KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
KUMASI, GHANA

SCHOOL OF ENGINEERING

WATER SUPPLY AND ENVIRONMENTAL SANITATION PROGRAMME

ADSORPTIVE REMOVAL OF ARSENIC AND MANGANESE FROM GROUNDWATER

A THESIS SUBMITTED TO THE BOARD OF POSTGRADUATE STUDIES (KNUST) IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN WATER SUPPLY AND ENVIRONMENTAL SANITATION

By

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JUNE 2005

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DEDICATION

This study is dedicated to my parents and siblings. God richly bless them for their support.

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ACKNOWLEDGEMENT

I am indebted to God, the Almighty father for the strength and the resources He placed at my disposal in bringing about this very important achievement.

I sincerely wish to extend my appreciation to my supervisor, Mr. Richard Buamah of the Civil Engineering Department, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana for his tremendous help, support and advice. Without him it would not have been possible.

I also want to place on record the role played by Mr. Emmanuel Botchwey and Mr. Bruce for being of help during the laboratory work. I also extend my gratitude to Mr. Tabas and Kwabena Anim for their unconditional trips to the laboratory whenever I called upon them.

I would always remember my colleague course participants; Messrs Gabriel Amanfu, Peter Obeng, Musah Saeed, Rajee Babalola, Mike Agbesi and Ebenezer Appiah, for travelling this extra mile together.

My final thanks to all and sundry that in various ways assisted me. I say may God bless you all.

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ABSTRACT

Groundwater remains the most important source of water supply for rural communities in Ghana. Currently, over 95% of the domestic water needs of rural communities are obtained from this source. In some localities, the quality of groundwater is affected by the occurrence of Arsenic (As) and Manganese (Mn) in concentrations above 10ug/l and 0.1mg/l respectively which are the World Health Organisation (WHO) acceptable limits for drinking water. This is a limiting factor in the choice of this resource. Water supply companies are currently seeking to improve the process of As and Mn removal from groundwater.

In this study, Adsorption capacity of locally available filter media namely, laterite and Iron Oxide Coated Sand (ICS) were investigated for removal of As and Mn from synthetic water. Batch studies were conducted under aerobic and anaerobic conditions. Changes in concentrations of As and Mn were determined using the Atomic Adsorption Spectrometer (AAS) and Graphite furnace AAS. Adsorption isotherms were prepared using different concentrations of Mn. Isotherms were not prepared for As due to constraints of time. The effect of pH on adsorptive trends was also investigated into. The filter media was then used for treatment of real groundwater seeded with different concentrations of Mn and As from Ayeduase Township.

Results of the study show that adsorption under conditions of anaerobic and aerobic is comparable prior to the attainment of equilibrium by the anaerobic case. However the aerobic adsorption process continues slowly and consistently probably because the adsorbed Mn^{2+} gets oxidized to form manganese oxides and manganese oxyhydroxide complexes. These complexes form a new external coating round the media and facilitate further adsorption of Mn^{2+} ions.

The anaerobic adsorption data of both ICS and laterite fitted well with the Freundlich's Isotherm. The results revealed that, iron oxide coated sand has higher adsorption capacity than laterite. This may be due to higher iron and manganese oxide content in the coating of the coated sand as compared to the amount in the laterite. The iron oxide coated sand also had higher adsorption intensity as compared to the laterite.

Better adsorption trends were realised at higher pH for both media.

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LIST OF ABBREVIATIONS

CWSA	Community Water and Sanitation Agency
CWSP	Community Water and Sanitation Programme
ICS	Iron Oxide Coated Sand
Lat	Laterite
WHO	World Health Organization
rpm	Revolutions per minute

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Water supply for the purposes of domestic and industrial use in Ghana is from both ground and surface water sources. Most urban communities obtain their drinking water supply from water sources that have treatment facilities and distribution network system. However, most rural communities obtain their water supplies from untreated surface sources such as rivers, streams, lakes, reservoirs and groundwater extracted from boreholes and hand dug wells. These untreated water sources expose the users to water related diseases (CWSA, 1994).

In 1994, the Government of Ghana adopted a rural water and sanitation strategy, which focused on the provision of potable water supply to rural communities. The Community Water and Sanitation Agency (CWSA) was subsequently formed by an Act of Parliament (Act 564 of 1998) to implement the Community Water and Sanitation Programme (CWSP). The policy strategy became the guiding principle for the development and implementation of water and sanitation programmes for rural communities in the country (CWSA, 1994).

Groundwater has become the most important source for most rural water supplies under the Community Water and Sanitation Strategy (CWSS). Groundwater represents about 97% of all freshwater supplies found on the earth. It has stable temperature and chemical composition. The natural purification processes which occur through filtration by the soil and other physical, chemical and microbiological processes make groundwater the most acceptable source for water supplies. Similarly, groundwater is less prone to pollution, especially in rural areas where problems of water associated with high industrialization are not serious issues. Less capital investment is therefore required for exploiting groundwater especially for small town projects than would be required for surface water treatment and distribution (*http://www.fao.org/docrep*).

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A recent emerged problem, which hitherto had not been investigated with keen interest, is the presence of arsenic(As) in groundwater, which may pose a health hazard to consumers. Arsenic contamination in drinking water was detected in 1958 (WHO, 2001). Arsenic as it is, even at high concentrations does not impart any taste, colour or odour to water. Arsenic contamination of drinking water is currently a world-wide problem but the biggest outbreak of arsenic poisoning has been discovered in Bangladesh and India. Countries like Taiwan, Hungary, Thailand, Argentina, Canada, Mexico etc also have a fair share of this prevailing problem and Ghana is no exception to such countries (Chien-Jen Chen et al. 1999; EAWAG, 2000). Norman et al (1999) investigating the occurrence of arsenic in 207 wells within a 6500 sq. km area of south-western part of Ghana found about 25% of the wells having arsenic contamination. The studies showed arsenic occurrence in studied wells ranging up to 200ug/l.

Concentration	**Bore Holes (No. of wells)**	**Hand Dug Wells (No. of wells)**	**WHO limit for arsenic in drinking water**
As > 5 ppb	23	2	10ug/l
As 0.5 to 5 ppb	30	6	"
As < 0.5 ppb	74	68	"

(Source: http://wwwbrr.cr.usgs.gov/Arsenic/FinalAbsPDF/norman.pdf.)

A strong correlation was found between skin problems and arsenic concentrations in well waters (Norman et al, 1999). A summary of noted skin problems in SW Ghana similar to those associated with arsenic poisoning is given in the table below.

As (ppb)	**Wells for which health effects noted in at least one person**	**Total wells**	**Percentage of wells with health effects**
2-120	14	27	52%
0.5-2	4	22	18%
<0.5	6	153	4%

(Source: http://wwwbrr.cr.usgs.gov/Arsenic/FinalAbsPDF/norman.pdf.)

Recently, there has been an upsurge in the incidence of cancer in Ghana. Other diseases such as conjunctivitis, gangrene, breaking palm and feet have been observed in areas such as Ntobroso and Takyikrom in the Ashanti region, Anyinase, Samahu and Seikwa all in the Western region and Bolgatanga in the Upper East region of Ghana where

drinking water wells have showcased arsenic contamination in excess of 50μg/l (Nkyerkyer, 2000).

Also aggravating the problem is the presence of Mn in some aquifers. Presently WHO (2004) recommended guideline value for manganese in drinking water is fixed at 0.1 mg/l. Mn in drinking water in concentrations greater than 0.1mg/l affects the aesthetic quality through conferring of turbidity and causing formation of brownish black deposits, poor taste, staining of laundry, porcelain and glassware. Consumption of drinking water with manganese concentrations in excess of 0.5 mg/l over four or more years may give rise to a disease condition similar to Parkinson's disease. In Ghana, several communities in several regions including Ashanti, Western, Eastern and Central have manganese levels in excess of the guideline value in their wells. Water extracted from these wells for drinking are normally not treated (CWSA- ER, 1998).

Several attempts have been made towards finding feasible technical options for the removal of manganese and arsenic from point sources. While there are several important arsenic minerals (e.g., arsenopyrite (FeAsS) and orpiment(As_2S_3), most arsenic in the solid phase is associated with common iron minerals, including iron oxyhydroxides (FeOOH) and pyrite (FeS_2). Arsenic may be released from these minerals by desorption or reductive dissolution of the arsenic-bearing mineral. Arsenic removal is strongly associated with removal of Iron (Fe) or Mn since these are able to form complexes with As. The removal plants so far designed are based on the principle of aeration, oxidation coagulation and filtration. This intervention has not been very successful due to the slow oxidation processes that occur during aeration and the rapid build up and penetration of Fe and/or Mn oxide flocs formed in the filter medium, resulting in the need for frequent rejuvenation of the media. This leads to high social and monetary cost for communities' (Welch et al, 2000).

Studies have shown that Iron oxide coated sand (ICS) and laterite have high adsorptive properties and are able to remove As, Mn and several other pollutants for water (Sebwato, 2000).

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This study is designed to further investigate the adsorptive capacity of ICS and laterite for removal of As and Mn from groundwater.

1.2 Goal of Study

The aim of the study is to remove As and Mn from drinking water using ICS and laterite.

1.3 Objectives

The objectives of the study are:

1. To determine the adsorption capacities of ICS and laterite for Mn and As under aerobic and anaerobic conditions.
2. To prepare adsorption isotherms using different concentrations of aqeous As and Mn for ICS and laterite.
3. To determine the effect of pH on the adsorptive capacities of ICS and laterite.
4. To determine the adsorbtion trend when Fe, Mn and As are all present in solution.

1.4 Structure of report.

This thesis covers five chapters, a list of references and appendices. Chapter one gives a background of the main problems leading to the need for the study, and the objectives set out for achieving the overall goal of removing As and Mn from drinking water. Chapter two gives relevant information available on the subject is discussed. The material and methods employed in the study are outlined in chapter three, whereas the results generated are discussed in chapter four. The conclusion and recommendations arrived at, based on the data generated are presented in chapter five.

1.5 Limitations of the study

The limitations of the study are listed below:

1. The ICS was obtained from Netherlands due to constraints of time and lack of resources to manufacture it in the laboratory.
2. Due to constraints of time, experiments to determine adsorption of arsenic under aerobic and anaerobic conditions using ICS and under anaerobic conditions using laterite was not performed. The unavailability of more reactors for the anaerobic experiment also delayed the process.
3. The aerobic experiments were performed using 500ml plastic bottles. A 1500ml glass reactor was used for the anaerobic experiments due to the fact that a 500ml

plastic reactor was not available in order to create the exact same conditions as in the aerobic case.

4. Though a pipette would have been more accurate, a syringe was used for sampling in order to prevent oxygen from entering the solution.
5. Acquisition of pure CO_2 and N_2 gas for the anaerobic batch experiment delayed and some of the cylinders had damaged valves which had to be fixed during which the experiment had to come to a standstill.
6. The Atomic adsorption spectrometer in the Environmental quality engineering laboratory was out of order. The samples had to be transported to IHE, Delft University in the Netherlands for analysis.

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CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Water Treatment Methods for Domestic Use

Water treatment involves processes that alter the chemical composition of water. Primary water availability includes surface or groundwater sources. Most municipal or public water comes from surface water such as lakes, reservoirs and rivers while private water supplies usually consist of groundwater pumped from wells. There are two main methods of water treatment. These are point of use methods and point of entry methods (http://www.randi.org).

2.1.1 Point of use (POU) methods:

POU methods treat water at the point where it is used.

2.1.1.1 Boiling

In an emergency, boiling is the best way to purify water that is unsafe because of the presence of protozoan parasites or bacteria. If the water is cloudy, it should be filtered before boiling. Boiling will also drive out some of the Volatile Organic Compounds (VOCs) that might also be in the water (http://www.randi.org).

Boiling is however not safe to use when toxic metals, chemicals (lead, mercury, asbestos, pesticides, solvents, etc.), or nitrates have contaminated the water. It may concentrate any harmful contaminants that do not vaporize as the relatively pure water vapor boils off (http://www.randi.org).

2.1.1.2 Distillation

In many ways, distillation is the reverse of boiling. To remove impurities from water by distillation, the water is usually boiled in a chamber causing water to vaporize, and the pure (or mostly pure) steam leaves the non volatile contaminants behind. The steam moves to a different part of the unit and is cooled until it condenses back into liquid water. The resulting distillate drips into a storage container. Anything that won't boil or evaporate such as salts, sediment and metals remain in the distiller and must be removed. Volatile organic compounds (VOCs) are a good example of a contaminant that will evaporate and condense with the water vapor. A vapor trap, carbon filter, or other device must be used along with a distiller to ensure the more complete removal of contaminants.

Distillation also removes pathogens in the water, mostly by killing and leaving them behind when the water vapor evaporates. As long as the distiller is kept clean and is working properly the high quality of treated water will be very consistent regardless of the incoming water (http://www.randi.org).

Distillation however takes time to purify the water. It can take two to five hours to make a gallon of distilled water. Distillers use electricity all the time the unit is operating. Most home distillation units require electricity, and will not function in an emergency situation when electrical power is not available. Distillers require periodic cleaning of the boiler, condensation compartment, and storage tank (http://www.randi.org).

2.1.1.3 Reverse Osmosis (RO)

Water pressure is used to force water molecules through a membrane that has extremely tiny pores, leaving the larger contaminants behind. Purified water is collected from the "clean" side of the membrane, and water containing the concentrated contaminants is flushed down the drain from the "contaminated" side. The average RO system is a unit consisting of a sediment/chlorine pre filter, the reverse-osmosis membrane, a water storage tank, and an activated-carbon post filter. Reverse osmosis significantly reduces salt, most other inorganic material present in the water, and some organic compounds. With a quality carbon filter to remove any organic materials that get through the filter, the purity of the treated water approaches that produced by distillation. Microscopic parasites (including viruses) are usually removed by properly functioning RO units, but any defect in the membrane would allow these organisms to flow undetected into the "filtered" water - they are not recommended for use on biologically unsafe water. Though slower than a carbon or sediment water filter, RO systems can typically purify more water per day than distillers and are less expensive to operate and maintain. Reverse Osmosis systems also do not use electricity, although because they require relatively high water pressure to operate, they may not work well in some emergency situations (http://www.randi.org).

The problems with this method are that point of use RO units makes only a few gallons of treated water a day for drinking or cooking. Also, RO systems waste water. Two to four gallons of "waste" water are flushed down the drain for each gallon of filtered water produced. Some pesticides, solvents and other volatile organic chemicals (VOCs) are not

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completely removed by RO. Although RO filters do not use electricity, they depend on a relatively high water pressure to force the water molecules through the membrane. In an emergency situation where water pressure has been lost, these systems will not function. RO systems also require maintenance. The pre and post filters and the reverse osmosis membranes must be changed according to the manufacturer's recommendation, and the storage tank must be cleaned periodically. Damaged membranes are not easily detected, so it is hard to tell if the system is functioning normally and safely (http://www.randi.org).

2.1.1.4 Fiber Filters

These filters contain cellulose, rayon or some other material spun into a mesh with small pores. If you take a piece of cloth and pour water containing sand through it you will get the picture. Suspended sediment (or turbidity) is removed as water pressure forces water through tightly wrapped fibers. Some small organic particles that cause disagreeable odors and taste may also be removed. These filters come in a variety of sizes and meshes from fine to coarse, with the lower micron rating being the finer. The finer the filter, the more particles are trapped and the more often the filter must be changed. Fiber filters are often used as pre-filters to reduce the suspended contaminants that could clog carbon or RO filters (http://www.randi.org).

The disadvantage is that fiber filters will not remove contaminants that are dissolved in the water, like chlorine, lead, mercury, trihalomethanes or other organic compounds (http://www.randi.org).

2.1.1.5 Ceramic Filters

Ceramic filters are much like fiber filters and use a process where water is forced through the pores of a ceramic filtration media. This provides mechanical filtration only. This type of filter can reduce asbestos fibers, cysts (if the pores are one micron or smaller), some bacteria (with pore sizes in the 0.2 - 0.8 micron range) and other particulate matter. The disadvantage is that ceramic filters will not remove contaminants that are dissolved in the water, like chlorine, lead, mercury, trihalomethanes or other organic compounds, nor will they remove viruses (http://www.randi.org).

2.1.1.6 Activated Carbon (AC) filter

AC is a highly porous material; therefore, it has an extremely high surface area for contaminant adsorption. AC is made of tiny clusters of carbon atoms stacked upon one another. The carbon source is a variety of materials, such as peanut shells, coconut husks, or coal. The raw carbon source is slowly heated in the absence of air to produce a high carbon material. The carbon is activated by passing oxidizing gases through the material at extremely high temperatures. The adsorption process depends on the following factors: 1) physical properties of the AC, such as pore size distribution and surface area; 2) the chemical nature of the carbon source, or the amount of oxygen and hydrogen associated with it; 3) chemical composition and concentration of the contaminant; 4) the temperature and pH of the water; and 5) the flow rate or time exposure of water to AC.

The effectiveness of carbon filters to reduce contaminants is affected by the factors affecting adsorption listed above and three additional characteristics of the filter, contact time between the water and the carbon material, the amount of carbon in the filter, and pore size. The length of contact time between the water and the carbon material, governed by the rate of water flow and the amount/volume of activated carbon, has a significant effect on adsorption of contaminants. More contact time results in greater adsorption. The amount of carbon present in a cartridge or filter affects the amount and type of contaminant removed. Less carbon is required to remove taste- and odor-producing chemicals than to remove trihalomethanes (http://www.randi.org).

2.1.2 Point of Entry (POE) methods

This is where all water entering the home is treated. The most common example is a water softening ion exchange system that removes calcium and magnesium ions (and some other ions) from the water. Other POE water treatment systems are designed to remove iron and manganese, adjust pH levels, add chlorine or other disinfectant, etc. People using water from a private well, spring, or surface sources are most likely to require POE treatment (http://www.randi.org).

2.1.2.1 Ultra Violet Light

Water passes through a clear chamber where it is exposed to Ultra Violet (UV) Light. UV light effectively destroys bacteria and viruses. However, how well the UV system works depends on the energy dose that the organism absorbs. If the energy dose is not

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high enough, the organism's genetic material may only be damaged rather than disrupted. No known toxic or significant non toxic by products are introduced. It removes some organic contaminants and leaves no smell or taste in the treated water. It also requires very little contact time. UV treatment improves the taste of water because some organic contaminants and nuisance microorganisms are destroyed. Many pathogenic microorganisms are killed or rendered inactive (http://www.randi.org).

UV radiation is however not suitable for water with high levels of suspended solids, turbidity, color, or soluble organic matter. These materials can react with UV radiation, and reduce disinfection performance. Turbidity makes it difficult for radiation to penetrate water and pathogens can be 'shadowed', protecting them from the light. UV light is not effective against any non-living contaminant, lead, asbestos, chlorine, etc. Tough cryptosporidia cysts are fairly resistant to UV light. It also requires electricity to operate. In an emergency situation when the power is out, the purification will not work (http://www.randi.org).

2.1.2.2 Water softeners and deionizers

Water softeners operate on the ion exchange process (specifically a cation exchange process where + ions are exchanged). In this process, water passes through a media bed, usually sulfonated polystyrene beads. The beads are supersaturated with sodium (a positive ion). The ion exchange process takes place as hard water passes through the softening material. The hardness minerals (positively charged Calcium and Magnesium ions) attach themselves to the resin beads while sodium on the resin beads is released simultaneously into the water. When the resin becomes saturated with calcium and magnesium, it must be recharged. The recharging is done by passing a concentrated salt (brine) solution through the resin. The concentrated sodium replaces the trapped calcium and magnesium ions which are discharged in the waste water. Softened water is not recommended for watering plants, lawns, and gardens due to its elevated sodium content (http://www.randi.org).

The disadvantages are that the process of regenerating the ion exchange bed dumps salt water into the environment. The elevated sodium concentration of most softened water can affect the taste and may not be good for people on low sodium diets, although sodium concentrations are typically quite low relative to sodium levels in most food. Typically,

approximately 50 gallons of rinse water per cubic foot of resin is required to totally remove hardness and excess salt from the resin after each regeneration. A potential problem with deionizers is that colonies of microorganisms can become established and proliferate on the nutrient-rich surfaces of the resin. When not regularly sanitized or regenerated, ion-exchange resins can contaminate drinking water with bacteria (http://www.randi.org).

2.1.2.3 Ozonation

Ozone is a naturally occurring component of fresh air. It can be produced by the ultraviolet rays of the sun reacting with the Earth's upper atmosphere (which creates a protective ozone layer), by lightning, or it can be created artificially with an ozone generator. The ozone molecule contains three oxygen atoms whereas the normal oxygen molecule contains only two. Ozone is a very reactive and unstable gas with a short half-life before it reverts back to oxygen. Ozone is the most powerful and rapid acting oxidizer man can produce, and will oxidize all bacteria, mold and yeast spores, organic material and viruses given sufficient exposure. Ozone is primarily a disinfectant that effectively kills biological contaminants. Ozone also oxidizes and precipitates iron, sulfur, and manganese so they can be filtered out of solution. Ozone will oxidize and break down many organic chemicals including many that cause odor and taste problems. Ozonation produces no taste or odor in the water. Since ozone is made of oxygen and reverts to pure oxygen, it vanishes without trace once it has been used (http://www.randi.org).

Ozone treatment can however create undesirable byproducts that can be harmful to health if they are not controlled (e.g., formaldehyde and bromate). The process of creating ozone in the home requires electricity. In an emergency with loss of power, this treatment will not work. Ozone is not effective at removing dissolved minerals and salts. (http://www.randi.org).

2.1.2.4 Activated Alumina

Activated Alumina is a granulated form of aluminum oxide. In this process, water containing the contaminant is passed through a cartridge or canister of activated alumina which adsorbs the contaminant. The cartridge of activated alumina must be replaced periodically. Activated alumina devices can accumulate bacteria, so treated water may

have higher bacteria counts than raw water. This method is an effective way to reduce levels of fluoride, arsenic, and selenium The disadvantage is that the use of other treatment methods would be necessary to reduce levels of other contaminants of health concern (http://www.randi.org).

2.2 Adsorption

Adsorption is a point of entry method of treating water. It involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated at the surface of that phase is the adsorbate. Four principal types of adsorption – exchange, physical, chemical and specific- may be distinguished. Exchange adsorption, involves electrostatic attachment of ionic species to sites of opposite charge at the surface of an adsorbent, with subsequent displacement of these species by other ionic adsorbates of greater electrostatic affinity. Physical adsorption results from the action of Van der Waals forces. Chemical adsorption involves a reaction between an adsorbate and an adsorbent resulting in a change in the chemical form of the adsorbate. Specific adsorption involves attachment of adsorbate molecules at functional groups on adsorbent surfaces which do not result in adsorbate transformation. The net dispersion, electrostatic, chemisorptive, and functional-group interactions broadly define the affinity of an adsorbent for a specific adsorbate (Weber, 1972).

In water purification processes, adsorption in rapid filtration systems remove finely divided suspended matter as well as colloidal and molecular dissolved impurities. The forces of adsorption exert their influence over short distances only between 0.01-0.1um. As the particles in the water are brought closer, the attractive forces of adsorption are exerted causing their extraction from the flowing water. Van der Waal's forces are the active promotion of adsorption of physical attraction between the two particles of matter. Where the distances between the centres of particle exceed 0.01nm the Van der Waal's forces of attraction becomes negligible and the most predominant forces that can keep the particles very close for adsorption to occur is electrostatic (Huisman, 1986).

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2.3 Factors affecting adsorption

2.3.1 Properties of the adsorbate relative to the solution phase

The extent of adsorption relates to certain properties of the adsorbate relative to the solution phase. These are:

- Solubility

Bonding between a substance and the solvent in which it is dissolved must be broken before adsorption from the solvent can occur. The greater the solubility of the compound, the stronger the bond and the smaller the extent of adsorption.

- Surface tension

Many organic compounds can effectively lower the surface tension of water. The lower the surface tension of the solution phase, the higher the adsorption (Bernadine, F. Jr., 1986).

2.3.2 Characteristics of the adsorbate

A number of parameters specific to the adsorbate can affect adsorption. They include concentration, molecular weight and size and molecular polarity. Large molecules of one chemical class may adsorb more rapidly than smaller ones of another if higher energies for adsorption are involved. A polar solute will be strongly adsorbed from a nonpolar solvent by a polar adsorbent. The amount of adsorbed material per unit weight of adsorbent is commonly found to increase with increasing concentration (Bernadine, F. Jr., 1986).

2.3.3 Characteristics of the Adsorbent

For the adsorbent they include surface area, the physical size and form of adsorbent particles, and the physiochemical nature of the surface. Specific area can be defined as that portion of the total surface area that is available for adsorption (Weber, 1972). The larger the specific surface area of the solid adsorbent, the higher the adsorption capacity. The adsorptive capacity per unit weight of media increases with a reduction of particle diameter (Bernadine, F. Jr., 1986).

2.3.4 Characteristics of the Solution

A major influence of the solution character on adsorption is the presence of competing adsorbate compounds. Few adsorbents demonstrate controllable selectivity for specific

compounds and therefore all adsorbable compounds present will compete for adsorption sites. System parameters such as temperature and pH can also markedly influence adsorption. Both adsorbate and adsorbent may have chemical characteristics which are affected by the concentration of hydrogen ions (H^+) in solution. Some adsorbents have affinity for H^+ or OH^- ions and can directly affect the solution pH and therefore solubility and adsorption capacity. The temperature of a solution has two major effects on adsorption. First, the rate of adsorption is usually increased at higher temperatures. This is due primarily to the increased rate of diffusion of adsorbate molecules through the solution to the adsorbent. Further, solubility and adsorption are inversely related; as temperature affects solubility it will therefore affect the extent of adsorption or capacity of the adsorbent for the particular adsorbate (Bernadine, F. Jr., 1986).

2.3.5 Double layer and Zeta Potential

Physiochemical properties such as zeta potential have influence on rate and adsorption capacity. The surface of filters can exhibit both positive and negative charges depending on the pH. The pH at zero point charge PZC is called isoelectric point. Above the PZC, the charge is negative and below the PZC, the charge is positive. Clays, silica and most organic particles for example are negatively charged at pH of 7 (Stern, 1924). The charge on a particle attracts solution ions of opposite charge to form a diffuse layer around the particle (Huisman, 1986). The particle together with the diffuse layer is called the electric double layer. The double layer is made of an inner layer where adsorbed water molecules are found and an outer layer where counter ions are found. There is a plane of shear separating the bulk solution and an envelope of water that moves with the particle. The potential at the plane of shear is called the zeta potential (ZP). The higher the ZP, the stronger the forces of repulsion and the more stable the particles. Particles are stable due to their affinity to adsorb water and electric charge (Huisman, 1986).

2.4 Adsorption Isotherms

Experimental isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate adsorbent, and for preliminary determination of adsorbent dosage requirements. The isotherm also plays a crucial role in predictive modeling procedures

for analysis and design of adsorption systems. Several models have been developed to describe adsorption isotherm relationships. Any particular one may fit experimental data accurately under one set of conditions, but fail entirely under another. No single model has been found to be generally applicable (Voice and Weber, 1983).

2.4.1 Langmuir model

This model is predicted on the assumptions that adsorption occurs on localized sites with no interaction between adsorbate molecules, and that maximum adsorption occurs when the surface is covered by a monolayer of adsorbate.

For solid-liquid systems, the equation is written as:

$$q_e = \frac{Q^0 b C_e}{1 + bC_e}$$

Where: qe is the amount of solute adsorbed per unit weight of adsorbent

Q is the solid phase concentration corresponding to complete coverage of available sites, or the limiting adsorption capacity.

Ce is the residual liquid phase concentration at equilibrium.

(Slejko, 1986).

2.4.2 Brunauer-Emmet-Teller model (BET model)

The BET model is an extended form of the Langmuir model and it includes multi-layer adsorption phenomena. The essential assumptions of the BET model are that any given layer need not be complete before subsequent layers can from, that the first layer of molecules adhere to the surface with an energy comparable to the heat of adsorption for monolayer attachment and that subsequent layers are essentially condensation reactions.

The BET equation is of the form:

$$\frac{Ce}{(Cs - Ce)q_e} = \frac{1}{BQ^0} + \left(\frac{B-1}{BQ^0}\right)\left(\frac{Ce}{Cs}\right)$$

Where;

Cs is the saturation concentration of the solute

B is a constant expressive of the energy of adsorption such that

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$$B = \frac{d_2 c_1}{d_1 c_2} e^{(E_1 - E_2)/RT}$$ where,

E_1 is the average heat of adsorption of the first layer

E_2 is the heat of condensation

d_2c_1/d_1c_2 is the ratio of evaporation-condensation coefficients for the adsorbed layers.

(Slejko, 1986).

2.4.3 The Freundlich Isotherm

The most important and widely used mathematical model for multiadsorption is the Freundlich isotherm. This equation often fits adsorption data on rough surfaces better than Langmuir equations. The equation that describes Freundlich Isotherm is given below:

$X/m = kCe1/n$

X is the amount of solute adsorbed

m is the weight or surface area of adsorbent

Ce is the equilibrium concentration of the solute

k and n are constants

when n=1, the equation reduces to the linear form: X/m=kCe

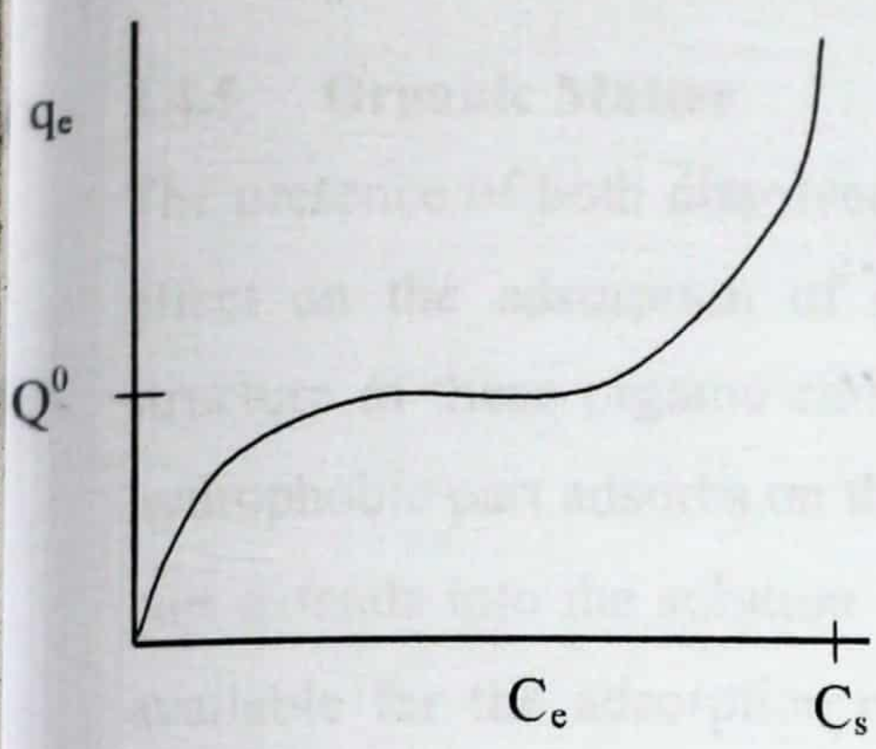
The equation becomes

$\log X/m = \log k + 1/n \log Ce$

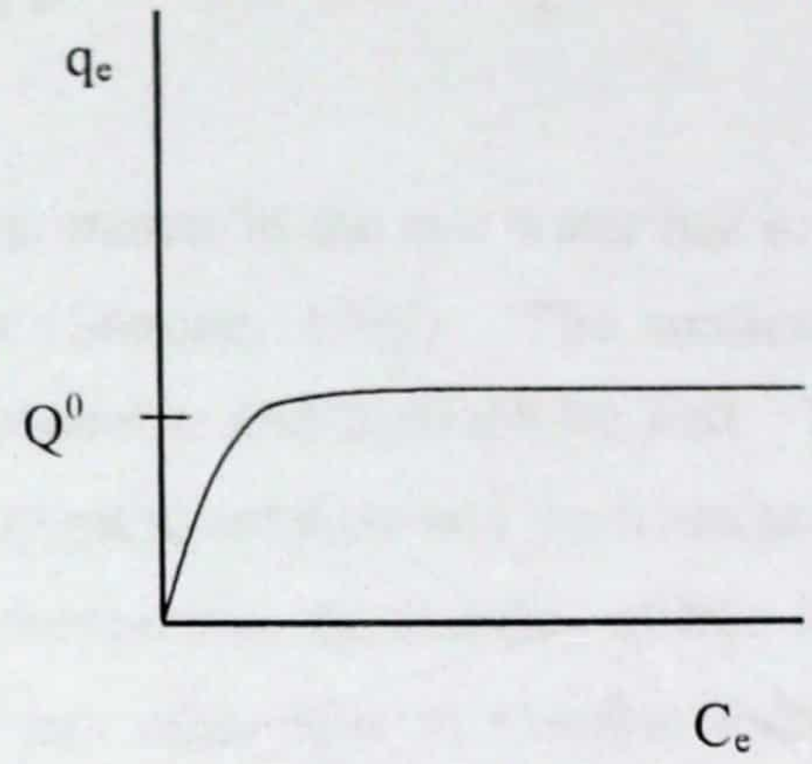
The value 1/n is the slope. Steep slopes, that is, 1/n close to 1 indicates high adsorption capacity at high equilibrium concentration. However, for relatively flat slopes, 1/n<<<1 show that the adsorptive capacity is slightly reduced at lower equilibrium concentrations. The adsorption capacity X/m depends on the equilibrium concentration of the solute and hence, higher adsorption capacities are obtained at higher equilibrium concentrations (Slejko, 1986).

2.4.4 Graphical representation of isotherms

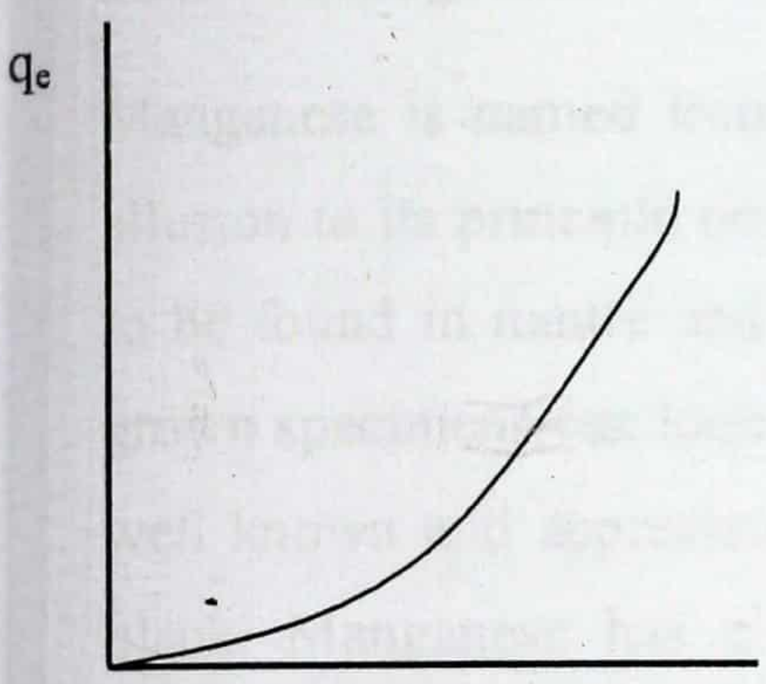
The general shapes corresponding to the equilibrium models described above are illustrated in figure 2.1 below. A comparison of these with a plot of qe vrs Ce data for a particular sorbate/sorbent/solvent system will indicate which of the models is most appropriate for that system (Voice and Weber, 1982).



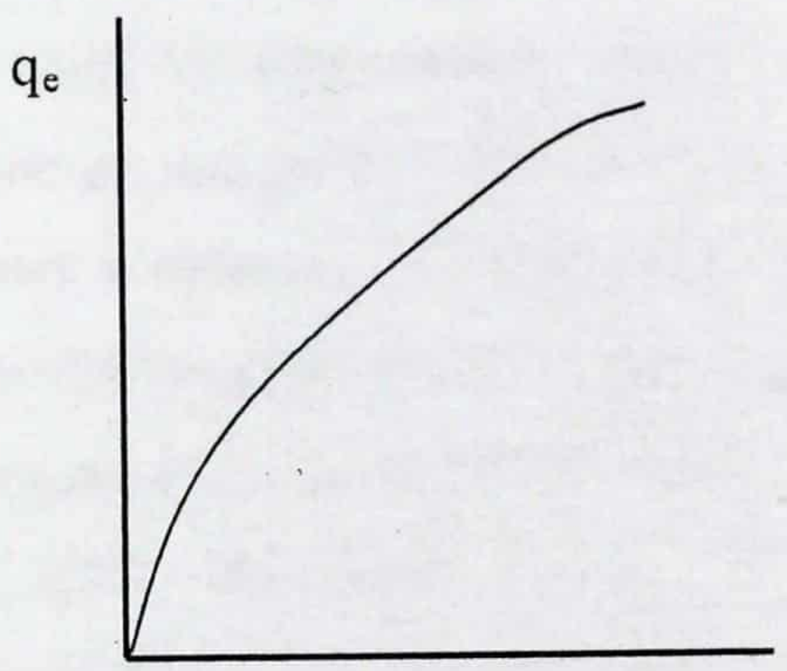
(a) BET



(b) Langmuir



(c) Freundlich 1/n > 1



(d) Freundlich 1/n <1

Figure 2-1 Graphical Representation of Isotherm models

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2.4.5 Organic Matter

The presence of both dissolved and suspended organic matter in the raw water has some effect on the adsorption of other ions in solution (Sharma, 1997). The molecular structure of these organic compounds has both hydrophobic and hydrophilic part. The hydrophobic part adsorbs on the surface of the ion present in solution and the hydrophilic part extends into the solution. As a result of these phenomena, the number of free sites available for the adsorption of iron, manganese or any other ions in solution reduces (Sharma, 1997).

2.5 Properties of Arsenic and Manganese

2.5.1 Manganese

Manganese is named from a corruption of the latin word for magnestism; magnes, in allusion to its principle ore's magnetic properties. However, manganese crystals have yet to be found in nature and therefore it is technically not a mineral, although laboratory grown specimens can look like a natural stone. Manganese coloring ability in minerals is well known and appreciated. Unfortunately most manganese oxide minerals tend to be black. Manganese has eight oxidation states: Mn, Mn^{2+}, $Mn_3O_4(s)$, Mn_2O_3, MnO_2, MnO_4^{2-}, MnO_4^{3-} MnO^{4-}. It is characteristically flexible, soft, easy to cut and can be bent. (http://www.lenntech.com/index.htm)

The table below shows some physical and chemical properties of manganese.

Atomic number	25
Atomic mass	54.9380 $g.mol^{-1}$
Density	7.43 $g.cm^{-3}$ at 20°C
Melting point	1247 °C
Boiling point	1962 °C
Vanderwaals radius	0.126 nm
Ionic radius	0.08 nm (+2) ; 0.046 nm (+7)
Isotopes	7
Electronic shell	[Ar] $3d^5$ $4s^2$
Energy of first ionisation	716 $kJ.mol^{-1}$
Energy of second ionisation	1489 $kJ.mol^{-1}$
Standard potential	- 1.05 V (Mn^{2+}/ Mn)
Colour	Silver grey
Luster	Metallic
Transparency	Opaque
Crystal system	Isometric
Discovered	Johann Gahn in 1774

Source: *http://www.lenntech.com/index.html*.

2.5.2 Sources of Manganese

Manganese-bearing minerals are quite common, with oxides, silicates and carbonates being the most common. Minerals such as Pyrolusite (MnO_2) and Rhodochriste ($MnCO_3$) rank amongst the most common manganese-bearing minerals. In addition to these sources, many large nodules of manganese (containing about 24% manganese) have been found on ocean floors and could provide another source of manganese (http://www.Azom.com).

2.5.3 Production of Manganese

Manganese is most commonly produced by the reduction of the oxide with sodium, magnesium or aluminium. Alternatively it can be produced by electrolysis (http://www.Azom.com).

2.5.4 Industrial Applications

Manganese is an important alloying agent. In steels, manganese improves the rolling and forging qualities, as well as strength, toughness, stiffness, wear resistance, hardness and

hardenability. In aluminium and antimony, manganese additions form highly ferromagnetic compounds, especially in the presence of small amounts of copper. It can also be used to produce an amethyst colour in glass. Manganese dioxide or pyrolusite is used to depolarise dry cells and green glass containing iron. Manganese permanganate is a powerful oxidising agent used in quantitative analysis techniques and medicine (http://www.Azom.com).

2.5.5 Health effects of Manganese

Manganese is a very common compound that can be found everywhere on earth. Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. When people do not live up to the recommended daily allowances their health will decrease. But when the uptake is too high health problems will also occur. The uptake of manganese by humans mainly takes place through food, such as spinach, tea and herbs. The foodstuffs that contain the highest concentrations are grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters. After absorption in the human body manganese will be transported through the blood to the liver, the kidneys, the pancreas and the endocrine glands.

Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson, lung embolism and bronchitis. When men are exposed to manganese for a longer period of time they may become impotent. A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches and insomnia.

Because manganese is an essential element for human health shortages of manganese can also cause health effects. These are the following effects:

-Fatness

-Glucose intolerance

- Blood clotting

- Skin problems

- Lowered cholesterol levels

- Skeleton disorders

- Birth defects
- Changes of hair colour
- Neurological symptoms

Chronic Manganese poisoning may result from prolonged inhalation of dust and fume. The central nervous system is the chief site of damage from the disease, which may result in permanent disability. Symptoms include languor, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps, and paralysis. A high incidence of pneumonia and other upper respiratory infections has been found in workers exposed to dust or fume of Manganese compounds (http://www.lenntech.com/index.htm).

For animals manganese is an essential component of over thirty-six enzymes that are used for the carbohydrate, protein and fat metabolism. With animals that eat too little manganese interference of normal growth, bone formation and reproduction will occur. For some animals the lethal dose is quite low, which means they have little chance to survive even smaller doses of manganese when these exceed the essential dose. Manganese substances can cause lung, liver and vascular disturbances, declines in blood pressure, failure in development of animal fetuses and brain damage. When manganese uptake takes place through the skin it can cause tremors and coordination failures. Finally, laboratory tests with test animals have shown that severe manganese poisoning should even be able to cause tumor development with animals (http://www.lenntech.com/index.htm).

2.5.6 Environmental effects of manganese

Humans enhance manganese concentrations in the air by industrial activities and through burning fossil fuels. Manganese that derives from human sources can also enter surface water, groundwater and sewage water. Through the application of manganese pesticides, manganese will enter soils. Manganese compounds exist naturally in the environment as solids in the soils and small particles in the water. Manganese particles in air are present in dust particles. These usually settle to earth within a few days.

In plants manganese ions are transported to the leaves after uptake from soils. When too little manganese can be absorbed from the soil this causes disturbances in plant

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and acidity and many trace elements. High As concentrations are also found in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or as adsorbed species. Adsorption of arsenate to hydrous iron oxides is strong, even at very low arsenic concentrations. As is also adsorbed at the surface of clays. Arsenic concentrations much higher than baseline values have been found in sediments and soils contaminated by the products of mining activity, including mine tailings and effluent. The high concentrations reflect increased abundance of primary arsenic-rich sulphide minerals, secondary iron arsenates and iron oxides formed as reaction products of the original ore minerals (Manning et al., 1996).

2.5.7.2 Acute and chronic effects of arsenic

Arsenic has been used since 3000 BC (Partington, 1935). In the United Kingdom, for example, it was used to extract iron from iron ore. It has long been known that arsenic is acutely toxic. Immediate symptoms on an acute poisoning typically include vomiting, oesophageal and abdominal pain, and bloody "rice water" diarrhoea. The symptoms and signs that arsenic causes appear to differ between individuals, population groups and geographic areas. Thus, there is no universal definition of the disease caused by arsenic.

Long-term exposure to arsenic via drinking-water causes cancer of the skin, lungs, urinary bladder, and kidney, as well as other skin changes such as pigmentation changes and thickening (hyperkeratosis). Increased risks of lung and bladder cancer and of arsenic-associated skin lesions have been observed at drinking-water arsenic concentrations of less than 0.05 mg/L. Absorption of arsenic through the skin is minimal and thus hand-washing, bathing, laundry, etc. with water containing arsenic do not pose human health risk. Following long-term exposure, some studies have reported hypertensive and cardiovascular disease, diabetes and reproductive effects. Exposure to arsenic via drinking-water has been shown to cause a severe disease of blood vessels leading to gangrene (Feroze A., 2002).

Yamamoto et al. (1995) showed that chronic exposure to DMA enhanced tumor development in the kidney, liver and urinary bladder. Results of studies by Chen et al. (1995) showed that most of water samples from wells in Northeast and Northwest

mechanisms. For instance disturbance of the division of water to hydrogen and oxygen, in which manganese plays an important part. Manganese can cause both toxicity and deficiency symptoms in plants. When the pH of the soil is low manganese deficiencies are more common. Highly toxic concentrations of manganese in soils can cause swelling of cell walls, withering of leafs and brown spots on leaves (http://www.lenntech.com/index.htm).

In deep wells, where oxygen content is low, the manganese bearing water is clear and colourless, but when exposed to air, manganese is oxidized and changes from colourless to black. This causes staining of clothes and utensils. Water containing manganese requires treatment for taste, aesthetic quality and toxicity. The limit of manganese in drinking water supplies is 0.1mg/l (WHO, 1994., GSB, 1998).

2.5.7 Arsenic

Arsenic is a metalloid toxic element also called "Secrete Poison." It is soluble in water and found in nature in the atmosphere, soils and sediments, rocks, natural waters and organisms. It is mobilized in the environment through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions, basin full of alluvial deposits, uranium and gold mining as well as through a range of anthropogenic activities such as smelting operations, fossil fuel combustion, and wastes from different uses of arsenic chemicals. Arsenic occurs in several different species depending on the pH and oxidation potential of the water. The four As species commonly reported are Arsenite [As(III)], Arsenate[As(V), monomethylarsinate(MMA), and dimethylarsinate (DMA) (Anderson et al., 1991).

2.5.7.1 Sources of Arsenic

Arsenic occurs as a major constituent in more than 200 minerals, mostly ore minerals and their alteration products. The most widespread As ore mineral is arsenopyrite(FeAsS). Other minerals are; Realgar (As_2S_2); orpiment (As_2S_3); arsenic trioxide (As_2O_3). Arsenic is also often present in varying concentrations in other common rock-forming minerals of which pyrite is the most abundant. Pyrite is also formed in low-temperature sedimentary environments under reducing conditions to form authigenic pyrite. Pyrite is not stable in aerobic systems and oxidizes to iron oxides with the release of large amounts of sulphate

Taiwan (an endemic area for blackfoot disease) had high DMA concentrations of up to 7ug/l. Elevated prevalence of mental retardation among children has also been reported in arseniasis endemic areas in Inner Mongolia (Ma et al, 1996).

2.5.7.3 Beneficial effects

Arsenic has been used for many years for medicinal purposes. It used to be used as a cure for diseases such as syphilis and has been shown to assist in curing some leukemias. (Feroze A., 2002).

2.5.7.4 Regulatory limits for continuous exposure

The regulatory limits on arsenic exposure were set primarily to be sure that these acute toxic effects were avoided. The first regulatory limit of which the webmasters are aware was set as a result of a public inquiry (subsequent to arsenic being found in beer) by the physicist William Thompson, first Lord Kelvin, about 1900. The regulatory limit for the U.K. was then set at 150 parts per billion (150 ppb, 0.15 ug/l). This was reduced three fold over the next century and until recently the limit set by Bangladesh, the United Kingdom, and the United States was 50 parts per billion (ppb). But the discovery that there are adverse effects of continuous chronic exposure led WHO to lower their recommendation to 10 parts per billion (10 ppb). The European Union (EU) plannned to enforce a standard of 10 ppb by 2003. After a long travail, on October 31st 2001, the administrator of US EPA confirmed a new standard for drinking water of 10 ppb to be enforced by 2006 (Feroze *A*., 2002).

2.5.7.5 *The worldwide scope of the catastrophe*

Arsenic contamination has become a problem in many parts of the world. At first as a result of leaching from mine tailings in Australia, Canada, Japan, Mexico, Thailand, United Kingdom, and the United States, but now also from the arsenic in natural aquifers now or recently used for water supply in Argentina, Bangladesh, Cambodia, Chile , China, Ghana, Hungary, Inner Mongolia, Mexico, Nepal, New Zealand, Philippines, Taiwan, the United States and Vietnam (http://phys4.havard.edu/2wilson/arsenic). Results of studies by Chen et al. (1995) showed that most of water samples from wells in Northeast and Northwest Taiwan (an endemic area for blackfoot disease) had high DMA concentrations of up to 7 μ g/l. Elevated prevalence of mental retardation among children

has also been reported in arseniasis endemic areas in inner Mongolia. Exposure to arsenic via drinking-water has been shown to cause a severe disease of blood vessels leading to gangrene in China (Province of Taiwan), known as 'black foot disease' (Ma et al 1996).

46 million people in Bangladesh drink water with concentrations of arsenic above the WHO's safety standard of 10ug/l. Millions of people in Bangladesh suffer from various skin lesions manifested by hyperpigmentation (dark spots), hypopigmentation (white spots) and keratoses of the hands and feet (http://phys4.havard.edu/2wilson/arsenic). According to some estimates, arsenic in drinking-water will cause 200,000 - 270,000 deaths from cancer in Bangladesh alone (NRC, 1998; Smith, et al, 2000).

Recently, there has been an upsurge in the incidence of cancer in Ghana (Buamah et al, 2005). Although the route cause has not been clearly detected, As(III) present in excess of the guideline value of 10 μ g/l provided by the World Health Organization(WHO), could be one of the major causes (Nkyerkyer, K., 2000). Arsenic has been found to be present in groundwater from areas in Ghana such as Ntobroso and Takyikrom in the Ashanti Region, Anyinase, Seikwa and Sanahu in the Western Region and Bolgatanga in the Upper East Region (Buamah et al, 2005). Due to the presence of Arsenic in the groundwater from these communities, diseases such as Gangrene, Breaking palm and feet and Conjunctivitis are endemic. There is also a high incidence of cancer in these areas (Nkyerkyer, K., 2000).

2.5.7.6 Release of Arsenic in Ground Water

The reasons that arsenic enters the water differ between all the major locations. Severe arsenic pollution of ground water in most alluvial aquifers worldwide is driven by the microbially-mediated metabolism of organic matter, with FeOOH acting as the source of oxygen: the oxide is reduced during the process and its sorbed arsenic is released to ground water. Another way is through oxidation of Arsenic Bearing Minerals (Arsenopyrite–FeAsS). Due to heavy groundwater extraction and fluctuation of water tables from pre-monsoon and post monsoon the underground aquifer is aerated. The alluvial consists of fine grained iron or manganese oxy-hydroxides. Due to aeration or

pyrite oxidation process, iron, sulfide and arsenic are released into surrounding water. Another process is the natural Process – Oxyhydroxide reduction, where arsenic is adsorbed into fine – grained iron or manganese oxyhdroxides, which are present in sediments. As time passes, oxygen level naturally decreases and under these conditions, the iron and manganese compounds dissolved and release the arsenic into the surroundings (Bhattacharya P., 2004.).

2.5.7.7 Arsenic removal at water treatment plants

Few water treatment plants are designed specifically for arsenic removal. However, some arsenic is typically removed at treatment plants designed for iron and/or manganese removal (McNeill and Edwards, 1995) and coagulation (Hering et al., 1997). In both processes, soluble arsenic sorbs to insoluble hydrous ferric or manganese oxide and gets filtered out. Many factors affect sorption of arsenic to metal oxides and, therefore, the efficiency of arsenic removal, including the metal to arsenic ratio, the pH, the arsenic oxidation state, and the concentrations of other substances that sorb to hydrous ferric oxide (HFO). Higher iron and/or manganese to arsenic ratios favor higher arsenic removal (Wilkie and Hering, 1996). Several substances that are commonly found in natural water, including bicarbonate (Appelo et al., 2002), silica (Swendlund and Webster, 1999), phosphate (Manning and Goldberg, 1996), and natural organic matter interfere with arsenic sorption to HFO (Redman et al., 2002).

Several arsenic removal techniques are used to treat drinking water. Primarily applied to public works, these methods include ion exchange, flocculation and filtration with ferric or ferrous salts, adsorption on activated alumina and on ferric iron-based adsorbents. Municipalities rarely use reverse-osmosis, However such systems are efficient at controlling and removing several contaminants from the raw water (Driehaus, W. et al, 1998).

In Germany, flocculation with ferric or ferrous iron is one of the applied forms of arsenic removal, as it meets national drinking water standards for arsenic. The technique entails dosing and mixing an acid ferric or ferrous solution in the raw water. The ferric iron precipitates and adsorbs arsenic during the flocculation. Filtration, usually with a sand

filter, is used to remove the arsenic-bearing precipitates. Backwashing removes the precipitates from the filter bed, leaving sludge residual high in water content. Despite its efficiency at removing arsenic, flocculation does have some disadvantages. These include chemical handling, required overdosing, maintaining dosing equipment, backwashing and sludge handling (Driehaus, W. et al, 1998).

Activated alumina has been used for more than two decades to adsorb arsenate-containing waters. The adsorbent does require regeneration due to its limited lifecycle. The optimal pH for arsenic removal with activated alumina is around 6.0. activated alumina is ineffective in arsenic III adsorption because it has to be regenerated. This regeneration technique may cause problems because it significantly lessens capacity, and more importantly, produces an arsenic-rich liquid waste stream (Driehaus, W. et al, 1998).

Jekel, M.R. in 1994 also developed a media known as granular ferric hydroxide(GEH) for removal of arsenic from small water systems. This media combines advantages of flocculation and filtration. The GEH media's high adsorption capacity, coupled with the fact that it does not produce contaminated sludge or require chemical dosing, gives it an edge over other arsenic removal treatment methods. The adsorption techniques rely on a simple filtration process over granular adsorbents like activated alumina or granular iron oxides and ferric hydroxides. Chemical dosing is usually not necessary. These techniques do not produce backwash sludge; the actual residual is the arsenic loaded adsorbent. More than 60 arsenic removal treatment plants in operation in Germany, Japan and the United States are using the described iron-based adsorbent.

In recent years, the United States has also begun investigating various arsenic treatment techniques to meet a lower arsenic standard of 10ug/l that goes into effect in 2006. in the last decade, iron oxide-based adsorbents have come to the forefront for treatment of arsenic contaminated water. Spurred on by the impending new US arsenic standard, the last few years have seen a renewed interest in developing new adsorption media for

arsenic removal. Looking into the future, iron-oxide based adsorbents are expected to play a major role in arsenic removal from potable water (Driehaus, W. et al, 1998).

2.5.7.8 Chemistry of Pyrite Weathering

A complex series of chemical weathering reactions are spontaneously initiated when surface mining activities expose spoil materials to an oxidizing environment. The following equations show the generally accepted sequence of pyrite reactions:

$2\ FcS_2 + 7\ 0_2 + 2\ H_20 \rightarrow 2\ Fc^{2+} + 4\ SO_4 + 4\ H^+$ (Equation I)

$4\ Fe^{2+} + 0_2 + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_20$ (Equation 2)

$4\ Fe^{3+} + 12\ H_20 \rightarrow 4\ Fe(OH)_3 + 12\ H^+$ (Equation 3)

$FeS_2 + 14\ Fe^{3+} + 8\ H_20 \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$ (Equation 4)

In the initial step, pyrite reacts with oxygen and water to produce ferrous iron, sulfate and acidity. The second step involves the conversion of ferrous iron to ferric iron has been termed the "rate determining" step for the overall sequence. The third step involves the hydrolysis of ferric iron with water to form the solid ferric hydroxide (ferrihydrite) and the release of additional acidity. The fourth step involves the oxidation of additional pyrite by ferric iron. The ferric iron is generated by the initial oxidation reactions in steps one and two (Bhattacharya P., 2004).

2.6 LATERITE

Laterite is a residual rock, a "duricrust" produced by weathering of pre-existing rocks by the action of rainwater. It is a red or brown superficial deposit of clay or earth which gathers on the surface of rocks and is produced by their decomposition. It is very common in tropical regions. In consistency it is generally soft and friable, but hard masses, nodules and bands often occur in it. These are usually rich in iron. The superficial layers of laterite deposits are often indurated and smooth black or dark-brown crusts occur where the clays have long been exposed to a dry atmosphere. In other cases the soft clays are full of hard nodules, and in general the laterite is perforated by tubules,

sometimes with veins of different composition and appearance from the main mass. The depth of the laterite beds varies up to 30 or 40 ft., the deeper layers often being soft when the surface is hard or stony. The transition to fresh, sound rock below may be very sudden (*chami-at-sunny.ncmc.cc.mi.us*). Laterite occurs in practically every tropical region of the earth, and is very abundant in Ceylon, India, Burma, Central and West Africa, and Central America. It is especially well developed where the underlying rock is crystalline and felspathic (as granite gneiss, syenite and diorite), but occurs also on basalts in the Deccan and in other places, and is found even on mica schist, sandstone and quartzite, though in such cases it tends to be more sandy than argillaceous. Many varieties have been recognized. In India a calcareous laterite with large concretionary blocks of carbonate of lime is called kankar and has been much used in building bridges because it serves as hydraulic cement. In some districts (e.g. W. Indies) similar types of laterite have been called "puzzuolana" and are also used as mortar and cement. Kankar is also known and worked in East Africa. The clay called cabook in Ceylon is essentially a variety of laterite. Common laterite contains very little lime, and it seems that in districts which have an excessive rainfall that component may be dissolved out by percolating water, while kankar, or calcareous laterite, is formed in districts which have a smaller rainfall. In India also a distinction is made between "high-level" and "low-level" laterites. The former are found at all elevations up to 5000 ft. and more, and are the products of the decomposition of rock in situ; they are often fine-grained and sometimes have a very well-marked concretionary structure. These laterites are subject to removal by running water, and are thus carried to lower grounds forming transported or "low-level " laterites. The finer particles tend to be carried away into the rivers, while the sand is left behind and with it much of the heavy iron oxides. In such situations the laterites are sandy and ferruginous, with a smaller proportion of clay, and are not intimately connected with the rocks on which they lie. On steep slopes laterite also may creep or slip when soaked with rain and if exposed in sections on roadsides or river banks has a bedded appearance, the stratification being parallel to the surface of the ground. Chemical and microscopical investigations show that laterite is not clay like those which are so familiar in temperate regions; it does not consist of hydrous silicate of alumina, but is a mechanical mixture of fine grains of quartz with minute scales of hydrates of alumina. The latter are easily

soluble in acid while clay is not, and after treating laterite with acids the alumina and iron leave the silica as a residue in the form of quartz. The alumina seems to be combined with variable proportions of water, probably as the minerals hydrargillite, diaspore and gibbsite, while the iron occurs as goethite, turgite, limonite, haematite. As already remarked, there is a tendency for the superficial layers to become hard, probably by a loss of the water contained in these aluminous minerals. These chemical changes may be the cause of the frequent concretionary structure and veining in the laterite. The great abundance of alumina in some varieties of laterite is a consequence of the removal of the fine particles of gibbsite from the quartz by the action of gentle currents of water. Where the iron concretions have been washed out by rains or by artificial treatment (often in the form of small shot-like pellets) they serve as an iron ore in parts of India and Africa. Attempts are being made to utilize laterite as an ore of aluminium, a purpose for which some varieties seem well adapted. There are also deposits of manganese associated with some laterites in India which may ultimately be valuable as mineral ores. (Encyclopedia Britannica, 1911.).

2.6.1 Formation

As warm rainwater soaks constantly through the rocks, it breaks down mineral grains forming the rock and dissolves away many of the chemical elements making them up. Some are easier to remove than others, such as sodium, potassium and calcium, and magnesium and silicon. However, the iron and aluminum tends to remain behind as their hydrated oxides, such as goethite and gibbsite. These minerals can form as layers of fine-grained material around very altered bits of the original rock, producing the round gravel pellets, as well as forming solid masses of oxide, or pellets which may be cemented together to produce a kind of conglomerate. The loose "ball-bearing" gravels are typical of the upper layers of the laterite deposits, while the lower parts are usually more solid. (Nahon, 1986).

Initial stages of weathering lead to the formation of kaolinite and iron oxyhydroxides. Micro and macro-level movements of iron through soil minerals also begin to occur (Nahon 1986). Next, mottled clay layers are formed. Iron oxyhydroxides continue to migrate within the soil profile, becoming more crystallized in the top horizons and

eventually forming large iron-rich nodes. These nodes are surrounded by yellow or white iron-depleted zones. The formation of the iron nodes occurs in a soil matrix made up of mostly weathered kaolinite and quartz and is called the "mottled clay layer." The soil at this point contains large tubules and alveoles, formed during the creation of the bleached zones (Coleman et al 1989). As weathering continues, these voids begin to fill with kaolinite and quartz grains. Further weathering leads to the ferruginization of these fill particles, as kaolinite and quartz are replaced with Fe, and purple to red indurated facies are produced. These processes complete the formation of the ferricrete soil horizon (Nahon 1986). Often ferruginous pebbly layers are formed in close association with the ferricrete horizon. They are formed from the break-down and downslope movement of pisolitic iron crusts. The end result is a "reddish matrix" made from kaolinite, goethite and fragments of the pisolitic iron crust converted in situ into a soft argillaceous material (Coleman et al, 1989). Laterite occurs in practically every tropical region of the earth, and is very abundant in Ceylon, India, Burma, Central and West Africa, Central America. It is especially well developed where the underlying rock is crystalline and felspathic (as granite gneiss, syenite and diorite), but occurs also on basalts in the Deccan and in other places, and is found even on mica schist, sandstone and quartzite, though in such cases it tends to be more sandy than argillaceous (Nahon 1986).

The conditions under which laterite are formed include, first, a high seasonal temperature, for it occurs only in tropical districts and in plains or mountains up to about 5000 ft. in height; secondly, a heavy rainfall, with well-marked alternation of wet and dry seasons (in arid countries laterite is seldom seen, and where the rainfall is moderate the laterite is often calcareous); third, the presence of rocks containing aluminous minerals such as felspar, augite, hornblende and mica. The restricted distribution of laterite deposits might then be due to the inhibiting effect of low temperatures on the reproduction of these organisms. This very ingenious hypothesis has not yet received the experimental confirmation which seems necessary before it can be regarded as established (Nahon 1986). The laterite beds are porous; in fact they are traversed by innumerable tubules which are often lined with deposits of iron oxide. We may be certain that, as in all soils during dry weather, there is an ascent of water by capillary

action towards the surface, where it is gradually dissipated by evaporation. The soil water brings with it mineral matter in solution, which is deposited in the upper part of the beds. If the alumina be at one time in a soluble condition it will be drawn upwards and concentrated near the surface. This process explains many peculiarities of laterites, such as their porous and slaggy structure, which is often so marked that they have been mistaken for slaggy volcanic rocks.

Laterites are not of much economic use. They usually form a poor soil, full of hard concretionary lumps and very unfertile because the potash and phosphates have been removed in solution, while only alumina, iron and silica are left behind. They are used as clays for puddling, for making tiles, and as a mortar in rough work. Where the iron concretions have been washed out by rains or by artificial treatment (often in the form of small shot-like pellets) they serve as an iron ore in parts of India and Africa. Attempts are being made to utilize laterite as an ore of aluminium, a purpose for which some varieties seem well adapted. There are also deposits of manganese associated with some laterites in India which may ultimately be valuable as mineral ores (Encyclopedia Britannica, 1911).

2.7 Iron Oxide Coated Sand

Various methods are used for the preparation of Iron oxide coated sand. Benjamin et al applied the following procedure for the sorption and filtration of heavy metals. The coating process contained the following steps: preparing the Fe(III) solution from $Fe(III)Cl_3$ followed by raising the pH-value with NaOH to 9.5 or 11.5 for ferrihydrite and goethite, respectively, mixing 100 ml Fe(III) solution with 200 g sand and heating at 105°C for 24 hours. Finally the surplus of precipitated iron oxides that were weakly bond to the surface of the sand grains were rinsed. A pre-coating step was added to obtain a more uniform final coating of the sand. The sand used for the coating was ordinary filter sand with a grain size of 0.32-0.71 mm, porosity of 38% and with a dispersion grade D_{60}/D_{10} of 1.5. The iron-oxides on the sand were by visual observations found to be ferrihydrite and goethite when the Fe(III) solution had a pH-value of 9.5 and 11.5, respectively. The amount of iron oxides coated on the sand grains was 1.7 mg Fe/ g sand for ferrihydrite and 4.2 for goethite (Benjamin, M.M. et al., 1996).

Yuan T, Luo Q. in his research on removal of arsenic from dispersed drinking water by iron oxide coated sand applied the following procedure. The iron oxide-coated sand (ICS) was developed by treating normal river sand with molysite and investigated by batch column tests and autoptic experiment to evaluate it's ability of eliminating arsenic from dispersed drinking water. The ICS did not require any activation pretreatment (Yuan T, Luo Q., 2001).

CHAPTER THREE

3.0 MATERIALS AND METHODOLOGY

To investigate the trends of adsorption of manganese and arsenic from aqueous medium under different process conditions such as aerobic and anaerobic conditions, different pH and different contact time, two adsorbents namely. laterite and iron-oxide coated sand were employed. Under the conventional treatment of water, metallic ion removal is often accomplished with aeration as one of the major processing unit (figure 3.1). Therefore in this study aerobic condition was considered as one of the process conditions.

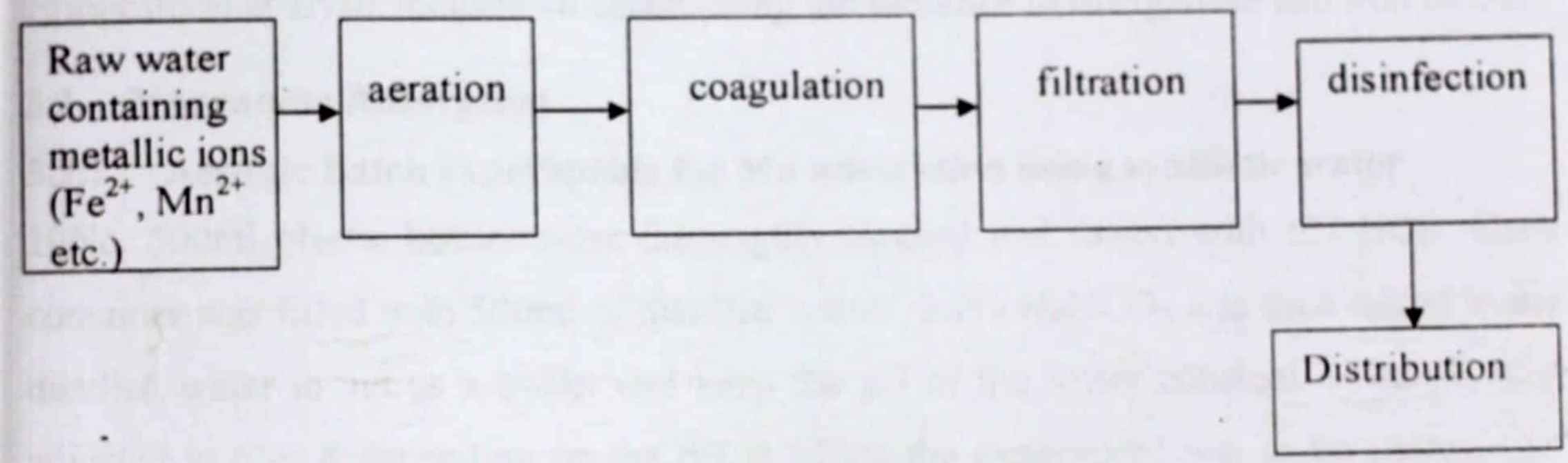


Figure 3-1 Line diagram of conventional treatment of water

In practice water extracted from deep wells or aquifers are almost always devoid of oxygen so in the experimentation it became relevant to monitor trends that pertain to anaerobic conditions. The experiments were carried out at pH 6 and pH 8 due to the fact that out of 300 borehole samples taken from Ashanti Region, 297 of the samples had pH range between 6 and 8. Only 3 samples had pH below 6 (Buamah et al, 2005).

In the experiments detailed out below synthetic water comprising de-mineralised water with 0.1% $NaHCO_3$ was used in the test experiments in order to clearly monitor the adsorption trends of the media for the different metallic ions. This was done to prevent the influence on the adsorption trend by other ions apart from Na^+ and HCO_3^- ions. The experiments were performed at temperatures of 28 – 32 °C.

3.1 Source of Adsorbents

Laterite was obtained from Nyinahin in the Ashanti Region. Due to time constraints, the iron oxide coated sand (ICS) was obtained from the Noord Bargeres Water Treatment plant in The Netherlands.

3.2 Preparation of Adsorbent

Rocky laterite was crushed and pulverized and sieved through a sieve with pore size of 75 μm. Iron-oxide coated sand aggregates of size ranging from 2.00mm to 3.15mm were pulverized and likewise sieved through 75 μm sieve. Portions of the various media were taken and added to concentrated HCl and aliquots of the resultant solution was analyzed at the Geological Survey Department in Accra, for the composition of the media. The composition analysis focused on ascertaining the presence of manganese and iron oxides.

3.3 Manganese Adsorption

3.3.1 Aerobic Batch experiments for Mn adsorption using synthetic water

10No. 500ml plastic bottles were thoroughly cleaned and rinsed with 6N HCl. Each container was filled with 500ml of distilled water. 0.1% $NaHCO_3$ was then added to the distilled water to act as a buffer and keep the pH of the water constant. The pH was adjusted to 6 or 8 depending on the pH at which the experiment was to be carried out. Different volumes of 1000 mg/l $MnSO_4$ stock solution was then added to the water to obtain initial Mn^{2+} ion concentrations of 2,3,4,5 and 6 mg/l in separate bottles. The volume of stock corresponding to a particular concentration is shown in table3.1 below.

Concentration Required (mg/l)	Volume of stock added (ml)
2	1
3	1.5
4	2
5	2.5
6	3

Table 3-1 Volume of stock corresponding to manganese concentration required

Each concentration was duplicated. A pair of blank solutions was also set up to determine whether the containers could contribute to the adsorption process. The

solutions in the plastic bottles were shaken vigorously and placed on a shaker operated at 110 rpm. Initial samples of volume 20ml were taken from each bottle with a 10 ml syringe to prevent oxygen from entering the bottles. 4g of the media was introduced into each bottle to commence the adsorption process. Sampling was done periodically for 5 days. Precisely sampling times were as follows: 15mins, and then 1, 2, 4, 8, 24, 48, 72, 96, 120 and 167 hours. The above sampling times were used because previous studies by Buamah et al have shown that there is an initial sharp drop in concentration from 0-15minutes. Between 15minutes and 1hour, significant adsorption does not take place. A 5minute sample was not taken because the sampling process takes time and it would be almost impossible to maintain the 5minute interval between one sampling and the next.

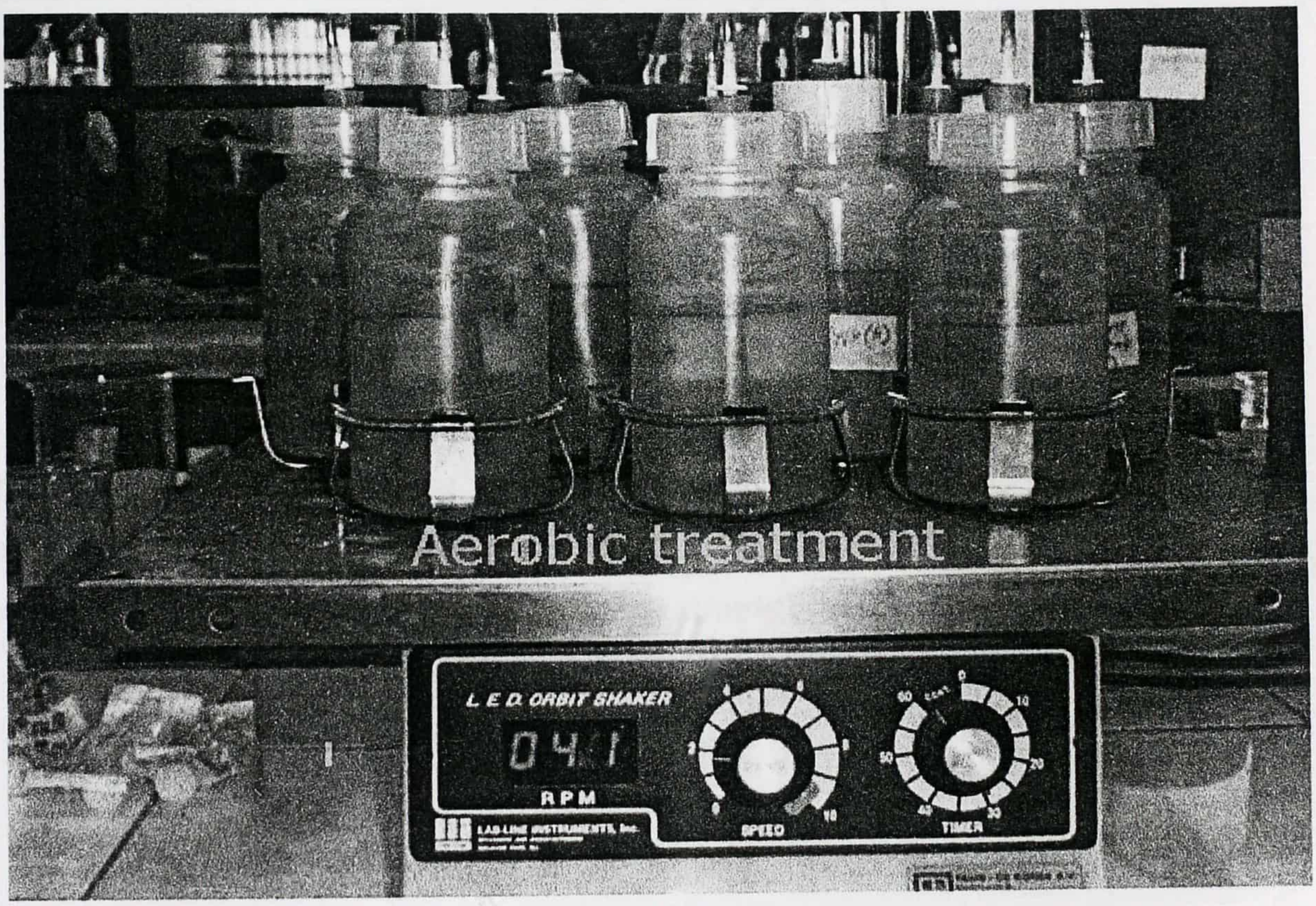


Figure 3-2 Experimental Setup for adsorption under aerobic conditions

3.3.2 Anaerobic Batch experiments for Mn adsorption using synthetic water

A 500ml plastic batch reactor was not available for the experiment under anaerobic condition. A 1500ml glass reactor was therefore used. A blank was initially set up to determine if the glass surface would affect the adsorption process. The reactor was filled

with distilled water and 0.1% $NaHCO_3$ was added to create buffering conditions within the solution. Pure N_2 gas was bubbled through for about an hour to create anaerobic conditions within the reactor. Pure CO_2 gas was then bubbled through to adjust pH to the value required (6 or 8). A pH meter and oximeter were used to read pH and oxygen levels in the reactor and necessary adjustments made when necessary. The volume of water corresponding to the required concentration was siphoned with a pipette. The amount of stock solution corresponding to the required concentration was introduced (table 3.2). The experiment was performed for concentrations of 2, 3, 4, 5 and 6mg/l.

Concentration Required (mg/l)	Volume of stock added (ml)
2	3
3	4.5
4	6
5	7.5
6	9

Table 3-2 Volume of stock corresponding to manganese concentration required

12g of the media was then introduced into the reactor in order that the amount of adsorbent would correspond to the volume of solution (1500ml). Samples were taken at intervals of 5mins, 15mins and then 1, 2, 4, 8, 12, 24 and 36hours. Since only one reactor was being used, it was possible to take a 5minute sample.

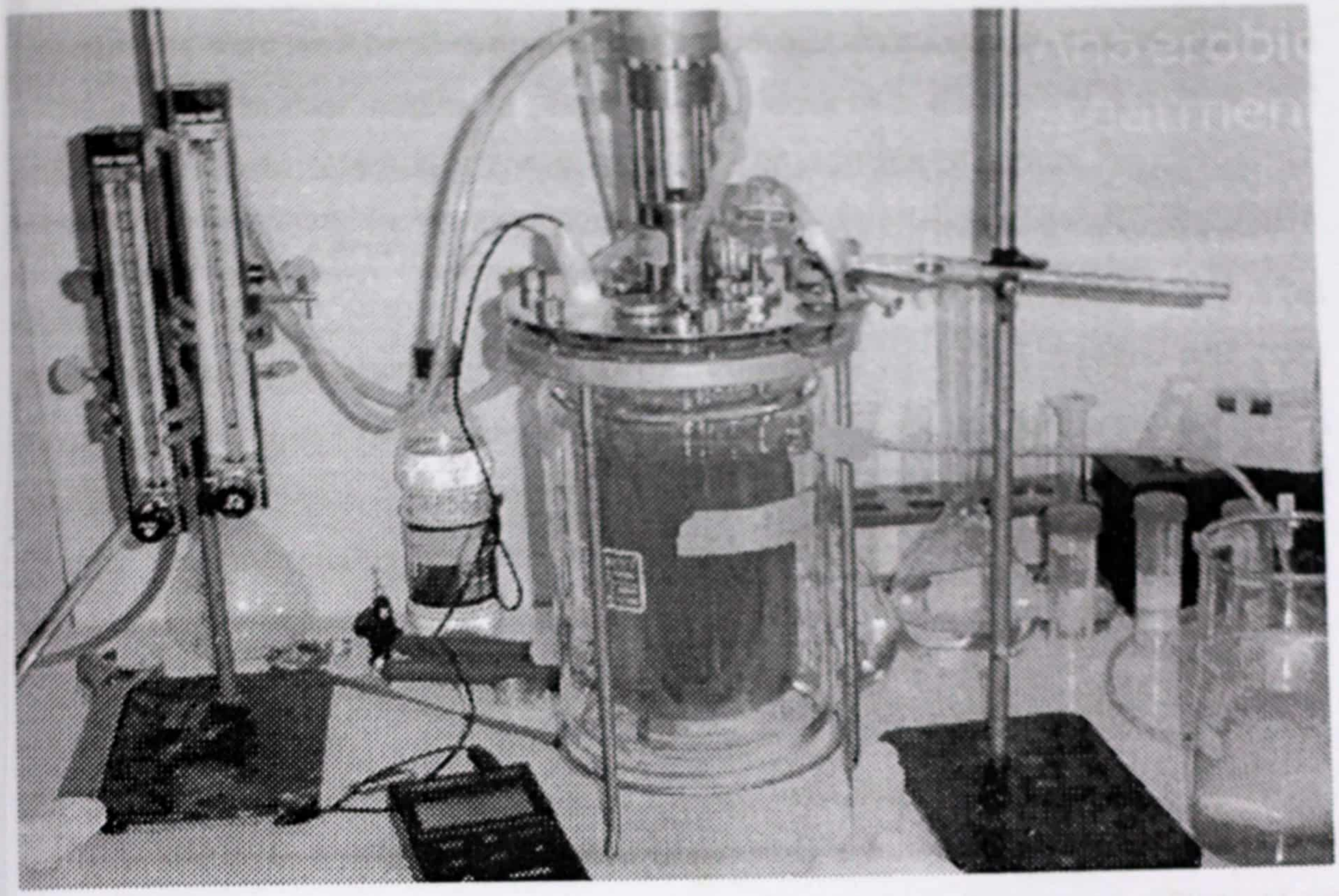


Figure 3-3 Experimental Setup for adsorption under anaerobic conditions

3.4 Arsenic Adsorption

3.4.1 Aerobic batch experiment for arsenic adsorption using synthetic water

The procedure under section 3.3.1 was repeated but with arsenic in place of manganese as the adsorbate. Initial aqueous arsenic concentrations of 30, 50, 100, 300 and 500 ug/l were used.

Concentration Required (ug/l)	Volume of stock to added(ml)
30	1.5
50	2.5
100	5
300	15
500	25

Table 3-3 Volume of stock corresponding to arsenic concentration required

Experiments were performed in duplicate with both adsorbents (i.e laterite and ICS). 4g of the media was then introduced. Sampling was done over a period of 5 days at time intervals of 15mins, and then 1, 2, 4, 8, 24, 48, 72, 96, 120 and 167 hours.

3.5 Competitive Adsorption

In real situations in deep wells or aquifers the metallic ions normally do not exist individually or in isolation but rather in combination and complexes together with other ions, so a competitive batch experiment was designed to simulate such a situation using modified groundwater. The groundwater was obtained from Ayeduase, a suburb of Kumasi. A water quality analysis of the groundwater was performed for parameters of As, Mn and Fe (Appendix A).

3.5.1 Aerobic batch experiment for adsorption of Mn, As and Fe using modified groundwater

To determine the behaviour of As (III) adsorption in the presence of Fe and Mn, the groundwater from Ayeduase was modified by dosing it with 1mg/l of Fe^{2+} and 2 mg/l of Mn^{2+} to represent the ratio in which they usually occur on the ground. 500ml of the modified groundwater was put in five separate 500ml plastic containers. Each container was then dosed with 0.1% $NaHCO_3$. The pH of the groundwater was 6.27. Each container was dosed with As (III) to obtain As (III) concentrations of 30, 50, 100, 300 and 500ug/l. The various solutions were duplicated. Solutions were thoroughly shaken, initial samples were taken and then 4g of the adsorbent was introduced to commence aerobic adsorption process as described in section 3.3.1 above. Periodic sampling was performed.

3.5.2 Anaerobic batch experiment for adsorption of Mn, As and Fe using modified groundwater

Using the same modified groundwater as in the aerobic case, manganese, arsenic and iron adsorption process under anaerobic conditions was monitored using similar procedure described in section 3.3.2. The pH was maintained at pH 6 and initial arsenic concentration kept at 300 ug/l. Periodic sampling was done and samples analyzed.

3.5.3 Preservation and analysis of samples

14 drops of 6N HCl was added to each sample taken periodically and then analyzed using the Perkin Elmer AA100 for the aqueous manganese level determination. In the case of

arsenic the graphite furnace spectrometer was employed using the standard methods (Greenburg et al, 1995).

3.5.4 Summary of experimental procedure

Part 1

Media	Medium	Adsorbate	Process Conditions
Laterite (pulverized)	Synthetic water 0.1% NaHCO3	Mn Different concentrations	D.O.–Aerobic & Anaerobic pH – 6&8 Temperature – 28-30^{0}C Stirring/Shaken 110rpm
ICS (pulverized)	Modeled water 0.1% NaHCO3	Mn Different concentrations	D.O.–Aerobic & Anaerobic pH – 6&8 Temperature – 28-30^{0}C Stirring/Shaken 110rpm

Part 2

Media	Medium	Adsorbate	Process Conditions
Laterite (pulverized)	Real groundwater	As Mn 1mg/l Fe 2mg/l	D.O. – Aerobic & Anaerobic pH – 6.27 Temperature – 28-30^{0}C
ICS (pulverized)	Real groundwater	As Mn 1mg/l Fe 2mg/l	D.O. –Anaerobic pH – 6.27 Temperature – 28-30^{0}C
Laterite (pulverized)	Modeled water 0.1% NaHCO3	As Different concentrations	D.O. – Aerobic pH – 6 Temperature – 28-300C Stirring/Shaken 110rpm

Due to constraints of time, anaerobic adsorption of As using laterite was not performed. Adsorption of As under aerobic and anaerobic conditions using ICS was also not carried out.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Media Composition

Analysis performed showed that the ICS has 510 mg of Fe and 24.5 mg of Mn in the coating per gramme of the ICS media. The other major component of the ICS was silica. In the case of the laterite Table 4.1 below shows the detailed composition of the laterite. The constituents of the two media showcase the presence of both iron and manganese therefore there is a high possibility of existence of several various oxides of these metallic ions within the media. This characteristic makes the media particles potential entities for adsorption of manganese and arsenic since these oxides are capable of forming complexes with these ions.

Table 4.1 Mineralogical analysis of laterite

SPECTRO X-LAB — Job Number: Test

Preset Sample Data

Sample Name:	**Afiba-03**	Dilution Material:	HWC
Description:		Sample Mass (g):	4.0000
Method:	Geo-4013	Dilution Mass (g):	0.9000
Job Number:	Test	Dilution Factor:	0.8163
Sample State:	Pressed tablet, 32 mm	Sample rotation:	No
Sample Type:	Preßtablette	Date of Receipt:	03/17/2005
Sample Status:	A A A A A X	Date of Evaluation:	03/17/2005

Results

The error is the statistical error with 1 sigma confidence interval

Minor Elements

15	P	0.0909	±	0.0012	%
16	S	412.3	±	6.4	ppm
17	Cl	141.9	±	2.9	ppm
22	Ti	> 0.9781	±	0.0017	%
23	V	> 635.6	±	6.0	ppm
24	Cr	809.7	±	3.1	ppm
27	Co	30.4	±	2.3	ppm
28	Ni	150.3	±	3.2	ppm
29	Cu	113.9	±	2.2	ppm
30	Zn	171.4	±	2.2	ppm
31	Ga	57.2	±	1.2	ppm
32	Ge	0.7	±	0.3	ppm
33	As	112.9	±	1.5	ppm
34	Se	4.2	±	0.4	ppm
35	Br	5.0	±	0.4	ppm
37	Rb	6.1	±	0.7	ppm
38	Sr	25.6	±	0.6	ppm
39	Y	29.2	±	0.6	ppm
40	Zr	442.2	±	1.8	ppm
41	Nb	26.6	±	0.5	ppm
42	Mo	5.1	±	0.5	ppm
47	Ag		<	0.8	ppm
48	Cd	3.1	±	0.3	ppm
50	Sn	9.9	±	0.4	ppm
51	Sb	7.3	±	0.4	ppm
52	Te		<	1.5	ppm
53	I	> 17.7	±	0.9	ppm
55	Cs	1.4	±	0.8	ppm
56	Ba	28.6	±	1.9	ppm
57	La	44.3	±	2.5	ppm
58	Ce	81.1	±	3.1	ppm
73	Ta		<	12	ppm
74	W	7.8	±	1.3	ppm
80	Hg	3.4	±	0.9	ppm
81	Tl	4.7	±	0.8	ppm
82	Pb	42.0	±	1.9	ppm
83	Bi		<	2.0	ppm
90	Th	21.0	±	2.0	ppm
92	U	8.4	±	1.3	ppm

Sum of concentration 41.17 %

Major Oxides

11	Na2O	1.86	±	0.14	%
12	MgO	0.366	±	0.053	%
13	Al2O3	28.27	±	0.06	%
14	SiO2	3.287	±	0.016	%
15	P2O5	0.2082	±	0.0028	%
16	SO3	0.1029	±	0.0016	%
19	K2O	0.02414	±	0.00073	%
20	CaO	0.04722	±	0.00070	%
25	MnO	0.00664	±	0.00014	%
26	Fe2O3	30.87	±	0.02	%

Sum 65.04 %

Date: 03/17/2005

Source: Geological Survey Department, Accra

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4.2 Manganese Adsorption

4.2.1 Aerobic Adsorption of Manganese using modeled water

Spectrometric analysis on the sample taken from the aerobic batch experiments for manganese showed a rapid decline in the levels of Mn in the aqueous phase within the first 4hours of the adsorption process as depicted in figures 4.1, 4.2 and 4.3.

The blank showed no adsorption implying that the material of the containers exhibited no contribution to the adsorption process.

From the graphs it is realised that equilibrium is not attained under aerobic adsorption. This is because the adsorbed Mn^{2+} gets oxidised to form manganese oxides and manganese oxyhydroxide complexes. These complexes form a new external coating round the media and facilitate further adsorption of Mn^{2+} ions. There is a gradual decrease in adsorption rate which could be due to the slow oxidation rate of the adsorbed Mn thus delaying the regeneration of new adsorptive sites.

From table B1, it can be inferred that, at pH 8 the percentage removal of Mn by laterite is 81.34 while it is 10.73 at pH 6. For ICS, the percentage removal at pH 8 is 98.84 while it is 87.50 at pH 6. This implies that better adsorption trends are realised at pH 8 than at pH 6 for both media. This can be attributed to the fact that, more OH^- ions are in solution at pH 8 and these are able to facilitate the formation of manganese oxides and oxyhydroxide complexes which enhance the adsorption. However, the percentage removal for ICS at pH 6 is relatively high because of the Fe and Mn oxide coating which facilitate better adsorption even under acidic conditions.

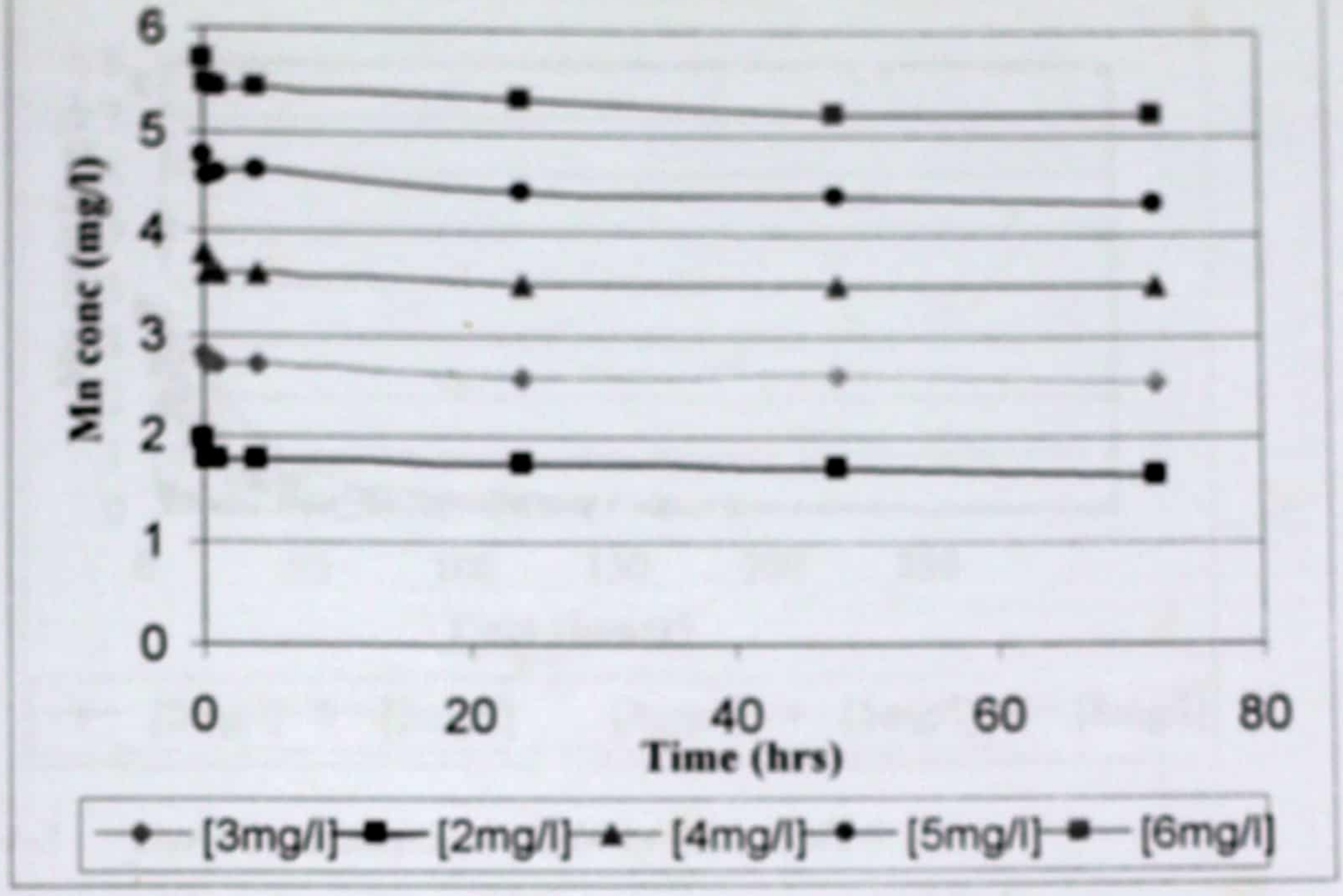


Figure 4-1 Aerobic adsorption of Mn at pH 6 using laterite

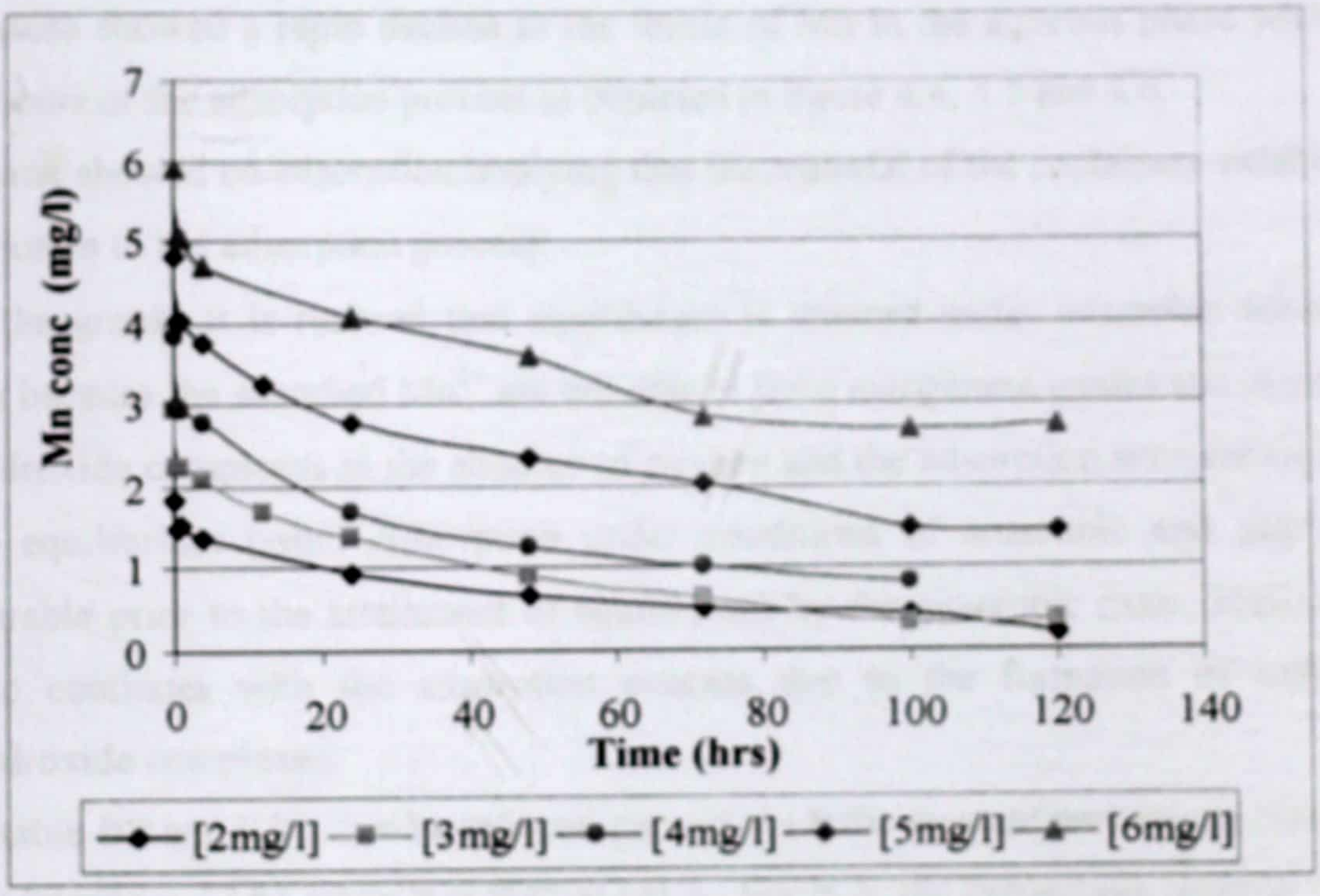


Figure 4-2 Aerobic adsorption of Mn at pH 8 using laterite

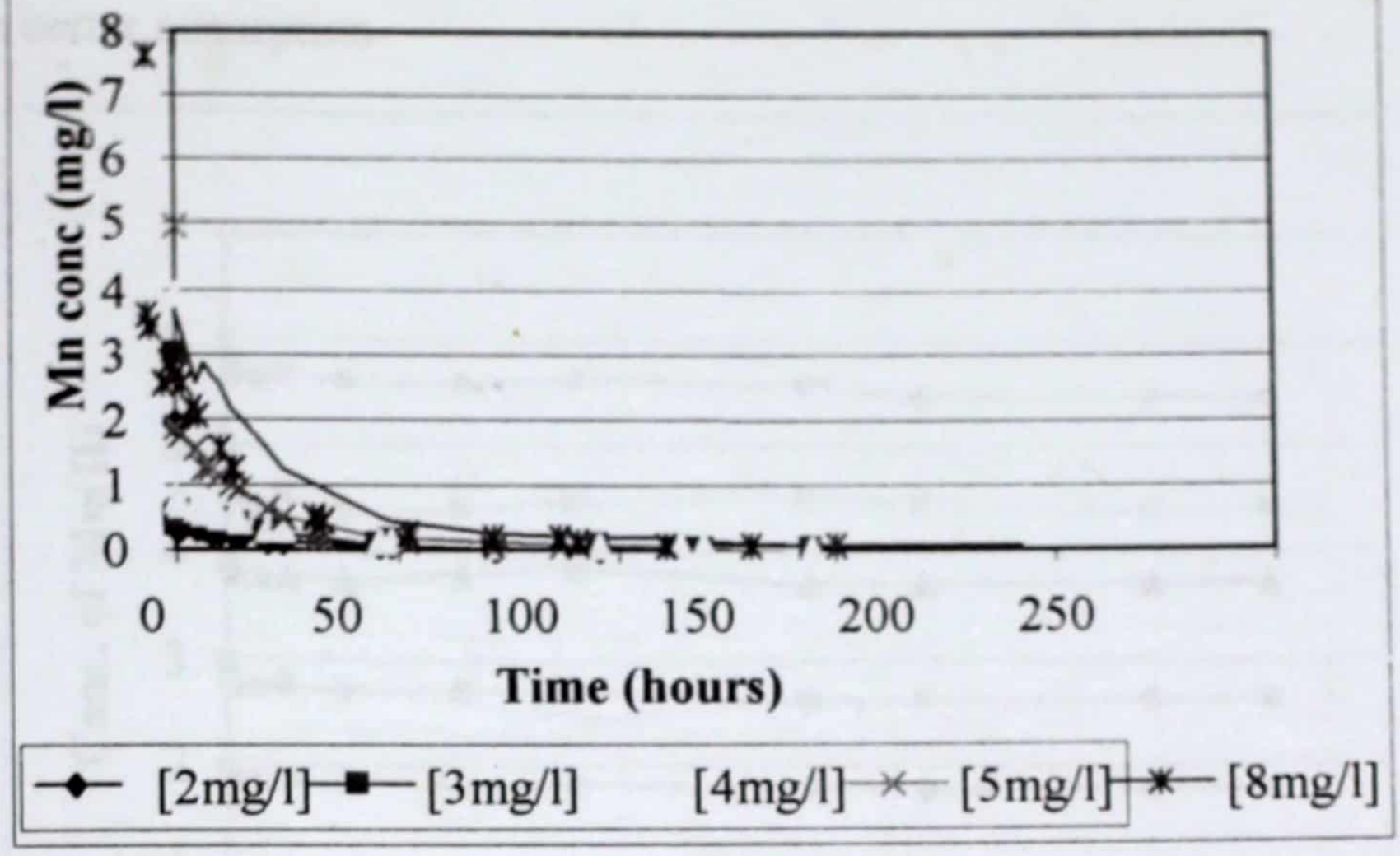


Figure 4-3 Aerobic adsorption of Mn by ICS at pH 8

4.2.2 Anaerobic Adsorption of Manganese using modeled water

Spectrometric analysis on the sample taken from the anaerobic batch experiments for manganese showed a rapid decline in the levels of Mn in the aqueous phase within the first 4hours of the adsorption process as depicted in figure 4.4, 4.5 and 4.6.

The blank showed no adsorption implying that the material of the containers exhibited no contribution to the adsorption process.

From the graphs it is realised that equilibrium is attained under anaerobic adsorption. This is because the adsorbed Mn^{2+} are not able to form manganese oxides and manganese oxyhydroxide complexes in the absence of oxygen and the adsorption sites are exhausted at the equilibrium point. Adsorption under conditions of anaerobic and aerobic are comparable prior to the attainment of equilibrium by the anaerobic case. However the aerobic continues with the adsorption process due to the formation of oxide and oxyhydroxide complexes.

From table B2 and B3 it can be inferred that, at pH 8 the average percentage removal of Mn by laterite is 47.83 while it is 9.45 at pH 6. For ICS, the percentage removal at pH 8 is 98.64 while it is 69.35 at pH 6. This implies that better adsorption trends are realised at pH 8 than at pH 6 for both media. This can be attributed to the fact that, more OH^- ions are in solution at pH 8 and these are able to facilitate the formation of manganese oxides

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and oxyhydroxide complexes which enhance the adsorption. However, the percentage removal for ICS at pH 6 is relatively high because of the Fe and Mn oxide coating which facilitate better adsorption.

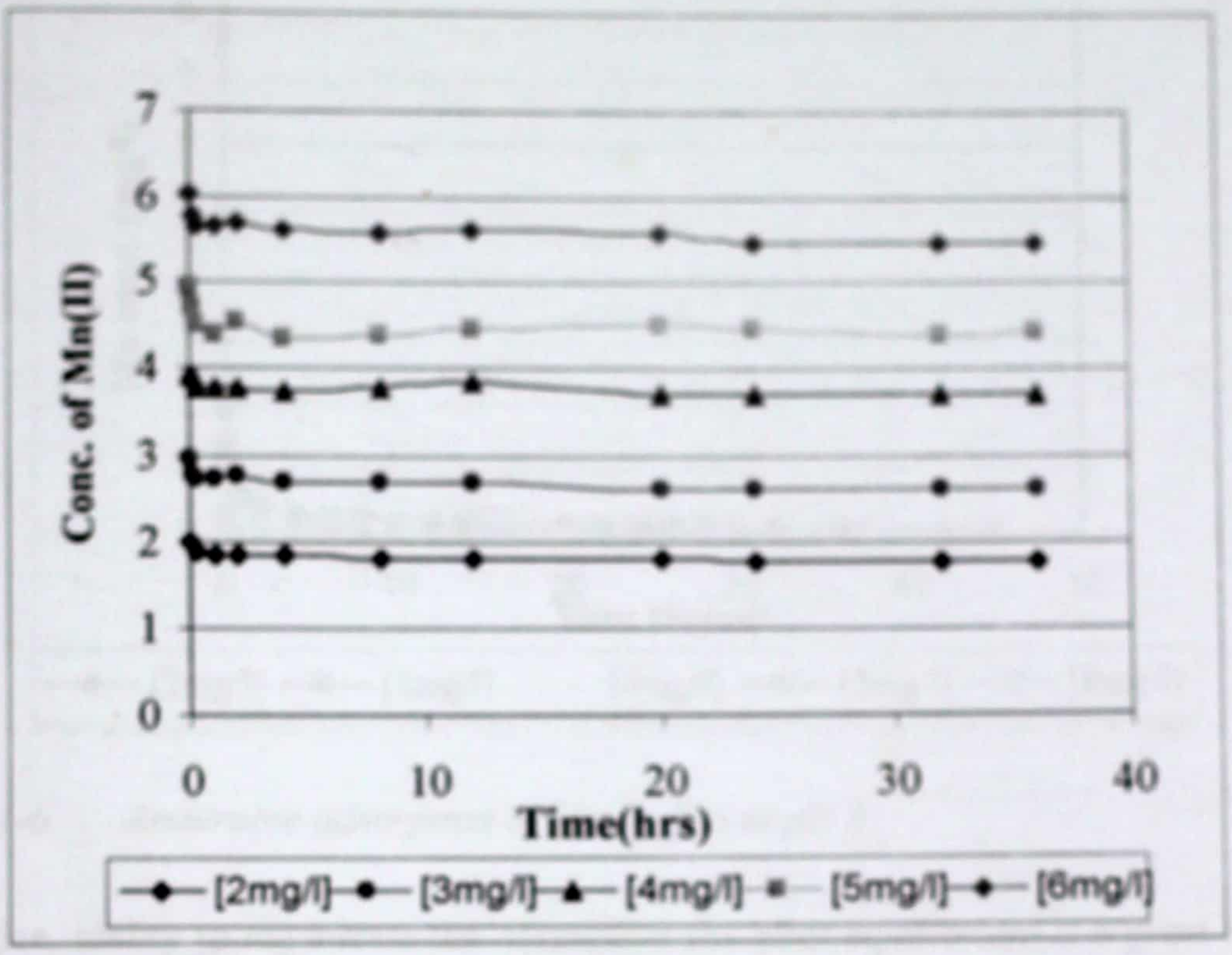


Figure 4-4 Anaerobic adsorption of Mn at pH 6 using laterite

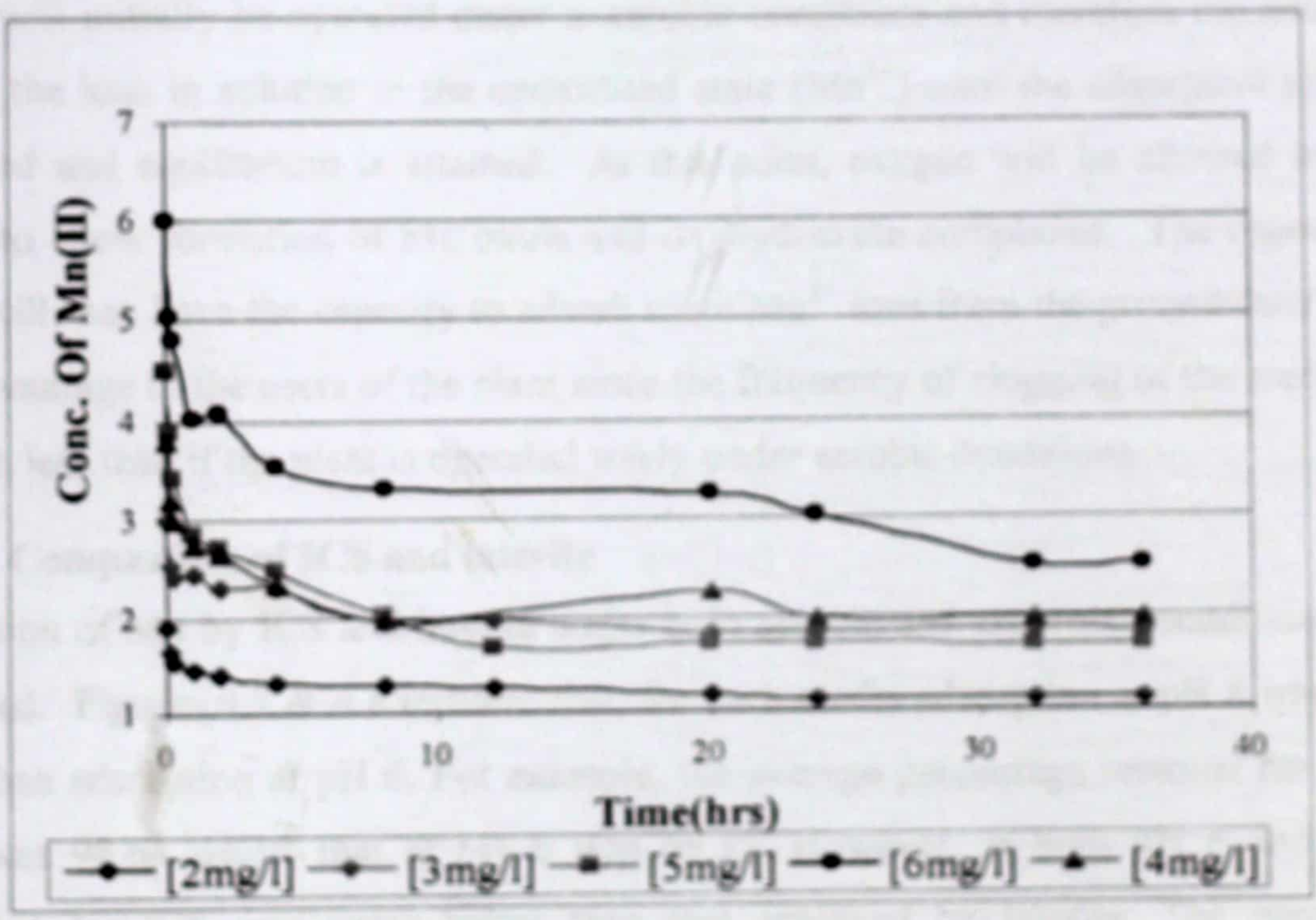


Figure 4-5 Anaerobic adsorption of Mn at pH 8 using laterite

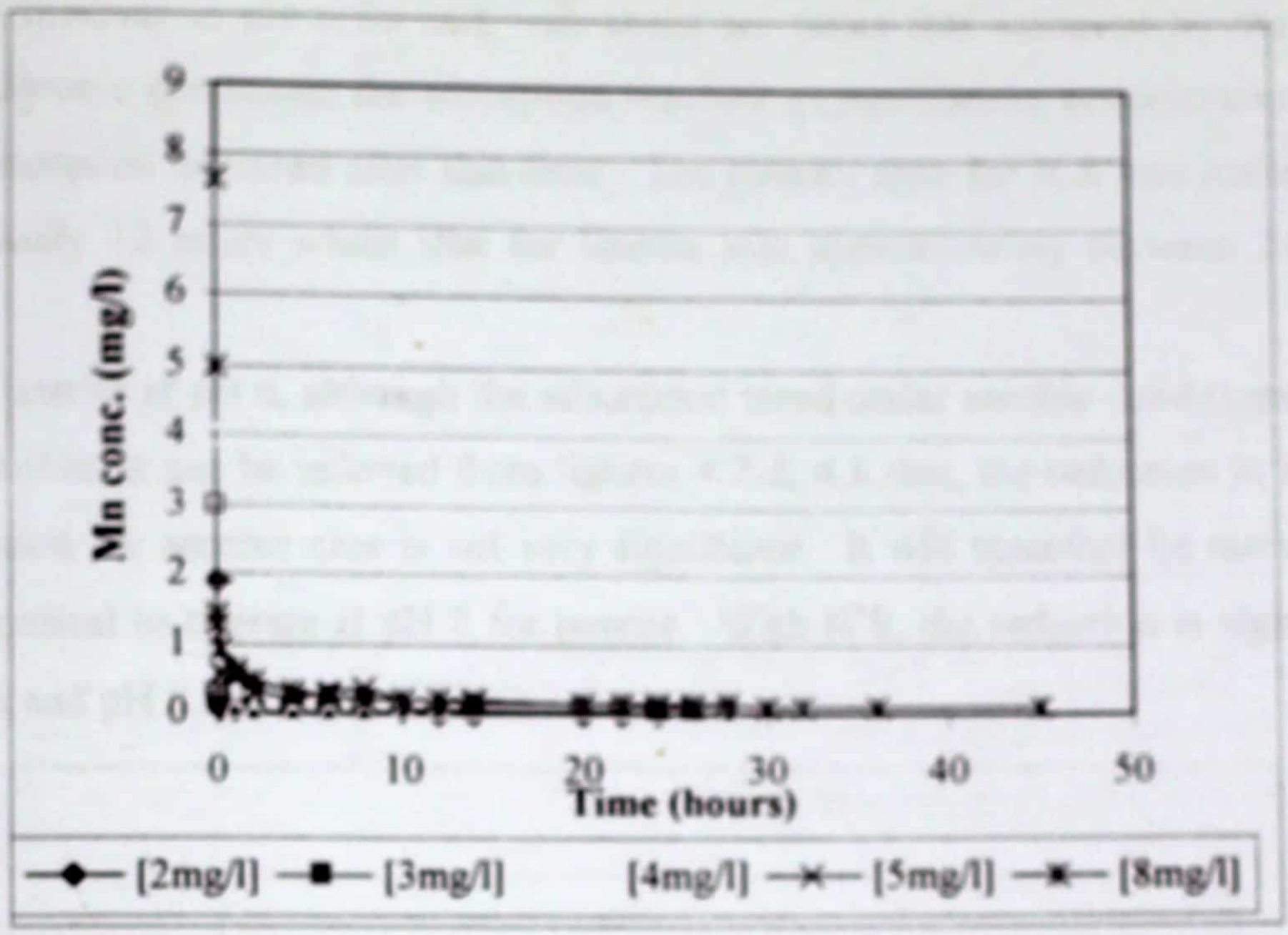


Figure 4-6 Anaerobic adsorption of Mn by ICS at pH 8

In practice, ability to regenerate the adsorptive site after equilibrium is a great advantage since no energy will used to aerate. Groundwater occurs in the anaerobic state. The system will initially be operated under anaerobic conditions and therefore the adsorbent adsorbs the ions in solution in the unoxidised state (Mn^{2+}) until the adsorptive sites are exhausted and equilibrium is attained. At this point, oxygen will be allowed into the system to allow formation of Mn oxide and oxyhydroxide complexes. The regenerated media will then have the capacity to adsorb more Mn^{2+} ions from the groundwater. This is an advantage to the users of the plant since the frequency of clogging of the media will be much less than if the plant is operated solely under aerobic conditions.

4.2.3 Comparison of ICS and laterite

Adsorption of Mn by ICS and laterite under both aerobic and anaerobic conditions were compared. Figures 4.7 & 4.8 indicate that, for each media adsorption at pH 8 was much better than adsorption at pH 6. For example, the average percentage removal for ICS at pH 8 was 98.64 whilst that at pH 6 was 69.35. However, at both pH 6 and pH 8, adsorption by ICS was much better than that achieved by laterite. The percentage

removal achieved by ICS at pH 8 for example was about twice that achieved by laterite while the removal at pH 6 for ICS was about six times that achieved by the laterite. Under anaerobic conditions the adsorption reached an equilibrium concentration and no further adsorption occurred after that time. The contact time for ICS was realised to be approximately 12 hours whilst that for laterite was approximately between 24 and 32 hours.

Also, for laterite at pH 6, although the adsorption trend under aerobic conditions is better than anaerobic, it can be inferred from figures 4.7 & 4.8 that, the reduction in adsorbate concentration for aerobic case is not very significant. It will therefore be more feasible and economical to operate at pH 8 for laterite. With ICS, the reduction is significant at both pH 6 and pH 8.

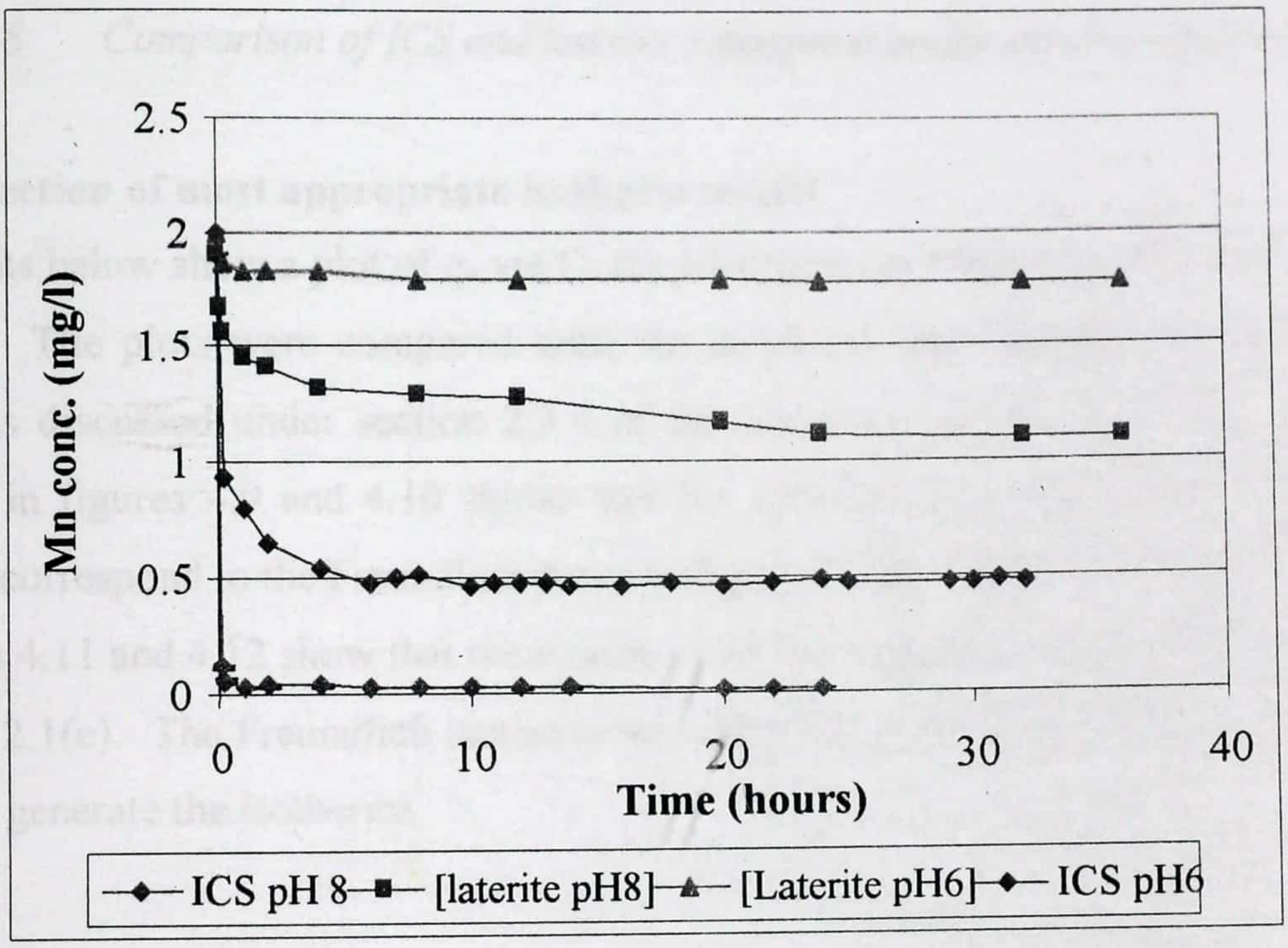


Figure 4-7 Comparison of ICS and laterite adsorption under anaerobic conditions

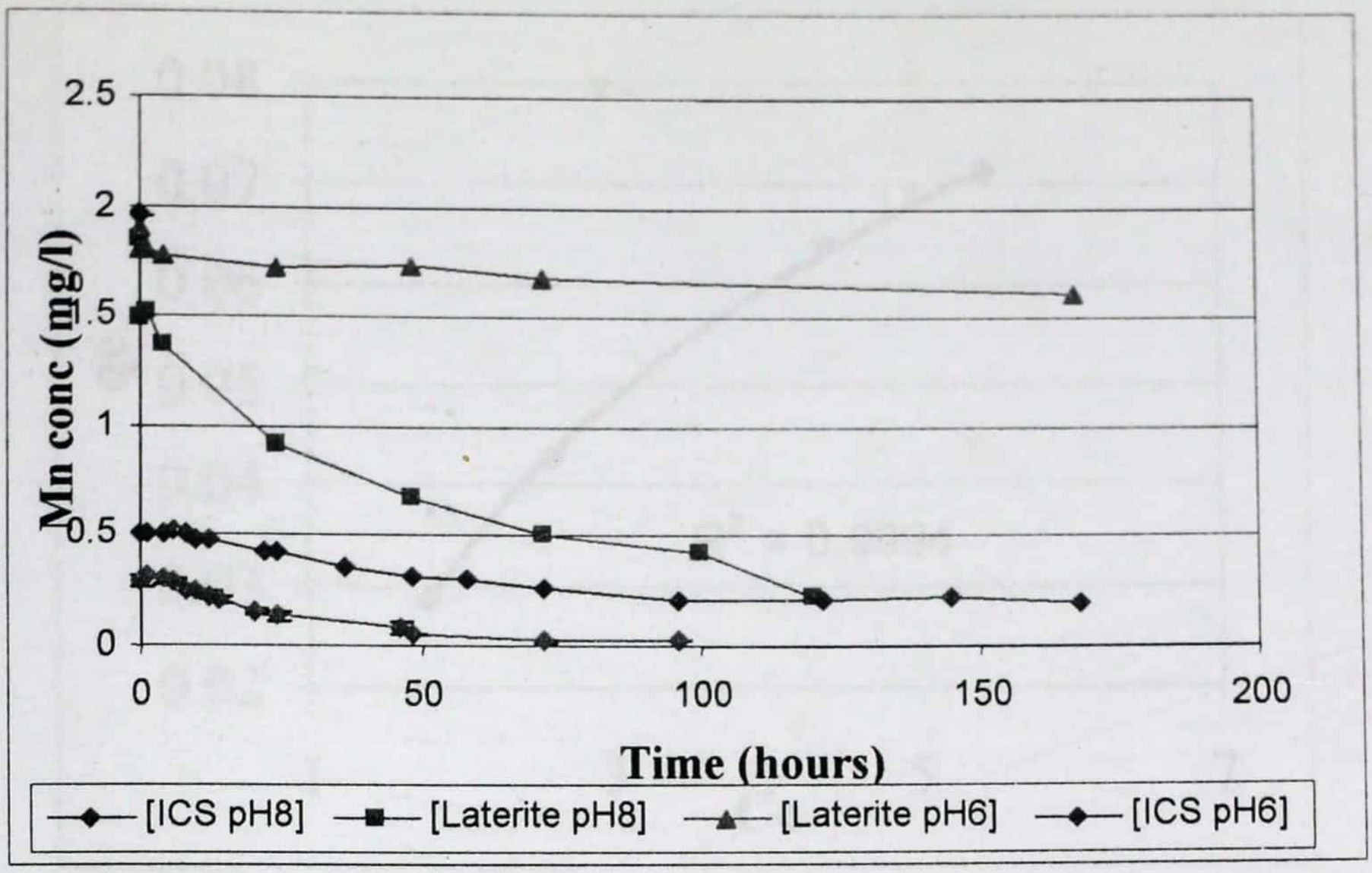


Figure 4-8 Comparison of ICS and laterite adsorption under aerobic conditions

4.3 Selection of most appropriate isotherm model

The graphs below show a plot of q_e vrs C_e for adsorption of Mn by laterite and ICS at pH 6 and 8. The plots were compared with the graphical representation of the isotherm models as discussed under section 2.3.4 of the literature review. The lines of best fit obtained in figures 4.9 and 4.10 shows that for adsorption of Mn at pH 6, the results obtained correspond to the Freundlich curve in figure 2.1(d). The lines of best fit obtained in figures 4.11 and 4.12 show that the results at pH 8 corresponds to the Freundlich curve in figure 2.1(c). The Freundlich isotherm was therefore selected as the most appropriate model to generate the isotherms.

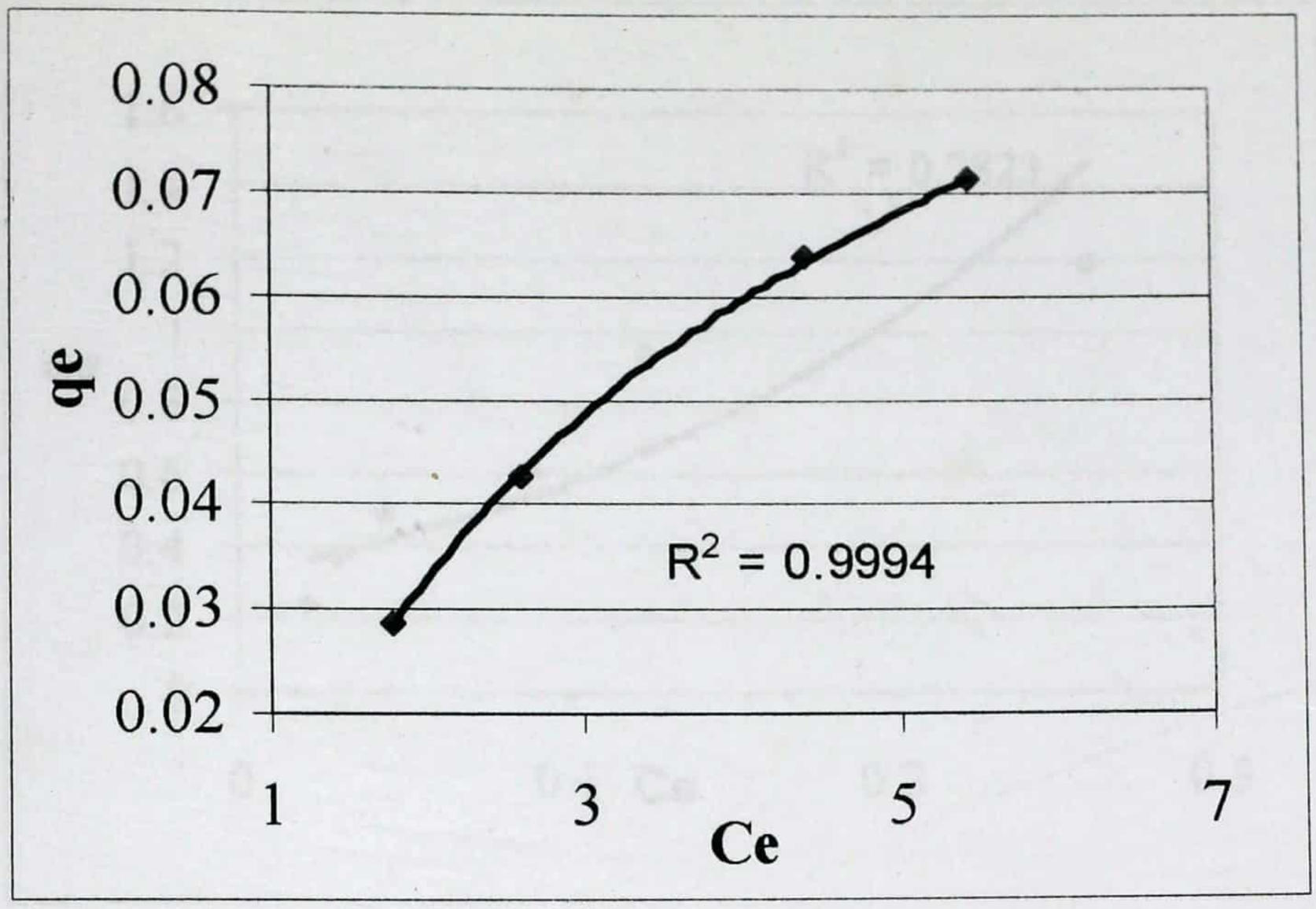


Figure 4-9 Line of best fit for ICS Isotherm results at pH 6

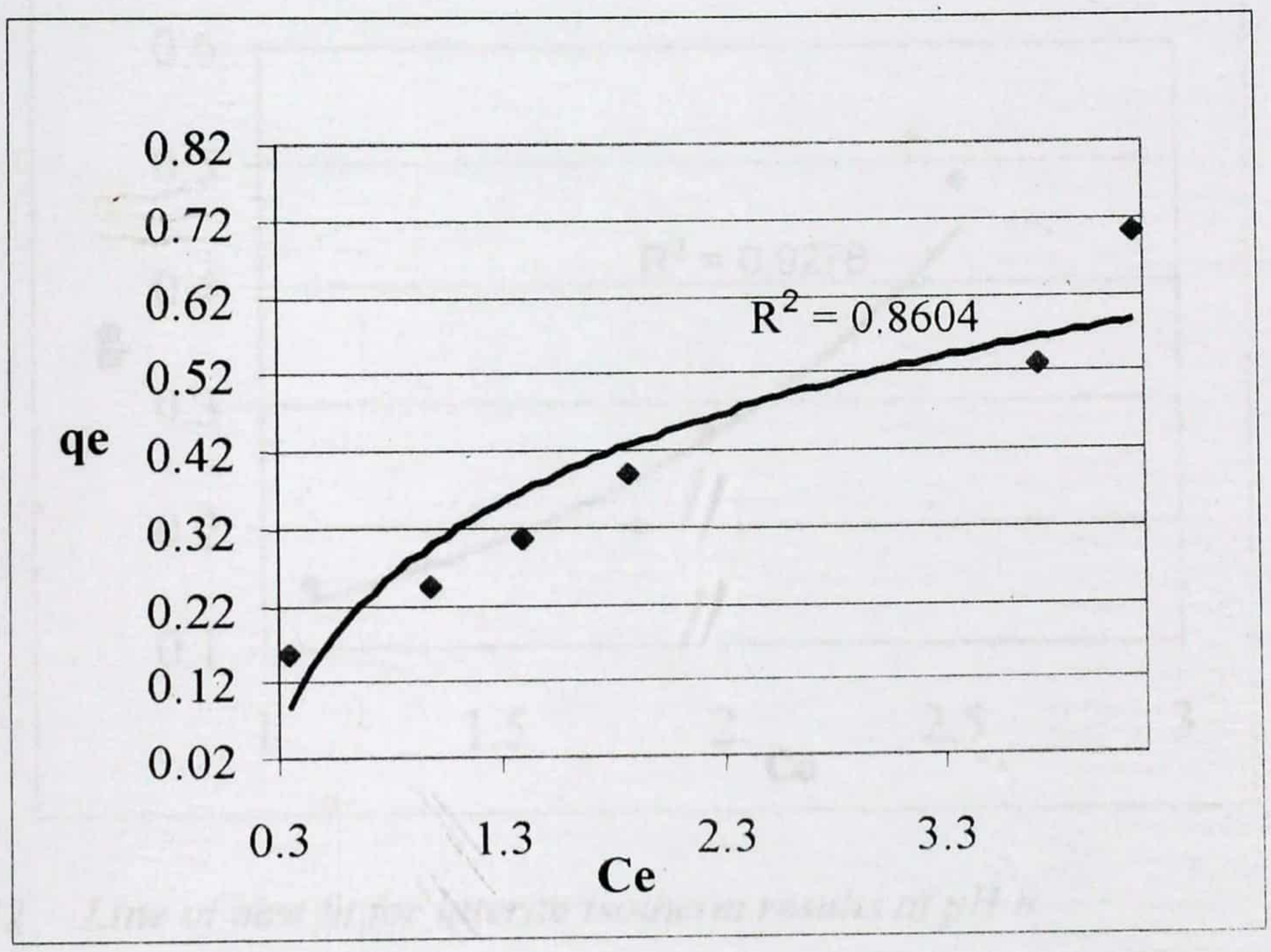


Figure 4-10 Line of best fit for laterite isotherm results at pH 6

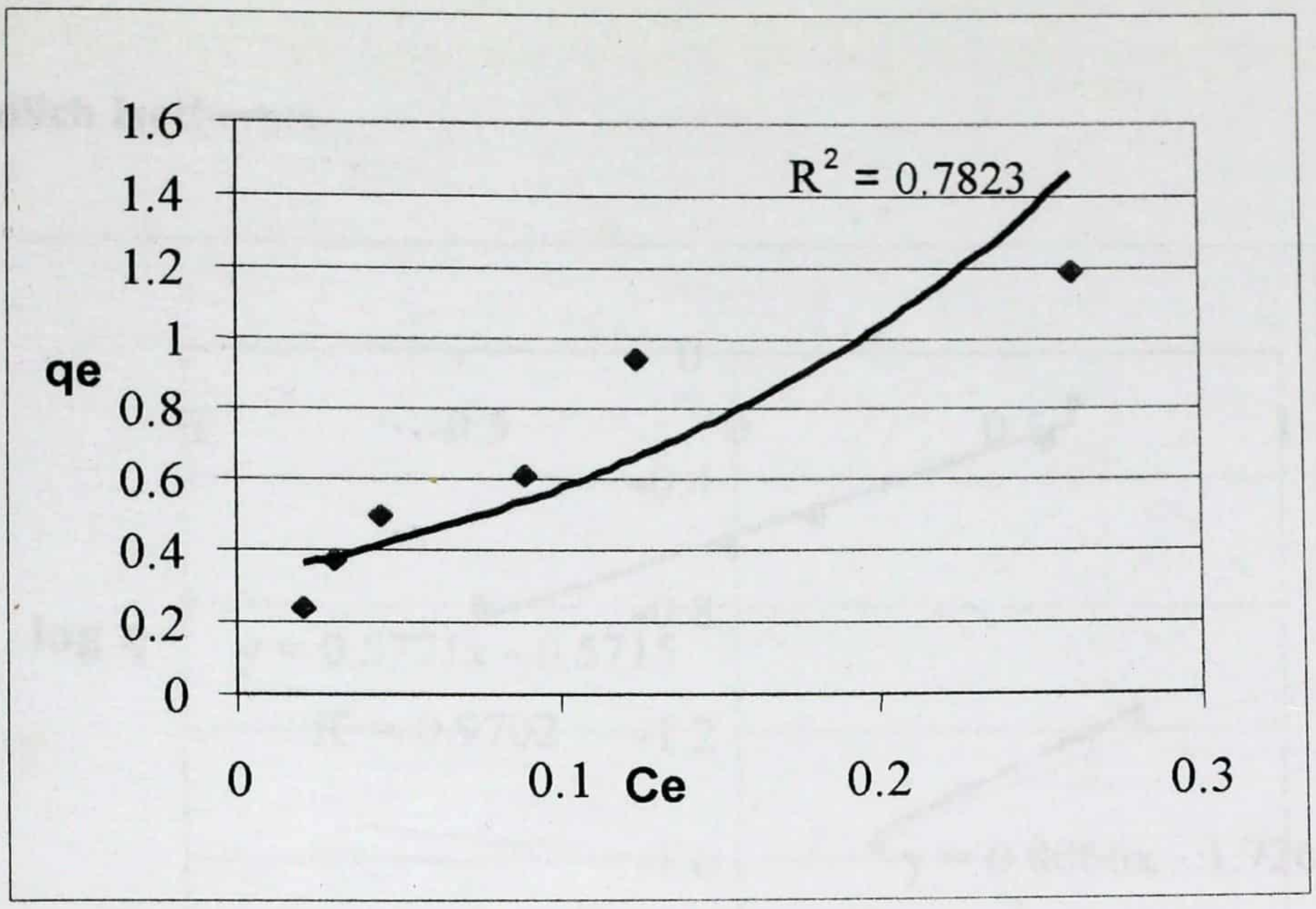


Figure 4-11 Line of best fit for ICS isotherm results at pH 8

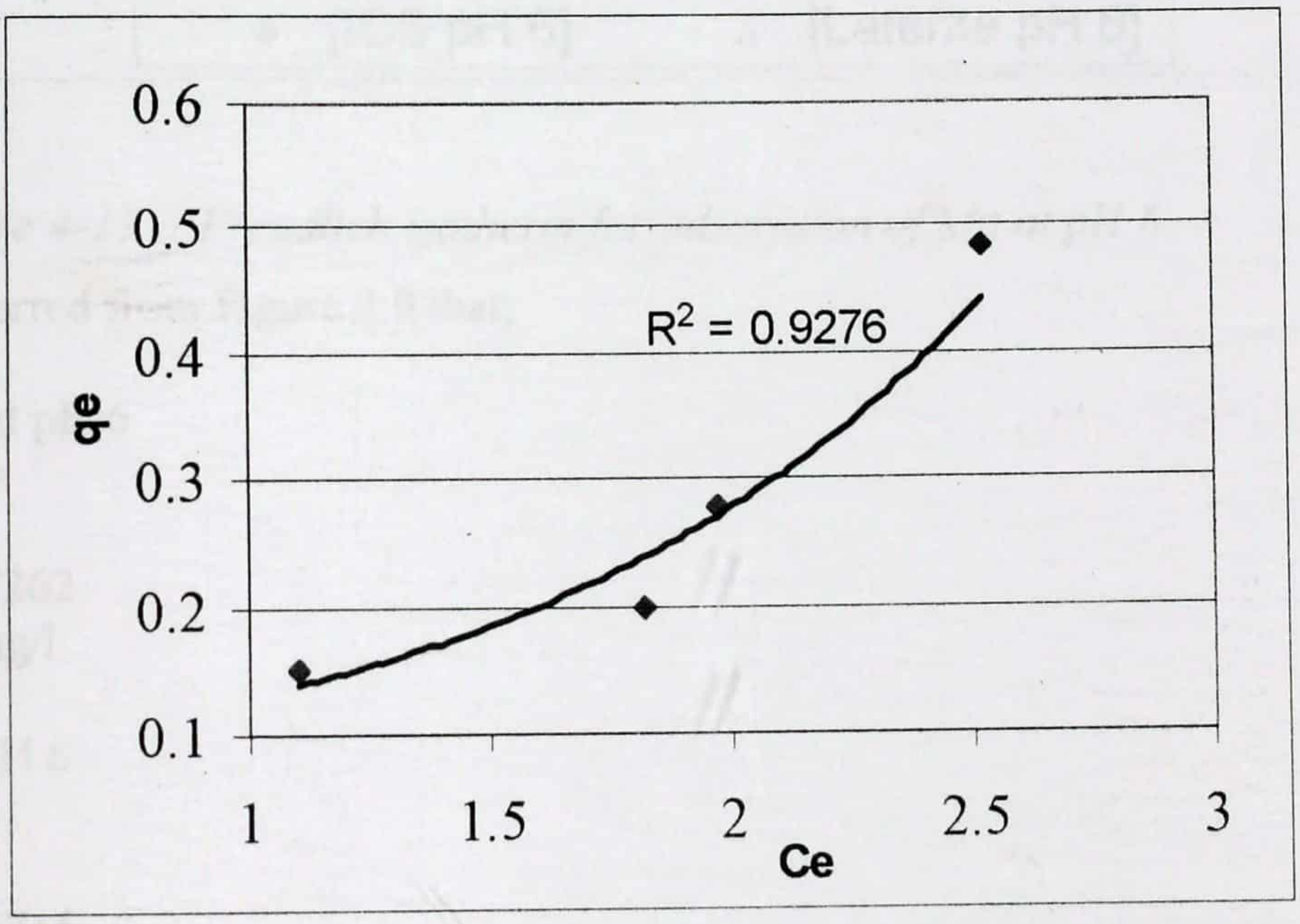


Figure 4-12 Line of best fit for laterite isotherm results at pH 8

4.4 Freudlich Isotherms

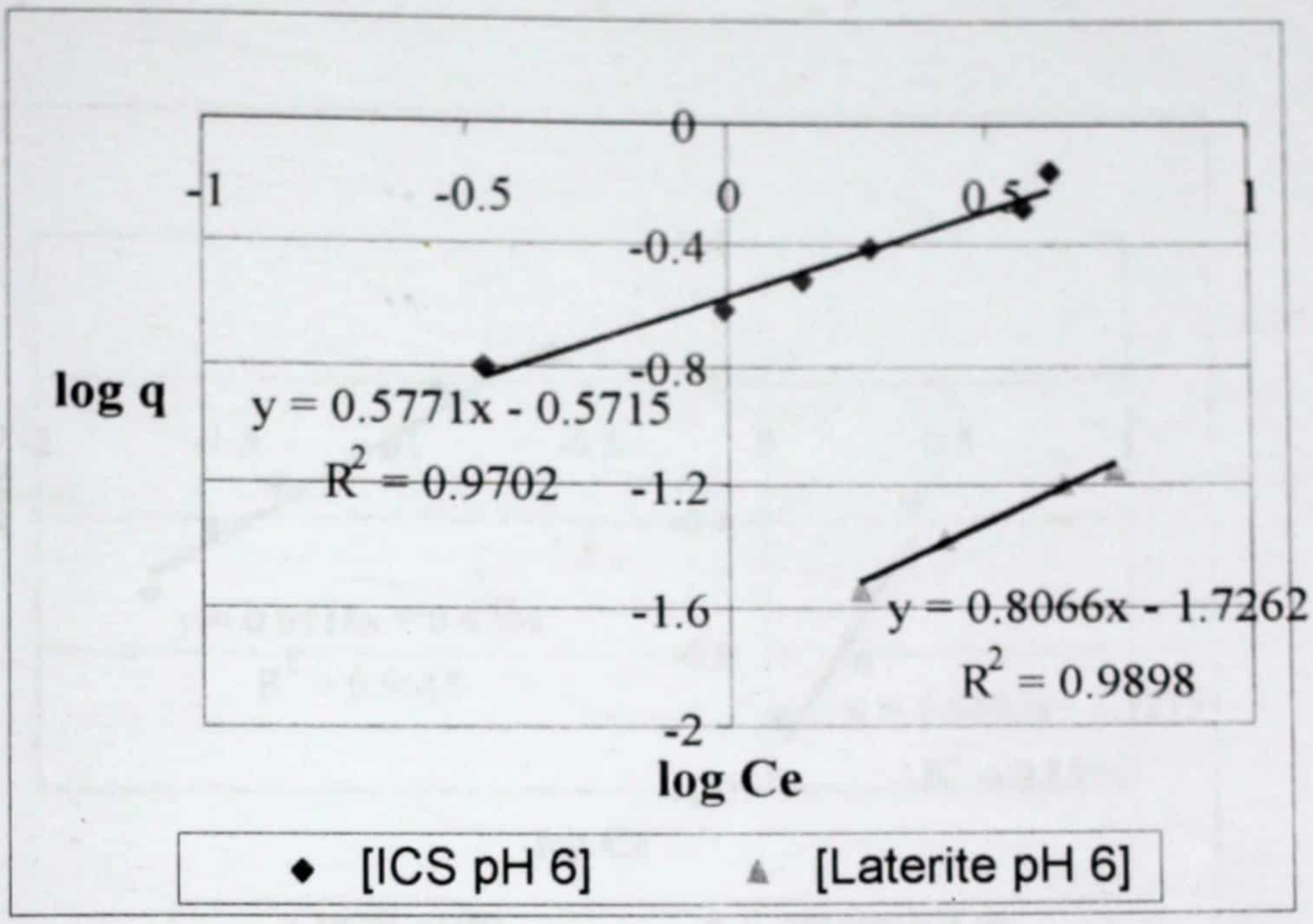


Figure 4-13 Freudlich isotherm for adsorption of Mn at pH 6

It can be inferred from Figure 4.9 that;

For laterite at pH 6
1/n = 0.8066
n = 1.239
Log k = -1.7262
k = 0.0188mg/l

For ICS at pH 6
1/n = 0.5771
n = 1.733
Log k = -0.5715
k = 0.2682

$\Rightarrow$ $n_{ICS} > n_{Lat}$
$k_{ICS} > k_{Lat}$

Iron Oxide Coated sand has higher adsorption capacity (k) and higher adsorption intensity (n) than laterite at pH 6. This could be attributed to the fact that, the ICS has higher iron and manganese oxide content in the coating than the laterite has in its

composition. The lower adsorption intensity for laterite also shows that during test runs, low turbulence should be applied since adsorbed solute will have higher tendency to desorb.

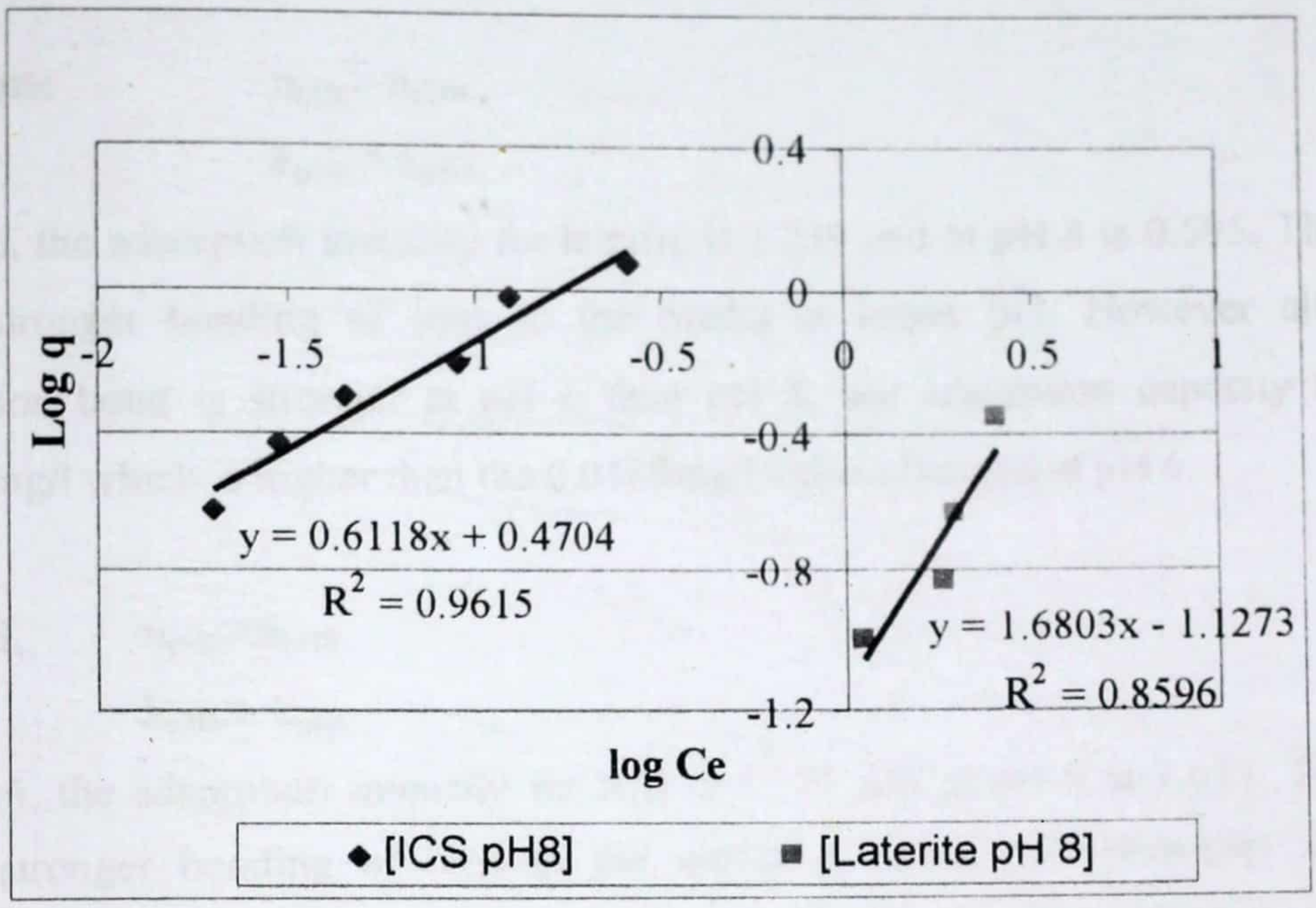


Figure 4-14 Freudlich isotherm for adsorption of Mn at pH 8

It can be inferred from Figure 4.10 that;

For laterite at pH 8
1/n = 1.6803
n = 0.595
Log k = -1.1273
k = 0.0746mg/l

For ICS at pH 8
1/n = 0.6118
n = 1.635
Log k = 0.4704
k = 2.954mg/l

$\Rightarrow \quad n_{ICS} > n_{Lat}$
$k_{ICS} > k_{Lat}$

Iron Oxide Coated sand has higher adsorption capacity and higher adsorption intensity than laterite at pH 8. This could be attributed to the fact that, the ICS has higher iron and manganese oxide content in the coating than the laterite has in its composition. The

lower adsorption intensity for laterite also shows that during test runs, low turbulence should be applied since adsorbed solute will have higher tendency to desorb.

For laterite $n_{pH6} > n_{pH8}$

$k_{pH8} > k_{pH6}$

At pH 6, the adsorption intensity for laterite is 1.239 and at pH 8 is 0.595. This shows a much stronger bonding of ions to the media at lower pH. However although the adsorption bond is stronger at pH 6 than pH 8, the adsorption capacity at pH 8 is 0.0746mg/l which is higher than the 0.0188mg/l value obtained at pH 6.

For ICS, $n_{pH6} > n_{pH8}$

$k_{pH8} > k_{pH6}$

At pH 6, the adsorption intensity for ICS is 1.733 and at pH 8 is 1.635. This shows a much stronger bonding of ions to the media at lower pH. However although the adsorption bond is stronger at pH 6 than pH 8, the adsorption capacity at pH 8 is 2.954mg/l which is much higher than the 0.2682 mg/l value obtained at pH 6.

4.5 Arsenic Adsorption

The figure below shows the trend for adsorption of As by laterite under aerobic conditions using different concentrations. The adsorption of As by laterite under aerobic conditions gave an average percentage removal of 93.48. Percentage removal increases with increase in initial manganese dosage. Laterite is a good material for adsorption of As under aerobic conditions. The adsorption does not reach an equilibrium value but continues until approximately zero. This is due to the formation of oxide and oxyhydroxide complexes in solution.

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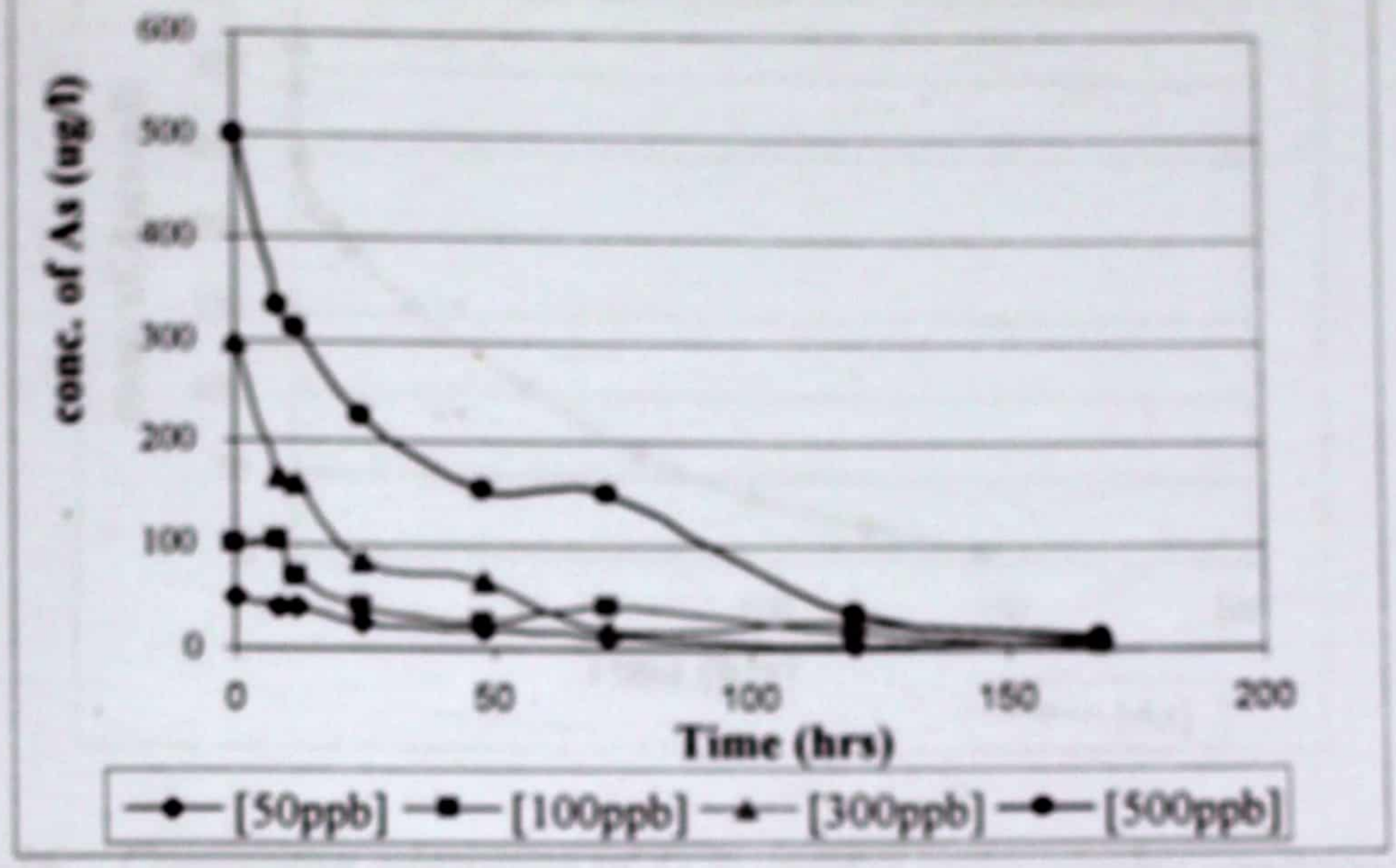


Figure 4-15 Aerobic adsorption of As by laterite

4.6 Competitive Adsorption

Raw ground water from Ford foundation hostel in Ayeduase Township was taken. The groundwater had the following quality with respect to the ions in question: [As] = 0 ug/l [Fe] = 0.13 mg/l and [Mn] = 0.06 mg/l.

4.6.1 Aerobic competitive adsorption of Mn, As and Fe using modified groundwater

The real groundwater samples dosed with 1mg/l Mn, 2mg/l Fe and different concentrations of As were tested with laterite and ICS under aerobic conditions. This was done in order to determine how the media will behave in the real situation and if the presence of one ion affected the adsorption of the other. The graphs below show the adsorptive trends for ICS and laterite under anaerobic conditions when all three ions are present in solution.

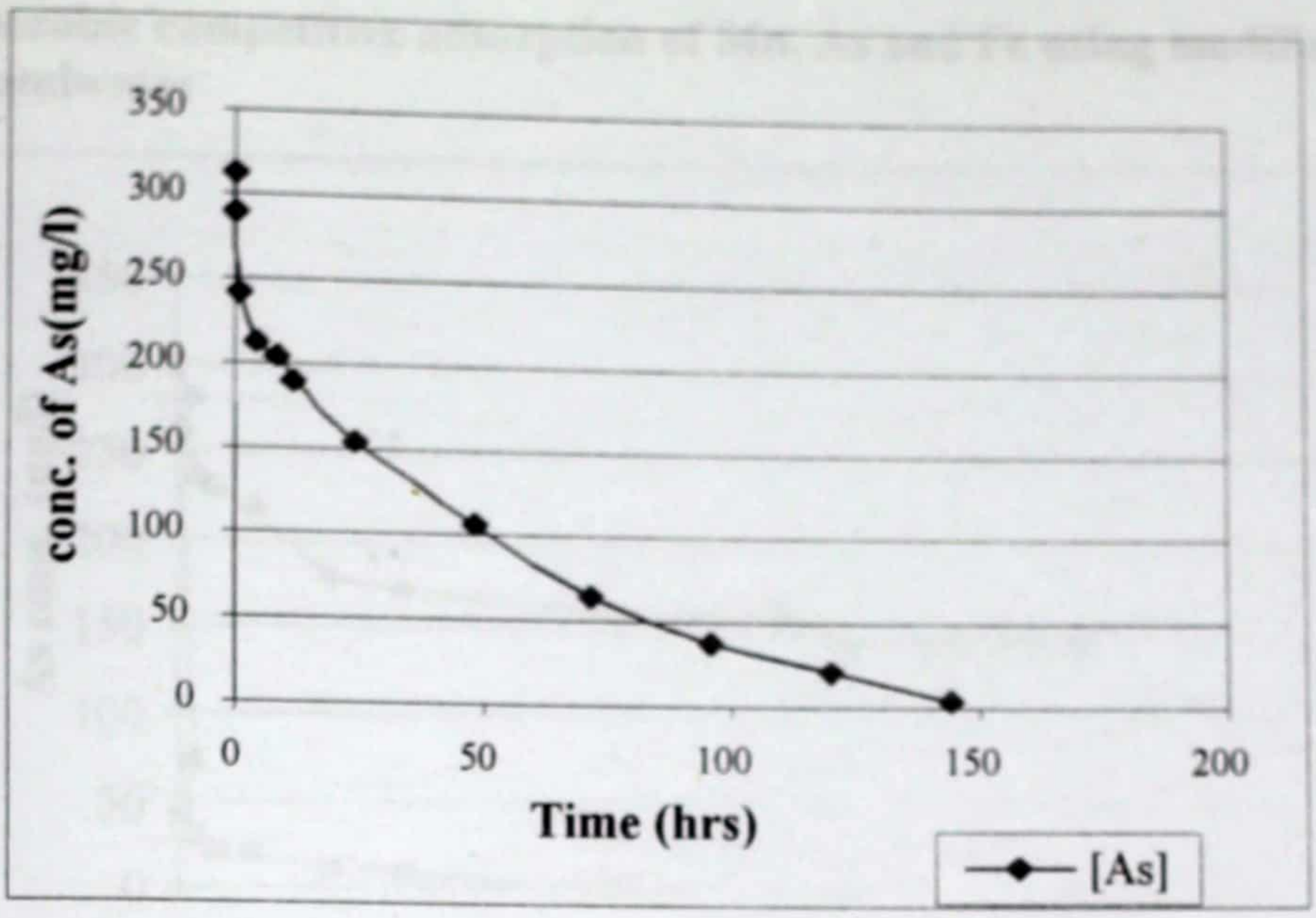


Figure 4-16 Competitive adsorption of As by laterite under aerobic conditions

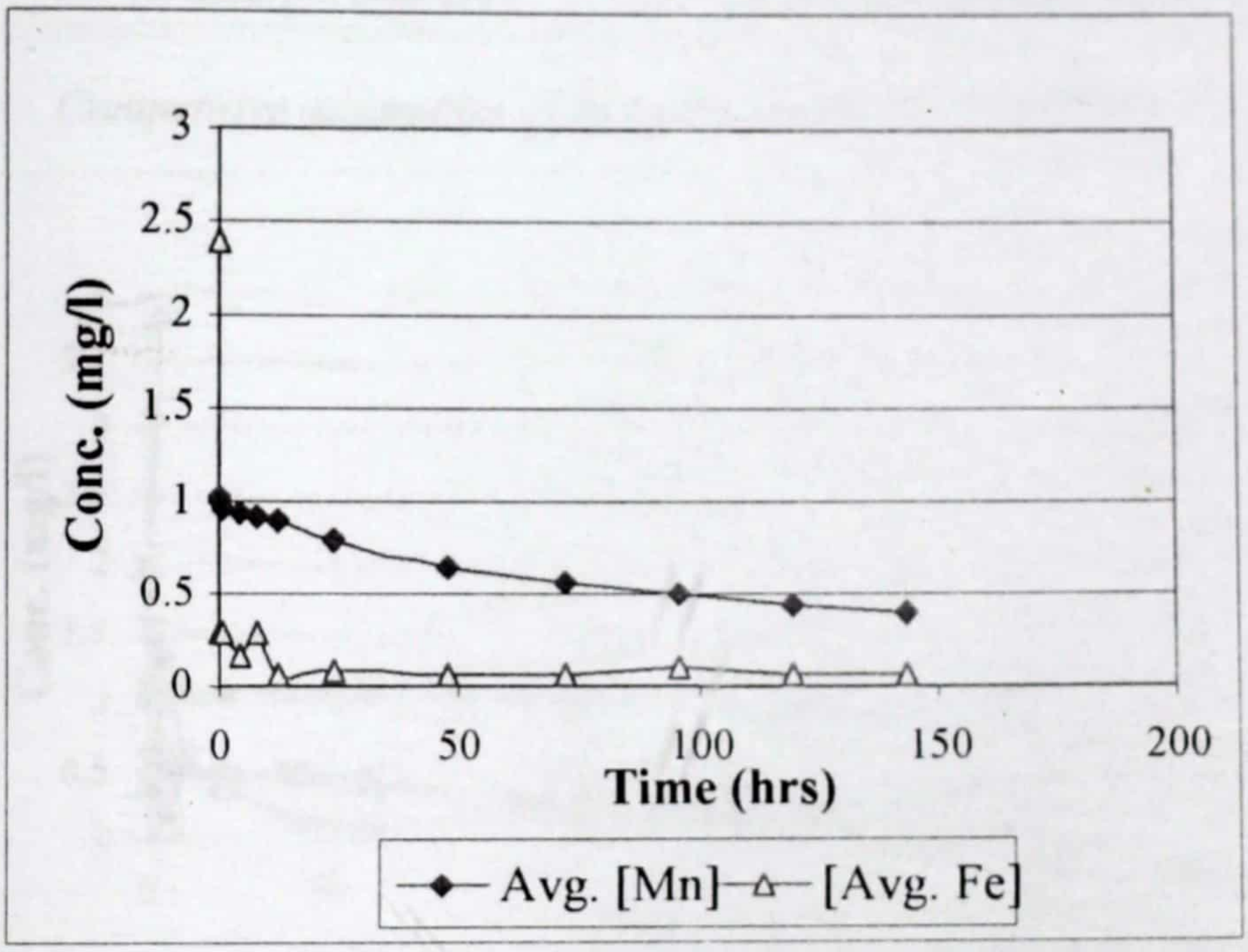


Figure 4-17 Competitive removal of Fe & Mn by laterite under aerobic conditions

From table A4, the average percentage removal achieved by laterite at pH 6 for removal of arsenic alone was 93.48. From table A6, in the presence of all three ions, the percentage removal decreases to 66.19. The presence of other ions in solution therefore reduces the adsorption capacity of the media for Arsenic.

4.6.2 Anaerobic competitive adsorption of Mn, As and Fe using modified groundwater

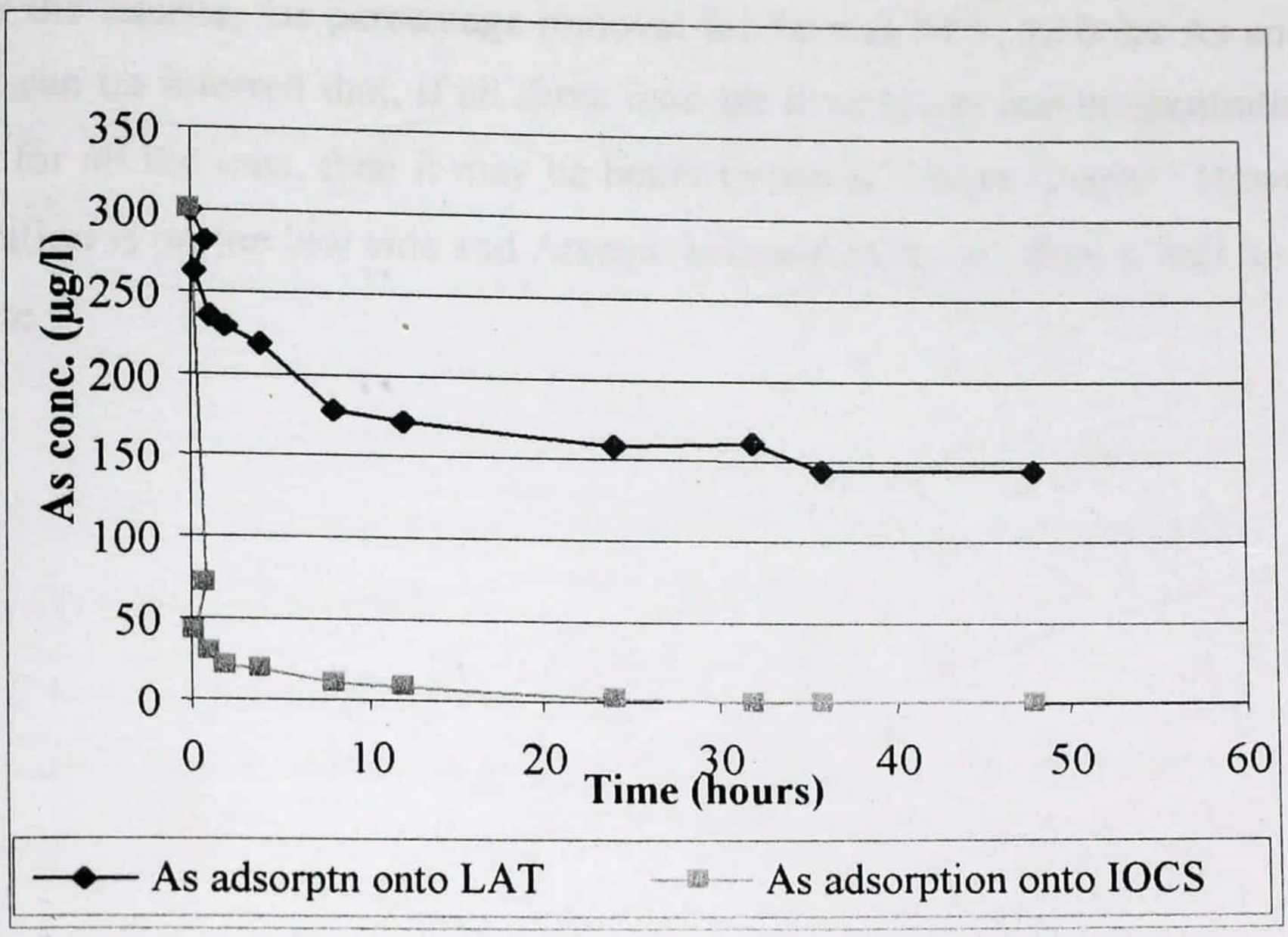


Figure 4-18 Competitive adsorption of As under anaerobic conditions

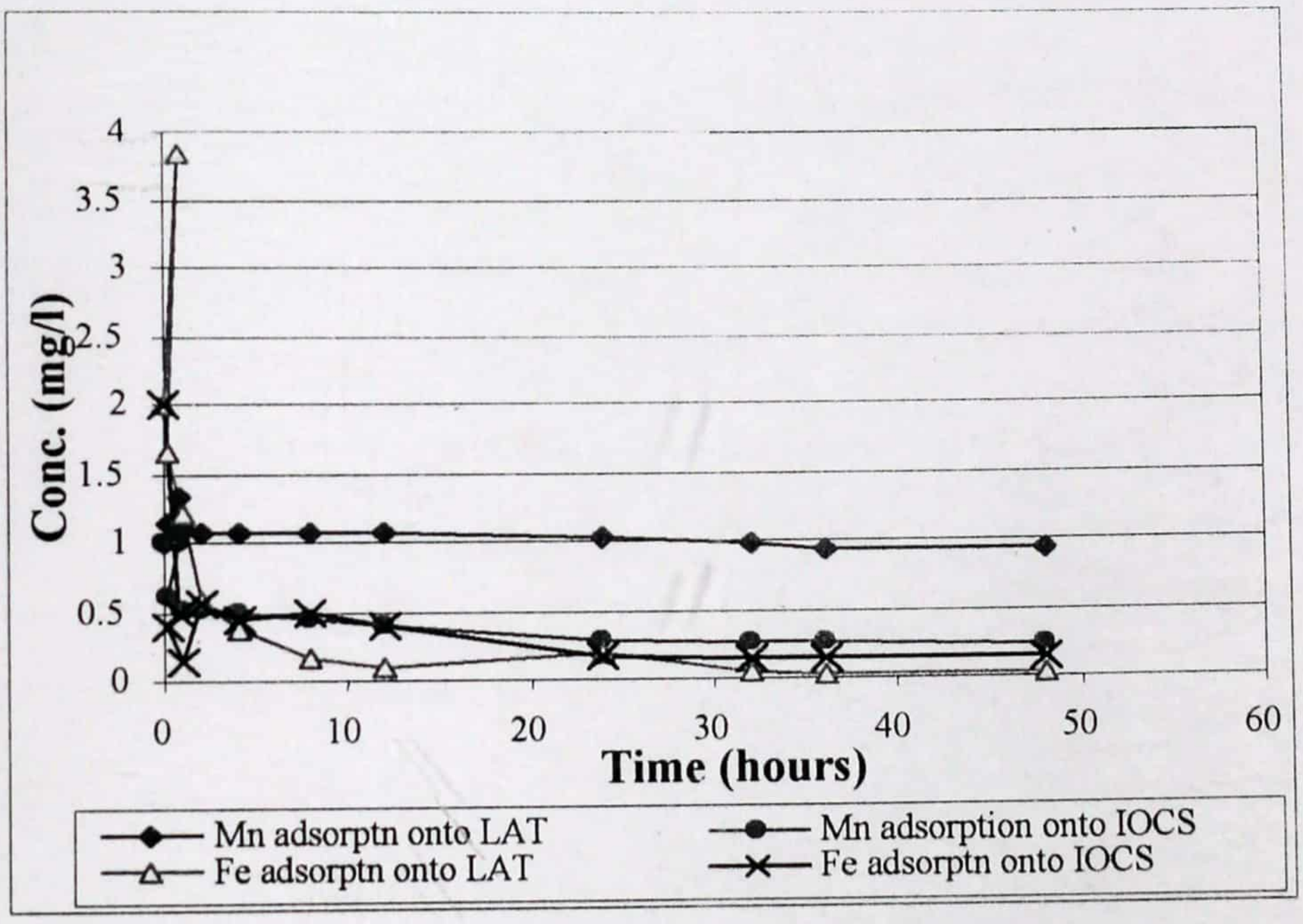


Figure 4-19 Competitive adsorption of Mn and Fe under anaerobic conditions

In the presence of all three ions, ICS showed highest percentage removal for As, followed by Fe and then Mn. However, laterite showed highest percentage removal for Fe, followed by As and then Mn. The percentage removals for ICS were satisfactorily high for all ions. From table B5 that for As was 100%, Fe was 92.5% and Mn was 76%.

However, for the laterite, the percentage removal for Fe was 98.5, 52.0 for As and 8 for Mn. Thus it can be inferred that, if all three ions are in solution and concentrations are equally high for all the ions, then it may be better to use ICS over laterite. However, if Mn concentration is on the low side and Arsenic is found in traces, then it will be safe to use the laterite.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- Both ICS and laterite exhibited appreciable adsorption capacities for Mn^{2+} and As in aqueous solutions under the given set conditions of the study.
- Adsorption under conditions of anaerobic and aerobic are comparable prior to the attainment of equilibrium by the anaerobic case. However the aerobic continues with the adsorption process slowly and consistently after the initial rapid adsorption. This trend of adsorption under aerobic conditions could be probably due to the fact that the adsorbed Mn^{2+} get oxidised to form manganese oxides and manganese oxyhydroxide complexes. These complexes form a new external coating round the media and facilitate further adsorption of Mn^{2+} ions.
- Adsorption data obtained under anaerobic conditions for both the ICS and laterite fitted the Freundlich Isotherm.
- At both pH 6 and 8, ICS has higher adsorption capacity and adsorption intensity as compared to laterite. Better adsorption trends were realised at higher pH for both ICS and laterite.
- Both media tested could be effective media for the design of a point of use filter system for removal of manganese and arsenic.
- In the presence of all three ions (Fe, Mn and As), similar adsorption trends are realised as in the case of the single ion. The laterite has highest affinity for Fe, then As and Mn while the ICS has highest affinity for As, then Fe and Mn.

5.2 Recommendations

- Arsenic adsorption by laterite under anaerobic conditions should be investigated and percentage removals compared to the aerobic case. Isotherms should be drawn from the data and adsorption intensity and capacity determined. The same should be done for ICS.
- The construction of the pilot plant should be completed and test runs carried out.
- The anaerobic batch experiments should be duplicated in order to confirm the results obtained.

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Appendix A *Water quality analysis of groundwater from Ayeduase*

Parameter	Unit	Value
Suspended Solids	mg/l	0.151
Total Dissolved Solids(TDS)	mg/l	728
Total Solids (TS)	mg/l	728.151
Conductivity	μ s/cm	1080
Hardness	mg/l	115
Alkalinity	mg/l	120
pH	-	6.42

Appendix B *Sample Calculations*

1. Preparation of 6N HCL

265ml of concentrated HCL was poured into a 500ml volumetric flask and diluted with distilled water to the 500ml mark.

Sample Calculation

$$\text{Given } V = \frac{100(N) \times M}{BPD}$$

Where V = volume of HCl to top to 1 litre

B = Basicity

D= specific gravity

M = Molar mass

N= normality

$$V = \frac{100(6) \times 36.5}{1x35x1.18} = 530.2663$$

$\therefore$ volume of HCl to top to 500ml = 530.26/2 = 265.13ml

2. Preparation of 1N NaOH

20g of NaOH was weighed and dissolved with distilled water to a volume of 500ml in a beaker.

Sample Calculation

Given n= m/M

Where n = no. of moles

m = mass in g

M = molar mass

Molar mass of NaOH = 40g

If 40g $\equiv$ 1 litre

500ml $\equiv$ 20g

3. Preparation of Mn stock solution

1000ppm Mn stock solution was prepared by dissolving 1mg of $MnSO_4.7H_2O$ to a litre in a volumetric flask.

Sample Calculation

1000ppm $\equiv$ 1000g in 1million ml

$$\therefore\ 1000\text{ml} \equiv \frac{1000}{1\text{mil}} \text{x}\, 1000\text{g} = 1\text{mg}$$

4. Preparation of Fe(II) sotck solution

0.25g of $Fe(II)SO_4.7H_2O$ was weighed and diluted to 100ml in a volumetric flask.

Sample Calculation

Molar mass ($Fe(II)SO_4.7H_2O$) = 279.02g

Atomic mass of Fe = 55.8g

$\Rightarrow$279.02g of $Fe(II)SO_4.7H_2O$ contains 55.8g of Fe(II).

For a stock solution of 500ppm in 100ml

500ppm = 0.5g/l

$\therefore$ 0.5g $\equiv$ 1litre

$\therefore$ 100ml $\equiv$ 0.05g of Fe(II)

$\therefore$ mass of $Fe(II)SO_4.7H_2O$ required

$$= \frac{279.02}{55.8} x\ 0.05 = 0.25\text{g of pure } Fe(II)SO_4.7H_2O$$

5. Preparation of As(III) stock solution

10ppm As(III) stock solution in 100ml was prepared by weighing 13.2mg of As2O3 and diluted with 0.1M HNO3.

Sample Calculation

Preparation of 10ppm $\equiv$ 10mg/l As_2O_3

100ml volume using HNO_3 (0.1M)

Stock salt $\rightarrow$ As_2O_3

Mwt. $\rightarrow$ 197.84g

%purity $\rightarrow$ 99.5%

Atomic mass (AsIII) = 74.92

$\Rightarrow$ 1 molecule $\equiv$ 2 atoms As(III)

197.84g contains 2(74.92)g of As(III)

97.84g $\equiv$ 149.84g As(III)

For 10mg of AsIIII)

$$\Rightarrow \frac{10}{149.84} \text{x}\, 197.84 = 13.203417$$

So 13.203417mg of pure salt contains 10mg of As(III)

However salt provided is 99.5% pure

$\therefore (\frac{100}{99.5} X 13.203417)$ salt of As(III) contains 10mg As(III)

$= 13.269766$mg of As_2O_3 needed

6. *Volume of stock*

i. For concentration of 2ppm in 500ml

$C_1V_1 = -C_2V_2$

$1000(V1) = (2x500)$

$V_1 = 1$ml

1ml of distilled water was siphoned and the same volume of stock solution was added to the solution.

Concentration Required (mg/l)	Volume of stock added (ml)
2	1
3	1.5
4	2
5	2.5
6	3

ii. For concentration of 30ppb in 500ml

$C_1V_1 = -C_2V_2$

$(10,000)V_1 = 30x500$

$= 1.5$ml

1.5ml of distilled water was siphoned and the same volume of 10,000ppb As stock solution added.

Concentration Required (ug/l)	Volume of stock to added(ml)
30	1.5
50	2.5
100	5
300	15
500	25

7. Adsorption capacity

Sample Calculation for adsorption of 2mg/l Mn by ICS at pH 6

From Table C4

C_0 = 1.585mg/l

Ce = 0.34mg/l

X = C_0-Ce

= 1.585-0.34

= 1.245mg/l

But volume of liquid used = 1.5l

$\therefore$ x = 1.245X 1.5 = 1.8675mg

m = 12g

q = x/m

= 1.8675/12

= 0.155625mg/g

From Figure 4.12

Isotherm equation $\equiv$ y =0.5771x-0.5715

Freudlich equation $\equiv$ log q = 1/nlogCe + log k

$\Rightarrow$ 1/n = 0.5771

Log k =- 0.5715

k = $\log^{-1}(-0.5715)$

= 0.2682

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Appendix C Percentage Removals

Table B 1 Aerobic percentage removal of Mn at pH 6 & 8

	pH 6		pH 8	
Average % removal	ICS	LAT	ICS	LAT
	87.50	10.73	98.84	81.34

Table B 2 Anaerobic percentage removal of Mn at pH 8

Anaerobic adsorption of Mn at pH 8		
Concentration (mg/l)	**%Mn removal (ICS)**	**%Mn removal (Lat)**
2	98.95	41.58
3	99.00	39.33
4	99.00	48.42
5	97.59	62.00
average	98.64	47.83

Table B 3 Anaerobic percentage removal of Mn at pH 6

Anaerobic adsorption of Mn at pH 6		
Concentration (mg/l)	**%Mn removal (ICS)**	**%Mn removal (Lat)**
2	83.00	11.50
3	67.00	11.56
4	65.00	5.58
5	62.40	9.15
average	69.35	9.45

Table B 4 *Aerobic percentage removal of As at pH 6*

Aerobic percentage removal of As at pH 6	
Concentration (ug/l)	**%As removal**
50	83.90
100	96.50
300	96.30
500	97.20
average	93.48

Table B 5 *Real groundwater sample under anaerobic conditions at pH 6*

Adsorbate	% removal (ICS)	% removal (Lat)
Fe	92.5	98.5
Mn	76.0	8.0
As	100.0	52.0

Table B 6 *Real groundwater sample under aerobic conditions at pH 6*

Adsorbate	% removal (Lat)
Fe	97.08
Mn	35.92
As	66.19

Appendix D Adsorption Results

Anaerobic batch reactor experiments at pH 6 for laterite

Table C 1 Anaerobic adsorption of 2mg/l Mn by laterite at pH 6

Adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	2	12	0	0.000	0.00
	0.25	1.87	12	0.13	0.016	6.50
	1	1.82	12	0.18	0.023	9.00
	2	1.83	12	0.17	0.021	8.50
	4	1.82	12	0.18	0.023	9.00
	8	1.79	12	0.21	0.026	10.50
	12	1.78	12	0.22	0.028	11.00
	20	1.78	12	0.22	0.028	11.00
	24	1.77	12	0.23	0.029	11.50
	32	1.77	12	0.23	0.029	11.50
	36	1.77	12	0.23	0.029	11.50

Table C 2 Anaerobic adsorption of 3mg/l Mn by laterite at pH 6

Adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	2.94	12	0	0.000	0.00
	0.083	2.74	12	0.2	0.025	6.80
	0.25	2.7	12	0.24	0.030	8.16
	1	2.72	12	0.22	0.028	7.48
	2	2.74	12	0.2	0.025	6.80
	4	2.66	12	0.28	0.035	9.52
	8	2.68	12	0.26	0.033	8.84
	12	2.68	12	0.26	0.033	8.84
	20	2.6	12	0.34	0.043	11.56
	24	2.6	12	0.34	0.043	11.56
	32	2.62	12	0.32	0.040	10.88
	36	2.6	12	0.34	0.043	11.56

Table C 3 Anaerobic adsorption of 4mg/l Mn by laterite at pH 6

Adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	3.94	12	0	0.00	0.00
	0.083	3.9	12	0.04	0.005	1.02
	0.25	3.8	12	0.14	0.018	3.55
	1	3.8	12	0.14	0.018	3.55
	2	3.8	12	0.14	0.018	3.55
	4	3.74	12	0.2	0.025	5.08
	8	3.8	12	0.14	0.018	3.55
	12	3.76	12	0.18	0.023	4.57
	20	3.72	12	0.22	0.028	5.58
	24	3.72	12	0.22	0.028	5.58
	32	3.72	12	0.22	0.028	5.58
	36	3.72	12	0.22	0.028	5.58

Table C 4 Anaerobic adsorption of 5mg/l Mn by laterite at pH 6

Adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	4.92	12	0	0.000	0.00
	0.083	4.71	12	0.21	0.026	4.27
	0.25	4.53	12	0.39	0.049	7.93
	1	4.41	12	0.51	0.064	10.37
	2	4.56	12	0.36	0.045	7.32
	4	4.44	12	0.48	0.060	9.76
	8	4.44	12	0.48	0.060	9.76
	12	4.47	12	0.45	0.056	9.15
	20	4.5	12	0.42	0.053	8.54
	24	4.47	12	0.45	0.056	9.15
	32	4.46	12	0.46	0.058	9.35
	36	4.44	12	0.48	0.060	9.76

Table C 5 Anaerobic adsorption of 6mg/l Mn by laterite at pH 6

Adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	6.03	12	0	0.000	0.00
	0.083	5.76	12	0.27	0.034	4.48
	0.25	5.67	12	0.36	0.045	5.97
	1	5.67	12	0.36	0.045	5.97
	2	5.7	12	0.33	0.041	5.47
	4	5.64	12	0.39	0.049	6.47
	8	5.58	12	0.45	0.056	7.46
	12	5.64	12	0.39	0.049	6.47
	20	5.58	12	0.45	0.056	7.46
	24	5.46	12	0.57	0.071	9.45
	32	5.46	12	0.57	0.071	9.45
	36	5.46	12	0.57	0.071	9.45

Anaerobic batch reactor experiments at pH 8 for laterite

Table C 6 Anaerobic adsorption of 2mg/l Mn by laterite at pH 8

Adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	1.9	12	0	0.000	0.00
	0.083	1.66	12	0.24	0.030	12.63
	0.25	1.55	12	0.35	0.044	18.42
	1	1.45	12	0.45	0.056	23.68
	2	1.41	12	0.49	0.061	25.79
	4	1.31	12	0.59	0.074	31.05
	8	1.29	12	0.61	0.076	32.11
	12	1.27	12	0.63	0.079	33.16
	20	1.16	12	0.74	0.093	38.95
	24	1.11	12	0.79	0.099	41.58
	32	1.1	12	0.8	0.100	42.11
	36	1.1	12	0.8 .	0.100	42.11

Table C 7 Anaerobic adsorption of 3mg/l Mn by laterite at pH 8

Adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	3	12	0	0.000	0.00
	0.083	2.54	12	0.46	0.058	15.33
	0.25	2.42	12	0.58	0.073	19.33
	1	2.46	12	0.54	0.068	18.00
	2	2.32	12	0.68	0.085	22.67
	4	2.32	12	0.68	0.085	22.67
	8	1.94	12	1.06	0.133	35.33
	12	1.98	12	1.02	0.128	34.00
	20	1.82	12	1.18	0.148	39.33
	24	1.82	12	1.18	0.148	39.33
	32	1.84	12	1.16	0.145	38.67
	36	1.82	12	1.18	0.148	39.33

Table C 8 Anaerobic adsorption of 4mg/l Mn by laterite at pH 8

Adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	3.8	12	0	0.000	0.00
	0.083	3.2	12	0.6	0.075	15.79
	0.25	3	12	0.8	0.100	21.05
	1	2.74	12	1.06	0.133	27.89
	2	2.64	12	1.16	0.145	30.53
	4	2.34	12	1.46	0.183	38.42
	8	1.96	12	1.84	0.230	48.42
	12	2.72	12	1.08	0.135	28.42
	20	2.24	12	1.56	0.195	41.05
	24	1.96	12	1.84	0.230	48.42
	32	1.98	12	1.82	0.228	47.89
	36	1.96	12	1.84	0.230	48.42

Table C 9 Anaerobic adsorption of 5mg/l Mn by laterite at pH 8

Adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	4.5	12	0	0.000	0.00
	0.083	3.87	12	0.63	0.079	14.00
	0.25	3.42	12	1.08	0.135	24.00
	1	2.85	12	1.65	0.206	36.67
	2	2.7	12	1.8	0.225	40.00
	4	2.49	12	2.01	0.251	44.67
	8	2.01	12	2.49	0.311	55.33
	12	1.68	12	2.82	0.353	62.67
	20	1.71	12	2.79	0.349	62.00
	24	1.71	12	2.79	0.349	62.00
	32	1.68	12	2.82	0.353	62.67
	36	1.68	12	2.82	0.353	62.67

Table C 10 Anaerobic adsorption of 6mg/l Mn by laterite at pH 8

Adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	6	12	0	0.000	0.00
	0.083	5.04	12	0.96	0.120	16.00
	0.25	4.8	12	1.2	0.150	20.00
	1	4.02	12	1.98	0.248	33.00
	2	4.08	12	1.92	0.240	32.00
	4	3.54	12	2.46	0.308	41.00
	8	3.3	12	2.7	0.338	45.00
	12	3.24	12	2.76	0.345	46.00
	20	3.03	12	2.97	0.371	49.50
	24	2.52	12	3.48	0.435	58.00
	32	2.52	12	3.48	0.435	58.00
	36	1.68	12	4.32	0.540	72.00

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Aerobic batch reactor experiments at pH 6 for laterite

Table C 11 Aerobic adsorption of 2mg/l Mn by laterite at pH 6

Aerobic adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	1.97	12	0	0.000	0.00
	0.25	1.76	12	0.21	0.026	10.66
	1	1.75	12	0.22	0.028	11.17
	4	1.75	12	0.22	0.028	11.17
	24	1.72	12	0.25	0.031	12.69
	48	1.70	12	0.27	0.034	13.71
	72	1.63	12	0.34	0.043	17.26
	167	1.52	12	0.45	0.056	22.84

Table C 12 Aerobic adsorption of 3mg/l Mn by laterite at pH 6

Aerobic adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	2.83	12	0	0.000	0.00
	0.25	2.7	12	0.13	0.016	4.59
	1	2.7	12	0.13	0.016	4.59
	4	2.7	12	0.13	0.016	4.59
	24	2.58	12	0.25	0.031	8.83
	48	2.6	12	0.23	0.029	8.13
	72	2.55	12	0.28	0.035	9.89
	100	0.24	12	2.59	0.324	91.52
	120	0.33	12	2.5	0.313	88.34

Table C 13 Aerobic adsorption of 4mg/l Mn by laterite at pH 6

Aerobic adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	3.8	12	0	0.000	0.00
	0.25	3.59	12	0.21	0.026	5.53
	1	3.58	12	0.22	0.028	5.79
	4	3.58	12	0.22	0.028	5.79
	24	3.5	12	0.3	0.038	7.89
	48	3.48	12	0.32	0.040	8.42
	72	3.5	12	0.3	0.038	7.89

Table C 14 Aerobic adsorption of 5mg/l Mn by laterite at pH 6

Aerobic adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	4.735	12	0.000	0.000	0.00
	0.25	4.545	12	0.190	0.024	4.01
	1	4.59	12	0.145	0.018	3.06
	4	4.62	12	0.115	0.014	2.43
	24	4.41	12	0.325	0.041	6.86
	48	4.365	12	0.370	0.046	7.81
	72	4.29	12	0.445	0.056	9.40
	100	1.83	12	2.905	0.363	61.35
	120	1.47	12	3.265	0.408	68.95
	145	0.44	12	4.295	0.537	90.71

Table C 15 Aerobic adsorption of 6mg/l Mn by laterite at pH 6

Aerobic adsorption of Mn by pulverized laterite at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	5.7	12	0.000	0.000	0.00
	0.25	5.45	12	0.250	0.031	4.39
	1	5.43	12	0.270	0.034	4.74
	4	5.415	12	0.285	0.036	5.00
	24	5.325	12	0.375	0.047	6.58
	48	5.19	12	0.510	0.064	8.95
	72	5.175	12	0.525	0.066	9.21
	100	2.49	12	3.210	0.401	56.32
	120	0.87	12	4.830	0.604	84.74
	145	0.48	12	5.220	0.653	91.58

Aerobic batch reactor experiments at pH 8 for laterite

Table C 16 Aerobic adsorption of 2mg/l Mn by laterite at pH 8

Aerobic adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	1.85	12	0.00	0.000	0.00
	0.25	1.495	12	0.36	0.044	19.19
	1	1.515	12	0.34	0.042	18.11
	4	1.365	12	0.49	0.061	26.22
	24	0.92	12	0.93	0.116	50.27
	48	0.67	12	1.18	0.148	63.78
	72	0.50	12	1.35	0.169	72.97
	100	0.42	12	1.43	0.179	77.30
	120	0.22	12	1.64	0.204	88.38

Table C 17 Aerobic adsorption of 3mg/l Mn by laterite at pH 8

Aerobic adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	2.93	12	0.00	0.000	0.00
	0.25	2.24	12	0.69	0.086	23.55
	1	2.22	12	0.71	0.089	24.23
	4	2.07	12	0.86	0.108	29.35
	12	1.69	12	1.24	0.155	42.32
	24	1.35	12	1.58	0.198	53.92
	48	0.9	12	2.03	0.254	69.28
	72	0.62	12	2.31	0.289	78.84
	100	0.31	12	2.62	0.328	89.42
	120	0.34	12	2.60	0.324	88.57

Table C 18 Aerobic adsorption of 4mg/l Mn by laterite at pH 8

Aerobic adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	3.82	12	0.00	0.000	0.00
	0.25	2.96	12	0.86	0.108	22.51
	1	2.94	12	0.88	0.110	23.04
	4	2.76	12	1.06	0.133	27.75
	24	1.68	12	2.14	0.268	56.02
	48	1.26	12	2.56	0.320	67.02
	72	1.02	12	2.80	0.350	73.30
	100	0.81	12	3.01	0.376	78.80

Table C 19 Aerobic adsorption of 5mg/l Mn by laterite at pH 8

Aerobic adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	4.81	12	0.00	0.000	0.00
	0.25	4.02	12	0.79	0.099	16.42
	1	4.02	12	0.79	0.099	16.42
	4	3.76	12	1.05	0.131	21.83
	12	3.26	12	1.55	0.194	32.22
	24	2.76	12	2.05	0.256	42.62
	48	2.34	12	2.47	0.309	51.35
	72	2.03	12	2.78	0.348	57.80
	100	1.48	12	3.33	0.416	69.23
	120	1.44	12	3.37	0.421	70.06

Table C 20 Aerobic adsorption of 6mg/l Mn by laterite at pH 8

Aerobic adsorption of Mn by pulverized laterite at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized Laterite	0	5.9	12	0.00	0.000	0.00
	0.25	5.09	12	0.81	0.101	13.73
	1	5.03	12	0.87	0.109	14.75
	4	4.71	12	1.19	0.149	20.17
	12	4.08	12	1.82	0.228	30.85
	24	3.59	12	2.31	0.289	39.15
	48	2.84	12	3.06	0.383	51.86
	72	2.68	12	3.22	0.403	54.58
	100	2.72	12	3.18	0.398	53.90

Anaerobic batch reactor experiments at pH 8 for ICS

Table C 21 Anaerobic adsorption of 2mg/l Mn by ICS at pH 8

Anaerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	1.91	12	0.000	0.000	0.00
	0.083	0.115	12	1.795	0.224	93.98
	0.25	0.06	12	1.850	0.231	96.86
	1	0.03	12	1.880	0.235	98.43
	2	0.035	12	1.875	0.234	98.17
	4	0.035	12	1.875	0.234	98.17
	6	0.03	12	1.880	0.235	98.43
	8	0.03	12	1.880	0.235	98.43
	10	0.03	12	1.880	0.235	98.43
	12	0.025	12	1.885	0.236	98.69
	14	0.025	12	1.885	0.236	98.69
	20	0.02	12	1.890	0.236	98.95
	22	0.02	12	1.890	0.236	98.95
	24	0.02	12	1.890	0.236	98.95

Table C 22 Anaerobic adsorption of 3mg/l Mn by ICS at pH 8

Anaerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	3	12	0.000	0.000	0.00
	0.083	0.235	12	2.765	0.346	92.17
	0.25	0.175	12	2.825	0.353	94.17
	1	0.065	12	2.935	0.367	97.83
	2	0.045	12	2.955	0.369	98.50
	4	0.04	12	2.960	0.370	98.67
	6	0.03	12	2.970	0.371	99.00
	8	0.04	12	2.960	0.370	98.67
	10	0.04	12	2.960	0.370	98.67
	12	0.045	12	2.955	0.369	98.50
	14	0.03	12	2.970	0.371	99.00
	20	0.04	12	2.960	0.370	98.67
	22	0.05	12	2.950	0.369	98.33
	24	0.03	12	2.970	0.371	99.00
	26	0.03	12	2.970	0.371	99.00
	28	0.03	12	2.970	0.371	99.00

Table C 23 Anaerobic adsorption of 4mg/l Mn by ICS at pH 8

Anaerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	4	12	0.000	0.000	0.00
	0.083	0.61	12	3.390	0.424	84.75
	0.25	0.62	12	3.380	0.423	84.50
	1	0.12	12	3.880	0.485	97.00
	2	0.07	12	3.930	0.491	98.25
	4	0.07	12	3.930	0.491	98.25
	6	0.04	12	3.960	0.495	99.00
	8	0.05	12	3.950	0.494	98.75
	10	0.08	12	3.920	0.490	98.00
	12	0.105	12	3.895	0.487	97.38
	14	0.1	12	3.900	0.488	97.50
	20	0.1	12	3.900	0.488	97.50
	22	0.1	12	3.900	0.488	97.50
	24	0.04	12	3.960	0.495	99.00
	26	0.05	12	3.950	0.494	98.75
	28	0.045	12	3.955	0.494	98.88
	30	0.045	12	3.955	0.494	98.88
	32	0.045	12	3.955	0.494	98.88

Table C 24 Anaerobic adsorption of 5mg/l Mn by ICS at pH 8

Anaerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l in solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	4.995	12	0.000	0.000	0.00
	0.083	1.295	12	3.700	0.463	74.07
	0.25	0.585	12	4.410	0.551	88.29
	1	0.52	12	4.475	0.559	89.59
	2	0.325	12	4.670	0.584	93.49
	4	0.23	12	4.765	0.596	95.40
	6	0.295	12	4.700	0.588	94.09
	8	0.35	12	4.645	0.581	92.99
	10	0.23	12	4.765	0.596	95.40
	12	0.185	12	4.810	0.601	96.30
	14	0.185	12	4.810	0.601	96.30
	20	0.13	12	4.865	0.608	97.40
	22	0.13	12	4.865	0.608	97.40
	24	0.12	12	4.875	0.609	97.60
	26	0.125	12	4.870	0.609	97.50
	28	0.13	12	4.865	0.608	97.40
	30	0.09	12	4.905	0.613	98.20
	32	0.08	12	4.915	0.614	98.40
	36	0.09	12	4.905	0.613	98.20
	45	0.09	12	4.905	0.613	98.20

Table C 25 Anaerobic adsorption of 8mg/l Mn by ICS at pH 8

Anaerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	7.68	12	0.000	0.000	0.00
	0.083	1.44	12	6.240	0.780	81.25
	0.25	0.92	12	6.760	0.845	88.02
	1	0.62	12	7.060	0.883	91.93
	2	0.445	12	7.235	0.904	94.21
	4	0.32	12	7.360	0.920	95.83
	6	0.25	12	7.430	0.929	96.74
	8	0.22	12	7.460	0.933	97.14
	10	0.19	12	7.490	0.936	97.53
	12	0.205	12	7.475	0.934	97.33
	14	0.165	12	7.515	0.939	97.85
	20	0.155	12	7.525	0.941	97.98
	22	0.15	12	7.530	0.941	98.05
	24	0.15	12	7.530	0.941	98.05
	26	0.14	12	7.540	0.943	98.18
	28	0.13	12	7.550	0.944	98.31
	30	0.125	12	7.555	0.944	98.37
	32	0.125	12	7.555	0.944	98.37
	36	0.125	12	7.555	0.944	98.37
	45	0.125	12	7.555	0.944	98.37

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Aerobic batch reactor experiments at pH 8 for ICS

Table C 26 Aerobic adsorption of 2mg/l Mn by ICS at pH 8

Aerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	1.95	12	0.000	0.000	0.00
	0.25	0.29	12	1.660	0.208	85.13
	1	0.315	12	1.635	0.204	83.85
	4	0.295	12	1.655	0.207	84.87
	6	0.285	12	1.665	0.208	85.38
	8	0.25	12	1.700	0.213	87.18
	10	0.24	12	1.710	0.214	87.69
	12	0.225	12	1.725	0.216	88.46
	14	0.205	12	1.745	0.218	89.49
	20	0.145	12	1.805	0.226	92.56
	24	0.13	12	1.820	0.228	93.33
	46	0.08	12	1.870	0.234	95.90
	48	0.055	12	1.895	0.237	97.18
	72	0.025	12	1.925	0.241	98.72
	96	0.03	12	1.920	0.240	98.46
	122	0.025	12	1.925	0.241	98.72
	145	0.025	12	1.925	0.241	98.72
	168	0.02	12	1.930	0.241	98.97
	192	0.02	12	1.930	0.241	98.97
	240	0.02	12	1.930	0.241	98.97

Table C 27 Aerobic adsorption of 3mg/l Mn by ICS at pH 8

Aerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	2.97	12	0.000	0.000	0.00
	0.25	0.52	12	2.450	0.306	82.49
	1	0.585	12	2.385	0.298	80.30
	4	0.455	12	2.515	0.314	84.68
	6	0.435	12	2.535	0.317	85.35
	8	0.415	12	2.555	0.319	86.03
	10	0.405	12	2.565	0.321	86.36
	12	0.375	12	2.595	0.324	87.37
	14	0.355	12	2.615	0.327	88.05
	20	0.265	12	2.705	0.338	91.08
	24	0.23	12	2.740	0.343	92.26
	46	0.09	12	2.880	0.360	96.97
	48	0.095	12	2.875	0.359	96.80
	72	0.035	12	2.935	0.367	98.82
	96	0.035	12	2.935	0.367	98.82
	114	0.025	12	2.945	0.368	99.16
	120	0.03	12	2.940	0.368	98.99
	144	0.015	12	2.955	0.369	99.49

Table C 28 Aerobic adsorption of 4mg/l Mn by ICS at pH 8

Aerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	3.9	12	0.000	0.000	0.00
	0.25	0.74	12	3.160	0.395	81.03
	1	0.675	12	3.225	0.403	82.69
	4	0.62	12	3.280	0.410	84.10
	6	0.555	12	3.345	0.418	85.77
	8	0.54	12	3.360	0.420	86.15
	10	0.515	12	3.385	0.423	86.79
	12	0.485	12	3.415	0.427	87.56
	14	0.45	12	3.450	0.431	88.46
	20	0.33	12	3.570	0.446	91.54
	24	0.285	12	3.615	0.452	92.69
	46	0.13	12	3.770	0.471	96.67
	48	0.12	12	3.780	0.473	96.92
	72	0.07	12	3.830	0.479	98.21
	96	0.07	12	3.830	0.479	98.21
	114	0.045	12	3.855	0.482	98.85
	120	0.045	12	3.855	0.482	98.85
	144	0.025	12	3.875	0.484	99.36

Table C 29 Aerobic adsorption of 5mg/l Mn by ICS at pH 8

Aerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	4.95	12	0.000	0.000	0.00
	0.25	1.87	12	3.080	0.385	62.22
	1	1.735	12	3.215	0.402	64.95
	4	1.53	12	3.420	0.428	69.09
	6	1.27	12	3.680	0.460	74.34
	8	1.235	12	3.715	0.464	75.05
	10	1.115	12	3.835	0.479	77.47
	12	1.02	12	3.930	0.491	79.39
	14	0.91	12	4.040	0.505	81.62
	20	0.645	12	4.305	0.538	86.97
	24	0.52	12	4.430	0.554	89.49
	46	0.21	12	4.740	0.593	95.76
	48	0.185	12	4.765	0.596	96.26
	72	0.105	12	4.845	0.606	97.88
	96	0.09	12	4.860	0.608	98.18
	114	0.065	12	4.885	0.611	98.69
	120	0.06	12	4.890	0.611	98.79
	144	0.035	12	4.915	0.614	99.29
	168	0.035	12	4.915	0.614	99.29

Table C 30 Aerobic adsorption of 8mg/l Mn by ICS at pH 8

Aerobic adsorption of Mn by pulverized ICS at pH 8						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	7.6	12	0.000	0.000	0.00
	0.25	3.6	12	4.000	0.500	52.63
	1	3.44	12	4.160	0.520	54.74
	4	2.54	12	5.060	0.633	66.58
	6	2.88	12	4.720	0.590	62.11
	8	2.68	12	4.920	0.615	64.74
	10	2.54	12	5.060	0.633	66.58
	12	2.18	12	5.420	0.678	71.32
	14	2.05	12	5.550	0.694	73.03
	20	1.57	12	6.030	0.754	79.34
	24	1.25	12	6.350	0.794	83.55
	46	0.525	12	7.075	0.884	93.09
	48	0.445	12	7.155	0.894	94.14
	72	0.255	12	7.345	0.918	96.64
	96	0.2	12	7.400	0.925	97.37
	114	0.16	12	7.440	0.930	97.89
	120	0.105	12	7.495	0.937	98.62
	144	0.075	12	7.525	0.941	99.01
	168	0.065	12	7.535	0.942	99.14
	192	0.065	12	7.535	0.942	99.14

Anaerobic batch reactor experiments at pH 6 for ICS

Table C 31 Anaerobic adsorption of 2mg/l Mn by ICS at pH 6

Anaerobic adsorption of Mn by pulverized ICS at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	2	12	0.000	0.000	0.00
	0.25	0.93	12	1.070	0.134	53.50
	1	0.8	12	1.200	0.150	60.00
	2	0.65	12	1.350	0.169	67.50
	4	0.545	12	1.455	0.182	72.75
	6	0.47	12	1.530	0.191	76.50
	7	0.495	12	1.505	0.188	75.25
	8	0.51	12	1.490	0.186	74.50
	10	0.46	12	1.540	0.193	77.00
	11	0.47	12	1.530	0.191	76.50
	12	0.47	12	1.530	0.191	76.50
	13	0.475	12	1.525	0.191	76.25
	14	0.465	12	1.535	0.192	76.75
	16	0.465	12	1.535	0.192	76.75
	18	0.475	12	1.525	0.191	76.25
	20	0.465	12	1.535	0.192	76.75
	22	0.47	12	1.530	0.191	76.50
	24	0.49	12	1.510	0.189	75.50
	25	0.475	12	1.525	0.191	76.25
	29	0.47	12	1.530	0.191	76.50
	30	0.47	12	1.530	0.191	76.50
	31	0.48	12	1.520	0.190	76.00
	32	0.47	12	1.530	0.191	76.50

Aerobic batch reactor experiments at pH 6 for ICS

Table C 32 Aerobic adsorption of 2mg/l Mn by ICS at pH 6

Aerobic adsorption of Mn by pulverized ICS at pH 6						
	Time (hrs)	[Mn] mg/l In solution	Adsorbent mass (g)	[Mn] mg/l Adsorbed	Mn (mg/g)	% [Mn] Adsorbed
Pulverized ICS	0	1.96	12	0.000	0.000	0.00
	0.25	0.495	12	1.465	0.183	74.74
	1	0.495	12	1.465	0.183	74.74
	4	0.495	12	1.465	0.183	74.74
	6	0.495	12	1.465	0.183	74.74
	8	0.48	12	1.480	0.185	75.51
	10	0.46	12	1.500	0.188	76.53
	12	0.46	12	1.500	0.188	76.53
	22	0.415	12	1.545	0.193	78.83
	24	0.405	12	1.555	0.194	79.34
	36	0.345	12	1.615	0.202	82.40
	48	0.305	12	1.655	0.207	84.44
	58	0.28	12	1.680	0.210	85.71
	72	0.245	12	1.715	0.214	87.50
	96	0.2	12	1.760	0.220	89.80
	122	0.205	12	1.755	0.219	89.54
	145	0.2	12	1.760	0.220	89.80
	168	0.185	12	1.775	0.222	90.56
	192	0.175	12	1.785	0.223	91.07
	240	0.14	12	1.820	0.228	92.86

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Aerobic batch reactor experiments at pH 6 for laterite

Table C 33 Aerobic adsorption of 50ug/l As by ICS at pH 6

Aerobic adsorption of As by pulverized Laterite at pH 6						
	Time (hrs)	[As] ug/l In solution	Adsorbent mass (g)	[As] ug/l Adsorbed	As (mg/g)	% [As] Adsorbed
Pulverized Laterite	0	50	12	0.000	0.000	0.00
	8	39.5	12	10.500	1.313	21.00
	12	39.5	12	10.500	1.313	21.00
	24	24	12	26.000	3.250	52.00
	48	18.9	12	31.100	3.888	62.20
	72	13.2	12	36.800	4.600	73.60
	120	3.8	12	46.200	5.775	92.40
	168	8.05	12	41.950	5.244	83.90

Table C 34 Aerobic adsorption of 100ug/l As by ICS at pH 6

Aerobic adsorption of As by pulverized Laterite at pH 6						
Pulverized Laterite	Time (hrs)	[As] ug/l In solution	Adsorbent mass (g)	[As] ug/l Adsorbed	As (ug/g)	% [As] Adsorbed
	8	104.5	12	0.000	0.000	0.00
	12	70.0	12	34.500	4.313	33.01
	24	40.0	12	64.500	8.063	61.72
	48	25.0	12	79.500	9.938	76.08
	72	41.0	12	63.500	7.938	60.77
	120	14.5	12	90.050	11.256	86.17
	168	3.5	12	101.000	12.625	96.65

Table C 35 Aerobic adsorption of 300ug/l As by ICS at pH 6

Aerobic adsorption of As by pulverized Laterite at pH 6						
	Time (hrs)	[As] ug/l In solution	Adsorbent mass (g)	[As] ug/l Adsorbed	As (ug/g)	% [As] Adsorbed
Pulverized Laterite	0	300	12	0.000	0.000	0.00
	8	166.4	12	133.600	16.700	44.53
	12	160	12	140.000	17.500	46.67
	24	85	12	215.000	26.875	71.67
	48	65	12	235.000	29.375	78.33
	72	20	12	280.000	35.000	93.33
	120	26.55	12	273.450	34.181	91.15
	168	11.05	12	288.950	36.119	96.32

Table C 36 Aerobic adsorption of 500ug/l As by ICS at pH 6

Aerobic adsorption of As by pulverized Laterite at pH 6						
	Time (hrs)	[As] ug/l In solution	Adsorbent mass (g)	[As] ug/l Adsorbed	As (ug/g)	% [As] Adsorbed
Pulverized Laterite	0	500	12	0.000	0.000	0.00
	8	332.5	12	167.500	20.938	33.50
	12	312.5	12	187.500	23.438	37.50
	24	227.5	12	272.500	34.063	54.50
	48	152.5	12	347.500	43.438	69.50
	72	151.5	12	348.500	43.563	69.70
	120	33.5	12	466.500	58.313	93.30
	168	13.8	12	486.200	60.775	97.24

Anaerobic batch reactor experiments at pH 6 for real groundwater

Table C 37 Anaerobic adsorption of 2mg/l Fe, 1mg/l Mn and 300ug/l As by laterite

Time (hours)	[As] (ug/l)	% As adsorbed	[Mn (II)] (mg/l)	% Mn adsorbed	[Fe(II)] (mg/l)	% Fe adsorbed
0	300	0.0	-	-	-	-
0.833	281	6.3	1.32	0.0	3.84	0.0
0.25	262	12.7	1.13	14.4	1.66	56.8
1	234	22.0	1.1	16.7	1.21	68.5
2	228	24.0	1.08	18.2	0.59	84.6
4	218	27.3	1.08	18.2	0.38	90.1
8	178	40.7	1.08	18.2	0.17	95.6
12	172	42.7	1.07	18.9	0.09	97.7
24	159	47.0	1.03	22.0	0.19	95.1
32	162	46.0	0.98	25.8	0.04	99.0
36	145	51.7	0.94	28.8	0.03	99.2
48	144	52.0	0.92	30.3	0.03	99.2

Table C 38 Anaerobic adsorption of 2mg/l Fe, 1mg/l Mn and 300ug/l As by ICS

Time (hours)	[As] (ug/l)	% As adsorbed	[Mn (II)] (mg/l)	% Mn adsorbed	[Fe(II)] (mg/l)	% Fe adsorbed
0	300	0.0	1	0	2	0.0
0.833	72	76.0	0.99	1	0.5	75.0
0.25	41	86.3	0.6	40	0.4	80.0
1	29	90.3	0.51	49	0.14	93.0
2	21.1	93.0	0.51	49	0.55	72.5
4	19.4	93.5	0.5	50	0.44	78.0
8	10.5	96.5	0.45	55	0.5	75.0
12	7.4	97.5	0.4	60	0.4	80.0
24	1.3	99.6	0.28	72	0.17	91.5
32	0.2	99.9	0.25	75	0.15	92.5
36	0	100.0	0.25	75	0.15	92.5
48	0	100.0	0.24	76	0.15	92.5

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Aerobic batch reactor experiments at pH 6 for real groundwater

Table C 39 Aerobic adsorption of 2mg/l Fe, 1mg/l Mn and 30ug/l As by laterite

Time (hours)	[As] (ug/l)	% As adsorbed	[Mn (II)] (mg/l)	% Mn adsorbed	[Fe(II)] (mg/l)	% Fe adsorbed
0	35.05	0.0	1.08	0.0	2.48	0.0
0.25	26.9	23.3	1.045	3.2	0.31	87.5
1	18.8	46.4	1.015	6.0	0.32	87.1
4	20.15	42.5	0.955	11.6	0.325	86.9
8	16.15	53.9	0.945	12.5	0.205	91.7
12	14.15	59.6	0.9	16.7	0.165	93.3
24	10.75	69.3	0.8	25.9	0.09	96.4
48	6.95	80.2	0.655	39.4	0.08	96.8
72	4.6	86.9	0.555	48.6	0.065	97.4
96	2.8	92.0	0.485	55.1	0.065	97.4
120	1.55	95.6	0.395	63.4	0.075	97.0
144	0.6	98.3	0.355	67.1	0.075	97.0

Table C 40 Aerobic adsorption of 2mg/l Fe, 1mg/l Mn and 50ug/l As by laterite

Time (hours)	[As] (ug/l)	% As adsorbed	[Mn (II)] (mg/l)	% Mn adsorbed	[Fe(II)] (mg/l)	% Fe adsorbed
0	53.5	0.0	1.08	0.0	2.455	0.0
0.25	39.45	26.3	1.01	6.5	0.625	74.5
1	36.75	31.3	1.025	5.1	0.615	74.9
4	35.75	33.2	0.975	9.7	0.47	80.9
8	27.6	48.4	0.96	11.1	0.395	83.9
12	23.2	56.6	0.935	13.4	0.38	84.5
24	19.5	63.6	0.76	29.6	0.075	96.9
48	12.2	77.2	0.74	31.5	0.085	96.5
72	8.15	84.8	0.66	38.9	0.07	97.1
96	4.3	92.0	0.615	43.1	0.075	96.9
120	2.1	96.1	0.52	51.9	0.045	98.2
144	1	98.1	0.52	51.9	0.045	98.2

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Table C 41 Aerobic adsorption of 2mg/l Fe, 1mg/l Mn and 100ug/l As by laterite

Time (hours)	[As] (ug/l)	% As adsorbed	[Mn (II)] (mg/l)	% Mn adsorbed	[Fe(II)] (mg/l)	% Fe adsorbed
0	102	0.0	1.02	0.0	2.555	0.0
0.25	151.5	0.0	1.05	0.0	1.25	51.1
1	75.5	26.0	1.005	1.5	0.625	75.5
4	65	36.3	0.99	2.9	0.4	84.3
8	58.5	42.6	0.97	4.9	0.545	78.7
12	49	52.0	0.955	6.4	0.18	93.0
24	41	59.8	0.875	14.2	0.155	93.9
48	25	75.5	0.79	22.5	0.11	95.7
72	18	82.4	0.725	28.9	0.06	97.7
96	11.85	88.4	0.65	36.3	0.065	97.5
120	6.2	93.9	0.555	45.6	0.11	95.7
144	1.35	98.7	0.545	46.6	0.13	94.9

Table C 42 Aerobic adsorption of 2mg/l Fe, 1mg/l Mn and 300ug/l As by laterite

Time (hours)	[As] (ug/l)	% As adsorbed	[Mn (II)] (mg/l)	% Mn adsorbed	[Fe(II)] (mg/l)	% Fe adsorbed
0	312	0.0	1.03	0.0	2.4	0.0
0.25	290	7.1	1.005	2.4	0.295	87.7
1	242.5	22.3	0.965	6.3	0.295	87.7
4	213	31.7	0.935	9.2	0.17	92.9
8	204.5	34.5	0.925	10.2	0.285	88.1
12	189.5	39.3	0.89	13.6	0.065	97.3
24	154	50.6	0.795	22.8	0.075	96.9
48	105.5	66.2	0.655	36.4	0.065	97.3
72	64.5	79.3	0.57	44.7	0.065	97.3
96	38.5	87.7	0.495	51.9	0.095	96.0
120	20.5	93.4	0.435	57.8	0.065	97.3
144	5	98.4	0.4	61.2	0.06	97.5

Table C 43 Aerobic adsorption of 2mg/l Fe, 1mg/l Mn and 700ug/l As by laterite

Time (hours)	[As] (ug/l)	% As adsorbed	[Mn (II)] (mg/l)	% Mn adsorbed	[Fe(II)] (mg/l)	% Fe adsorbed
0	738	0.0	1.05	0.0	2.5	0.0
0.25	695	5.8	1.025	2.4	0.305	87.8
1	620	16.0	1	4.8	0.425	83.0
4	580	21.4	0.975	7.1	0.13	94.8
8	526	28.7	0.95	9.5	0.295	88.2
12	494	33.1	0.935	11.0	0.15	94.0
24	417	43.5	0.85	19.0	0.17	93.2
48	308.5	58.2	0.735	30.0	0.115	95.4
72	228.5	69.0	0.68	35.2	0.085	96.6
96	167	77.4	0.595	43.3	0.04	98.4
120	96	87.0	0.545	48.1	0.07	97.2
144	46	93.8	0.515	51.0	0.075	97.0

Appendix E Freudlich Isotherms

Table D 1 Freudlich Isotherm for Mn adsorption by ICS at pH 8

Initial Mn conc. (mg/l)	C_e mg/l	Ce (mg/l)	X (mg/l)	m (g)	q (mg/l/g)	q (mg/g)	Log q	log Ce
2	1.91	0.02	1.89	12	0.1575	0.23625	-0.62663	-1.69897
3	3	0.03	2.97	12	0.2475	0.37125	-0.43033	-1.52288
4	4	0.045	3.955	12	0.329583	0.494375	-0.30594	-1.34679
5	4.995	0.09	4.905	12	0.409167	0.613751	-0.21201	-1.04576
8	7.68	0.125	7.555	12	0.629583	0.944375	-0.02486	-0.90309
10	9.8	0.26	9.54	12	0.795	1.1925	0.076458	-0.58503

Table D 2 Freudlich Isotherm for Mn adsorption by laterite at pH 8

Initial Mn conc. mg/l	C_0 mg/l	Ce mg/l	X	m (g)	q (mg/l/g)	q (mg/g)	Log q	Log Ce
2	1.9	1.1	0.8	12	0.066667	0.10000	-1.00000	0.041393
3	3	1.82	1.18	12	0.098333	0.14750	-0.83121	0.260071
4	3.8	1.97	1.83	12	0.1525	0.22875	-0.64064	0.294466
5	4.5	1.68	2.82	12	0.235	0.35250	-0.45284	0.225309
6	6	2.52	3.48	12	0.29	0.43500	-0.36151	0.401401

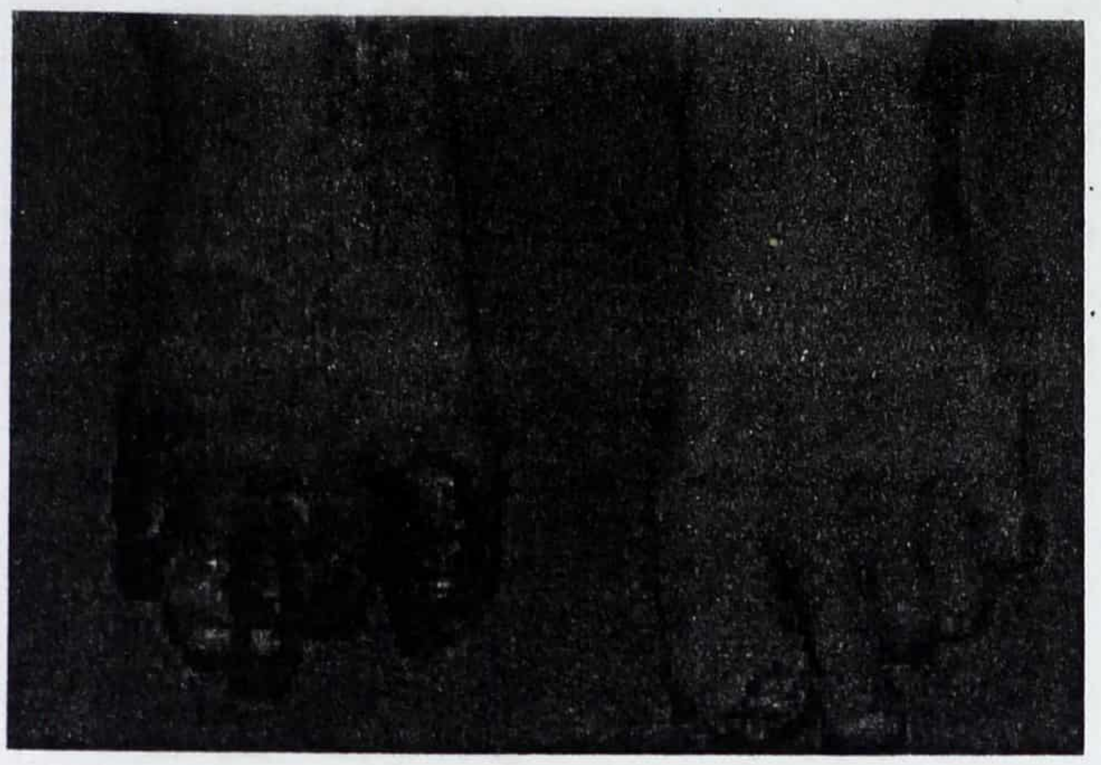
Table D 3 Freudlich Isotherm for Mn adsorption by Laterite at pH 6

Initial Mn conc. mg/l	C_0 mg/l	Ce mg/l	X mg/l	m (g)	q mg/l/g	q mg/g	LOG q	LOG Ce
2	2	1.77	0.23	12	0.019167	0.02875	-1.54136	0.247973
3	2.94	2.6	0.34	12	0.028333	0.0425	-1.37161	0.414973
4	3.94	3.72	0.22	12	0.018333	0.0275	-1.56067	0.570543
5	4.92	4.41	0.51	12	0.0425	0.06375	-1.19552	0.644439
6	6.03	5.46	0.57	12	0.0475	0.07125	-1.14722	0.737193

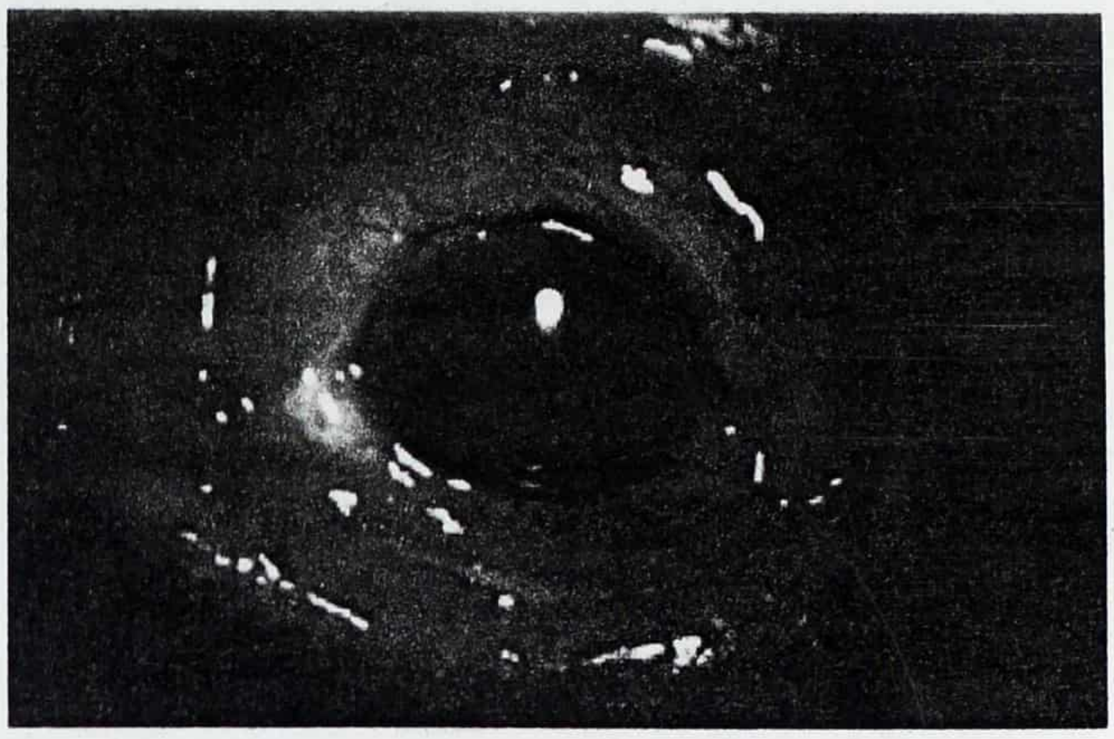
Table D 4 Freudlich Isotherm for Mn adsorption by ICS at pH 6

Initial	C_0	Ce	X	m	q	q	LOG q	log Ce
(mg/l)	mg/l	(mg/l)	mg/l	(g)	(mg/lg)	(mg/g)		
2	1.585	0.34	1.245	12	0.10375	0.155625	-0.80792	-0.46852
3	2.95	0.99	1.96	12	0.163333	0.245	-0.61083	-0.00436
4	3.83	1.4	2.43	12	0.2025	0.30375	-0.51748	0.146128
5	5	1.88	3.12	12	0.26083	0.391245	-0.40755	0.274158
8	7.96	3.72	4.24	12	0.35333	0.529995	-0.27573	0.570543
10	9.78	4.16	5.62	12	0.46833	0.702495	-0.15336	0.619093

Appendix F Pictures of Arsenicosis sufferers



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