission on Environmental Pollution (RCEP) differentiates between 'contamination' and 'pollution' in a way which makes it difficult to define contaminated land. According to the RCEP, contamination is a necessary, but not a sufficient, condition for pollution, whilst in the United States contamination and pollution are used interchangeably.[5,6] The second definition in the United Kingdom is the one used by the Department of the Environment (DoE). According to the DoE, land is considered contaminated only on the basis of its actual or potential use.[7] The third is the one proposed by the British Standards Institution (BSI) which defines contaminated land as land which poses hazards irrespective of whether or not it is to be used, which basically conflicts with the DoE view of contaminated land.[8]

The widely accepted definition which more or less echoes the views of other countries is from the NATO-Committee on the Challenges of Modern Society (CCMS):

> ... land that contains substances that when present in sufficient quantity or concentration are likely to cause harm, directly or indirectly to man, to the Environment or on occasions to other targets.

The emphasis in this definition is on the presence of contaminants that bring about pollution rather than the current or future use of the land.[5,9,10]

Virtually all industrial activities emit contaminants which eventually give rise to contaminated land. Consequently more and more incidents of pollution are being reported and efforts to tackle the problem are increasing. Hopefully, with our increasing knowledge of contaminants and their genesis the 'hidden agenda' for not dealing with them, which is exercised for political/economic reasons, will disappear and instead the problem will be addressed with the benefit of better insight, and parity of emphasis.

Knowledge of the exact nature of the contaminating species present in the soils and the reactions and transport of these species through soils is vital to the development of remedial techniques. Polluting species can react with soil components in a number of ways, e.g. by adsorption on the surface of soil particles, by exchange with hydroxide and other groups in clays and aluminosilicates, by interaction with organic soil components as humic acids, by reactions with the aqueous component of the soils leading to precipitation and dissolution of derivatives of the contaminating species and by uptake by microorganisms and plants. Transfer of contaminating species in soils is further complicated by the physical nature of the soil, particularly the extent of fissures which will affect the transport of dissolved and suspended species through the soil to the aquifer.

An aspect of transport of heavy metals that must be addressed is their availability to biota. The ability of living matter to take up potentially toxic species depends upon a number of factors including the nature of the polluting species and the metabolism of the organisms. Toxicity is, of course, dose-dependent and many organisms can adapt to the levels of available heavy metal species. There are, for example, a number of plants native to Africa which are hyperaccumulators of cobalt. The soils in which they grow can contain up to 1% cobalt which is extremely poisonous to most plant life but the hyperaccumulators can concentrate cobalt in their leaves at very high levels.[11] Because pollutants are generally present in the environment in very dilute concentrations (even though they are harmful at these low levels) we are faced with the fact that there is a major lack of detailed knowledge of the fundamental nature and properties of the behaviour of species in very low concentrations in complicated systems such as soils.

The purpose of this paper is to describe the current legislative situation and the developments in remedial techniques that are important in the waste management of contaminated land.

3 CONSPECTUS OF LEGISLATION AND ITS IMPLEMENTATION

Contaminated land, like other pollution problems, is a legacy of industrialization which is regarded as a threat to society in the developed market economies, even though the threat is worse in the industrialized former eastern bloc and developing market economies. In the developing market economies, public and political attention has only recently begun to be turned to environmental issues, and they are not regarded as a priority. The struggle to provide and secure basic necessities such as food, shelter, and basic health care for the general population is considered more important.

On the other hand, in spite of public awareness and political commitment in North America and western Europe, countries manage the problem differently, regulated by unparallel legislation. The following account considers the practices in identification, clean-up, and financing of remedial action concerning contaminated land within the United States, Canada, the United Kingdom, The Netherlands and Germany (Table 1). The respective standards, guidelines and legislative regulations are discussed; the similarities and differences are highlighted and practical experiences summarized.

3.1 Identification of contaminated sites

In the United States the two major legislative instruments dealing with contaminated land are the 1976 Resource Conservation and Recovery Act (RCRA) and the 1980 Comprehensive Environmental Response Compensation

TABLE 1
Profile of Countries Surveyed

Country	*Area* (*'000 km²*)	*Population* (*millions*)	*Density* (*pop. km⁻²*)
USA	9373	246·33	26
Canada	9221	26	3
West Germany	249	61·2	246
UK	244	57·1	234
The Netherlands	37	14·8	396

and Liability Act (CERCLA) and their amendments and reauthorization. The RCRA establishes a 'cradle-to-grave' regulatory programme for current hazardous waste activities while CERCLA establishes a comprehensive response programme for past hazardous waste activities by providing funds and authority. Accordingly, national contingency plan (NCP) regulations are set in which owners and operators of any facility are required to notify the release of reportable quantities of hazardous substances and pollutants or contaminants to the national response centre of the Environmental Protection Agency (EPA) in Washington.[6]

There are more than 720 hazardous substances listed by the EPA as presenting a substantial danger to human health and the environment. In addition, according to CERCLA a 'pollutant or contaminant' can be any other substance not on the list of hazardous substances which 'will or may reasonably be anticipated to cause any type of adverse effects in organisms and/or their offspring'. The list of hazardous substances is regularly updated by the EPA and by the end of 1990 there were approximately 33 000 sites in the EPA's inventory of potentially hazardous sites. Out of these, 31 000 sites have undergone preliminary assessment by the EPA. As a result of preliminary assessment it was decided that 19 000 sites would be handled by local government together with the parties potentially responsible and not by federal action, leaving 12 000 sites on the National Contingency Plan (NCP).[12]

In contrast, in the United Kingdom the existing laws including the Control of Pollution Act of 1974 (COPA) and the Environmental Protection Act 1990 (UK EPA) are not designed to investigate or identify contaminated land. Instead they aim to minimize pollution by controlling activities which have the potential to contaminate. In addition they are designed to respond to specific contaminants in the case of redevelopment.[12] There is no centrally managed identification of contaminated land except through pilot studies carried out in a few locations, including a comparatively detailed study made in Wales.[13–15] It is estimated that 100 000 sites in the United Kingdom, covering more than 100 000 hectares, are contaminated.[16] The Environmental Protection Act 1990 requires local authorities to maintain a register of land exposed to contaminative use. The contaminative use list issued by the Department of the Environment covers a wide range of processes and operations.[17] It includes processes for producing energy, chemicals and raw materials, operations such as the burial of diseased livestock, activities of research or educational laboratories, and dry cleaning services. As stipulated in the UK EPA the scheduled compilation of contaminated land registers should have commenced by April 1992 and should have been available to the public by April 1993. The government has postponed the action after complaints by developers and landowners that such registers could blight their property. It was also revealed that further consultations would take place but there is no target date for implementing the register.[18] It is worth noting here that the register is still mainly intended for use in property transactions.

In Canada the major piece of legislation that deals with contaminated land is the 1988 Canadian Environment Protection Act (CEPA). CEPA is a comprehensive act and has created the 'priority substance list'. Using data on priority substances, a list of 'hot spots' has been identified. The list of 'priority substances' is comparable to the United States' list of hazardous substances even though it is much shorter. The list comprises substances proved or suspected to have negative effects on human health and the environment.[19] There is, however, no structured system, as in the United States, for identifying contaminated land at national level, even though CEPA and other laws and regulations require compulsory reporting of spills, pollution and emission of contaminants.[19,20] In contrast to the national situation in Canada, the city of Toronto has an inventory of contaminated land compiled from previous contaminative use and the province of Quebec has a list of companies whose operations are suspected of causing contamination.[7]

In The Netherlands the legislation dealing with the identification of contaminated land is contained in the 1983 Soil Clean-up Act (interim) referred to as IBS and the 1987 Soil Protection Act.[7] The provincial authorities are responsible for investigation and clean-up. Although the national survey of contaminated land was started in 1980, since 1983 there has been an extensive programme to identify contaminated sites.[21] The survey has helped in the production of lists of sites considered likely to be hazardous in the future to human health and the environment. According to the summary of various studies carried out by the national and provincial authorities, there are 650 000 contaminated sites of varying size throughout the country. About 110 000 are thought to be sufficiently contaminated to need remediation and of these 25 000 were considered to need urgent action because they posed a serious threat to human health and the environment.[22–24]

In West Germany the eleven states and the federal government have been working since the early 1970s to abate the problem of contaminated land. The legal foundation of the contaminated land problem is contained in three federal acts and various state laws and regulations, the federal acts are: the 1972 Waste Disposal Act, the 1986 Waste Disposal Act and the 1974 Environmental Protection Act. These pieces of legislation have been criticized for containing no direct regulations on contaminated land.[25] In spite of the lack of direct legal regulations an enormous amount of work has been undertaken towards tackling the problem of contaminated land. The responsibility of identification of contaminated land rests with state authorities and contaminated sites are considered as a historical burden. There is a similar approach in most states towards identification of contaminated land.[25,26] The state of Hamburg follows three stages in the identification process: documentation and surveying, preliminary studies, and detailed studies. The first stage consists of gathering information from different sources regarding the suspected site. From the information gathered a 'contaminated site reference register' and accompanying site map is produced. These documents are used as support documents for any undertaking related to the use of the land. According to the state of Hamburg the sites are divided into four categories, A, B, C, and X, depending on the risk to human health and the environment. The state has adopted the United States Environment Protection Agency's hazard ranking system and the Dutch A, B, and C reference value to fit its needs.[27] If the initial evaluation reveals a high risk a preliminary study is undertaken, followed by detailed studies which prepare an action plan for remediation.[25] According to the German authorities, in 1989 there were 50 000 suspect sites of which 5000 to 6000 were thought to require urgent remedial action. Table 2 summarizes the situation on contaminated sites.

TABLE 2
Summary of Contaminated Sites

Country	*Potentially contaminated sites*	*Sites with preliminary assessment*	*Sites requiring remediation*
USA	33 000	31 000	20 200[a]
Canada	NA	NA	NA
West Germany	50 000	NA	6 000[b]
UK	100 000	NA	NA
The Netherlands	650 000	650 000	110 000[c]

[a] This include 19 000 sites to be handled by local governments and potential responsible parties and 12 000 sites for federal agency action.
[b] These are the sites that need immediate action only.
[c] This includes 25 000 sites that require immediate action.
NA, Not available.

3.2 Clean-up of contaminated land

In the United States CERCLA directs the EPA to protect human health and the environment by meeting strict clean-up standards at each site. The EPA undertakes 'removal' and/or 'remedial' action whenever the hazardous substance or the pollutant/contaminant on the site presents threatening and actual danger to humans and nature. Removal is a short-term limited response to a more manageable problem whereas remedy is a longer term, more expensive solution for a more complex problem.[6] The remediation action aims to reduce to background or natural level many contaminants that are on the hazardous substance list and/or pollutant or contaminant. CERCLA clearly states that treatment is strongly preferred to off-site disposal and to leaving the contaminant on-site.[6]

The clean-up process begins with investigation of each site to determine the nature and extent of the contamination and assess the attendant risks. Concurrently, a feasibility study is conducted which considers the techno-economic and social factors involved. The process continues with public participation in the records of decision, in which the EPA announces and explains its tentative selection from the remedial options available. It is compulsory that the EPA should do all it can to secure public participation and incorporate the public response in its final decision. Finally the detailed design is undertaken and upon completion the construction contract is awarded. Two conditions must be satisfied before the EPA starts the long remedial action process:

(1) A 'contract or cooperative agreement' should be reached with the state in which the site is located to finance 10 or 50% of the remedy cost for non-state operated and state-operated sites respectively, provided liable parties are not identified.
(2) The site should be on the National Priority List (NPL).

Once the site has fulfilled the two conditions it goes through the chain of remedial process activities. This process provides a site-specific decision concerning the remedial action to be taken. According to the EPA by the end of 1990 there were 1200 NPL sites and 412 of them received an emergency response to eliminate any immediate danger to human health and the environment. NPL sites vary in size, location, and nature and level of contaminants, viz. from a metal plating workshop covering a quarter of an acre to larger mining areas and waste dump sites.[12] It is worth noting here that one of the most difficult and complex areas in CERCLA and accompanying laws relating to contaminated land is how to determine the appropriate extent of the remedy at the particular ste and to answer the question 'how clean is clean?'. Despite all the details in CERCLA much of the decision-making on remediation is left to the EPA decision-makers on a site-by-site basis. This mandate has cast a shadow on the human element of the decision on 'how clean is clean?' and EPA's ability to control and maintain the quality of the decision. In 1988 this uncertainty forced the EPA to prepare new regulations and guidelines to deal with this issue but still the problem exists, and is likely to remain in the foreseeable future.

In the United Kingdom there is no statutory force specially related to the remediation of contaminated land as in the United States or The Netherlands. But it is subject to the Control of Pollution Act 1974, the Environmental Protection Act 1990 and the Water Resources Act 1991. Instead, current practice is based on the guidance notes issued by the Interdepartmental Committee on Redevelopment of Contaminated Land (ICRCL).[28] ICRCL guidance notes set out two 'trigger values' for a number of contaminants. These are 'action trigger' and 'threshold trigger'. The term 'action trigger' refers to concentrations above which the risk is unacceptable; while 'threshold trigger' refers to concentrations below which no action is required. In between the two there is a grey area in which risk is dependent upon the planned next use of the land and the form of development, and should be judged on a site-by-site basis. The 'trigger concentrations' are available for both organic and inorganic contaminants for certain elements and compounds (Table 3). In general in the United Kingdom the problem of contaminated site remediation is addressed, only if and when the problem comes to light. Furthermore the preferred methods of treatment are excavation, cover, and off-site disposal which merely shift the problem and are not treatment in the real sense of decontamination. Moreover, only a limited number of contaminants are considered and the risk is analysed narrowly in relation to the intended use of the land rather than in the wider context of environmental pollution.[4,26]

In Canada, the remediation of contaminated sites excluding federally controlled areas, viz. airports, armed force bases and national parks, is the direct responsibility of the provinces. Environment Canada, which is the equivalent of the Environmental Protection Agency of the United States, coordinates the investigation and remediation of contaminated sites with participating provinces and territories.[20] The Canadian Environmental Protection Act of 1988 (CEPA) has created the priority substance list which assists in determining remediation methods. The list contains 44 substances identified as potentially hazardous and their detailed assessment is planned to be completed by 1994.[20,29]

Apart from mandatory reporting of spillage which facilitates the identification of contaminated land, there is no aggressive 'search and tackle' programme. The remediation is mainly undertaken whenever there is a need for redevelopment, and it aims as far as possible to eliminate or destroy the contaminants. In 1989 the Canadian Council of Ministers of the Environment initiated a five year programme to clean 30 abandoned high risk sites. One of these is the remediation operation in the Sydney tar ponds chemical dump site, claimed to be the largest of its kind in North America.[20]

TABLE 3
UK Trigger Concentrations

Contaminant	*Planned use*	*Threshold trigger concentration (mg kg^{-1})*
Arsenic	Domestic gardens, allotments	10
	Parks, playing fields, open spaces	40
Cadmium	Domestic gardens, allotments	3
	Parks, playing fields, open space	15
Lead	Domestic gardens, allotments	500
	Parks, playing fields, open space	2000
Chromium	Domestic gardens, allotments	600
	Parks, playing fields, open space	1000
Mercury	Domestic gardens, allotments	1
	Parks, playing fields, open space	20
Selenium	Domestic gardens, allotments	3
	Parks, playing fields, open space	6
Copper	Any use where plants are to be grown	130
Nickel	Any use where plants are to be grown	70
Zinc	Any use where plants are to be grown	300
Coal tar	Domestic gardens, allotments, playing fields	200–5000
Phenols	Domestic gardens, playing fields, buildings	5
Sulphate	Domestic gardens, playing fields, buildings	2000

In The Netherlands, contamination of land has serious repercussions because of the country's topography and geological setting. Therefore land is considered to be a scarce and valuable resource that needs to be reclaimed and protected from further pollution whenever possible. Accordingly, remediation operations aim to restore soil to 'natural' or 'background' levels to permit 'multifunctionality' of the soil. 'Multifunctionality' of a soil is a concept to describe the various potentials of the soil, within its natural limit. The soil is required to be fit for many functions for present and future use; for this reason treatment and/or destruction of contaminants are the methods usually employed. The Soil Clean-up Act (interim) of 1983 (IBS) empowers respective authorities with the mandate to implement remediation operations, thus giving the authorities power to shut down an offending process, to oblige site owners to cooperate in the remedial action and, if the need arises, to demand the right of ownership to the contaminated site to facilitate the remediation operations.[26] Currently the remediation operations are performed by two parties, IBS sites, where a responsible party is not identified, are handled by the government and non-IBS sites are dealt

TABLE 4
The Netherlands' Standard for Inorganic Contaminants in Soil

Contaminant	*A* (*mg kg*$^{-1}$)	*B* (*mg kg*$^{-1}$)	*C* (*mg kg*$^{-1}$)
Arsenic	15 + 0·4(L + H)	30	50
Barium	200	400	2000
Cadmium	0·4 + 0·007(L + 3H)	5	20
Cobalt	20	50	300
Copper	15 + 0·6(L + H)	100	500
Chromium	50 + 2L	250	800
Lead	50 + L + H	150	600
Mercury	0·2 + 0·0017(SL + H)	2	10
Molybdenum	10	40	200
Nickel	10 + L	100	500
Tin	20	50	300
Zinc	50 + 1·5(2L + H)	500	3000

A: Reference level.
B: Levels that require scientific judgment.
C: Levels for detailed investigation for redevelopment.
L: Weight percentage of clay in the soil.
H: Weight percentage of organic matter in the soil.

with by private parties. A recent estimate revealed that there are more than 110000 sites that need remediation, and 6000 of them should be remediated by 1994.[21,23]

The Dutch reference values for remediation standard are known as 'A, B, C' values and are intended to reflect 'clean' concentrations of elements and compounds both in the soil and ground water (Table 4).

It is interesting to note the rationale behind the Dutch approach. A substantial portion of the country is on a common delta of three rivers Rhine, Meuse and Scheldt from other countries. This delta is believed to be a terminal for the deposit of wash from the rivers. The topography is flat, the elevation reaches or falls below sea level in most places, and the water table is kept at an acceptable level by continual pumping to the sea.[30] In addition the country has many industrial sites, high population density of both humans and livestock, heavy use of motor vehicles, and high energy demand. The animal population (12 million pigs and 5 million cattle) generates 100 million tons of dung annually.[31] It is evident from the foregoing how much human activity and nature can affect the quality of the land, surface water and ground water. The country draws 80% of its drinking water from ground water, and this is the major reason why the Dutch have enforced the strictest regulations towards contaminated land in Europe, if not in the world.

In Germany, state governments are responsible for implementing and enforcing the requirements of clean-up. Most states have an Environmental Protection Agency. There is no uniform standard between the states regarding clean-up, it depends on local regulations and industrial history.[27] The remedial action is carried out by government authorities and responsible parties. The latter can undertake the remediation on a voluntary basis or by order of competent authorities. The aim of remedial action in most instances is to treat the soil with the best available technique regardless of the cost involved to achieve land 'fit for all purposes'. Different remedial techniques are employed, including underground mine disposal. The government is also encouraging better techniques by financing projects for the review of remedial techniques and major research and development activities.[24,31] Despite the increasing number of contaminated sites discovered, a uniform approach to the problem is difficult because of technical, financial and legal constraints. For this reason and because of the on-going nature of the problem, the federal government adopted the notion of soil protection in 1987. Its basic premise is that soil is a scarce and vulnerable resource which needs conservation and protection to enable it to be used both at present and in the future. It is believed to influence industries with contaminative operations to work seriously towards prevention of soil contamination. Regulations are currently being drawn up to enforce this.[32]

3.3 Remediation liability

In the United States CERCLA has established a trust fund called 'superfund' which is primarily drawn from tax on the petroleum and chemical industries. The maxim behind 'superfund' is 'shovels first and lawyers later'.[33] The EPA pays for the remediation from superfund and whenever possible recovers the cost from responsible parties. CERCLA puts the liability for remedial action on potential responsible parties (PRPs). PRPs include past and present owners of the site and also persons who arranged for the transport, disposal and treatment of a contaminant.[6] Once the PRPs are identified and an enforcement agreement is reached, PRPs are compelled to execute the remediation under the EPA directive. If agreement is not reached in good time the EPA can order PRPs to take action towards remediation. If PRPs fail to comply with an enforcement order the EPA can undertake the remediation and recover the actual costs, plus three times the actual cost in damages. Remediation settlement figures showed that the financing by PRPs has increased drastically, from 123 settlements worth US$230 million in 1987 to 285 settlements worth US$1300 million in 1990. In 1987 the share of remediation costs borne by PRPs was 40% and in 1990 this rose to 60%.[6,12] It should also be noted that the liability costs also apply to the 'natural resources damage' even though such damage to the ecosystem is difficult to quantify. Natural resources include flora, fauna, groundwater, surface water, etc., which are managed by the federal or state governments.

In the United Kingdom there is no legislation which particularly compels the remediation of contaminated land. Rather, it is dealt with as a condition of planning permission. Here the guiding principle is '*caveat emptor*', consequently remediation costs are borne by those who own or purchase contaminated land with a view to redevelopment. The environmental lobbies have urged the adoption of the 'polluter pays principle' as in other countries but the concept has failed to be accepted by the law commission. The law commission insisted that the 'polluter pays principle' will invite more litigation; instead they recommended 'let the buyer be well informed'.[34] This will leave in doubt the effectiveness of remedial action taken by developers using the existing undemanding guidelines of the Department of the Environment (DoE). Furthermore, the consequences to human health and the environment of leaving aside untreated contaminated sites for which there is no demand for development remain to be seen.

In Canada, the six provinces and the six territories have laws which empower them to stop contaminative operations and undertake remediation at the polluter's expense. As in the United States, authorities can also order responsible parties to carry out remediation; if they fail to carry out the order the authorities can undertake the remediation and recover the cost and expenses. As an exception to the above, the province of Quebec places responsibility for remediation on the purchaser or developer of the contaminated site.[7] The Canadian government's Green Plan published in 1990 mentions the allocation of C$250 million for remediation between 1992 and 1996. In addition to enforcement stipulated in the Canadian Environmental Protection Act (CEPA) of 1988, the federal government has promoted the 'life cycle' management of toxic substances which is planned to ease the burden on land and ultimately the contamination of the soil.

In The Netherlands the financing of remediation is laid down in the two acts of Soil Clean-up and Soil Protection. The main tenet is that the 'polluter pays principle' should be adhered to as far as is possible. Reasonable success has been recorded in the recovery of costs from those who are responsible for contamination. In the early 1980s clean-up was undertaken by provincial authorities and costs were covered from contributions by local authorities within whose boundaries the site is located, and from national authorities. Local authorities pay a maximum of UK£50000 plus 10% of the remaining cost. The national authorities are authorized to recover the cost from the polluter. The objective of this proactive government involvement was to remediate, in the shortest possible time, those sites which posed a serious threat to human health and the environment.[35] In the mid and late 1980s the involvement of responsible parties and developers also made some progress. This breakthrough gave an opportunity to the government authorities to concentrate on and tackle the more urgent and serious sites that are threats to human health and the environment. Developers are also obliged to investigate the site before they commence any construction work and if they find the site is contaminated they are authorized to take remedial action and recover the cost from the previous operator or owner of the site. If the remedial cost is found to be beyond the developer's resources, and provided the project is in the public's interest, the government will make available the resources necessary to carry out the work.[23] Nowadays the government adheres more and more to be 'polluter pays principle' as the number of sites discovered has increased and a huge amount of money is required for remediation. Above all it is now realized that remediation will not be completed in a short time span but will take considerably longer and should be planned for accordingly. Up until the end of the 1980s UK£650 million had already been spent and with the recent figures from contaminated sites the cost may reach UK£25000 million. This will be impossible to finance from government resources alone, hence wider involvement from industry must be secured.

In Germany remedial costs are covered by the state budget, by a reclamation fund and by responsible parties. Although the 'polluter pays principle' is the guiding regulation it is not always applicable for several reasons.[36] Many previous polluters are unknown as contamination may have originated in the late 19th century, the time at which the chemical and other industries started. Even if the polluters are located, most cannot afford the cost or they are protected by other laws dealing with special production. They may also have been responsible for plant operation during and after wars, when emergency situations led to improper disposal practices.

4 REMEDIAL TECHNIQUES

The development of commercially viable efficient remedial techniques for soil decontamination is an important area of current research and development. A wide range of remedial techniques have been considered and most of them are summarized in this section. Most techniques for treating contaminated land aim to protect and rescue humans, animals and the environment from exposure to hazards by dealing with the source and pathways of contaminants. Many of the techniques being used to clean up contaminated land have been developed from knowledge and experience in other disciplines, especially mining where low grade ores are treated to obtain a concentrate for smelting or hydrometallurgy.[37–39] Furthermore the multi-faceted nature of the problem has benefited from the input of several disciplines, viz. chemistry, microbiology, soil science, environmental science, civil and chemical engineering, and recently computer science, in designing appropriate remedial techniques.

According to Sims[40] remedial techniques at contaminated sites can be classified under three headings, viz. in-situ, prepared bed, and in-tank reactors. Within these techniques the separation process involved can be physical, chemical or biological. These methods and their appropriate processes aim to achieve separation, volume reduction, immobilization and detoxification where possible.

An in-situ method treats contaminated soil in the place where the contamination is located without excavation. Conceptually, this method appeals most since it entails the minimum disturbance of the ground. The prepared bed method deals with contaminated soil in one of two ways: (1) by physically moving the contaminated soil for on-site treatment to avoid transport of contaminants, or (2) by provisional removal of soil from the site in order to prepare the site for use, then return of the soil after treatment is complete. The bed contains the soil to be treated within a lining of clay or plastic to prevent the outward migration of contaminants. It can also be achieved by adding 'clean soil' to provide a favourable medium for treatment. As with the in-situ method, chemical, physical or biological techniques or any combination of these, can be used to improve treatment. The in-tank method utilizes industrial processes in which the soil is removed off-site to be treated in an enclosed reactor. The soil may be in an unsaturated or a saturated form, and treatment techniques include composting, slurry-phase and solid-phase methods.[40]

It is worth mentioning here that the remedial techniques which will be overviewed are mostly limited to the soil that lies at or near the surface. However, it should be noted that this pollution is followed by pollution of the deep lying strata of the soil and groundwater, and that this is even more difficult and complex to deal with. Groundwater pollution will remain in the system longer because of its very slow movement through the aquifer and the residual impact of the desorption of the contaminants.

4.1 Physical techniques

4.1.1 Excavation

Excavation is apparently the simplest prepared bed method. Its aim is to transfer the contaminants elsewhere or to prepare the contaminated soil for on-site and off-site treatments. The drawbacks are the determination of the boundary of soil contamination, the identification of an area acceptable for disposal, the requirement for large quantities of clean fill material and the increase in groundwater pollution which results from disturbing the soil column. Other problems include traffic movement, noise, atmospheric and surface water pollution.[5]

4.1.2 Entombment

This is a prepared bed method which is used to collect most of the contaminated soils together at one or more places on a site and to construct tombs to avoid dispersion. It can be applied to soil contaminated with a range of contaminants. The drawbacks are contamination of the collection area, movement of contaminants and the fact that an effective structure has to be constructed.[5]

4.1.3 Cover

This applies to in-situ and prepared bed methods and is widely used in the United Kingdom, although it is considered an inappropriate method by the environmental cognoscenti. The cover materials vary from asphalt and concrete to clean soil. The drawbacks of this method are that the covered soil remains contaminated and there can be lateral migration of contaminants under the influence of surface waters and groundwater.[41,42]

4.1.4 Soil washing

This is an in-tank method for separation and volume reduction of contaminants. It is used for the removal of organic and inorganic contaminants, but is most suitable for soils polluted with non-volatile hydrophilic and hydrophobic organic compounds and heavy metals. The washing process is less effective with soil that contains appreciable amounts of clay, organic matter and semi-volatile substances. Apart from the overall ineffectiveness of the soil-washing process, treatment of the washing fluid presents another problem with its high toxicity, low treatability, and its effect on soil permeability.[40,43–47]

4.1.5 Soil flushing

This is an in-situ method that aims to separate and reduce the volume of contaminants. Flushing solutions that may be used include water, acidic and basic solutions, surfactants and solvents. The difference between soil flushing and soil washing methods is that the former involves in-situ application and the latter is basically an on-site and/or off-site process. Therefore the problems discussed in Section 4.1.4 above also apply here.[40,45,46]

4.1.6 Soil vacuum extraction

This applies to in-situ and prepared bed methods and uses air-stripping to extract contaminants from unsaturated soil by injecting clean air or allowing air to pass into the unsaturated zone. The close contact causes a mass migration of contaminating chemicals from soil water into soil air. The limitations of this method are the difficulties of handling non-homogeneous and saturated soil materials.[40,46,48]

4.1.7 Electro-reclamation

This is an in-situ method of electro-kinetics which occurs when the soil is electrically charged with direct current by one or several electrode arrays. The method also requires the insertion of a water circulation system to facilitate the collection of metals at the cathode. The method is based on the movement of soil moisture containing metals from the anode to the cathode, and the effectiveness of the technique depends on the chemical composition of the parent soil. The drawbacks of this method are the limitations on the electric current that can be used, and the length of time required for the process.[40,49]

4.1.8 Particle size separation

This is an in-tank method for particle size separation by gravity. It involves removal of the finest particles from the site and is based on the assumption that the contaminants will be associated with the finest soil particles. The drawback of this method is its complexity and the difficulty of treating fine particles.[50]

4.2 Chemical techniques

4.2.1 Neutralization

This is a detoxification and immobilization process designed to reduce the reactivity and corrosiveness of acid- and alkali-containing systems. It can be carried out by in-situ, prepared bed and in-tank methods. The main shortcoming of this process is the difficulty of achieving compatibility of contaminants and treatment chemicals to prevent formation of more toxic or hazardous compounds.[37,40,46]

4.2.2 Oxidation

This process can be used as in-situ, prepared bed and in-tank methods for the detoxification of oxidizable contaminants. The major problems with this process are the possibility of explosive reactions, the production of more toxic or hazardous products and the non-selective nature of the process.[37,40,47]

4.2.3 Photolysis

This is a prepared bed method which uses a photochemical reaction and generally involves using sunlight in natural systems. It is used in the detoxification of dioxins and nitrated contaminants. The inability of light to penetrate deep into the soil is the major drawback of this technique.[40,46]

4.2.4 Precipitation

This technique can be carried out in three ways: in-situ, prepared bed and in-tank methods. The main function of the technique is the separation, volume reduction and immobilization of metals and certain anions, by the formation of insoluble precipitates. The long term effect of the precipitation technique has not yet been tested, and its use could have unfavourable effects on soil permeability.[37,40,46]

4.2.5 Reduction

This is a detoxification process for chromium, silver and mercury, using in-situ prepared bed and in-tank methods. The drawbacks of the process are the risk of explosive reactions and the production of more toxic and hazardous substances and its possible effect on other substances.[37–40,46,50]

4.2.6 Carbon adsorption

This is a separation and immobilization technique, suitable for organic contaminants and contaminants with high molecular weight, high boiling point, low solubility and polarity. It can be used in in-situ and in prepared bed methods but the long-term stability of the adsorbed complexes is unknown.[40,46]

4.2.7 Ion exchange

This is a separation and immobilization technique, suitable for metal contaminants. It uses in-situ and prepared bed methods. The drawbacks are that its use is limited to a few inorganic contaminants in suitable soils and that it requires the pH to be controlled.[40,46]

4.3 Thermal techniques

Thermal techniques are in-tank processes that use high temperatures as the primary method of volume reduction, destruction and/or detoxification of contaminants.[37,40,46,51–53]

4.3.1 Fluidized bed

This is a thermal process of volume reduction and detoxification for halogenated and non-halogenated organics and organic cyanides. The drawbacks of this process are the high maintenance requirements, and the necessity to use homogeneous soil which has small particles and a low content of sodium and other metal.[40,46]

4.3.2 Rotary kiln

This is a volume reduction and detoxification process for combustible organic and inorganic contaminants. The drawbacks are that it produces high particulate emissions and the fact that only small particles can be treated, which necessitates the additional use of size reduction equipment.[40,46]

4.3.3 Pyrolysis

This is a volume reduction and detoxification process for contaminated soil which is unsuitable for conventional incineration and soils containing volatile metals or recoverable residues. Experience to date has shown that this process can handle only small amounts of treatable material at any one time. No significant industrial uses have been described.[40,46]

4.4 Solidification and stabilization

4.4.1 Cement solidification

This is a storage and immobilization technique carried out in a tank and *in situ* for metal cations, latex and solid plastic wastes. It is carried out by mixing Portland cement with the soil to form a hardened matrix. The drawbacks are its incompatibility with large amounts of dissolved sulphate salt or metallic anions such as arsenate or borates and difficulty in achieving cement hardening in a short time when organic matter, lignite, silt and clay are present. Moreover the long term stability of this method is unknown, in particular it may reduce soil permeability and increase run-off.[37,40]

4.4.2 Pozzolanic solidification

This is a storage and immobilization technique which is carried out in-tank and in situ for metals, waste oils and solvents. It is based on the reaction of lime with fine-grained siliceous material. The drawbacks with this technique are that a complete and uniform mixture of soils and reagents must be used and that it reduces soil permeability.[37,40,54]

4.4.3 Thermoplastic stabilization

This is a volume reduction, storage, immobilization technique carried out in-tank and in situ for complex soils that are difficult to treat. Basically it involves sealing the soils in a matrix such as asphalt bitumen, paraffin, or polyethylene. This technique has very limited use in contaminated soil with a high water content or which contains strongly oxidizing contaminants, anhydrous inorganic salts, tetraborates, iron and aluminium salts, or organics with low molecular weight and high vapour pressure.[37,40]

4.4.4 Vitrification

This storage and immobilization technique is carried out in a tank and in situ for inorganics and some organics. The drawback is its high energy requirement especially in soils with high water contents.[37,40,46,55–57]

4.5 Biological techniques

Biological techniques use microorganisms to break down organic molecules to simpler compounds and/or detoxify contaminants provided the soil is not so polluted as to be biocidal. It is mainly effective with organic contaminants, but it has been utilized in certain circumstances to oxidize or reduce inorganic contaminants through biochemical reactions. Most biological processes require long treatment times and are difficult to substantiate.[5,7,58–64]

4.5.1 Aerobic bioremediation

This is a technique for detoxification of biodegradable contaminants by aerobic microorganisms using in-tank, prepared bed and in-situ methods. The drawbacks are the maintenance of conditions conducive to biodegradation, the generation of transformation products which may also be toxic, and the requirement for a large area in which the process can be carried out, which is costly.[37–39,40,50,59]

4.5.2 Anaerobic bioremediation

This is a technique for the detoxification of certain halogenated organic contaminants by the use of anaerobic microorganisms. The drawbacks are the length of time required for the treatment, and the additional need to use aerobic techniques to complete the break-down process.[37,40,61]

4.5.3 Land-farming

This is a technique for detoxification of many biodegradable organic contaminants with microorganisms using techniques applied in agriculture. In view of the number of external uncontrollable factors occurring in the local environment it is difficult to achieve optimum performance of the microorganisms used in this technique.[40,63]

4.5.4 Composting

This is a detoxification technique for biodegradable organic contaminants which may be carried out either as an in-tank or prepared bed method. Like land farming, the drawbacks are the difficulty in maintaining optimum environmental conditions for biological activity and the large amount of compost required to treat small amounts of contaminated soil.[40,65]

4.5.5 Enzyme process

This detoxification technique may be carried out as an in-tank, prepared bed or in-situ method for treatment of certain biodegradable organic contaminants by introducing enzymes derived from plant cell cultures. The enzymes help to form a non-toxic polymer. This technique is in the early stages of its development, and to date has only been used on a pilot scale, so the efficiency and stability of the enzymes in the natural environment is yet to be seen.

5 CONCLUDING REMARKS

Contaminated and polluted land and its remediation have become major environmental concerns in nations with developed market economies. Furthermore, as knowledge of environmental issues increases, there is a greater awareness of the existence of more and more potentially contaminated sites. The different attitudes and approaches to the problem reflect the relative importance given in individual countries to pollution control despite the universal nature of the problem.

In countries like the United Kingdom and Germany, contaminated land is the legacy of nearly two centuries of industrial operations which started during the industrial revolution. Any thought that the problem would be eliminated in a decade or less has proved to be unthinkable from the experience of the 1980s. In The Netherlands alone remediation costs have been estimated to be £250 million per year for the next hundred years.

The 1980s was the decade of aggressive action in the United States, The Netherlands and Germany who adopted the proactive approach. These countries have managed to bring under control cases of immediate threat to human health and the environment, although many sites still need remediation, demanding considerable use of time and financial resources. On the other hand, countries such as the United Kingdom and Canada have opted for a reactive approach. This approach, especially in the United Kingdom, is justified by its proponents on the basis of the country's geological setting, controlled waste disposal and the lack of major incidents. Although the Lasoe incident of 1986 caused by a methane gas explosion is among the few publicized incidents in the United Kingdom it was not of the same magnitude as that of the Love canal in the United States or Lekkerkerk in The Netherlands. The reactive approach however underestimates the problem, with the hidden motive of policy-makers being to avoid blight, litigation and huge remediation costs.

Many invaluable results have been achieved in investigation, risk assessment, remediation, follow up, prevention and legislation, but a lot remains to be accomplished in order to secure a near 'natural' or a near risk-free land environment. Remedial technique experience with respect to contaminated land is relatively brief, dating back only to the 1970s, although there are techniques with a long history of use in the mining industry. It is also important in the long term to understand the detailed transport mechanisms of the transfer of pollutants in soil and to develop new and effective means of soil decontamination. These are the aims of the Brunel University Centre for Environmental Chemistry which is working with industrial sponsors.

Risk assessment is another area where a clear picture and understanding of the polluted land problem is still lacking. The posed question 'How clean is clean?', is still unresolved and open to debate. It is very difficult, in realistic conditions, to achieve a risk-free environment. Furthermore whatever technique is employed to remediate the site the chance of transfer of pollutants to another medium is inevitable. It may be said that the remedial technique attempt alone is a gain with no net benefit. International endeavour as observed in NATO-CCMS cooperation on remedial technique research is appreciable, but would be more effective if extended to other countries outside NATO, e.g. China and the former eastern bloc.

Legislative enforcement has created a regulatory programme to address the problem in most developed countries. Much tougher legislation is emerging in the 1990s to control contaminative operations that contribute pollutants to the environment. Although there are significant differences in legislation between individual countries, there is a sign of convergence towards preventing land becoming contaminated as part of an overall protection of the environment. This might help the long-awaited realization of soil standardization which is undertaken by the International Organization for Standardization (ISO). Soil standardization, however, is technically complex and difficult and a compromise solution will have to be secured. Achieving broad-based agreement on soil standardization will assist as a tool for further pollution prevention and its remediation. International effort should also be extended to curb illegal dumping of pollutants in developing nations. Many pollutants deemed to be operational waste from industry are finding their way to developing countries where the regulations are lenient or non-existent, and where they have caused human and animal fatalities and further polluted the environment. The cross-boundary agreement existing within OECD countries should be strictly adhered to and extended globally in order to safeguard the soil environment.

Finally, it should be stressed that problems associated with contaminated land should neither be overstated nor underestimated. The problem will remain with us for longer than previously anticipated, but plans should be geared towards a concerted long term effort with realistic targets.

REFERENCES

1. Carson, R., *Silent Spring*. Penguin, London, 1962.
2. Galbraith, J. K., *The Affluent Society*. Penguin, Suffolk, 1969.
3. FAO, *Land, Food and People*. Food and Agriculture Organization of the United Nations, Rome, 1984.
4. Great Britain—House of Commons (GB—HC), *First Report. Contaminated Land*, Volume 1. HMSO, London, 1990.
5. Great Britain—House of Commons (GB—HC), *First Report. Contaminated Land*, Volume 3. HMSO, London, 1990.
6. Stoll, R. G., Comprehensive Environmental Response, Compensation and Liability Act (CERCELA or Superfund). In *Environmental Law Handbook*, eds J. G. Arbuckle, M. E. Bosco, D. R. Case, E. P. Lans, J. C. Martin, M. L. Miller, R. V. Randle, R. G. Stoll, T. F. P. Sullivan, T. A. Vanderver, Jr., P. A. J. Wilson. Government Institutes Inc., Rockville, 1989, pp. 75–123.
7. Great Britain—House of Commons (GB—HC), *First Report. Contaminated Land*, Volume 2. HMSO, London, 1990.
8. BSI, Code of Practice for the identification of potentially contaminated land and its investigation. Draft for development DD 175:1988. BSI, London, 1988.
9. Smith, M. A., Report of the NATO-CCMS pilot study on contaminated land. In *Contaminated Land, Reclamation and Treatment*, ed. M. A. Smith. Plenum, New York and London, 1989, pp. 1–11.
10. Harris, M. R., Recognition of the problem. In *Reclaiming Contaminated Land*, ed. T. Cairney. Blackie, Glasgow and London, 1987, pp. 1–29.
11. Donaldson, J. D., Clark, S. J. & Grimes, S. M., *Cobalt in Medicine, Agriculture and the Environment*. Cobalt Institute, London, 1986.
12. Clay, D. R., Ten years of progress in the superfund programme. *Journal of Air and Waste Management Association*, 41(2) (1991) 144–7.

13. Anonymous, Scottish contaminated land survey. *Environmental Data Services Report*, (183) (1990) 27.
14. UK—DoE, *Pilot Survey of Potentially Contaminated Land in Cheshire: A Methodology for Identifying Potentially Contaminated Sites*. Department of the Environment, London, 1990.
15. UK—Welsh Office, *Survey of Contaminated Land in Wales*. Welsh Office, Cardiff, 1988.
16. Anonymous, £10–30 billion and rising UK's contaminated land clean up. *Environmental Data Services Report* (201) (1991) pp, 4–5.
17. UK—DoE & Welsh Office, *Public Registers of Land which May be Contaminated, a Consultative Paper*. Department of the Environment, London, 1991.
18. Hunt, J., Contaminated land register postponed. *Financial Times*, 11 March, 1992, p. 10.
19. Davies, J., CEPA—The Canadian Environmental Protection Act. *JAPCA—The International Journal of Air Pollution Control and Waste Management*, 38(9) (1988) 111–13.
20. Government of Canada, *Canada's Green Plan for a Healthy Environment*. Ministry of Supply and Services, Canada, 1990.
21. Keuzenkamp, K. E., Von Meijenfeldt, H. G. & Roels, J. M., Soil protection in the Netherlands. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 3–10.
22. Hinsenveld, M., Soczo, E. R. & Van de Leur, G. J., Alternative physico-chemical and thermal cleaning technologies for contaminated soil. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 873–81.
23. Gravestlyn, L. T. J., Contaminated industrial sites in the Netherlands. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 3–10.
24. Sondermann, W. D., Questions of law to danger inquiry, risk assessment and rehabilitation of ontaminated soil. In *Contamined Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 1595–603.
25. Herrnring, H. W., Clean-up of contaminated sites in Hamburg. In *Contaminated Soil '88*, eds K. Wolf, W. J. Van der Brink, F. J. Colon. Kluwer, Dordrecht, 1988, pp. 1543–8.
26. Ministry of Housing, Physical Planning and Environment, Soil Clean-up (interim) Act. Central department for information and international relations. The Hague, 1984.
27. Anonymous, Germans prepare for the cleaning of the 5000. *New Scientist*, 22(1676) (1989) 34.
28. ICRCL, Guidance on the assessment and development of contaminated land. Guidance note 59/83 2nd edn. Department of the Environment, London, 1987.
29. Orchard, D., The green plan: a national challenge for Canada. *Journal of Air and Waste Management Association*, 41(3) (1991) 268–71.
30. Brasser, L. J., Solid waste disposal in the Netherlands. *Journal of Air and Waste Management Association*, 40(10) (1990) 1364–7.
31. Adamson, D., *Defending the World*. I. B. Tauris, London and New York, 1990.
32. Scheneider, U., Contaminated sites and soil protection. Communal strategies with the example of Berlin (west). In *Contaminated Soil '88*, eds K. Wolf, W. J. Van der Brink, F. J. Colon. Kluwer, Dordrecht, 1988, pp. 1583–7.
33. Clay, D. R., Twenty years of EPA: an anniversary retrospective. *Journal of Air and Waste Management Association*, 41(2) (1991) 140–3.
34. UK—Law Commission, *Let the Buyer be Well Informed*. Law Commission, London, 1989.
35. Meijenfelot, G. V. & Schippers, E. C. M., The bill is presented: motives behind the recovery of soil clean-up costs in the Netherlands. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 11–16.
36. Giesler, G., Contaminated land in the EC. In *Contaminated Soil '88*, eds K. Wolf, W. J. Van der Brink, F. J. Colon. Kluwer, Dordrecht, 1988, pp. 1555–62.
37. Smith, M. A., Available reclamation methods. In *Reclaiming Contaminated Land*, ed. T. Cairney. Blackie, Glasgow and London, 1987, pp. 114–43.
38. Donaldson, J. D. & Grimes, S. M., Private communication, 1992.
39. Boddington, S. C., Studies on the recovery of useful chemicals from waste and secondary materials. PhD thesis, City University, 1990.
40. Sims, R. C., Soil remediation techniques at uncontrolled hazardous waste sites: a critical review. *Journal of Air and Waste Management Association*, 40(5) (1990) 704–32.
41. Parry, G. D. R. & Bell, R. M., Covering system. In *Contaminated Land, Reclamation and Treatment*, ed. M. A. Smith. Plenum, New York and London, 1985, pp. 113–29.
42. Cairney, T., Soil cover reclamations. In *Reclaiming Contaminated Land*, ed. T. Cairney. Blackie, Glasgow and London, 1987, pp. 144–69.
43. Werther, J. & Willchowski, M., Investigation of the physical mechanisms involved in the purification of contaminated soils by washing process. In *Contamined Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 907–20.
44. Rudat, D., Experience with Dywinex washing process to clean soil contaminated by metals. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 929–30.
45. Raghavan, R., Coles, E. & Dietz, D., Cleaning excavated soil using extraction agent: a state-of-the-art review. *Journal of Hazardous Materials*, 26(1) (1991) 81–7.
46. Sims, R. C., Sorensen, D. L., Sims, J. L., McLean, J. E., Mahmood, R. & Dupont, R. R., *Contaminated Surface Soils In-Place Treatment Techniques*. Noyes, New Jersey, 1986.
47. Ziggler, M. & Reintless, R. C., Decontamination of a former gasworks site with an in situ high pressure soil washing technique. In *Reclaiming Contaminated Land*, ed. T. Cairney. Blackie, Glasgow and London, 1987, pp. 921–7.
48. Anonymous, First UK soil clean up with vacuum extraction process. *Environmental Data Services Report*, (201) (1991) 6.
49. Lageman, R., Pool, W. & Seffinga, G. A., Electroreclamation state of the art and future development. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 1071–8.
50. Elias, F. & Wiesmann, U., Laboratory tests on the characterization of contaminated soils and on the assessment of decontamination technique. In *Contaminated Soil '90*, ed. F. Ardent, M. Hinsenveld, W. J. Van der Brink. Kluwer, Dordrecht, 1990, pp. 935–6.
51. Sanning, O. E., Soczo, E. R. & Stief, K., NATO/CCMS pilot on demonstration of remedial action technologies for contaminated land and ground water. December 1990 update of activities. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 853–71.
52. Daescher, H. P., Lehbrink, R. & Leifhold, K., Combined thermal treatment and in situ rehabilitation of contaminated soils on the area of an incineration plant for industrial use. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 895–901.
53. Schuller, C. & Reintless, R. C., Ten years experience in thermal soil treatment. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 885–93.
54. Anonymous, New process may offer clean up solutions for acid tar dumps. *Environmental Data Services Report*, (220) (1991) 7–8.
55. Anonymous, Successful trial for contaminated land clean-up technology. *Environmental Data Services Report*, (184) (1990) 6–7.

56. Kastern, J., The long, sharp shock for contaminated land. *New Scientist*, **126**(1721) (1990) 34.
57. Clerey, D., Where there's muck, there's glass. *New Scientist*, **126**(1721) (1990) 34.
58. Anonymous, Bacteria show promise in soil clean up. *Chemical Week*, **142**(18) (1988) 43.
59. Lapinskas, J., Bacterial degradation of hydrocarbon contamination in soil and ground water. *Chemistry and Industry*, (12) (1989) 784–9.
60. Wainwright, M., Novel uses of fungi in biotechnology. *Chemistry and Industry*, (2) (1990) 31–4.
61. Soczo, E. R. & Staps, T. J. H., Review of biological soil treatment techniques in the Netherlands. In *Contamined Soil '88*, eds K. Wolf, W. J. Van der Brink, F. J. Colon. Kluwer, Dordrecht, 1988, pp. 665–9.
62. Spenger, B. & Ebner, H. G., Determination of the biotechnical treatability of contaminated soils, eds F. Ardent, M. Hinsenveld, W. J. Van der Brink. Kluwer, Dordrecht, 1990, pp. 959–66.
63. Maag, J. & Lokke, H., Land farming of DEHP contaminated soil. In *Contaminated Soil '90*, ed. J. Ardent. Kluwer, Dordrecht, 1990, pp. 975–82.
64. Dekreuk, J. F., The microbiological decontamination of excavated soil. In *Proc 1st TNO Conference on Contaminated Land, Utrecht, Netherlands*, eds W. Assink & W. J. Van Den Brink. Martinus Nijhoff, Dordrecht, 1986, pp. 669–77.
65. Williams, R. T. & Myler, C. A., Bioremediation using composting. *Biocycle*, November (1990) 78–82.