Low-cost Technology for Removal of Arsenic from Water: With Particular Reference to Bangladesh

by

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Declaration of Author's Rights

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ABSTRACT

The contamination of groundwater by arsenic is currently a major concern in Bangladesh. Arsenic in groundwater was first detected in 1993 following reports of many people suffering from arsenical diseases. Further investigations showed the extent of the problem with large areas of the country's water supply being affected and millions of people at serious risk of arsenic poisoning.

Technology for arsenic removal from water already exists. However, the socio-economic conditions which prevail in Bangladesh, do not permit implementation of this type of technology on grounds of cost. The main objective of this study was to develop a low cost technique for the removal of arsenic from contaminated groundwater using the naturally occurring iron, which is another water quality constraint in Bangladesh. The approach was to form arsenic-iron complexes by co-precipitation and adsorption of arsenic on iron. It has been demonstrated that provided the iron levels are sufficiently high (say ≥ 1.2 mg/l), simple shaking of a container and allowing the arsenic-iron complex to settle out for 3 days could reduce the concentration of arsenic from 0.10 mg/l to Bangladesh standard (0.05 mg/l).

In experimental program, As(III) form of arsenic was used as this form is more likely to be present in groundwater. From laboratory studies, it was shown that the removal rate was largely controlled by the Fe/As ratio, pH and the As concentration. Arsenic removal increases with increasing Fe/As ratio and is favoured by increasing pH in the range of 5 to 8. Separation of the precipitates was achieved by settlement. Following prolonged settlement, it was found that arsenic removal could exceed the removal achieved by filtration through a 0.45 μm filter paper. The experiments demonstrated that about 77% arsenic removal could be achieved from water containing 0.2 mg/l As(III), 4.0 mg/l Fe at pH 7.5 by manual flocculation (1 min manual mixing) and 3 days settlement.

The use of ordinary charcoal, which is cheap and easily available, was investigated for removal of arsenic and was found to be ineffective.

From maps of the known distributions of As, Fe and pH, it was evident that 63% of the area in Bangladesh complied with the Bangladesh standard for arsenic. By interpreting the maps and applying the potential removal by coprecipitation-adsorption and settlement technique, it was estimated that a further 8% of area would comply with the Bangladesh standard freeing an additional 7 million people from arsenic contamination.

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Symbols and Notations

C_e	Residual equilibrium concentration
q_e	Amount of substance adsorbed per unit weight of adsorbent
pK_a	pH at which the dissociation of the reactant is 50% complete
V_s	Settling velocity of particle
g	Gravity constant
D_s	Diameter of solid particle
C_D	Drag coefficient
ρ_s	Density of particle
ρ	Density of water
R	Reynolds number
μ	Dynamic viscosity
ν	Kinematic viscosity
K_{ads}	Adsorption rate constant
r	Regression coefficient

Acronyms and Abbreviations

ACIC	Arsenic Crisis Information Centre
APHA	American Public Health Association
AsRT	Arsenic Remediation Technology
ASTM	American Society for Testing Materials
AWWA	American Water Works Association
BDH	British Drug House
BGS	British Geological Survey
BRAC	Bangladesh Rural Advancement Committee
BUET	Bangladesh University of Engineering and Technology, Dhaka
DCH	Dhaka Community Hospital
DOE	Department of Environment, Bangladesh
DPHE	Department of Public Health Engineering, Bangladesh
EGIS	Environment and GIS Support Project for Water Sector Planning
GAC	Granular Activated Carbon
GIS	Geographic Information System
MHFW	Ministry of Health and Family Welfare, Bangladesh
NIPSOM	National Institute of Preventive and Social Medicine
NOM	Natural Organic Matter
WEF	Water Environment Federation
WHO	World Health Organisation

Chapter 1

INTRODUCTION

1.1 BACKGROUND

Bangladesh, a densely populated country with a low per capita income, has recently been hit by a major environmental disaster — contamination of the groundwater with high levels of arsenic.

Use of untreated surface water for drinking purposes was discouraged in Bangladesh as it harboured different water borne diseases (Mortoza, 1998). On the other hand, groundwater was seen to be safe for drinking, even without treatment. For this reason, the Bangladesh government and different donor agencies promoted the use of groundwater. Presently about 95% of the people of Bangladesh depend on groundwater for drinking and domestic purposes. About 4 million tubewells have been sunk all over the country during the last three decades. Because of the lack of suitable central treatment facility and piped distribution system, these tubewells play a crucial role in providing the nation with safe drinking water.

However, in the early nineties (1993), reports of arsenic related diseases started to emerge and investigations found arsenic in groundwater much higher than the limits set by both WHO (0.01 mg/l) and Bangladesh standards (0.05 mg/l). Concentrations exceeding 1 mg/l have been reported (BGS and MottMacdonald Ltd, 1999) in some parts of Bangladesh. This far exceeds even the relatively lenient Bangladesh standard for drinking water.

The extent of the problem is already very acute. Around 85% of the total area of Bangladesh is contaminated with arsenic (Dainichi, 1998) and between 50 to 75 million people are at risk due to ingesting contaminated groundwater (Bridge and Hussain, 1998). A clinical survey in 22 districts (out of the total 64) revealed that one third of the population in affected areas have already shown symptoms of arsenic poisoning (DCH, 1998). Up to 1997, National Institute of Preventive and Social Medicine (NIPSOM) and Dhaka Community Hospital (DCH) have registered over 2,000 cases of chronic arsenocosis (EGIS, 1997).

With such a huge population having to consume highly contaminated water for lack of any alternative, Bangladesh is perhaps facing one of the largest environmental disaster of the century.

Technologies for removal of arsenic from water already exist (Kartinen and Martin, 1995) as incidences of arsenic contamination in groundwater have already been reported from various parts of the world (e.g. Chile, Hungary, New Zealand, Taiwan and India). Arsenic can be removed effectively using iron coagulation or adsorption on to activated carbon (Cheng *et al*, 1994; Scott *et al*, 1995; and Gupta and Chen, 1978). However, the socio-economic conditions that prevail in Bangladesh do not permit the implementation of much of this type of technology on grounds of cost. This aspect also couples with the fact that the water supply system is not centralised (as in the developed countries) — individual household or small groups being served by their own tubewell. Solutions to the problem of arsenic removal from drinking water in Bangladesh necessitate the development of technology that can be implemented both at household level and at virtually zero cost.

A related problem in Bangladesh is the presence of iron in groundwater (Chapter 2). It is known that arsenic and iron co-exist geologically (Ahmed *et al*, 1998). While each of arsenic and iron pose problems, their association in groundwater provides a basis for generating a simple means of removing arsenic by coprecipitation (Edwards, 1994; McNeill and Edwards, 1997).

1.2 OBJECTIVE OF THE STUDY

The objective of this study was to develop a practical method for reducing arsenic levels in groundwater in Bangladesh at near zero cost.

1.3 SCOPE OF THE STUDY

In order to achieve the stated objective, the scope of study included the following:

1. Prospects of charcoal for removing arsenic were examined because, unlike activated carbon, it can be locally manufactured.

2. Prospects of removing arsenic on the basis of adsorption and coprecipitation with iron were examined.

3. Implications of arsenic removal technology at field level were evaluated.

1.4 ORGANISATION OF THE THESIS

The study is presented in seven chapters. Chapter 1 sets out the background to the problem of arsenic contamination in Bangladesh, including the objective and scope of the study. Chapter 2 provides a brief discussion of the sources of arsenic and its mobilisation in the groundwater in Bangladesh. It also encompasses the extent and distribution of iron. Besides, data on other water quality parameters are also reviewed. Chapter 3 compiles a selection of relevant literature, which provides insight into the arsenic and iron chemistry, arsenic removal mechanisms and techniques, and the factors influencing arsenic removal. The bulk of the experimental work together with results is described in Chapter 4. It covers work on charcoal and interaction of arsenic with iron including mixing, solid-liquid separation, factors influencing removal and draw-off arrangements. It also presents a summary of the preliminary findings. Chapter 5 presents the outcome of the experimental works and implications of the removal technique in the field level. Chapter 6 concentrates on arsenic removal mechanisms and discusses experimental results in detail. This is followed by conclusions of the study reported in Chapter 7.

Appendix A presents a comparison of arsenic data obtained from the Department of Public Health Engineering (DPHE) and EGIS, and Appendix B reproduces the data obtained from Bangladesh University of Engineering and Technology (BUET) on a study visit in January 1998.

Chapter 2

GROUNDWATER IN BANGLADESH: ARSENIC AND IRON

2.1 INTRODUCTION

This chapter begins with a brief discussion of the sources of arsenic in the environment and is followed by more detailed discussion on the probable sources of arsenic in the groundwater in Bangladesh and the causes of its mobilisation. The review also encompasses the extent and distribution of iron, this representing a problem in its own right in groundwater with potable usage and interacts with the removal of arsenic. Besides iron, data on other water quality parameters (pH, turbidity, chloride, alkalinity, hardness, iron, magnesium, manganese, nitrate and sulphate) are also reviewed.

2.2 BACKGROUND INFORMATION OF ARSENIC

The occurrence of arsenic in groundwater is linked to two principal sources: geogenic and anthropogenic. Arsenic is the twentieth most abundant element in the earth crust and is a component of more than 245 minerals. Common mineral forms of arsenic compounds are arsenopyrite ($FeAsS$), realgar (AsS) and orpiment (As_2S_3).

Arsenic forms permanent compounds in virgin soil at a concentration varying between 1.3 and 2.5 ppm (Galba and Konstantin, 1960). The hazard of groundwater contamination is also known to occur frequently in alluvial aquifers with a significant sulphide component and in areas in gold mineralisation where arsenopyrite is present (BGS, 1998). Interaction of the aqueous phase with the different mineral phases of the aquifer sediments plays a predominant role in controlling the retention and /or mobility of arsenic under different redox conditions within the subsurface environment.

The source of arsenic in sediments is mainly the parent rock materials from which it is derived. Sediments can contain substantial amounts of total arsenic that can be a major source of contamination when arsenic particles are detached and carried as sediments during erosion. During the formation of sedimentary rocks, arsenic is carried down by precipitation of iron hydroxides and sulphides (Bhattacharya *et al*, 1998). In moist climate, arsenic sulphides are easily oxidised, become water-soluble, are washed out of the sediment particles by meteoric precipitation, and are transported with run off (Lalor *et al*, 1999). Mobilisation of arsenic in groundwater is governed by natural bio-geochemical cycling. Arsenic undergoes reactions of oxidation-reduction, precipitation-dissolution, adsorption-desorption and organic and biochemical methylation. All of these reactions control mobilisation and accumulation of arsenic in the environment. The redox conditions within the aquifers are mainly controlled by biological activity and by chemical processes (Robertson, 1986; Bhattachariya *et al*, 1997).

Aside from naturally occurring arsenic, it has also industrial, agricultural and domestic usages, which add to the quantities already existing in the environment. Arsenic has been used in agriculture for many years as insecticides and herbicides. Industrial applications of arsenic compounds include as weed-killers, rodenticides, wood preservatives etc. Arsenic is added to the environment when fertilisers are made using calcined phosphate, which may contain over 20 ppm of arsenic (Helling *et al*, 1969). Similarly, arsenic is found in detergents as a constituent of phosphate builders at concentration of 70- 80 ppm (Gulledge and O'Conor, 1973).

2.3 ARSENIC IN GROUNDWATER IN BANGLADESH

The presence of arsenic in groundwater in Bangladesh is the most serious health hazard the country has ever faced. In terms of population exposed, it is the largest groundwater arsenic problem in the world. Fig. 2.1 shows the groundwater arsenic contamination throughout the country.

The source of arsenic contamination of groundwater in Bangladesh is said to be geogenic. However, the situation is complicated due to a number of factors involved such as sedimentology, geomorphology, bio-geochemical and hydro-chemical patterns and most importantly, due to the massive extent of the contamination. Because of the combination of these factors, there is controversy among researchers regarding the occurrence, mobilisation and transportation of arsenic in groundwater in Bangladesh.

Many hypotheses have been put forward to explain the complex mechanisms behind its occurrence (i.e. the presence of arsenic in the aquifer sediments), mobilisation (the release of arsenic from the sediments to the groundwater) and transportation (the flushing of arsenic into the groundwater circulation). A summary of the main hypotheses put forward by researchers based on various direct findings as well as indirect supporting evidence is shown in Table 2.1

Hypothesis 1: Oxidation of Arsenopyrite

This hypothesis states that arsenic is derived from the oxidation of arsenic rich pyrite in the shallow aquifer. Arsenic is bound up in pyrite minerals in the alluvium and excessive withdrawal of ground water lowers the water table and allows the penetration of atmospheric oxygen to diffuse into the pore spaces of the soil/sediment and also into the ground water. The oxygen oxidises the arsenic laden pyrites and coverts insoluble arsenic into a soluble form in water.

Table 2.1 Summary of hypotheses on arsenic occurrence

Hypothesis	Reference	Comment
1. Oxidation of arsenopyrite	Chakraborti (1996)	This is less likely to happen as the condition in groundwater is reducing
2. Reduction of oxyhydroxides	Nickson *et al* (1988)	This is more likely to happen and further research is needed to establish this
3. Oxidation-reduction within the aquifer underlain by peaty clay / clay layer	This is not really a hypothesis but the combination of the above two hypotheses linked to a particular situation (from newspaper discussion)	This is highly unlikely to be a major cause of extensive arsenic contamination

Hypothesis 2: Reduction of Oxyhydroxides

This theory argues that arsenic is derived by desorption from ferric hydroxide minerals present as coatings in the aquifer sediments under reducing conditions. Here arsenic is released when arseniferrous iron-oxyhydroxides are reduced in anoxic ground water — a process that solubilises iron and its adsorbed load and increases bicarbonate concentration. It therefore assumes that a high proportion of arsenic in the sediments is present as adsorbed arsenic form (MHFW, 1998; Nickson *et al*, 1998; BGS, 1998; Rahman, 1999 and The Guardian, 1998).

Hypothesis 3: Aquifers subjected to Oxidation-reduction

This theory suggests that unconfined aquifers that are subjected to oxidation and reduction and underlain by peaty clay and /or clay layers, are responsible for arsenic contamination. Mine wastes, specially carbonaceous shale, dumped to the surface from coal mining in India are transported and deposited along with the river and flood born sediments may be responsible for the formation of peaty clay layer in the deltaic region. The continued abstraction of water from unconfined aquifer releases

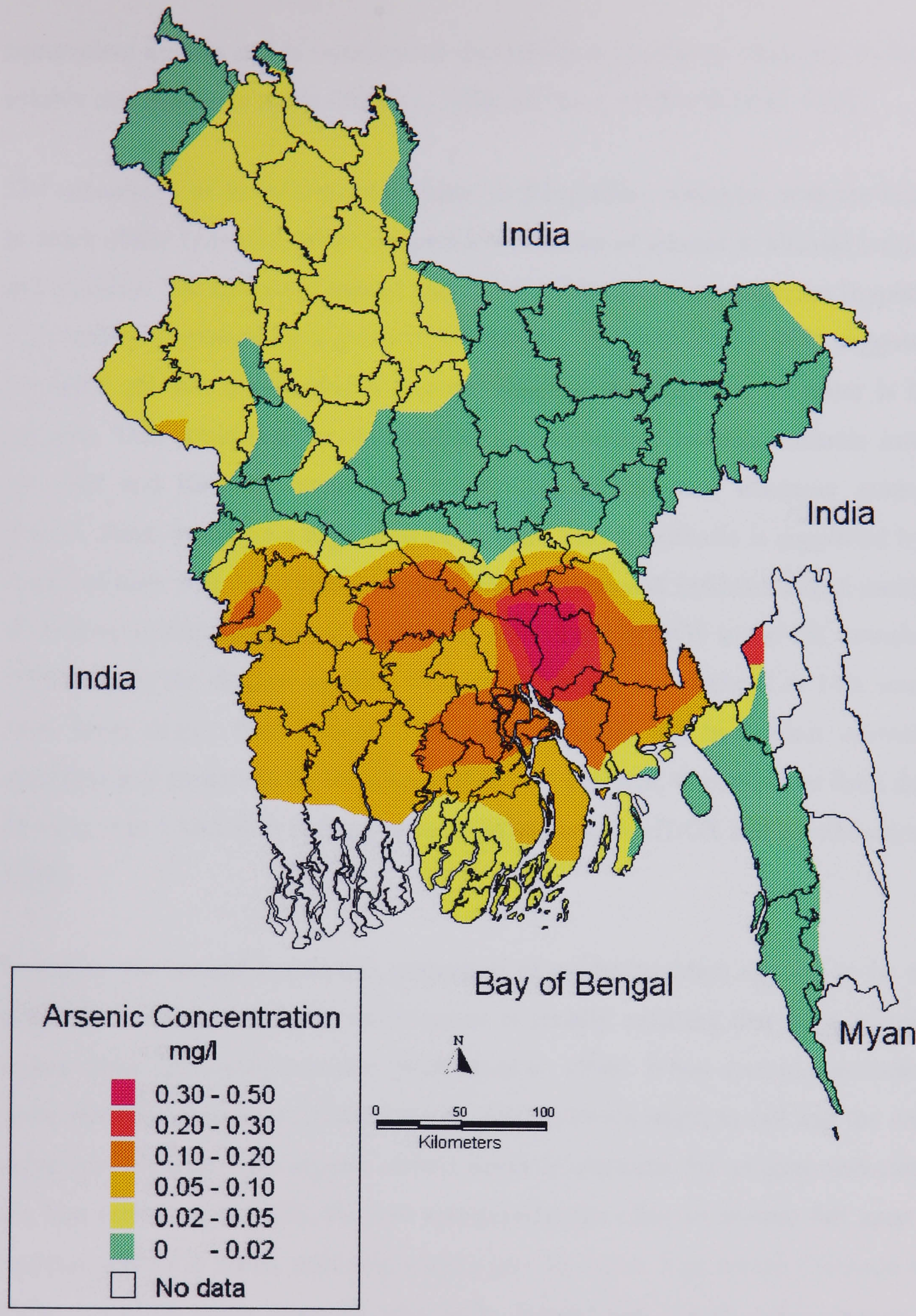


Fig 2.1 Extent of arsenic contamination in Bangladesh (EGIS, 1997)

pentavalent arsenic and is transformed into trivalent arsenic on reduction to become soluble and mobile in water (MHFW, 1998; Mortoza, 1998 and BGS, 1998).

The occurrence of arsenic in groundwater in Bangladesh coincides with the findings in much of the literature, which suggest a prevalence of arsenic in alluvial sediments and aquifers. The release of arsenic due to the oxidation of arsenopyrites (hypothesis 1) is widely supported by a group of researchers. Nickson *et al* (1998) suggest that air could get into the boreholes through which a large amount of water is being pumped. This could lead to oxidation of certain arsenic bearing minerals into the sediment and liberate arsenic into water. This implies that wherever arsenic is present, there would be a high level of oxygen. This hypothesis is supported by the results of tube well water tested by most organisations and indicates a high incidence of shallow aquifer contamination. A study carried out by BGS in the UK reveals that 41% wells in the shallow aquifers were contaminated as compared to 14% samples from wells deeper than 200 m. The shallow aquifer has been most extensively exploited and appears to be the source of arsenic problem. Groundwater from depths of more than 150-200 m is found essentially arsenic free (BGS and MottMacdonald, 1999).

However, the second hypothesis (reduction of oxyhydroxides) appears to be more plausible as the groundwater environment is usually reducing that helps to release arsenic from iron-oxyhydroxides (Nickson *et al*, 1998). When arsenic-adsorbed iron oxide dribbles deeper into ground water, oxygen levels begin to fall and the micro-organisms together with organic carbon begin to consume the oxygen molecules in the iron oxide. As a result, the iron compounds that cling to arsenic fall apart and become soluble in water, releasing arsenic into the water. Test results (Nickson *et al*, 1998) based on water from 44 tube wells showed that arsenic concentration was found lower (0.05 mg/l) in shallow wells compared with samples from deep wells (0.26 mg/l). The BGS also consider the reduction of oxyhydroxides as the main cause of arsenic mobilisation in groundwater.

The third hypothesis advocates both the explanations of oxidation-reduction process of the previous theories. A counter argument is that the transport of arsenic rich sediments or formation of peaty clay layer in the short-term geological time scale is unlikely (BGS, 1998). Apart from this, this hypothesis considers arsenic rich sediments as the source of arsenic, hence, the reason for spatial variability of arsenic concentrations in the whole region remains unexplained.

2.4 IRON AND OTHER WATER QUALITY PARAMETERS IN GROUNDWATER IN BANGLADESH

Irrespective of its source of origin, groundwater contain mineral salts and other chemical compounds such as iron, manganese, nitrate, chloride, calcium, sodium, fluoride etc. The type and concentration of the constituents depend on various geological, geohydrological and physical factors of the aquifers. The quality of groundwater may vary from place to place and from season to season. Iron problems in groundwater are acute in different parts of Bangladesh. For the purpose of this study, data on groundwater quality parameters were collected and the following sections present the sources of collected field data, the iron distribution and other water quality parameters in groundwater in Bangladesh.

2.4.1 Collection of Field data

A field visit was undertaken to Bangladesh in 1998 to collect data on arsenic, iron and pH together with other water quality parameters from different sources as listed in Table 2.2.

Of these, only the data from EGIS covered most of Bangladesh and had information on location in a map form. However, EGIS did not provide the actual field data as the maps represented them as different contour ranges.

Table 2.2 Field data collected from Bangladesh

Source of data	Data Type	Remark
Environmental and GIS Support Project for Water Sector Planning (EGIS)	Maps of arsenic, iron and pH distribution	Maps are presented in sections 2.3, 2.4.2 and 2.4.3 respectively
Department of Public Health Engineering (DPHE)	Arsenic	A comparison of arsenic data from DPHE and EGIS is shown in Appendix A
Bangladesh Univ. of Engineering and Technology (BUET)	General water quality parameters	Reproduced in Appendix B

Although providing raw data on arsenic concentration, DPHE did not have any locational information and only covered part of the country. For the purpose of this study, the data from EGIS was used to determine the prevailing ranges of arsenic, iron and pH that were used in the laboratory test programme. The same data set was used for development of the potential arsenic removal maps discussed in Chapter 5.

2.4.2 Iron in groundwater in Bangladesh

Iron compounds are widely distributed in shale, sandstone and alluvial deposits. Groundwater is usually low in dissolved oxygen and is supersaturated with carbon dioxide. The lower pH value of groundwater due to presence of carbon dioxide and mineral acids and absence of dissolved oxygen creates favourable condition to hold iron in high concentration in groundwater as ferrous carbonate (Bell, 1965). When tubewells are drilled in places rich in iron compounds, a high iron contamination is likely to occur in tubewell water supply system. Upon exposure to the atmosphere, dissolution of carbon dioxide occurs, leading to an increase in pH value. At the same time, aeration also increases the dissolved oxygen concentration. Thus the combination of aeration and the dissolution of carbon dioxide increases the rate of oxidation of soluble ferrous iron into insoluble form; these precipitates from solution as hydrous ferric oxides as shown in eqn. 2.1.

$$2Fe^{2+} + 4HCO_3^{-} + H_2O + \frac{1}{2} O_2 \rightarrow Fe(OH)_3 + 4CO_2 \qquad (2.1)$$

The presence of dissolved iron in groundwater in Bangladesh is also an existing water quality constraint in water supply system based on tube wells (Fig. 2.2). It has been found that hand tube well water in 65% of the area of Bangladesh contains dissolved iron in excess of 2 mg/l and in many areas concentration is around 15 mg/l (Ahmed *et al*, 1998). Allowable limit of iron for drinking in Bangladesh is 0.3- 1.0 mg/l. and this limit may be relaxed up to 5.0 mg/l for areas with no alternative suitable drinking water sources (DOE, 1991), whereas the WHO standard for iron is 1.0 mg/l (WHO, 1971).

The major causes of non-usage of water with excessive iron are its unpleasant taste and colour, and its role in promoting the stickiness of hair and the roughness of skin. As a result, the rural population is generally reluctant to use tubewell water in "iron problem" areas and are more inclined to use unprotected surface water sources. Unfortunately many of these have the potential for causing water-borne diseases (e.g. cholera, diarrhoea) and are completely unsuitable for domestic use without any treatment. As a result it was found that the attack rate of water-borne diseases in iron problem areas is much higher than the non-iron problem areas (Ahmed, 1987). It is also estimated by WHO that more than 50% of cases of mortality among infants in Bangladesh is due to diarrhoeal diseases (Ahmed, 1987)).

2.4.3 Other water quality parameters in groundwater in Bangladesh

General water quality data were collected from BUET and are presented in Appendix B. These data include pH, turbidity, chloride, alkalinity, hardness, iron, magnesium, manganese, nitrate and sulphate. This data set is a compilation of the results of field investigation in different areas and not a systematic survey. They are broadly classified into six administrative regions (divisions). Information of geographical location was not available and it was not possible to carry out any meaningful statistical analysis. However, representative concentrations of the required parameters (pH, turbidity, alkalinity, nitrate, and sulphate) were determined

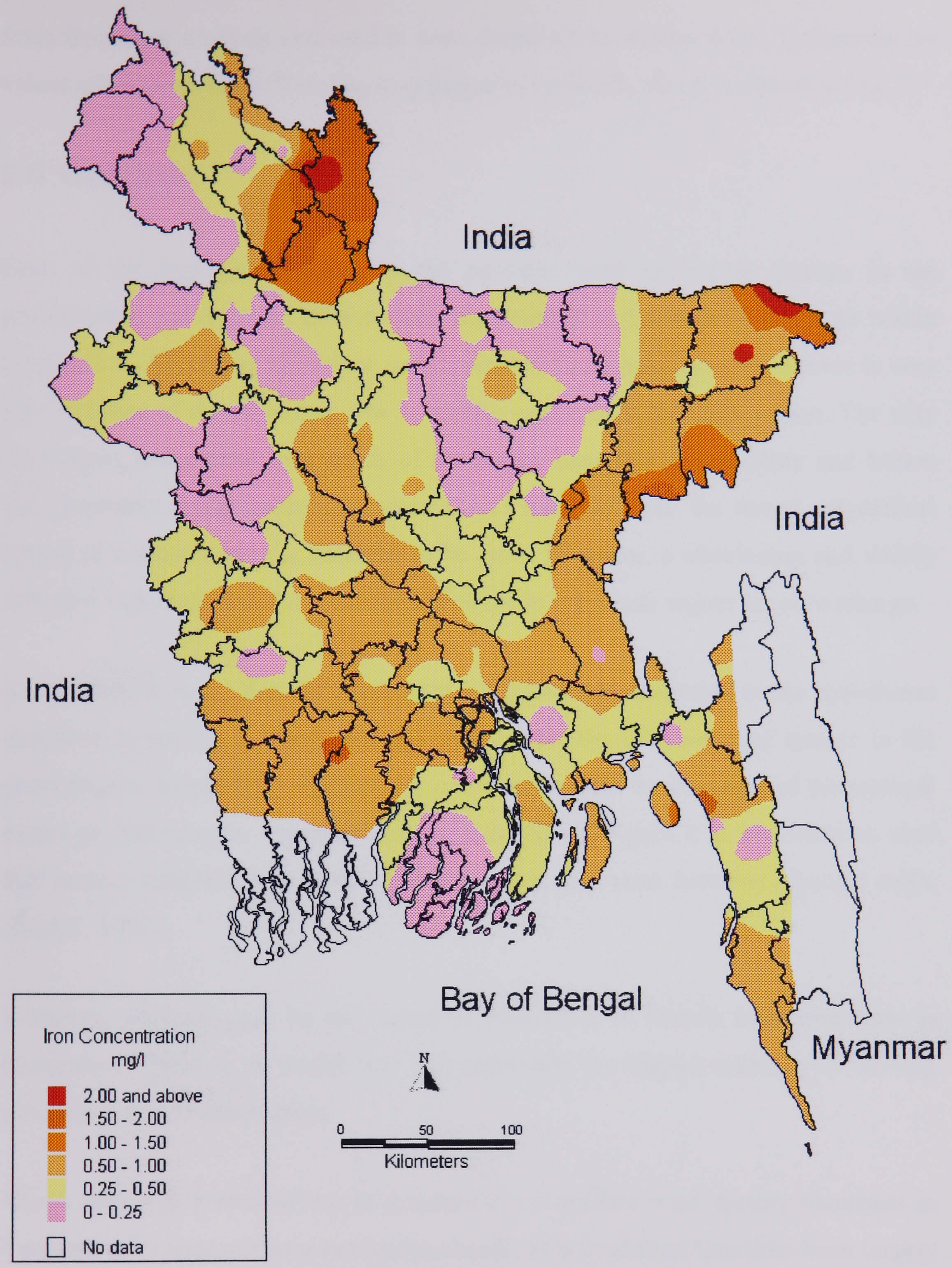


Fig 2.2 Extent of Iron contamination in Bangladesh (EGIS, 1997)

from frequency analysis and used in tests described in section 4.5.5. Representative values of pH were taken from the map prepared by EGIS, which is shown in Fig. 2.3.

2.5 OVERVIEW

Each of the hypotheses discusses the possible ways of arsenic release in the groundwater, but does not fully explain the mobility and transport of arsenic within the aquifers. According to various survey reports, the groundwater movement is very slow because of the extremely low hydraulic gradients in the delta region. The silty clay layers that extend over much of the region have low permeability and hence, tend to protect strong leaching of arsenic. As a result of these, the lateral and vertical spread of contamination is believed to be slow. However, a convincing and widely accepted explanation of the presence of arsenic in the whole region is yet to emerge.

It is important to say that the arguments put forward by scientists in the hypotheses described in section 2.3 only partially account for the occurrence of arsenic in the groundwater. None of the explanations can fully account for the cause of the regional extent of groundwater contamination in Bangladesh. Again it is important to note that arsenic concentration in well water vary widely even between adjacent wells (BRAC, 1997).

However, whatever may be the reason of occurrence of arsenic in groundwater in Bangladesh, there is no doubt that this represents the biggest calamity of arsenic poisoning in recorded history.

The existence of dissolved iron in groundwater is another water quality constraint in Bangladesh. It does not pose any serious health effects and has therefore been largely ignored. However, interest in naturally occurring iron has been aroused because of its potential for enabling the removal of arsenic from groundwater (Ahmed *et al*, 1998).

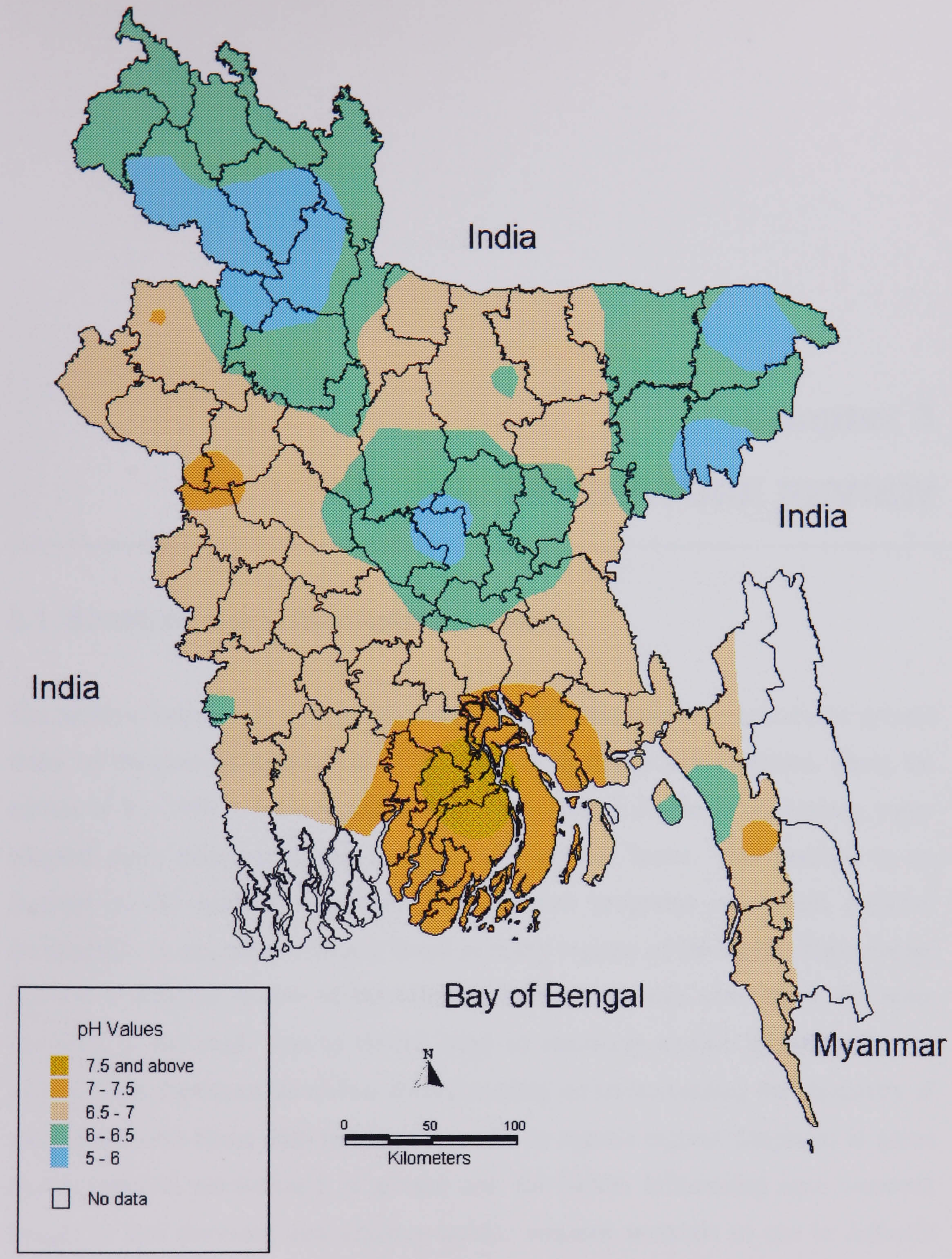


Fig 2.3 pH distribution in Bangladesh (EGIS, 1997)

Chapter 3

LITERATURE REVIEW

3.1 SCOPE OF THE LITERATURE APPRAISAL

The problem being dealt with in this research is the existence of arsenic in the ground water of Bangladesh where iron is also present in significant quantities. Since the middle of the 1990's, various national and international standards of drinking water adopted more stringent criteria on allowable arsenic limits. This resulted in an increase in the interest and number of research programs on arsenic removal mechanisms as arsenic problem is faced in many regions of the world. This chapter presents a detailed review of the relevant literature on this area. Since the main objective of the study was to devise ways of removing arsenic by using the co-existing iron, the literature review focuses mainly on understanding the chemistry of arsenic and iron along with cycling of arsenic in aquatic regime. Emphasis is given on the removal mechanisms of arsenic and the factors influencing such removal. Insight is also provided into existing arsenic removal methods in use in different parts of the world, but which generally engender more sophisticated technologies.

3.2 ARSENIC CHEMISTRY

Arsenic is a trace element with an average crustal abundance of 1.8×10^{-4} % (Pierce, 1981). It is a non-metal in group VA in the periodic chart. Since the physical appearance of arsenic resembles that of a metal, it is therefore referred to as a metalloid to distinguish from a non-metal. Arsenic forms both organic and inorganic compounds. The inorganic compounds are more toxic than organic compounds. Arsenic occurs in water in several different forms depending upon the pH and oxidation-reduction potential (E_h) of the water. Arsenic can occur in four oxidation states in water: arsenate (As^{5+}), arsenite (As^{3+}), arsenic (As) and arsine (As^{3-}). But is generally found in As(III) and As(V) forms. Fig. 3.1 shows distribution diagrams for As(III) and As(V) as a function of pH.

Arsenate (As(V)) generally predominates in surface waters as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. $HAsO_4^{2-}$ predominates from pH 7 to 11.5, indicating that this is the form most likely to occur in surface water supplies. At $pH < 7$, $H_2AsO_4^-$ dominates.

Arsenite (As(III)) is present as H_3AsO_3 in aqueous solution; this undissociated weak acid is predominant in the pH range of 2 to 9. $H_2AsO_3^-$ occurs within pH range of 9.5 to 12 and $HAsO_3^{2-}$ exists in pH above 12 (Fig. 3.1).

Fig. 3.2 is an E_h-pH diagram for arsenic in a system including oxygen, sulphur and H_2O. This diagram represents the equilibrium conditions of arsenic under various redox potentials. Well-aerated surface waters would tend to induce high E_h values, therefore, arsenic should be in the As(V) form. Mildly reducing conditions, such as can be found in ground water, should produce As(III).

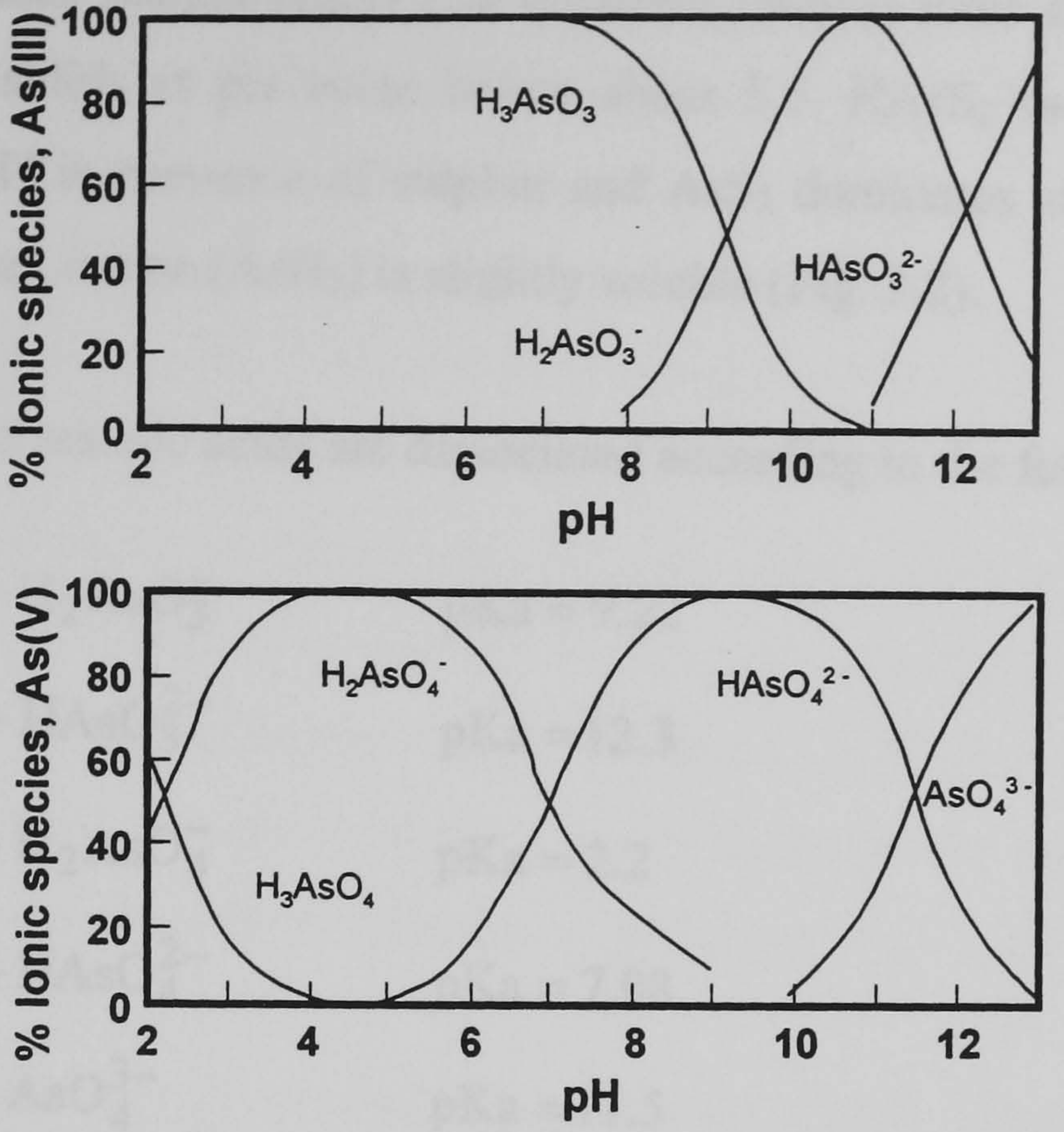


Fig. 3.1 Predominance diagram for As(III) and As(V) as a function of pH (Gupta and Chen, 1978)

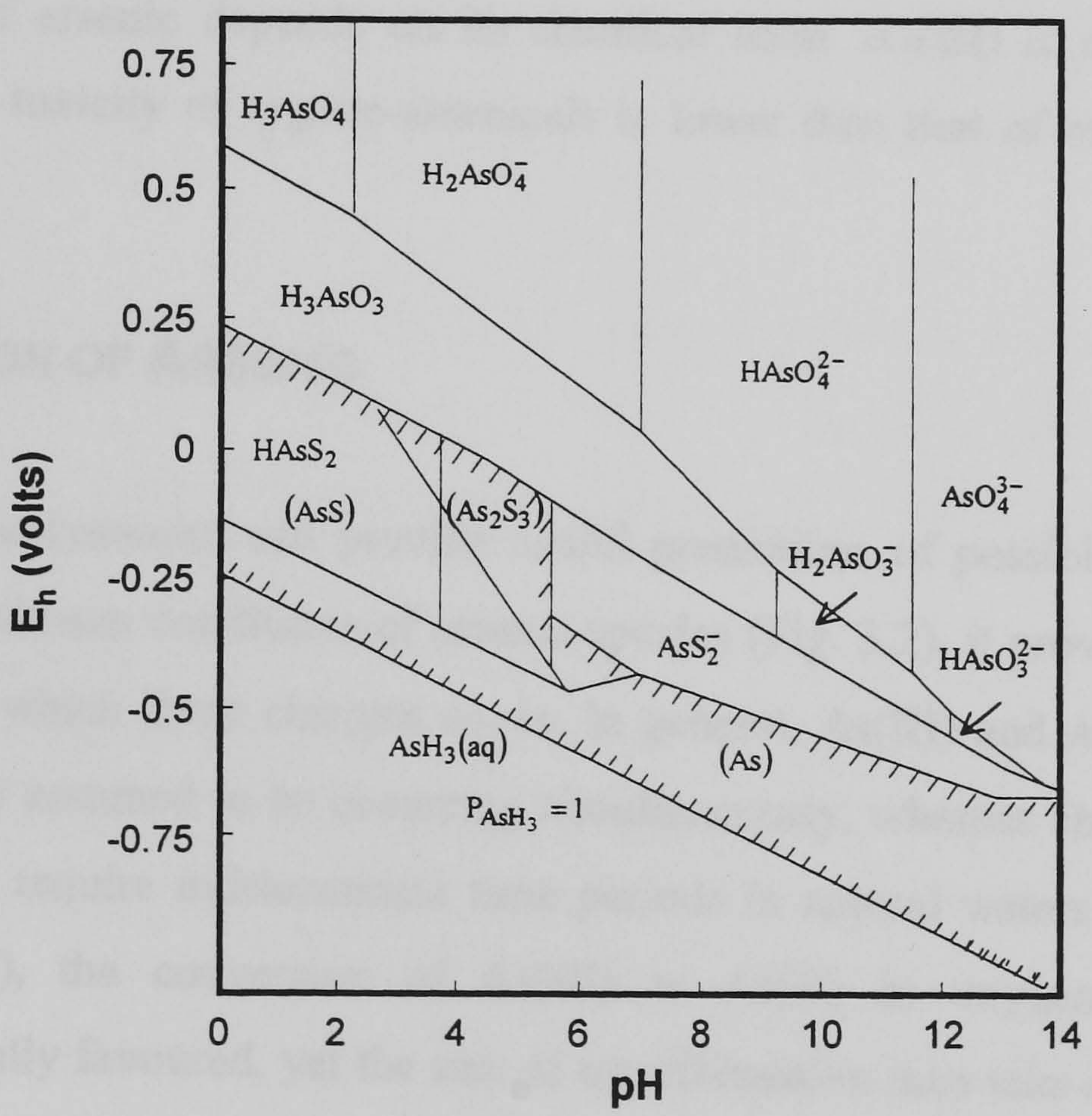


Fig. 3.2 The E_h-pH diagram for arsenic at 25°C (Ferguson and Gavis, 1972)

Arsenic compounds realgar (AsS) and orpiment (As_2S_3) have low solubilities and occur as stable solids at pH value below about 5.5. $HAsS_2$ (aq) is the dominant species at low pH in presence of sulphur and AsS_2 dominates at pH above 5.5. At very low E_h values, arsine (AsH_3) is slightly soluble (Fig. 3.2).

The arsenious and arsenic acids are dissociated according to the following equations:

$$H_3AsO_3 = H^+ + H_2AsO_3^- \qquad pKa = 9.22 \qquad (3.1)$$

$$H_3AsO_3^- = H^+ + HAsO_3^{2-} \qquad pKa = 12.3 \qquad (3.2)$$

$$H_3AsO_4 = H^+ + H_2AsO_4^- \qquad pKa = 2.2 \qquad (3.3)$$

$$H_2AsO_4^- = H^+ + HAsO_4^{2-} \qquad pKa = 7.08 \qquad (3.4)$$

$$HAsO_4^{2-} = H^+ + AsO_4^{3-} \qquad pKa = 11.5 \qquad (3.5)$$

(pKa is the pH at which the dissociation of the reactant is 50% complete).

The toxicity of arsenic depends on its chemical form. As(III) is more toxic than As(V) and the toxicity of organo-arsenicals is lower than that of inorganic arsenic species.

3.3 OXIDATION OF ARSENIC

Although thermodynamics can provide useful predictions of possible changes in a given non-equilibrium conditions of arsenic species (Fig. 3.2), it provides no insight into the rate at which these changes occur. In general, As(III) and As(V) acid-base reactions can be assumed to be occurring simultaneously, whereas changes between oxidation states require indeterminate time periods in natural waters. According to Edwards (1994), the conversion of As(III) to As(V) in oxygenated water is thermodynamically favoured, yet the rate of transformation may take days, weeks or months depending on the specific conditions. Strongly acidic or alkaline solutions, the presence of copper salts, carbon, unknown catalysts and higher temperature can increase the oxidation state (Ferguson and Gavis, 1972; Johnson and Pilson, 1972;

and Johnson, 1972). Manganese oxide, chlorine, hydrogen per oxide, ozone, permanganate etc. can directly transfer As(III) to As(V) in the absence of oxygen (Oscarson *et al*, 1983; Frank and Clifford, 1986; and Lauf and Waer, 1993). When selecting an appropriate oxidising agent in water treatment, there are important considerations such as a list of permitted chemicals, residuals of oxidants, oxidation by-products and the oxidation of other organic and inorganic water constituents play a major role in selecting an appropriate oxidising agent. Chlorine is widely used for oxidation, but may lead to chlorinated by-product, namely trihalomethanes (THMS) from reactions with natural organic matter. Clifford *et al* (1983) suggest that oxygen is a preferred oxidant, because it avoids some of the problems associated with other chemicals. However, the rate of oxidation by dissolved oxygen is very slow.

Fig. 3.3 shows the rate of catalytic oxidation of As(III) achieved by powdered activated carbon and dissolved oxygen in stirred reactors. Jekel (1994) states that this rate of oxidation is not fast enough and necessitates high concentrations of powdered active carbon to oxidise greater than 90% of As(III) in 20 to 30 minutes. It is not feasible to use this method in a treatment plant because of the excessive amount of residual active carbon, which are generated by the process.

According to Jekel's study (1994), the most feasible oxidants are potassium permanganate and Fenton's reagent (H_2O_2/Fe^{2+}) in precipitation-coagulation and rapid filtration processes. Permanganate oxidises As(III) specifically and quickly.

Unexpectedly, As(III) oxidation has been observed to be independent of oxygen concentration in sea water (Johnson and Pilson, 1972). Likewise the reduction of As(V) to As(III) in the absence of oxygen is chemically slow and requires bacterial mediation (McBride and Wolfe, 1971).

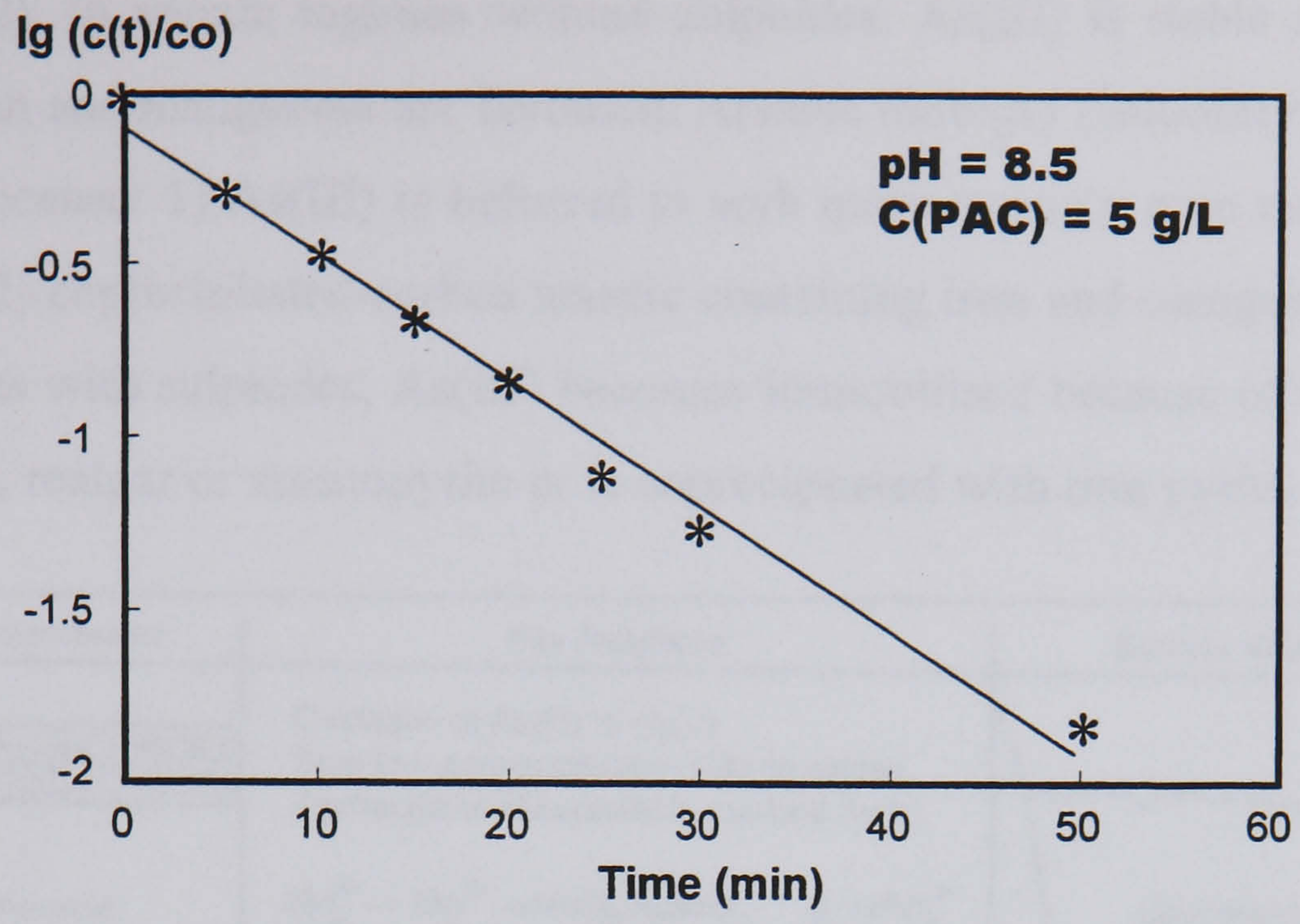


Fig. 3.3 Rate of catalytic oxidation of As(III) according to a first order rate equation with 40 mg/l initial As(III) concentration, 5 g/l powdered active carbon at pH 8.5 (Gottshalk *et al*, 1992)

3.4 LOCAL CYCLING OF ARSENIC IN AQUATIC REGIMES

A cycle for arsenic reactions in aquatic systems is illustrated in Fig. 3.4 (Edwards, 1994). These reactions apply generally to ground and surface water sources and include the transition from solution to the solid phase, and conversion from one oxidation state to another. For each water source, three distinct zones are evident i.e. aerobic, anaerobic without sulphide, and anaerobic with sulphides. These zones might correspond to the epilimnion, hypolimnion and sediments within a strata, lake or analogously, to increasing depth with a ground water aquifer. In an aerobic epilimnetic water, reduced forms of arsenic tend to be oxidised to arsenate, and coprecipitates with ferric hydroxide (Ferguson and Gavis, 1972). High concentrations of orthophosphate may compete with arsenic for adsorption sites in this zone, increasing soluble arsenic concentration and mobility (Edwards, 1994). Turbulent dispersion and convection transport some of the arsenate across the thermocline to the oxygen-depleted hypolimnion, where reductions to $HAsO_2$ and AsS_2^- take place, depending on the sulphur concentration and E_h (Ferguson and

Gavis, 1972). In anoxic regimes without sulphides, As(III) is stable and dissolved forms of iron and manganese are favoured. Arsenic mobility (solubility) is highest in this zone because: 1) As(III) is believed to sorb more strongly onto oxides than the As(V) and 2) coprecipitated-sorbed arsenic containing iron and manganese oxides in anoxic zones with sulphides, As(III) becomes immobilised because of the formation of orpiment, realgar or arsenopyrite or is coprecipitated with iron pyrite.

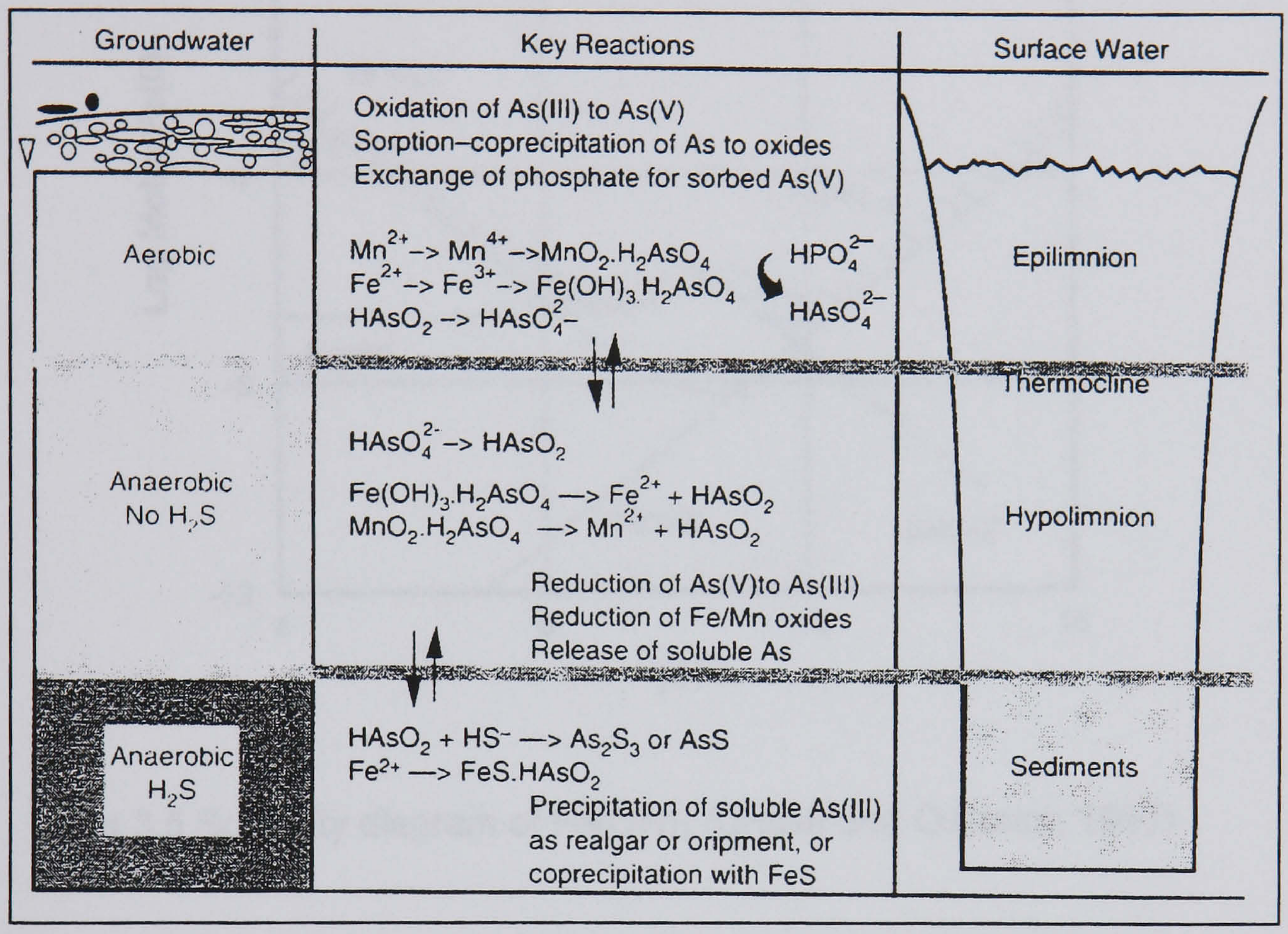


Fig. 3.4 Cycling of arsenic in aquatic regimes (Edwards, 1994)

3.5 IRON CHEMISTRY

3.5.1 Solubility of Iron

In the pH range of natural water, soluble ferrous iron consists of Fe^{2+} and $FeOH^+$ (Morgan and Stumm, 1964). As found by Ghosh and O'Conor (1966), alkaline natural water containing 5× 10^{-3} moles/l of total carbonic species, e.g. H_2CO_3, HCO_3^- and CO_3^{2-}, the solubility of ferrous carbonate in the pH range of 6-9 (Fig. 3.5). Theoretically, iron that precipitates from a supersaturated solution of this type would be either ferrous carbonate or ferrous hydroxide depending on the pH. Under practical condition, the precipitation of basic carbonates e.g. ($Fe(OH)_2$. $FeCO_3$) is probable — especially in the pH range of 8 to 11 (Ghosh and O'Conor, 1966).

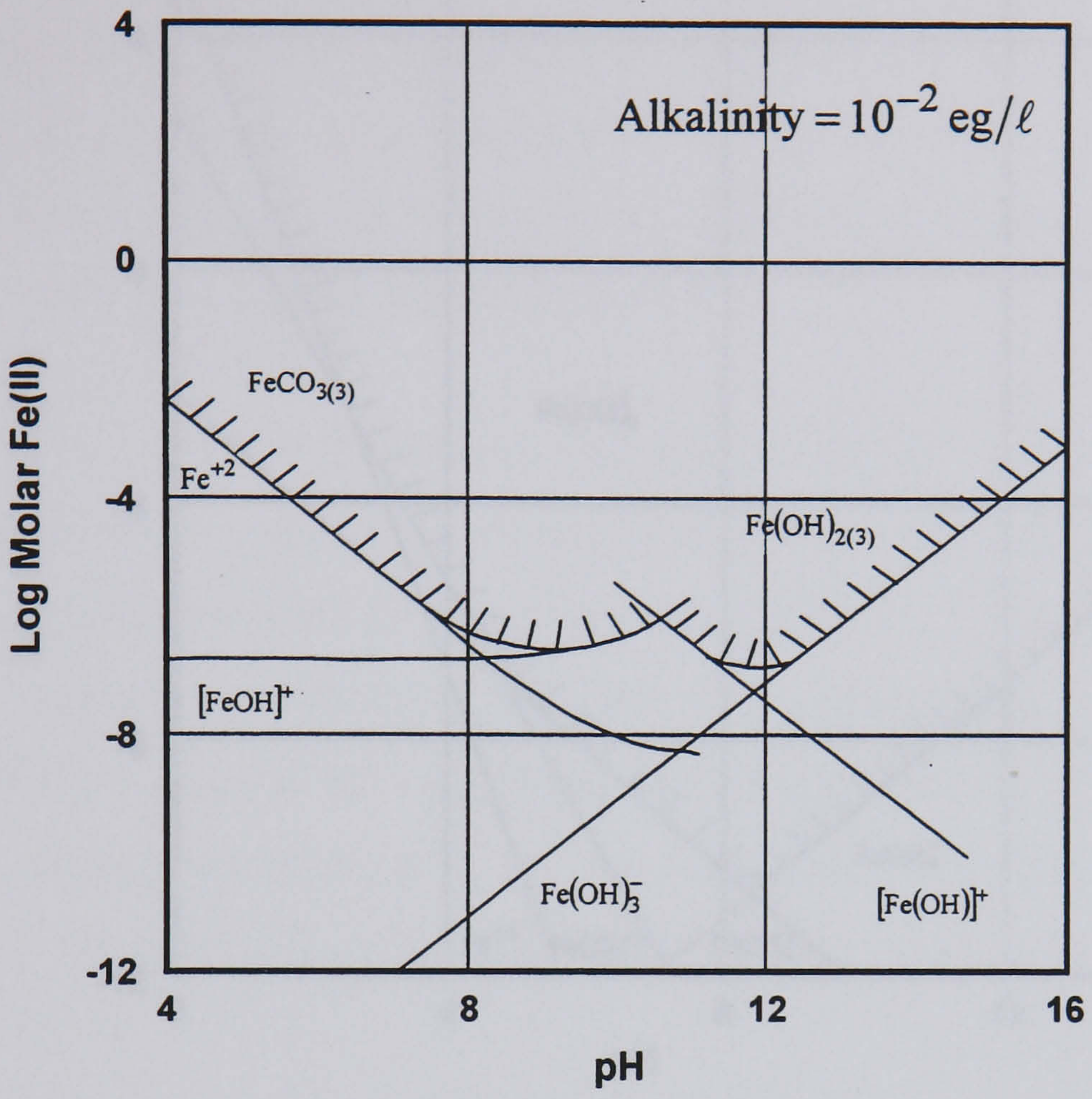


Fig 3.5 Solubility diagram of $Fe(OH)_2$ (Ghosh and O'Conor, 1966)

On aeration or by the addition of oxidising agents, iron is oxidised from the ferrous to ferric form. The solubility of ferric iron in natural water is generally governed by the solubility of $Fe(OH)_3$ or ferric oxy-hydroxide, FeOOH. Once oxidised, the solubility of iron is severely limited over a wide range of pH values from 4 to 13 by the solubility of ferric hydroxide (Fig. 3.6). Ferric ion has generally a stronger tendency to form complexes than the ferrous ions.

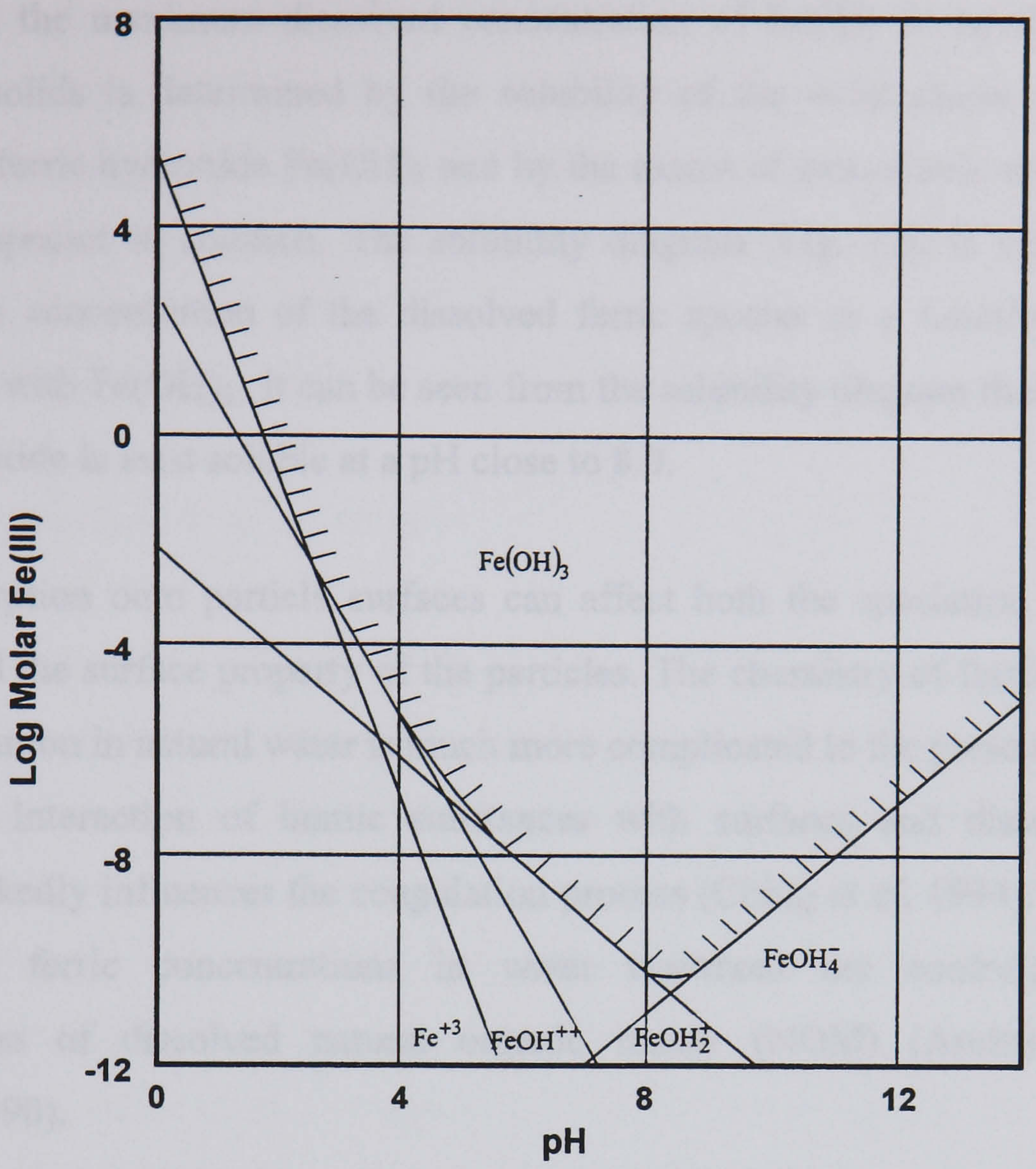


Fig. 3.6 Solubility diagram of Fe(OH)3 (Ghosh and O'Conor, 1966)

When Fe(III) salts are dissolved in water, the metal ion hydrates, co-ordinating with six water molecules to form $Fe(H_2O)_6^{3+}$. This $Fe(H_2O)_6^{3+}$ ion then can hydrolyse and form monomeric and polymeric ferric species, the formation of which is highly pH dependent (Stumm and Morgan, 1981). It is possible to describe the formation of several hydrolysis species that are positively charged: $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$; neutral $Fe(OH)_3^o$ and negatively charged: $Fe(OH)_4^-$. In general the hydrolysis reactions of Fe(III) in aqueous solution can be written as (Ching *et al*, 1994):

$$xFe^{3+} + yH_2O = Fe_x(OH)_y^{(3x-y)+} + yH^+ \qquad (3.6)$$

At any pH, the maximum dissolved concentration of Fe(III) in equilibrium with hydroxide solids is determined by the solubility of the solid phase, in this case amorphous ferric hydroxide $Fe(OH)_3$ and by the extent of monomeric and polymeric hydrolysis species in solution. The solubility diagram (Fig. 3.6) is very useful to describe the concentration of the dissolved ferric species as a function of pH, at equilibrium with $Fe(OH)_3$. It can be seen from the solubility diagram that amorphous ferric hydroxide is least soluble at a pH close to 8.0.

Ferric adsorption onto particle surfaces can affect both the speciation of ferric in solution and the surface property of the particles. The chemistry of ferric adsorption and precipitation in natural water is much more complicated in the presence of humic substances. Interaction of humic substances with surfaces and dissolved ferric species markedly influences the coagulation process (Ching *et al*, 1994). It is known that actual ferric concentrations in water treatment are controlled by the concentration of dissolved natural organic matter (NOM) (Amirtharajah and O'Melia, 1990).

3.5.2 Oxidation of Iron

The reaction of ferrous iron with oxygen leads to the formation of ferric oxides or hydroxides. The stoichiometric relationship is as follows:

$$Fe^{2+} + \tfrac{1}{4}O_2 + 2OH^- + \tfrac{1}{2}H_2O \rightarrow Fe(OH)_3 \qquad (3.7)$$

which indicates that 1 mg/l of O_2 will oxidise 7 mg/l of ferrous iron.

Ghosh and O'Conor (1966) stated that the rate of ferrous iron oxidation is of the first order with respect to ferrous iron concentration and the partial pressure of oxygen. According to Ahmed (1987), the oxidation of ferrous iron increases rapidly at pH 7.0 or above and is very slow below pH 6.0. Solubility of ferric hydroxide decreases with increasing pH only about 10.0. Oxidation reaction is incomplete and very slow for low alkaline water. He states that an increase of 1 pH unit causes 100 fold increase in the rate of reaction. Robinson and Dixon (1968) mentioned that in order to obtain complete oxidation of the ferrous iron, the bicarbonate alkalinity of the water should be in excess of 100 mg/l as $CaCO_3$. Temperature also plays a positive role in increasing oxidation-reaction rate. The oxidation rate increases about 10 fold for a 15°C increase in temperature (Ahmed, 1987).

3.6 ARSENIC REMOVAL MECHANISMS FROM SOLUTION

3.6.1 Coagulation-precipitation

Arsenic can be successfully removed by coagulation-precipitation process where addition of coagulant facilitates the conversion of soluble arsenic species into insoluble products (Shen, 1973; Pierce and Moore, 1982; and Frank and Clifford, 1986). These products may form through a coprecipitation-adsorption process. Coprecipitation is defined as an incorporation of soluble arsenic species into a growing hydroxide phase via inclusion, occlusion or solid-solution formation. Inclusion is the mechanical entrapment of solution inside the growing precipitate whereas occlusion refers to the entrapment of adsorbed contaminant in the interior of the growing particle. The solid-solution formation is the incorporation of the contaminant into the bulk phase rather than only onto the surface of the precipitate.

Adsorption is a process of formation of surface complexes between soluble arsenic species and the solid oxy-hydroxide surface site. Edwards (1994) expresses the adsorption of arsenic onto ferric oxy-hydroxide as follows:

$$\equiv \mathrm{Fe}-\mathrm{OH} + \mathrm{H_2AsO_4^-} + \mathrm{H^+} \rightarrow \mathrm{Fe}-\mathrm{H_2AsO_4^-} + \mathrm{H_2O} \qquad \text{(arsenate sorption) (3.8)}$$

$$\equiv \mathrm{Fe}-\mathrm{OH} + \mathrm{H_3AsO_3} \rightarrow \mathrm{Fe}-\mathrm{H_2AsO_4} + \mathrm{H_2O} \qquad \text{(arsenite sorption) (3.9)}$$

in which $\equiv \mathrm{Fe}-\mathrm{OH}$ is an oxy hydroxide surface site.

3.6.1.1 Concepts of arsenic removal during iron precipitation

Arsenic in raw water may be either in soluble or particulate form, with particulate arsenic seemingly sorbed to Fe solids (Chen and Edwards, 1996). Likewise, iron may be present in true solution (Fe^{2+}) or particulate ($Fe(OH)_3$) form, that can influence transport and removal of arsenic during treatment processes (McNeill and Edwards, 1997). Freshly precipitated iron oxides solid can form during water treatment by oxidation of soluble Fe^{2+} species or by direct addition of $FeCl_3$ or $Fe_2(SO_4)_3$ coagulants. Thus for any sample collected at a water treatment plant using iron coagulants or containing iron in the raw water, there is a quantifiable concentration of particulate iron oxide surface $[\equiv Fe]_{total}$, soluble arsenic $(As)_{soluble}$ and arsenic that is sorbed or coprecipitated with iron oxide solids $[As]_{sorbed}$ (McNeill and Edwards, 1997).

3.6.2 Adsorption

Adsorption is a physical process occurring when liquids, gases or suspended matter adheres to the surfaces of, or in the pores of adsorbent medium. Adsorption is a dominant mechanism in removing arsenic from water. Several adsorptive mediums such as activated carbon, activated alumina, preformed ferric hydroxide etc. (Gupta and Chen, 1978; Driehaus *et al*, 1998; and Hering *et al*, 1996) are reported to have removed arsenic from water effectively.

Eguez and Cho (1987) suggest that the adsorption of arsenic is by physiosorption and due to weak forces such as Van der Waals forces. Little is known about the adsorption mechanism of arsenic species onto activated carbon and alumina. A general view is that the arsenic adsorption mechanism may not be solely explained in terms of molecule-surface interaction, electrostatic interaction or occlusion (Gupta and Chen, 1978). For As(V) adsorption, $H_2AsO_4^-$ is the major species removed by activated carbon. It may be the result of the reaction of the monovalent species with the oxofunction groups on the carbon surface as suggested by Huang and Wu (1975). There is probably little affinity between carbon surface and the non-ionic, divalent, and trivalent forms of As(V). For As(V), negatively charged molecules are removed effectively onto the slightly positive or neutral charge surfaces. For As(III) adsorption, neutral H_3AsO_3 molecules are removed on relatively neutral charged surfaces. Based on previous studies of anion adsorption onto goethite (FeOOH)

(Hingston *et al*, 1972), for adsorption of As(V) and As(III) species, point of inflection should result around pK values of these species, if electrostatic interactions and specific adsorption mechanisms are dominant. A study carried out by Gupta and Chen (1978) demonstrates the point of inflection around pH 7.0 and 9.0 for As(V) and As(III) adsorption onto activated alumina and bauxite respectively (Figs. 3.7a, 3.7b and Fig. 3.8). It seems that electrostatic interaction and specific adsorption are important mechanisms for arsenic removal by activated alumina and bauxite.

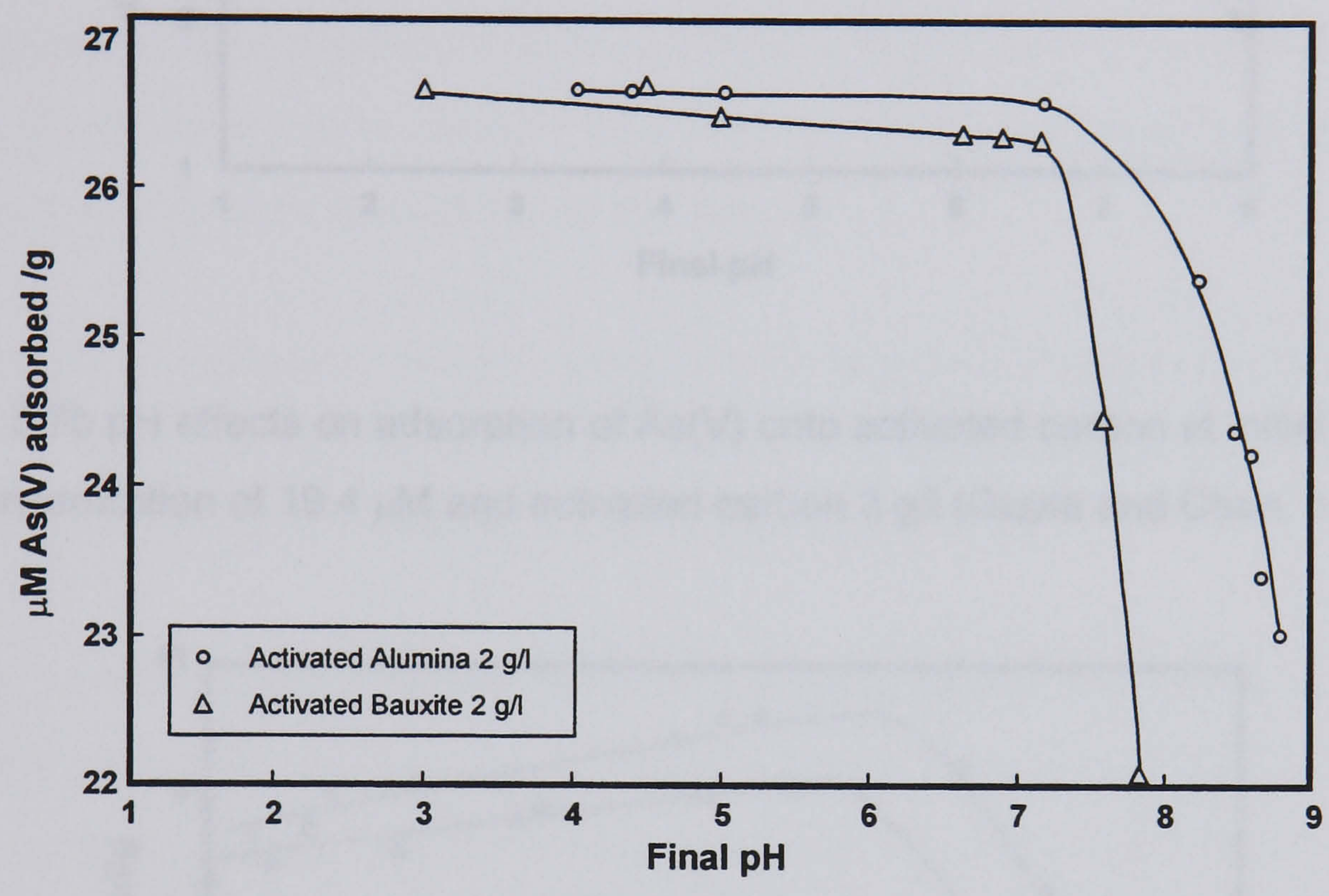


Fig. 3.7a pH effects on adsorption of As(V) onto activated alumina and bauxite at initial As(V) concentration of 53.4 µM (Gupta and Chen, 1978)

Many adsorption models have been developed to describe adsorption behaviour at the solid solution interface such as ion-exchange model and surface complexation model. Most of the adsorption data has been explained on the basis of surface complexation model (Bachelor and Dennis, 1987; and Westall, 1987). Surface complexation may occur when a proton from an undissociated arsenic ion forms a molecule of water with the hydroxyl group of the hydrous oxide followed by its displacement by the arsenic ions. The potential for surface complexation depends on the protonation state of arsenic ion and is more favourable at lower pH (Prashad, 1994).

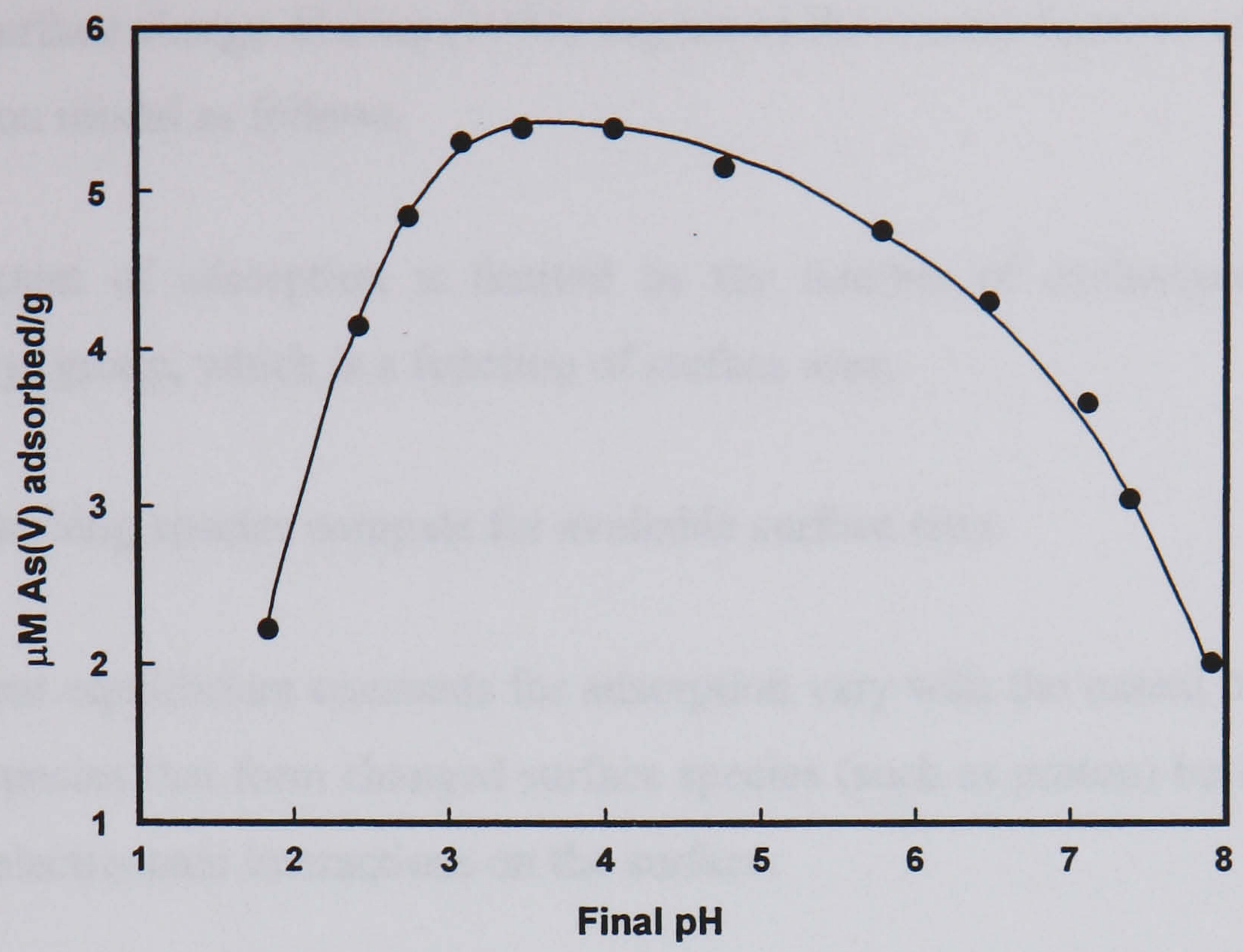


Fig. 3.7b pH effects on adsorption of As(V) onto activated carbon at initial As(V) concentration of 19.4 µM and activated carbon 3 g/l (Gupta and Chen, 1978)

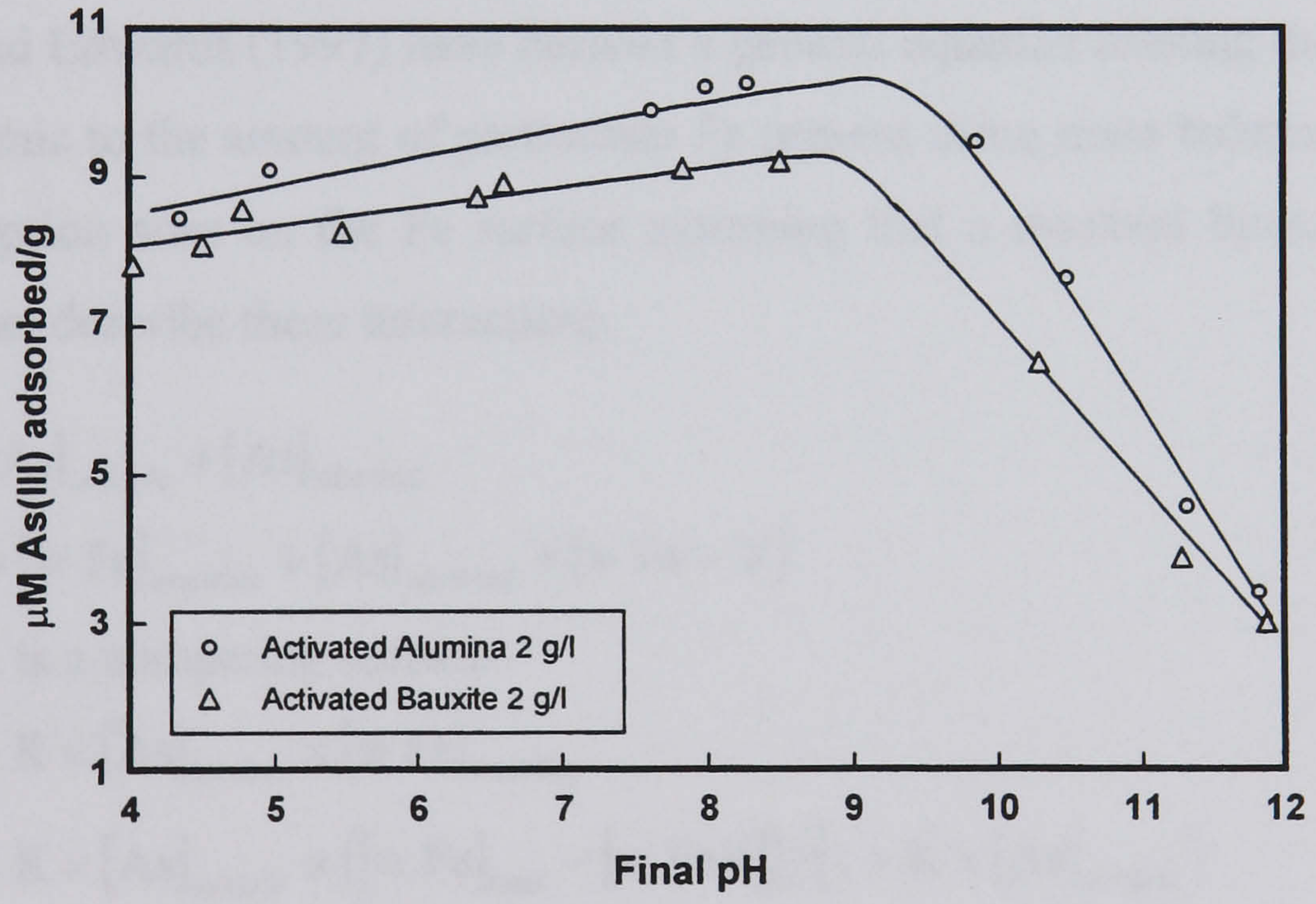


Fig. 3.8 pH effects on adsorption of As(III) onto activated alumina and bauxite at initial As(III) concentration of 26.0 µM (Gupta and Chen, 1978)

Formation of surface complexes at the oxide surface can be modelled by using mass balance and equilibrium expressions where the apparent equilibrium constant for formation of surface complex contains a coloumbic term due to the electrostatic effects of surface charge. Hering (1994) expressed the central features of the surface complexation model as follows:

1) The extent of adsorption is limited by the number of exchangeable surface hydroxyl group, which is a function of surface area.
2) All adsorbing species compete for available surface sites.
3) Apparent equilibrium constants for adsorption vary with the extent of adsorption of all species that form changed surface species (such as proton) because of long range electrostatic interactions on the surface.

This surface complexation model allows the calculation of the extent of adsorption of dissolved species at varying sorbate and sorbent concentrations and as a function of pH, ionic strength and concentrations of co-occurring solutes.

McNeill and Edwards (1997) have derived a general equation relating the amount of sorbed arsenic to the amount of particulate Fe present using mass balance on arsenic and on sorption sites on the Fe surface assuming that a standard linear adsorption isotherm can describe these interactions.

$$[\mathrm{As}]_{\mathrm{total}} = [\mathrm{As}]_{\mathrm{soluble}} + [\mathrm{As}]_{\mathrm{adsorbed}} \tag{3.10}$$

$$[\equiv \mathrm{Fe}]_{\mathrm{total}} = [\equiv \mathrm{Fe}]_{\mathrm{available}} + [\mathrm{As}]_{\mathrm{adsorbed}} + [\equiv \mathrm{Fe} - \mathrm{X}] \tag{3.11}$$

in which X is a competing sorbate.

$$[\mathrm{As}]_{\mathrm{sorbed}} = \mathrm{K} \times [\mathrm{As}]_{\mathrm{soluble}} \times [\equiv \mathrm{Fe}]_{\mathrm{available}} \tag{3.12}$$

$$[\mathrm{As}]_{\mathrm{sorbed}} = \mathrm{K} \times [\mathrm{As}]_{\mathrm{soluble}} \times \left([\equiv \mathrm{Fe}]_{\mathrm{total}} - [\equiv \mathrm{FeX}]\right) / \left(1 + \mathrm{K} \times [\mathrm{As}]_{\mathrm{soluble}}\right) \tag{3.13}$$

At low arsenic concentration, $\left(\mathrm{K} \times [\mathrm{As}]_{\mathrm{soluble}} << 1\right)$, the denominator is approximately equal to 1. If competition from other species (X) is weak, then $[\equiv \mathrm{Fe} - \mathrm{X}]$ is negligible compared with $[\equiv \mathrm{Fe}]_{\mathrm{total}}$. Eq. 3.13 then becomes

$$[\mathrm{As}]_{\mathrm{adsorbed}} = \mathrm{K} \times [\mathrm{As}]_{\mathrm{soluble}} \times [\equiv \mathrm{Fe}]_{\mathrm{total}} \tag{3.14}$$

Rearranging equation 3.14 in terms of $[As]_{sorbed}$ for convenience yields

$$[As]_{sorbed}(\%) = (K \times [Fe]mM)/(1 + K \times [Fe]mM) \times 100 \qquad (3.15)$$

Eq. 3.15 can be easily used for prediction of arsenic removal in any system if a single constant (e.g., K, mM^{-1}) and the quantity of iron hydroxide are known.

3.6.2.1 Adsorption Isotherm

Adsorption of substances onto adsorbent takes place because there are forces that attract the adsorbate to the solid surface from solution. Thermodynamically adsorbate has a lower free energy at the surface than in solution and during equilibration, the adsorbate is driven onto the surface to the lower energy state. The specific forces or mechanism by which adsorbate is attracted to the solid solution interface can be physical or chemical.

The common way to depict this adsorption is to express the amount of substance adsorbed per unit weight or mole of adsorbent, q_e, as a function of the equilibrium concentration, C_e, of substance remaining in the solution phase, termed as “adsorption isotherm”. It is termed as isotherm because it describes the equilibrium state of adsorbent, adsorbate and solute at a given temperature. The determination of isotherm is probably the most useful way of characterising the adsorbing properties of a substance in presence of an adsorbing surface. Different adsorption isotherm models are as follows: Langmuir, Freundlich, Gibbs, Brunauer, Emmet and Teller (BET) and the linear model (Weber, 1985). These models are graphically presented in Fig. 3.9.

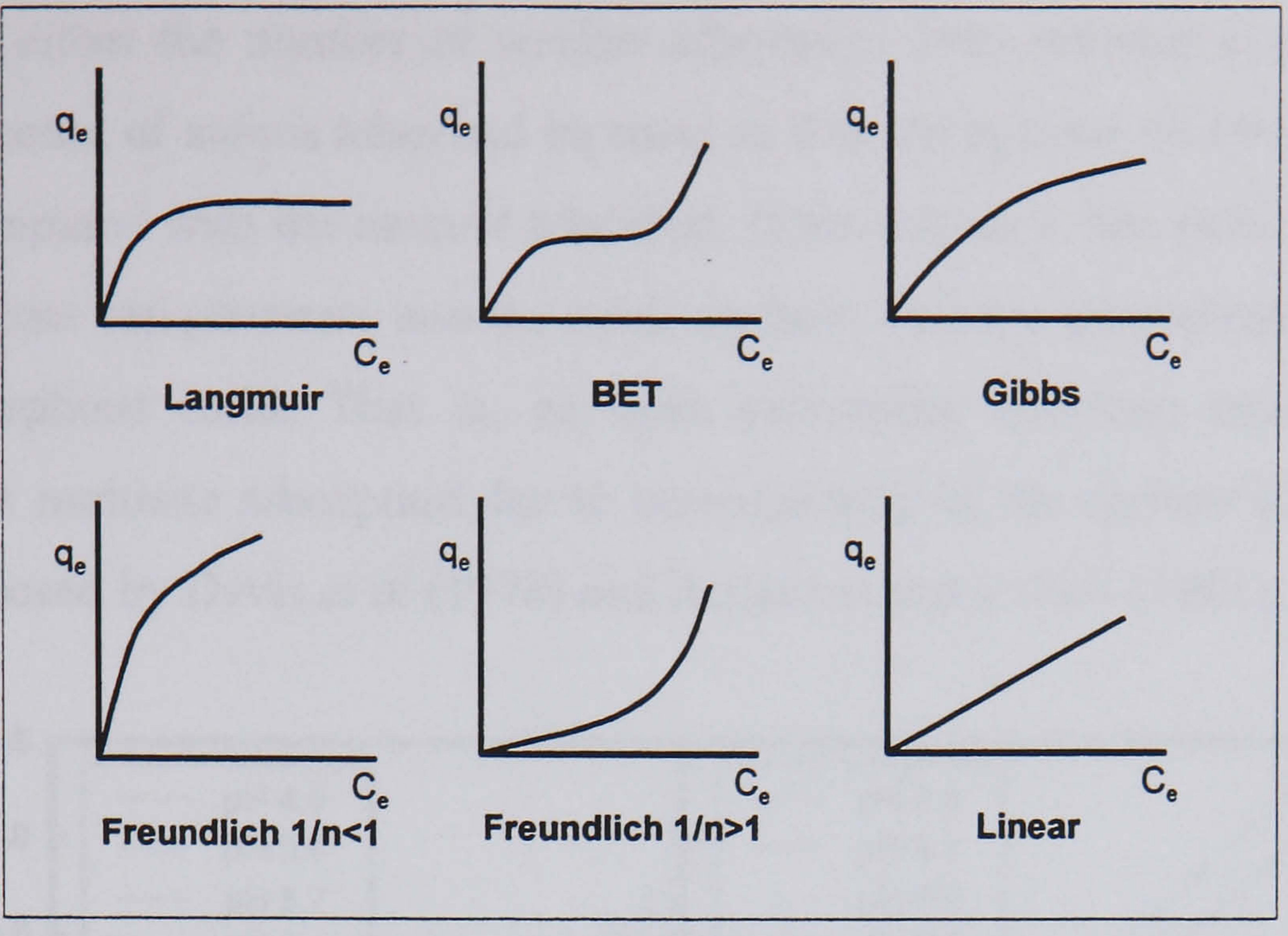


Fig. 3.9 Graphical representation of adsorption isotherm models (Voice and Weber, 1983)

Several studies were carried out to investigate the adsorption behaviour of As(V) and As(III) onto different adsorbents like iron hydroxide, activated carbon, alumina, bauxite etc. Most of the studies showed that both As(V) and As(III) followed Langmuir isotherm (Ferguson and Anderson, 1974 and Gupta and Chen, 1978). Pierce and Moore (1982) extensively studied the adsorption characteristics of arsenic and found two different adsorption behaviour of arsenic onto amorphous ferric hydroxide depending on the initial concentration of arsenic over a wide pH range of 4.0 to 10.0. The isotherms plotted at constant pH at the concentrations of 0.667-13.3 µm/l shows that As(III) adsorption is best described by a Langmuir isotherm (Fig. 3.10a). But the adsorption of As(III) onto $Fe(OH)_3$ using higher initial concentrations from 33.4 to 667.3 µm/l shows that the Langmuir isotherm is not obeyed any more in this range, rather a linear isotherm is followed (Fig. 3.10b). Pierce and Moore (1982) partially explained this dependence on two different isotherms as follows: the oxide surfaces have different types of surface sites, with different affinities for adsorbate ions. The surface density of the strong binding sites would be much less than the weaker binding sites. Therefore, adsorption proceeds until all the strong binding sites are occupied, which would allow a Langmuir isotherm. Then the anions would start to adsorb on the weaker binding sites. The linear isotherm at the high concentrations indicates that either the number of weaker adsorption sites remains constant even though the amount of anions adsorbed increase or that the number of weaker sites is very large compared with the amount adsorbed. If the former is the case, it suggests that the adsorbate can penetrate into the oxide surface, which is theoretically possible with an amorphous solid. That is, an open permeable structure exists for am $Fe(OH)_3$. This multisite adsorption due to heterogeneity of the surface is consistent with that proposed by Davis *et al* (1978) and Benjamin and Leckie (1981).

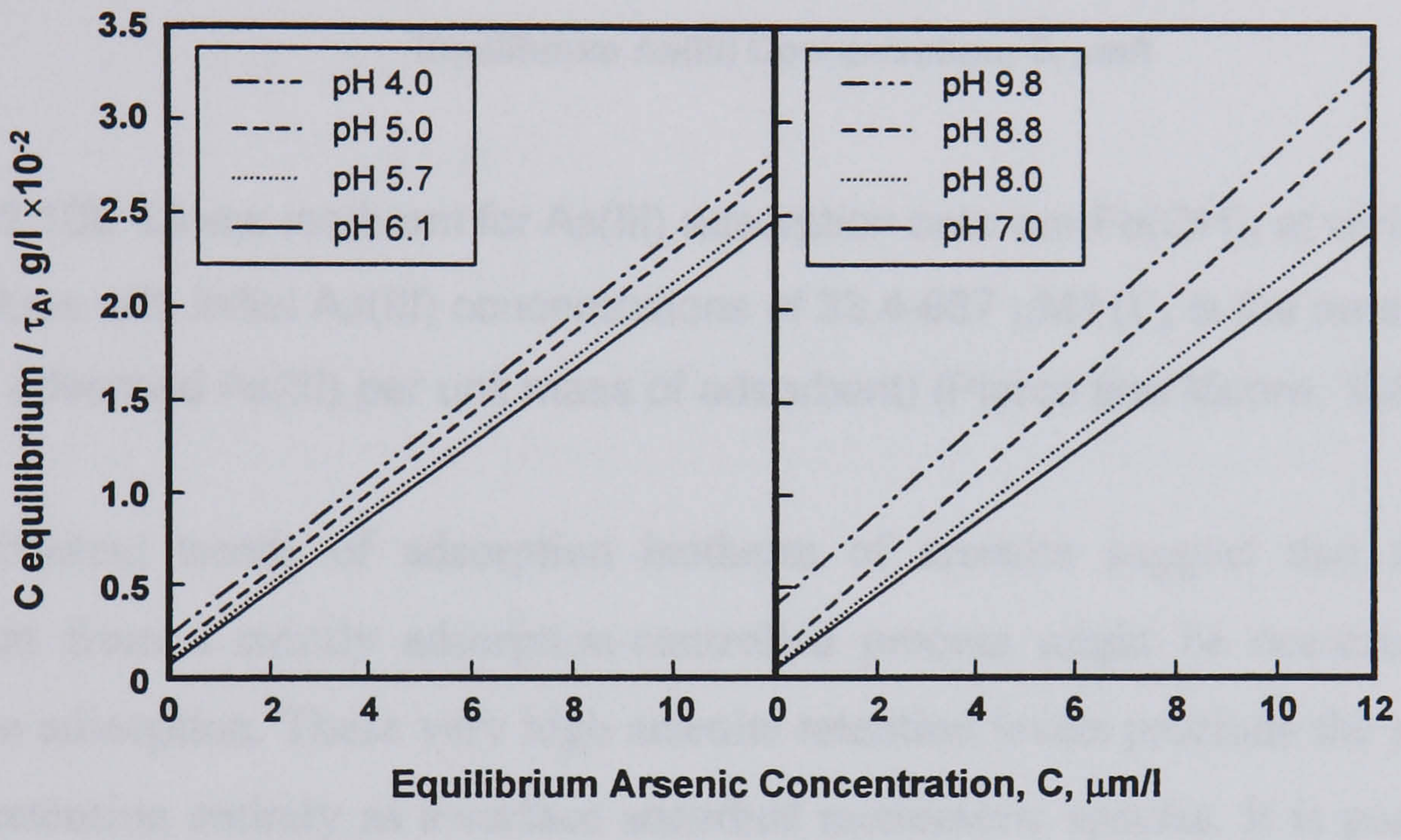


Fig 3.10a Langmuir isotherm for As(III) adsorption onto am-$Fe(OH)_3$ at various pH values with initial As(III) concentrations of 0.667-13.3 μM/l (Γ_A is the amount of adsorbed As(III) per unit mass of adsorbent) (Pierce and Moore, 1982)

Pierce and Moore (1982) obtained the same trend of adsorption isotherm of As(V) onto amorphous $Fe(OH)_3$ i.e. for initial concentration of 0.667- 13.3 μm/l, it follows Langmuir isotherm and for concentration of 33.4 –667 μm/l, it follows linear isotherm.

Ferguson and Anderson (1974) stated that As(III) adsorption did not reach a state of saturation and observed a maximum adsorption density of 0.54 mg As / mg Fe.

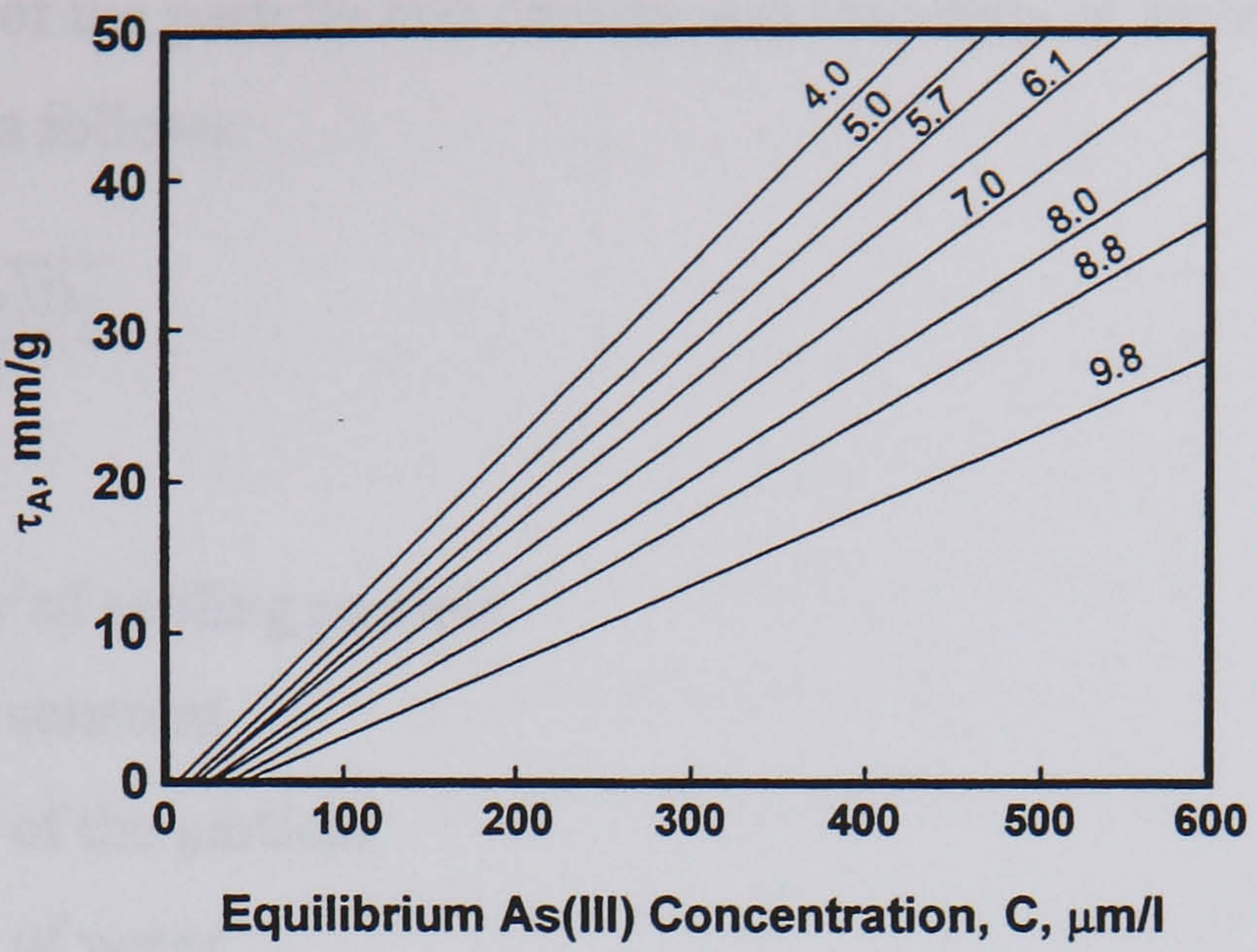


Fig 3.10b Linear isotherm for As(III) adsorption onto am-Fe(OH)$_3$ at various pH values with initial As(III) concentrations of 33.4-667 μM/l (Γ_A is the amount of adsorbed As(III) per unit mass of adsorbent) (Pierce and Moore, 1982)

The different trends of adsorption isotherm of arsenite suggest that something different from a strictly adsorption-controlled process might be occurring during arsenite adsorption. These very high arsenite retention levels preclude the possibility of its retention entirely as a surface adsorbed monomeric species. It is possible that upon reaction with arsenite, the ferrihydrite was reordered as a ferric arsenate phase, although this hypothesis would require verification by other means (Raven *et al*, 1998).

Gupta and Chen (1978) showed that arsenic adsorption onto activated carbon, alumina and bauxite appeared to confirm to Langmuir isotherms.

3.6.3 Sedimentation

Gravity separation of suspended particles from water is the most widely used low-cost technique in water treatment. Several factors control the sedimentation process, such as concentration and size of the particle, flocculation, viscosity and density of water etc. For isolated discrete particles, the settling velocity is a function of size, shape and density of the particle and density and viscosity of water. The relationship can be expressed as follows:

$$V_s = \sqrt{\frac{4}{3}\frac{g}{C_D}\frac{(\rho_S - \rho) D_S}{\rho}} \quad (3.16)$$

where

V_s = velocity of settling particle

g = gravity constant

ρ_s = density of the particle

ρ = density of water

D_s = diameter of the particle

C_D = drag coefficient

The drag coefficient varies as a function of density, relative velocity, particle diameter and fluid viscosity, which are expressed by the dimensionless Reynolds number, R:

$$R = \rho V D / \mu \quad (3.17)$$

Where,

ρ = density of fluid

μ = viscosity of fluid

D = diameter of particle

V = relative velocity

For Reynolds numbers less than 2, C_D is related to R by the expression

$$C_D = 24/R \quad (3.18)$$

which is formulated by Stokes law and equation 3.16 can be substituted as follows:

$$V_s = (g\,(\rho_s - \rho)\, D_s^2) / 18\nu\rho \quad (3.19)$$

where

ν = kinematic viscosity (μ/ρ)

From the eqn. 3.19, it is seen that settling velocity is proportional to the square of particle diameter and inversely proportional to the kinematic viscosity of water. The kinematic viscosity is dependent on temperature — if temperature increases, the kinematic viscosity decreases and therefore the settling velocity increases.

Furthermore, flocculation has a major influence on settleability. Flocculation depends on the number of particles and the probability of collision. Collision may result from variable velocity of suspended particles and mixing condition. Particle transport of small colloidal particles is motivated by Brownian motion, and is called Perikinetic transport whereas transport of large particles is motivated by velocity gradient promoting the physical agitation and is called Orthokinetic transport. According to Tekippe and Ham (1971), coagulation is sometimes used to describe the formation of tiny agglomerates often called "unit flocs" that develop by perikinetic transport of primary particles. Flocculation is used to describe the growth of unit flocs into large, visible agglomerates through orthokinetic transport and bond formation. In a poorly mixed system, local variations of pH and particle concentration will produce more heterogeneous flocculent particles than would be found in a well-mixed system. Therefore, to enhance settling character, flocculation plays a major role in particle settling.

In case of iron removal process, oxidation of soluble iron is not the entire picture. According to Sung and Forbes (1984), when the initial iron concentration was in the range of 2- 5 mg/l, the precipitate was roughly concentrated in the sub micron size range. To enhance the settling, they proposed to promote flocculation before settling. Owens (1963) has also suggested using lime as the coagulant to accelerate the settling of iron precipitates.

3.7 ARSENIC REMOVAL TECHNIQUES IN PRACTICE

The techniques for removing arsenic can be split into two main groups: 1) coagulation-precipitation techniques and 2) adsorption techniques. Coprecipitation-adsorption by alum and iron salts followed by coagulation, lime softening and combination of iron and manganese removal with arsenic are commonly used precipitation techniques. In adsorption techniques, several sorption media such as preformed granular ferric hydroxide, activated carbon, activated alumina, bauxite etc. are usually used for removing arsenic. In general, the removal of arsenic by precipitation is the most effective process when smaller quantities of high concentration of arsenic water are treated. The cost effectiveness of precipitation is diminished in case of large quantities of low concentration arsenic water. In this situation, adsorption technology becomes cost-effective, especially if the adsorbent is regenerable (Huang and Vane, 1989). Some sophisticated techniques like ion exchange, membrane filtration and electrodialysis are sometimes used in the removal of arsenic (Legault *et al,* 1993; Kartinen and Martin, 1995; and Waypa *et al*, 1997).

3.7.1 Coagulation-precipitation

3.7.1.1 Iron and alum coagulation

Iron salts such as ferric sulphate or ferric chloride and alum are commonly used in coagulation-precipitation process for removing arsenic. The effectiveness of these coagulants depends mainly on the pH and on the oxidation state of arsenic. It has been found that higher removal is achieved if an oxidising agent such as chlorine is added to the treatment system for both cases of alum and iron salts (Kartinen and Martin, 1995). In the typical pH range of natural water (4-10), As(III) species are found neutral and As(V) species are usually negatively charged (Fig. 3.1) and probably due to the neutral charge of As(III), the removal efficiency of As(III) is much lower than that of As(V). Therefore, for an effective removal of arsenic, it is useful to oxidise As(III) to As(V) by adding any oxidant. Arsenic removal by alum is greatly influenced by pH. Generally around pH 7.0 is considered to be the optimum for alum coagulation (Karcher *et al*, 1999) whereas the influence of pH is not as significant as with iron salts within the pH range of 5- 8 (Sorg and Logsdon, 1978 and Kartinen and Martin, 1995).

Table 3.1 presents a summary of the arsenic removal capacity in different treatment processes. It is seen from Table 3.1 that $FeCl_3$ has a higher percentage of arsenic

Table 3.1 Efficiency of arsenic removal during coprecipitation –adsorption process.

Treatment process	Reference	Test parameters	%Arsenic removal
Iron coagulation	Cheng *et al* (1994)	$FeCl_3$: 30 mg/l As(V): 20 μg/l pH: 7.0	97.0
	Hering *et al* (1996)	$FeCl_3$: 20 mg/l pH: 7.0 As(V): 20 μg/l	> 90.0
		$FeCl_3$: 20 mg/l pH: 7.0 As(III): 20 μg/l	> 75.0
	Beltran (1993) (coagulants are formed in situ)	Fe(III): 90 μM As(III): 0.3 mg/l pH: 7.0	> 80.0
	Scott *et al* (1995)	$FeCl_3$: 20 mg/l As(V): 1.6 μg/l	92.0
Fe(III) ion precipitation with prechlorination to oxidise As(III) to As(V)	Jekel (1986)	As(V)+As(III): 135 μg/l Fe(III) ions: 4 mg/l pH: 6.1-6.5	> 95.0
Alum coagulation	Cheng *et al* (1994)	Alum: 30 mg/l As(V): 21.3 μg/l pH: 7.0	91.0
	Beltran (1993) (coagulants are formed in situ	Alum: 90μM As(III): 0.3 mg/l pH: 7.5	45.0
	Scott *et al* (1995)	Alum: 20 mg/l As(V): 2.2 μg/l	69.0

removal than alum. It is also observed that As(III) removal is less than As(V) removal for both alum and iron salts except the study carried out by Jekel (1986) (removal is > 95.0%) where oxidation of As(III) to As(V) was carried out prior to treatment. Therefore, it can be noted that for effective removal of arsenic by the coagulation process depends on many factors like type and dosage of coagulant, pH and oxidation state of arsenic. In this process, disposal of the arsenic contaminated sludge may be a concern.

3.7.1.2 Lime softening

Arsenic can be removed by lime softening process. The removal mechanism may be adsorption and / or coprecipitation with solids formed during softening (including $Mg(OH)_2$, $Mn(OH)_2$ and $CaCO_3$) possible precipitation of arsenic bearing solids such as calcium arsenate (Jekel, 1994; McNeill and Edwards, 1997a; and Edwards, 1994). The removal efficiency is significantly affected by pH. According to Dutta and Chaudhuri (1991), As(III) could be removed from 0.6 mg/l to less than 0.05 mg/l by lime softening (dosage 800 mg/l). Sorg and Logsdon (1978) present data indicating more than 90% removal of As(V) at pH above 10.5 and 75% removal of As(III) at pH above 11.0 with initial arsenic concentration of 0.4 mg/l and lime dosage of 300 mg/l as $CaCO_3$ (Fig. 3.11).

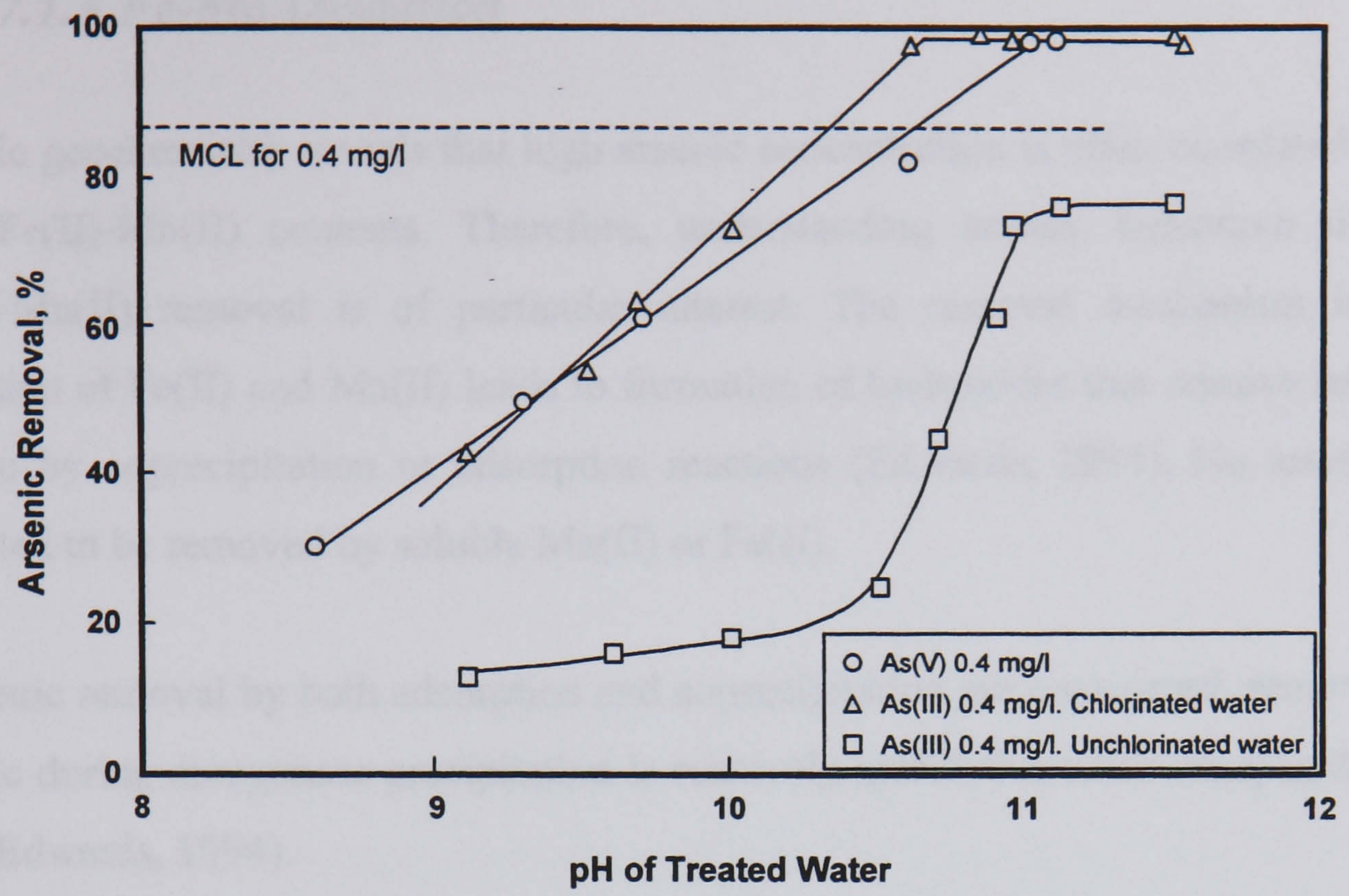


Fig. 3.11 Effects of pH on arsenic removal by lime softening (Sorg and Logsdon, 1978)

In this method, the chemical dosages were quite high and pre-oxidation would have been beneficial. McNeill and Edwards (1997a) studied the removal of arsenic using precipitative softening. Arsenic removal was facilitated by a variety of solids formed during softening including $CaCO_3$, $Mg(OH)_2$, and $Mn(OH)_3$. The following equations show an example of the reactions in the process.

$$Ca^{2+} + AsO_4^{3-} \rightarrow Ca_3(AsO_4)_2 \tag{3.20}$$

$$CaO + H_3AsO_3 \rightarrow CaHAsO_3 + H_2O \tag{3.21}$$

$$CaO + H_3AsO_4 \rightarrow CaHAsO_4 \tag{3.22}$$

They observed that presence of orthophosphate and carbonate slightly decreased the As(V) removal. For systems initially containing on Mn^{2+}, arsenic removal occurred by adsorption onto $Mn(OH)_3$ rather than formation of $Mn_3(AsO_4)_2$ precipitate. The addition of small amount of iron to waters before softening can greatly increase As(V) removal. However, due to its high lime requirements and high pH, the lime softening process in removing arsenic may be limited to very hard waters.

3.7.1.3 Fe-Mn Oxidation

Arsenic geochemistry reveals that high arsenic concentration is often correlated with high Fe(II)-Mn(II) contents. Therefore, understanding arsenic behaviour during Fe(II)-Mn(II) removal is of particular interest. The removal mechanism is the oxidation of Fe(II) and Mn(II) leads to formation of hydroxides that remove soluble arsenic by coprecipitation or adsorption reactions (Edwards, 1994). No arsenic is expected to be removed by soluble Mn(II) or Fe(II).

If arsenic removal by both adsorption and coprecipitation are considered, removal of arsenic during manganese precipitation is relatively ineffective when compared with iron (Edwards, 1994).

3.7.2 Adsorption techniques

3.7.2.1 Adsorption onto preformed $Fe(OH)_3$ / Hydrous ferric Oxide (HFO)

Adsorption of arsenic onto preformed $Fe(OH)_3$ or hydrous ferric oxide (HFO) is a successful method of removing arsenic (Pierce and Moore, 1982; Hering *et al*, 1996; Wilkie and Hering, 1996 and Driehaus *et al*, 1998).

$Fe(OH)_3$ or HFO adsorbents can be prepared by neutralising and precipitating iron salts such as ferric chloride, ferric sulphate or ferric nitrate using NaOH solution. After precipitation, suspensions may then be centrifuged and washed with nano pure water and suspended in ageing medium.

Like coagulation, As(V) is better removed than As(III) in adsorption. Hering *et al* (1997) showed that at pH 7.0, HFO concentration equivalent of 16.0 mg/l of $FeCl_3$ and initial arsenic concentration of 10 µg/l, 85% removal was obtained for As(V) whereas for As(III), it was 50% for the same test conditions. In contrast, Raven *et al* (1998) observed that As(III) adsorbed on ferrihydrite in larger amounts than As(V) at high arsenic concentrations. At pH 9.2, As(III) was adsorbed in larger amounts than As(V) even at low arsenic concentration. In the pH range of 4.6-9.2, neutral H_3AsO_3 (pK = 9.2) is the dominant As(III) species in solution. Therefore, the adsorption of As(III) would be less strongly influenced by the anion repulsion forces that would likely play an important role in the adsorption of As(V) species at high pH. Also, adsorption of neutral H_3AsO_3 would have less influence than the adsorption of negatively charged As(V) species on the total negative charge character of the ferrihydrite surface (Raven *et al*, 1998).

Driehaus *et al* (1998) has examined the removal efficiency of granular ferric hydroxide (GFH) for arsenic and found it as an effective media for adsorption. The adsorption density of arsenate in model system was in the range of 1 mM As/g Fe at a residual concentration of 10 µg/l at pH 7.0. The application of GFH in test adsorbers shows a high treatment capacity up to 40000 bed volumes.

However, arsenic removal during coagulation with $FeCl_3$ is noticeably more efficient than arsenic adsorption onto preformed HFO (Fig. 3.12). According to Driehaus *et al* (1998), the adsorption on freshly prepared ferric hydroxide is slightly greater than preformed GFH, which agrees with Pierce and Moore (1982). The high adsorptive capacity of amorphous $Fe(OH)_3$ (freshly prepared) can be explained by visualising a loose, highly hydrated structure which is permeable to hydrated ions. The ions are diffused throughout the structure and are not restricted to external surface sites such as the case with some crystalline solids like preformed GFH.

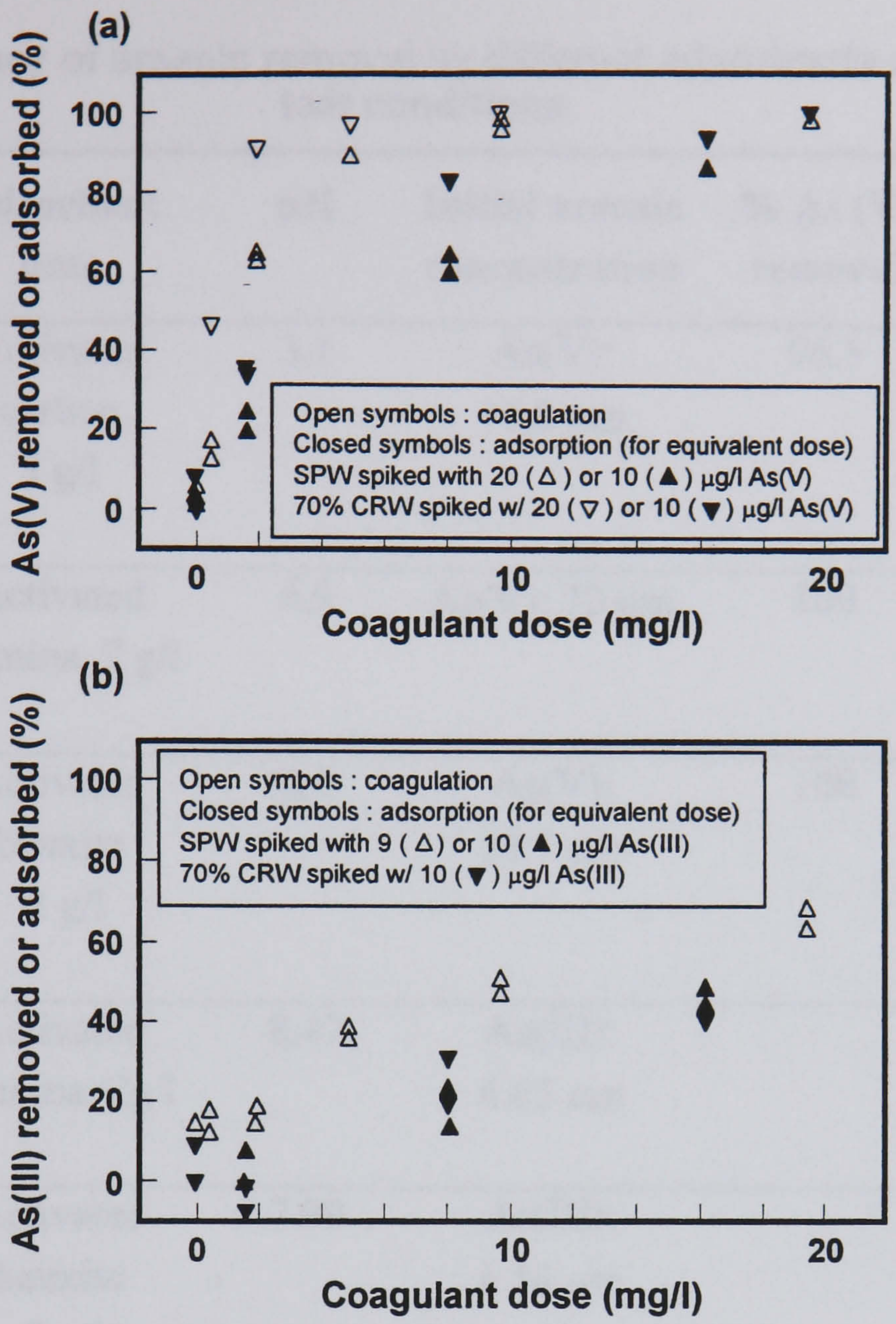


Fig. 3.12 Comparison of (a) As(V) and (b) As(III) removal and adsorption at pH 7.0; removal by $FeCl_3$ and adsorption onto HFO shown as a function of coagulant dose (or equivalent coagulant dose for adsorption) (Hering *et al*, 1997).

3.7.2.2 Adsorption onto activated carbon and activated alumina

Due to its easy handling, sludge free operation and regeneration capability, adsorption is a preferred technique for the removal of arsenic. Arsenic has been successfully removed by adsorption onto activated carbon (Huang and Fu, 1984), metal treated activated carbon (Huang and Vane, 1989), activated alumina and bauxite (Gupta and Chen, 1978) and hematite and feldspar (Singh *et al*, 1988 and Prashad, 1994) (Table 3.2).

Table 3.2 Efficiency of arsenic removal by different adsorbents under different test conditions

Reference	Adsorbent dose	pH	Initial arsenic concentration	% As (V) removal	% As(III) removal
Gupta and Chen (1978)	Activated carbon 3 g/l	3.1	As(V): 12.8 μm	96.5	
	Activated alumina, 2 g/l	6.9	As(V): 32 μm	100	
	Activated bauxite 2 g/l	6.5	As(V): 24.7 μm	100	
	Activated alumina, 2g/l	8.47	As(III): 6.65 μm		88.8
	Activated bauxite 2 g/l	7.99	As(III): 6.54 μm		79.6
Prashad (1994)	Hematite	4.2	As(V): 0.13 mM/l	80	
	Feldspar	6.2	As(V): 0.13 mM/l	75	
Huang and Fu (1984)	Powdered activated carbon (D-XI), 1 g/l	4.0	As(V): 5×10^{-5} M	84	
Huang and Vane (1989)	Fe^{2+} treated activated carbon 10 g/l	4.5	As(V): 2×10^{-4} M/l	100	

From the summary in Table 3.2, it is evident that activated alumina is the most effective adsorbent in removing arsenic and activated carbon and bauxite are also effective. Fe^{2+} treated activated carbon appears as a successful adsorbent medium in removing arsenic. Nevertheless, the adsorbent medium requires periodic cleaning with an appropriate regenerant such as caustic soda. Activated alumina is especially useful if water has very high total dissolved solids. However, it may not be efficient in the long term and disposal of high concentration of brine containing wastewater may be another problem.

The adsorption of arsenic onto activated carbon depends on several factors: carbon type, ash content, specific surface area, pH, and carbon pre-treatment etc. Generally, powdered activated carbon has better adsorbing capacity (84%) than granular activated carbon (61%) in As(V) removal (Huang and Fu, 1984). The effect of carbon type on the adsorption of arsenic onto untreated activated carbon is presented in Table 3.3 (Lorenzen *et al*, 1995).

Table 3.3 The effect of carbon type on the adsorption of arsenic onto activated carbon (Lorenzen *et al*, 1995)

Carbon type	Ash content %	Surface area, m^2/g	Arsenic (As(V)) loading, mg/g carbon
Coconut shell carbon	3.0	1200	2.40
Coal based carbon	5.5	1125	4.09
Peat based extruded carbon	5.0	975	4.91
Pre-treated coconut shell carbon with copper salt, $CuCl_2.2H_2O$	_	_	5.79

Table 3.3 shows that increasing amount of ash content increases the adsorption capacity of carbon whereas increased surface area plays a negative role in the adsorption of arsenic. This agrees with the findings obtained by Diamodopoulous *et al* (1992). According to Diamodopoulous *et al* (1992), the high ash carbon enhances

As(V) removal up to five times. This is explained as follows: when a substance like arsenic interacts with mineral matter (which is a major constituent of the carbon ash), its removal is enhanced by the presence of ash. In this case, the role of surface area may be less important than the ash content, which also agrees with Huang and Fu (1984).

A method of pre-treating activated carbon by a ferrous salt to enhance arsenic removal was studied by Huang and Vane (1989). They have increased the carbon capacity by a factor of 10, due primarily to adsorption of Fe^{2+} and formation of Fe^{2+} arsenate complexes. They have not indicated whether oxidation of Fe occurred or whether ferric hydroxide, which should have a high capacity, was formed. The proposed method of coating a porous supporting media with an adsorbent is in fact a promising technique, as also demonstrated by Edwards and Benjamin (1989) for metal-bearing waste waters treated with a coated sand.

3.7.3 Low-cost techniques

Many conventional and advanced processes for the removal of arsenic involve high cost, well-trained operators and multiple chemical requirement, these being inappropriate for Bangladesh and other developing countries where there is a need to develop low-cost techniques. The following sections describe some of the low-cost techniques for the removal of arsenic.

3.7.3.1 Sedimentation

Shen (1973) carried out plain sedimentation to observe the effectiveness of this method in removing arsenic. The arsenic-containing raw water (As(V) and As(III)) was placed in a beaker and settled without agitation. At different settling intervals, the supernatant was drawn by pipette for arsenic analysis. The tests showed that plain sedimentation has some effect on removal of arsenic (Table 3.4). After one full day of settling, the arsenic concentration is reduced only from 0.8 mg/l to 0.73 mg/l i.e. only 8.7% removal had occurred. Removal by sedimentation progressed asymptotically — the level of arsenic remaining in water reached a near equilibrium after ten days.

The test results demonstrated that plain sedimentation is only capable of removing half of the arsenic (removal 48.7%) and this occurs after a prolonged period (15 days). Therefore, it is evident that although this technique involves zero cost, it appears as an ineffective means of removing arsenic.

Table 3.4 Arsenic removal by sedimentation (Shen, 1973)

Settling time, days	As concentration in the supernatant, mg/l	% As removal
1	0.8	0
2	0.73	8.7
3	0.66	17.5
4	0.60	25.0
5	0.55	31.3
6	0.53	33.7
7	0.50	37.5
8	0.48	40.0
9	0.40	50.0
10	0.45	43.7
11	0.44	45.0
12	0.43	46.2
13	0.42	47.5
14	0.42	47.5
15	0.41	48.7

3.7.3.2 Arsenic removal by iron filter

According to Nikolaidis *et al* (1997), a simple filter based on sand and iron filing could prevent millions of people from being poisoned by arsenic in drinking water. The filter is a tube filled with sand and iron filings (zero valent iron), designed to fit in a well outlet. In the presence of $BaSO_4$ (this can be cheaply added if it is not already in the water) the iron oxidises and reacts with arsenic to form arsenopyrite, which precipitates out and remains trapped in the filter. Laboratory experiment showed that 97% of arsenic can be removed for initial concentration of 45 to 8,600 ppb when the combination of iron filings and sand is 1:1 (by weight). Nikolaidis *et al* (1997) stated that the principal ingredients in the filter are very cheap. A tonne of iron filings costs $350 and a tonne of sand is $10 and the life span of this filter is expected 20 years, therefore, the cost of supplying drinking water per person per year will be around 15 cents.

Joshi and Chaudhury (1996) developed a home arsenic removal unit using iron-coated sand, which showed a promising medium (70-80% removal) for arsenic removal. Iron coated sand was prepared by mixing the washed and dried sand with 2M $Fe(NO_3)_3 \cdot 9H_2O$ solution (adjusted to pH 11.0 with NaOH) and then drying in an oven for 14 h. According to their estimate, such a home arsenic removal unit would cost about $8. However, the study did not take account of the pH, possible selectivity of As(III) and As(V) over one another for removal and concentration and type of competing ions that may affect sorption. Furthermore, field trials should be carried out to assess its long-terms effects, such as loss of medium capacity, fouling and clogging of iron oxide coating on its performance.

3.7.3.3 Microbiological process

Paknikar (1998) studied the performance of microbiological process in removing arsenic. He stated that two types of metal microbiological interactions could be potentially used for the removal. They are 1) microbial oxidation of As(III) to As(V) and its subsequent precipitation and 2) bio-accumulation of arsenic by microbial biomass. The oxidation method could either be operated in an immobilised reactor containing the arsenic contaminated water collected in a pond. A cheap source of organic substrate such as beet pulp or sugarcane juice could be added to the pond water along with iron fillings (Paknikar, 1998; and Macy and David, 1998). The addition of iron fillings promotes the development of a variety of iron-oxidising bacteria, e.g. leptothrix, which oxidises ferrous iron to ferric iron and adsorbs arsenic and settle in the pond. Overflow of water can typically contain arsenic less than 0.05 mg/l for water containing arsenic up to 4.0 mg/l. The reaction is 50,000 times faster than the chemical oxidation of iron. Therefore, microbiological based techniques can be effective low-cost option for arsenic removal.

3.8 FACTORS INFLUENCING THE REMOVAL OF ARSENIC FROM SOLUTION

The parameters which are thought to influence the removal of arsenic are: pH, oxidation of As(III), type and dosages of coagulants, adsorbent/adsorbate ratio, initial arsenic concentration, presence of co-occurring solutes and natural organic matter in water, temperature and filtration. All the factors are described briefly below.

3.8.1 Influence of pH

Arsenic removal by coagulation-precipitation process is very much pH dependent and the favourable pH range varies according to the oxidation state of arsenic present in water. According to Gulledge and O'Conor (1973), As(V) removal decreases at pH 8.0 for both alum and iron salts which also agrees with the findings obtained by Edwards (1994) and Cheng *et al* (1994). The reason may be the result of the change in anionic form of the As(V) from $H_2AsO_4^-$ to $HAsO_2^{2-}$ around this pH. The effects of pH on the removal of arsenic are presented in Fig. 3.13 (Sorg and Logsdon, 1978). In the pH range of 5 to 7, 0.09 mM/l dosages of metal ions achieved greater than 90% removal of As(V). Above pH 7.0 alum removal efficiency decreased with increasing pH to 47% at pH 8.0, whereas ferric sulphate removal efficiency remained above 95% at the same pH.

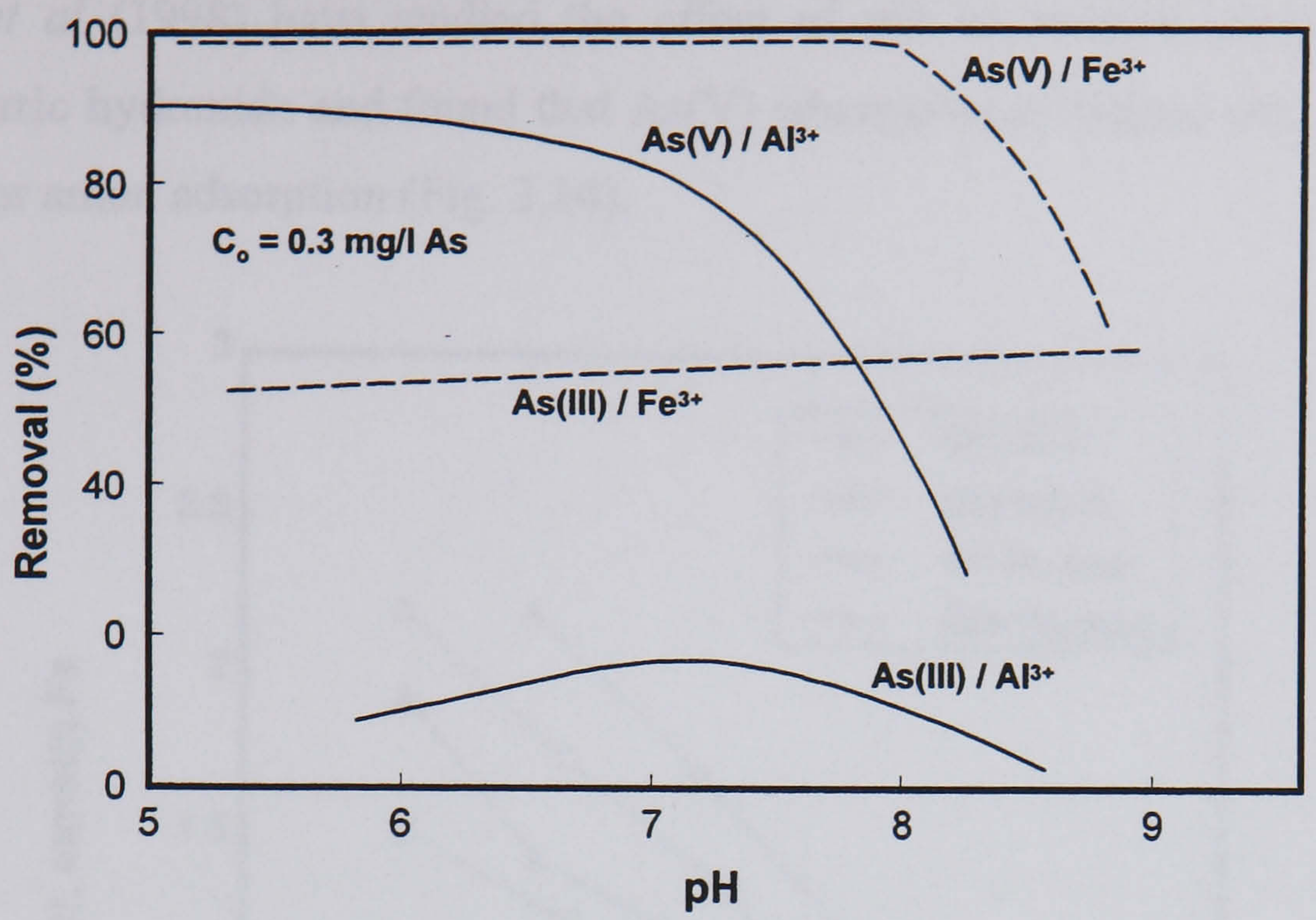


Fig 3.13 Influence of pH on As(III) and As(V) removal by ferric and aluminium ions with arsenic concentration of 0.3 mg/l and dosage of metal ions of 0.09 mM/l (Sorg and Logsdon, 1978)

As(III) removal by iron coagulation increases with pH in the range of 5-9 and for alum coagulation, removal increases within pH 5-7 and above pH 7.0, removal decreases (Fig. 3.13).

The difference in the pH ranges for alum and $FeCl_3$ coagulation for arsenic removal corresponds to the greater solubility of the amorphous aluminium hydroxide solid compared with iron (III). In contrast to turbidity removal, which can be accomplished by charge neutralisation, arsenic removal requires amorphous hydroxide solids as a substrate for arsenic adsorption. In typical water treatment processes applying coagulation, the pH range over which the amorphous hydroxide solid is stable is much narrower for aluminium than for iron(III). Consequently, the possible application of alum for arsenic removal is restricted to a narrower pH range than the corresponding application of ferric chloride (Amirtharajah and O'Melia, 1990; McNeill and Edwards, 1995).

Driehaus *et al* (1998) have studied the effect of pH on arsenic adsorption onto granular ferric hydroxide and found that As(V) adsorption decreases with pH which is typical for anion adsorption (Fig. 3.14).

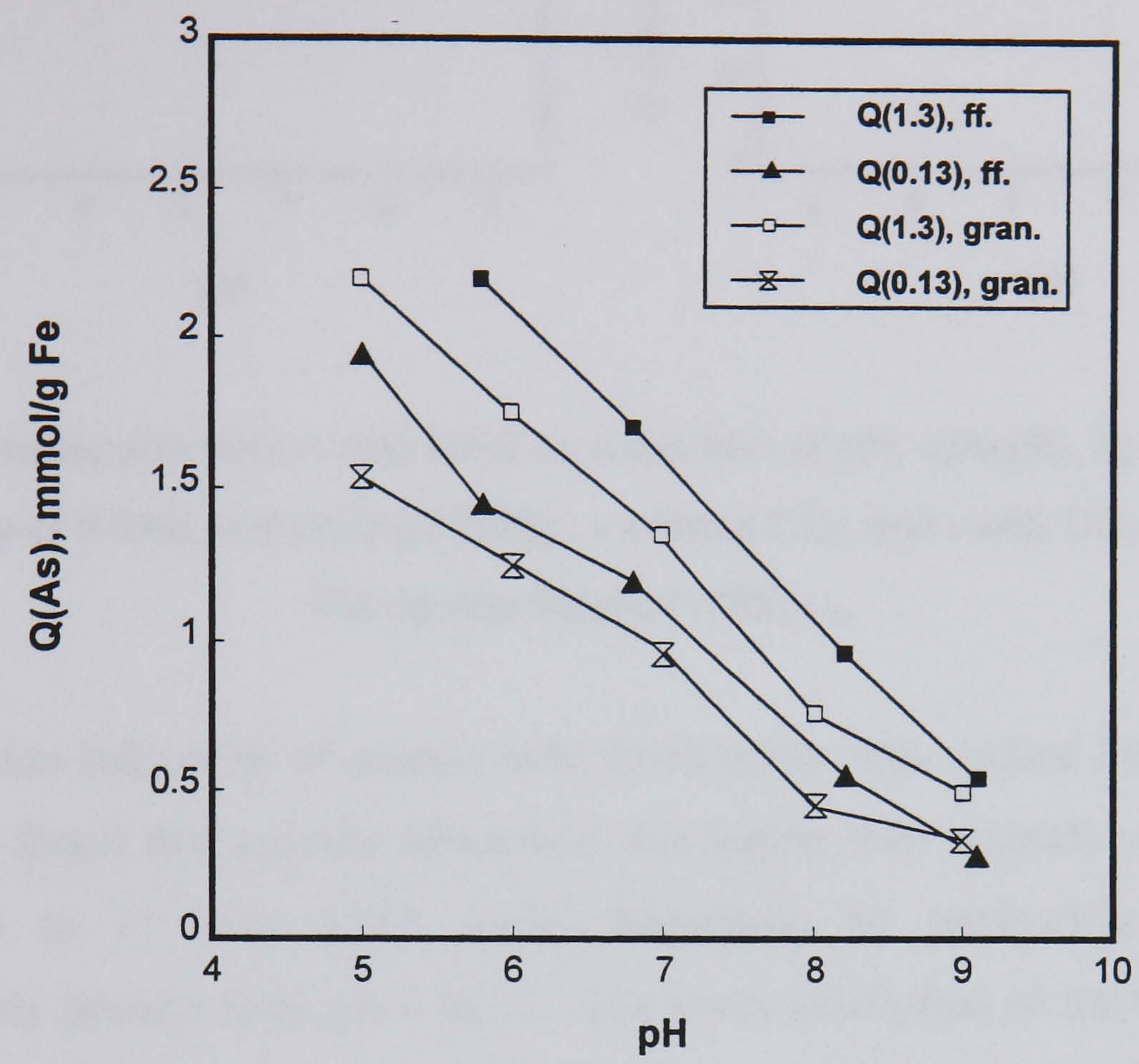


Fig 3.14 As(V) adsorption density (Q) on granular ferric hydroxide (gran) and on freshly prepared ferric hydroxide (ff) at residual concentrations of 0.13 and 1.3 μm/l (Driehaus *et al*, 1998)

Wilkie and Hering (1996) observed that adsorption of As(III) onto the hydrous ferric oxide over the pH range of 4 to 9 is not strongly dependent on pH which agree with the findings obtained by Pierce and Moore (1982). But for As(V) removal, less adsorption and a somewhat stronger effect of pH were observed by Pierce and Moore (1982) than those observed by Wilkie and Hering (1996) (Fig. 3.15).

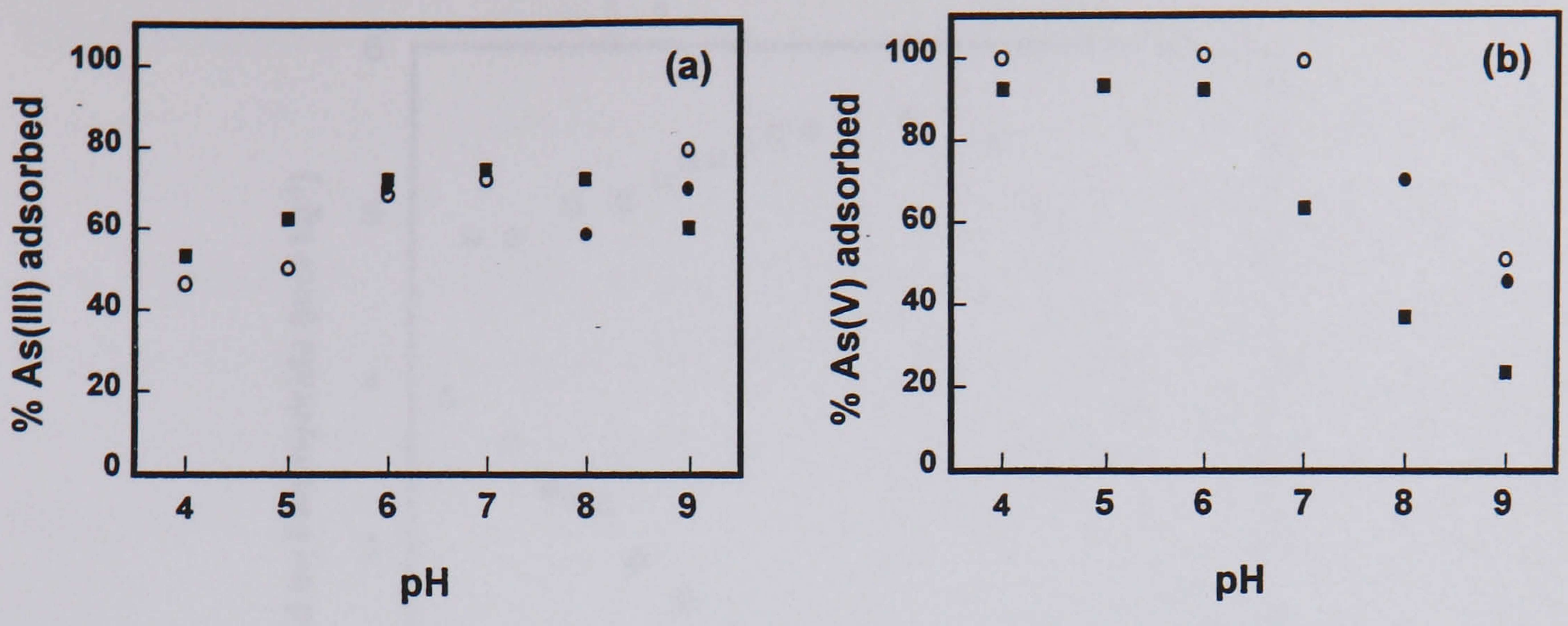


Fig 3.15 Arsenic adsorption onto HFO as a function of pH; a)As(III), b) As(V). Data from study of Wilkie and Hering (1996).: ○ without CO_3 and ● with CO_3; data from Pierce and Moore (1982) : ■.

The adsorption behaviour of arsenic onto Ferrihydrite was studied by Raven *et al* (1998) who found that arsenite adsorption was higher than arsenate within the pH range of 3 to 11 (Fig. 3.16). As(V) adsorption by ferrihydrite decreased approximately linearly from pH 4 to 10. The lower adsorption of As(V) at high pH values was attributed to an increased repulsion between the more negatively charged arsenate species and negatively charged surface sites. Since arsenite has a less negatively charged character than the arsenate species at the same pH value, it does not exhibit as much repulsion. As a result, the adsorption decreases less with increasing pH. Again Raven *et al* (1998) observed that As(III) adsorption is faster than that of As(V) at pH 9.2, while Pierce and Moore (1982) reported that As(V) adsorption was much faster than that of As(III) at pH 8.0 and pH 9.9. This discrepancy could be attributable to the different experimental conditions.

Another study carried out by Papassiopi *et al* (1996) showed that the pH for maximum arsenic removal depends on the Fe/As ratios during Fe-As precipitation process. Optimum pH is seen to be shift from 3 to 5 to 6 as the Fe/As ratios (molar) increases from 2 to 4 to 6 (Fig. 3.17).

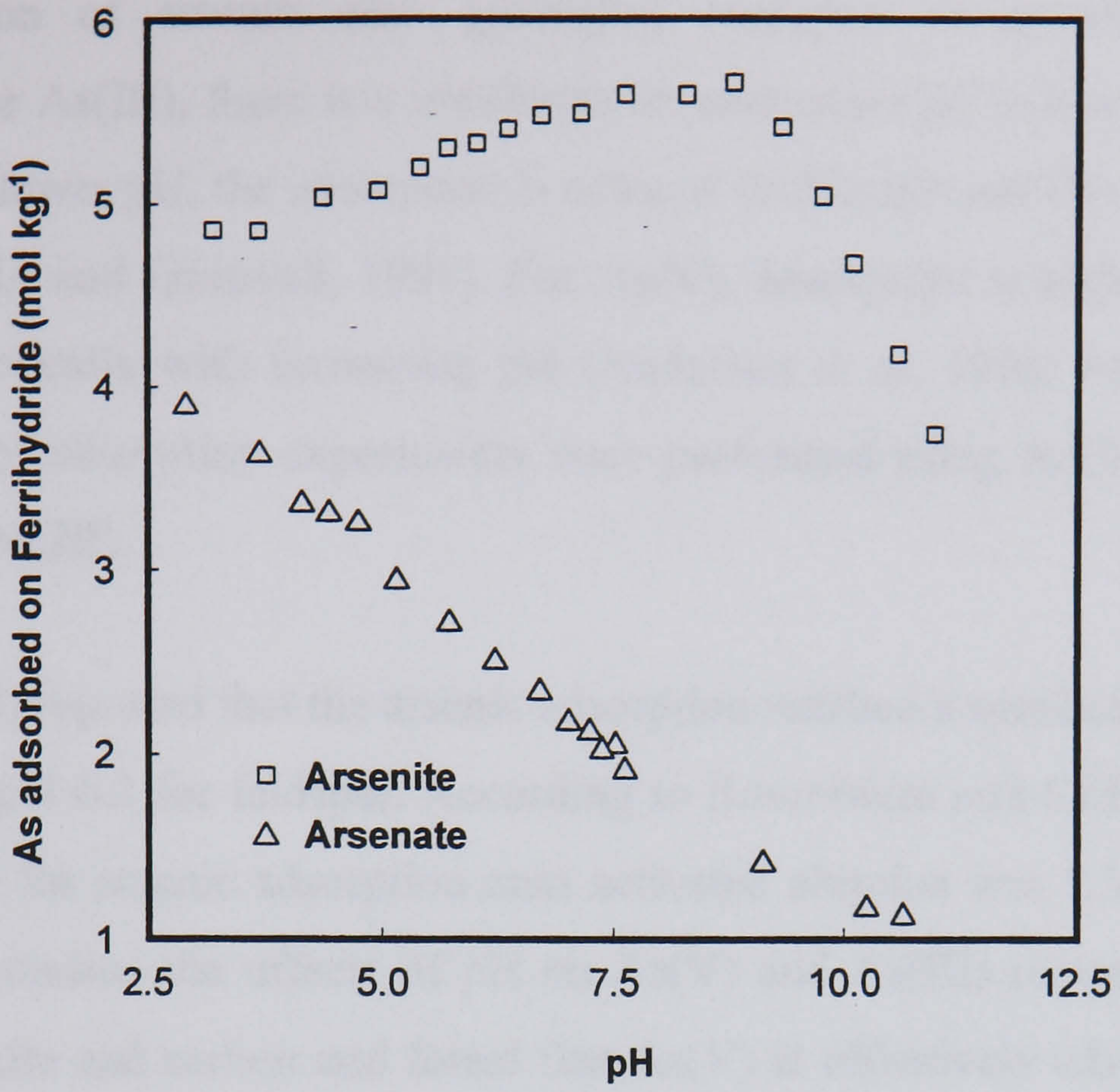


Fig 3.16 Effects of pH on adsorption of arsenic onto 2-line ferrihydrite following the addition of 13.3 mole As/kg ferrihydrite (Raven *et al*, 1998)

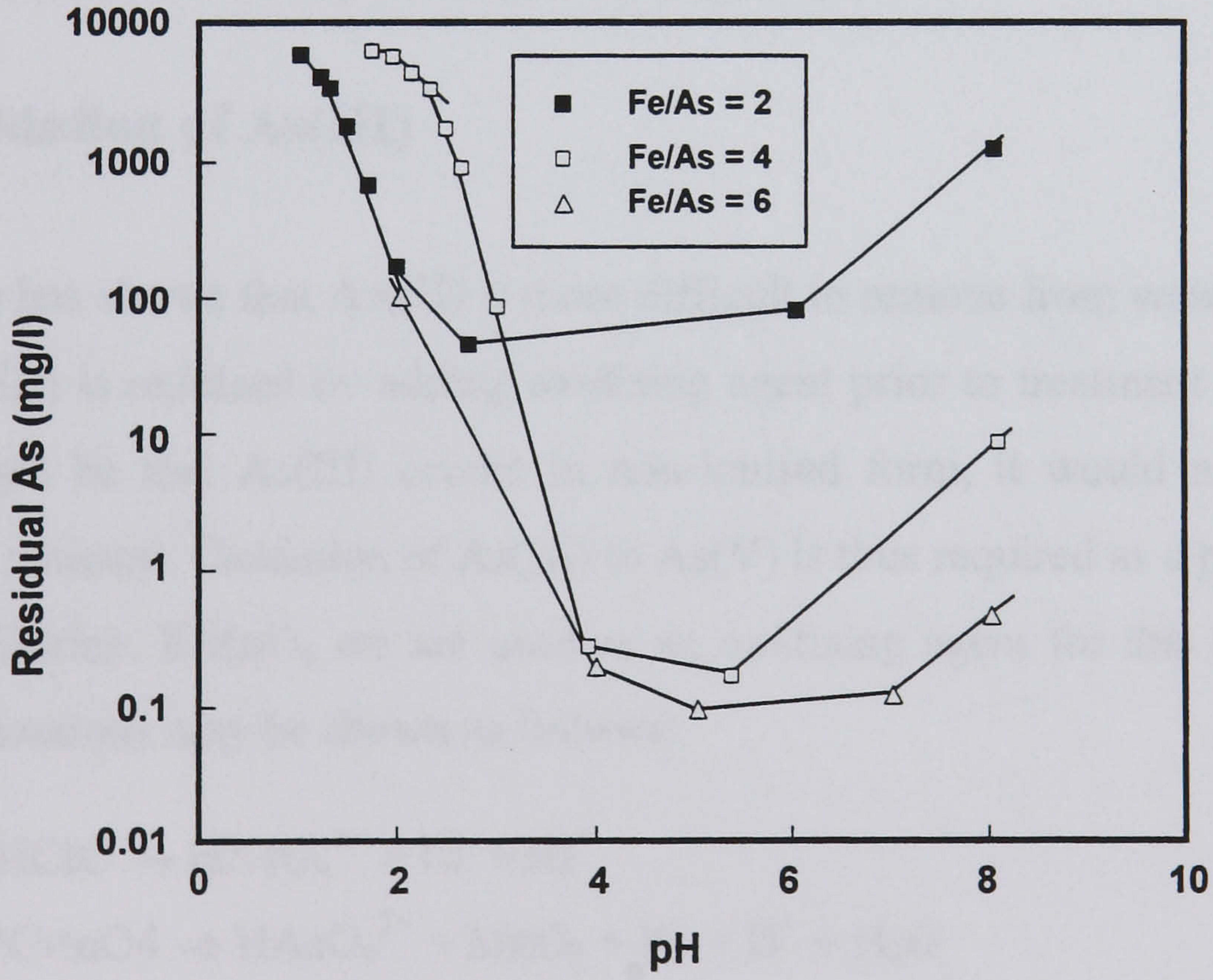


Fig 3.17 Residual arsenic concentration as a function pH (Papassiopi *et al*, 1996)

The adsorption of arsenic onto geological materials is generally highly pH dependent. For As(III), there is a maximum in adsorption by oxides and hydroxides at pH 7-8. At lower pH, the adsorption is reduced (Schlicher and Ghosh, 1985; Singh *et al*, 1988; Xu and Grimvall, 1991). For As(V), adsorption is high at low pH and decreases drastically with increasing pH (Anderson *et al*, 1976; Frost and Griffin, 1977). Most of adsorption experiments were performed using As(V) and in a very few cases of As(III).

Prashad (1994) reported that the arsenic adsorption reached a maximum at pH 4.2 for hematite and pH 6.2 for feldspar. According to Rosenblum and Clifford (1984), the best pH value for arsenic adsorption onto activated alumina was 5.5-6.0. Gupta and Chen (1978) studied the effects of pH on As(V) and As(III) removal by activated alumina, bauxite and carbon and found that As(V) is effectively adsorbed in the pH range of 4 to 7 for activated alumina and bauxite and activated carbon adsorbs As(V) better in the acidic pH range between 3 and 5.0 (Figs. 3.7a and 3.7b). The adsorption of As(III) on activated alumina and bauxite increased over the pH range of 4 to 9 and adsorption decreased sharply above pH 9.0 (Fig. 3.8).

3.8.2 Oxidation of As(III)

Experience has shown that As(III) is more difficult to remove from water than As(V) unless As(III) is oxidised by adding oxidising agent prior to treatment process. The reason might be that As(III) occurs in non-ionised form, it would not subject to significant removal. Oxidation of As(III) to As(V) is thus required as a pre-treatment. Usually, chlorine, $KMnO_4$ etc are used as an oxidising agent for this purpose. The chemical reactions may be shown as follows:

$$H_3AsO_3 + HClO \rightarrow HAsO_4^{2+} + Cl^- + 3H^+ \qquad (3.23)$$

$$H_3AsO_3 + KMnO4 \rightarrow HAsO_4^{2+} + MnO_2 + K^+ + H^+ + H_2O \qquad (3.24)$$

Fig. 3.18 (Jekel, 1994) shows that 1 to 2 ppm of Fe^{3+} are sufficient for removal of more than 95% arsenic if prechlorination is introduced to oxidise As(III). Also alum is very effective in removing arsenic if an oxidising agent such as chlorine is added.

At pH below 7.0, without chlorine, about 10% of arsenic were removed and using chlorine, removal increased to about 90% (Kartinen and Martin, 1995).

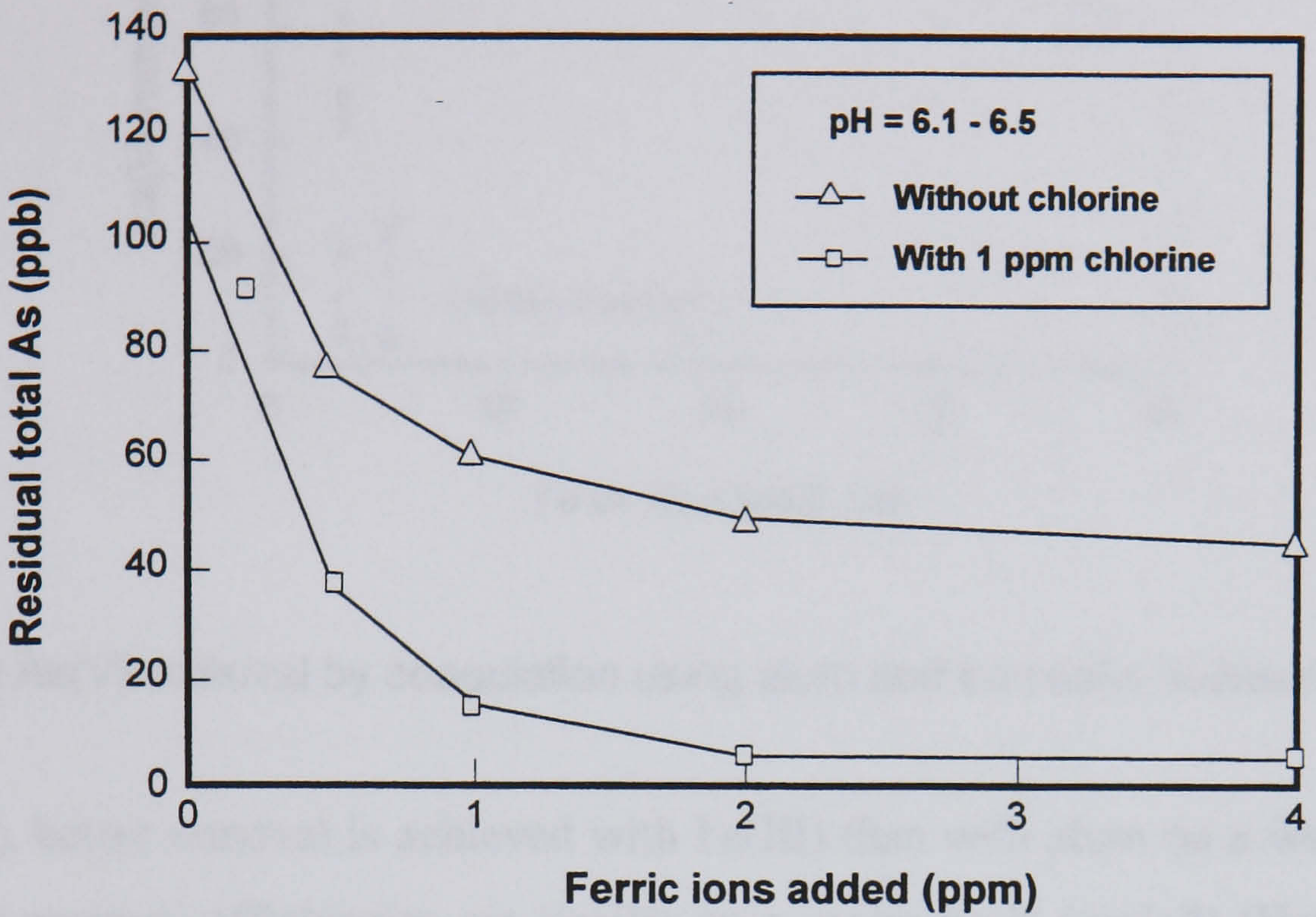


Fig 3.18 Arsenic removal by ferric ion precipitation without and with prechlorination to oxidize As(III) at initial total arsenic concentration of 135 μg/l and initial As(III) concentration of 60 μg/l (Jekel, 1994)

3.8.3 Types and dosages of coagulants

Alum and iron salts are widely used for the removal of arsenic in coagulation-precipitation processes. Edwards (1994) reported that at pH ≤ 7.0, alum and ferric salts are nearly equally effective (Fig. 3.19) which agrees with McNeill and Edwards (1997). The advantages of ferric over alum become significant at higher pH values. At pH 7.0 –7.5, average removals at a coagulant dose of 10 mg/l $FeCl_3$ were 87% compared to 67% for same alum dosage. If the alum dose is higher than 30 mg/l, As(V) removals exceeded 70% as long as the pH < 7.8. At lower alum dosages or higher pH, arsenic removal decreases (Edwards, 1994).

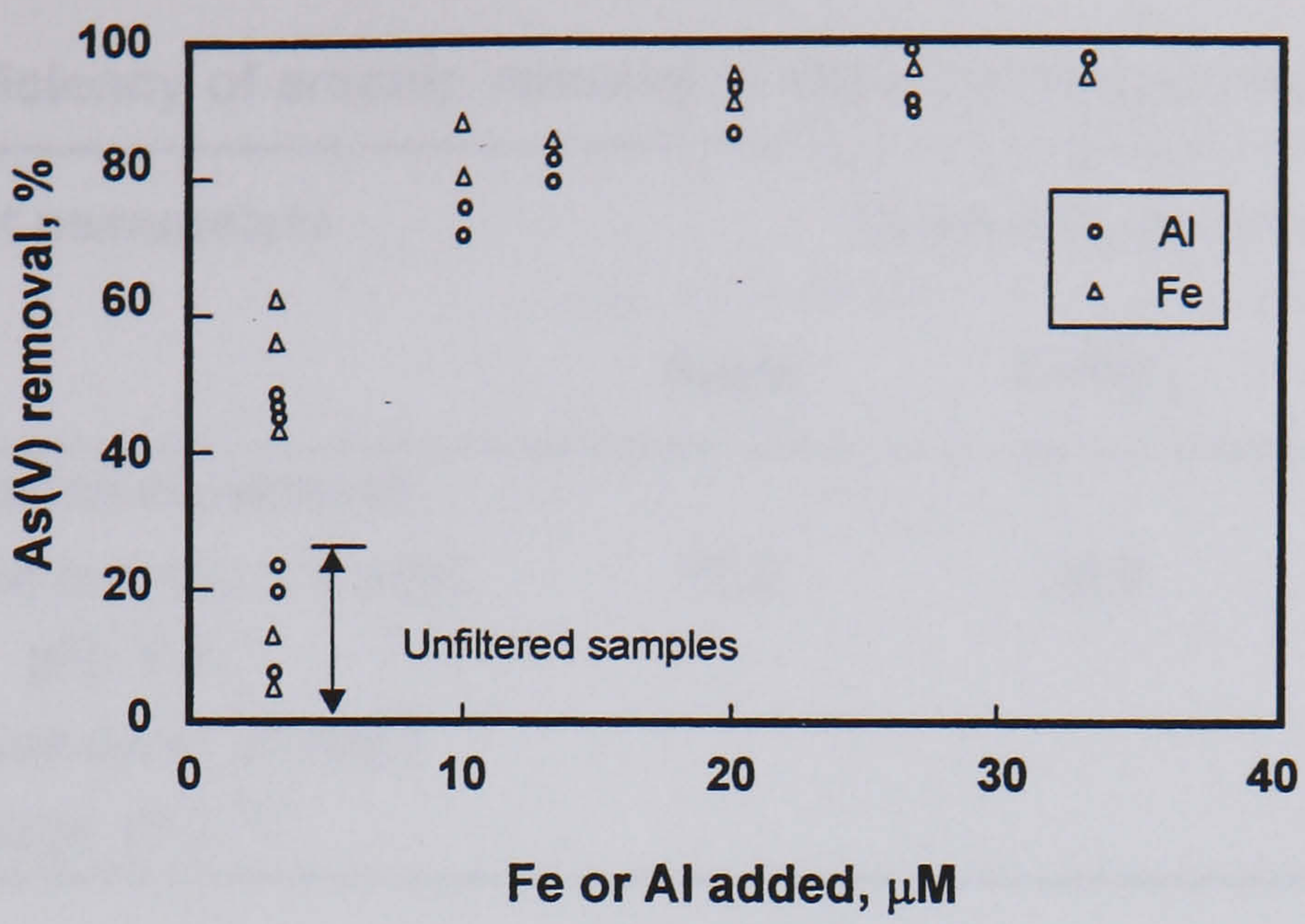


Fig 3.19 As(V) removal by coagulation using alum and iron salts (Edwards,1994)

For As(V), better removal is achieved with Fe(III) than with alum on a weight basis (mg/l) but removal efficiencies are similar on a molar basis (mole/l) (Hering *et al*, 1996). Table 3.5 shows a comparison of arsenic removal efficiency among different coagulants according to a study carried out by Shen (1973).

From Table 3.5, it is evident that the performance of $FeCl_3$ in removing arsenic is the best and $FeSO_4$ is not practically effective.

Bench scale work carried out in the University of Colorado at Boulder as presented in Fig. 3.20 confirmed that iron coagulants are much more effective in removing As(III) than aluminium based coagulants which is consistent with Sorg and Logsdon (1978).

Table 3.5 Efficiency of arsenic removal at different coagulants (Shen, 1973)

Test parameters	% arsenic removal		
	Alum	$FeSO_4$	$FeCl_3$
Coagulation experiment Initial total arsenic: 1.0 mg/l pH: 6.8 Coagulant dose: 20 mg/l Temp: 19.5 °C	32.0	24.0	82.0

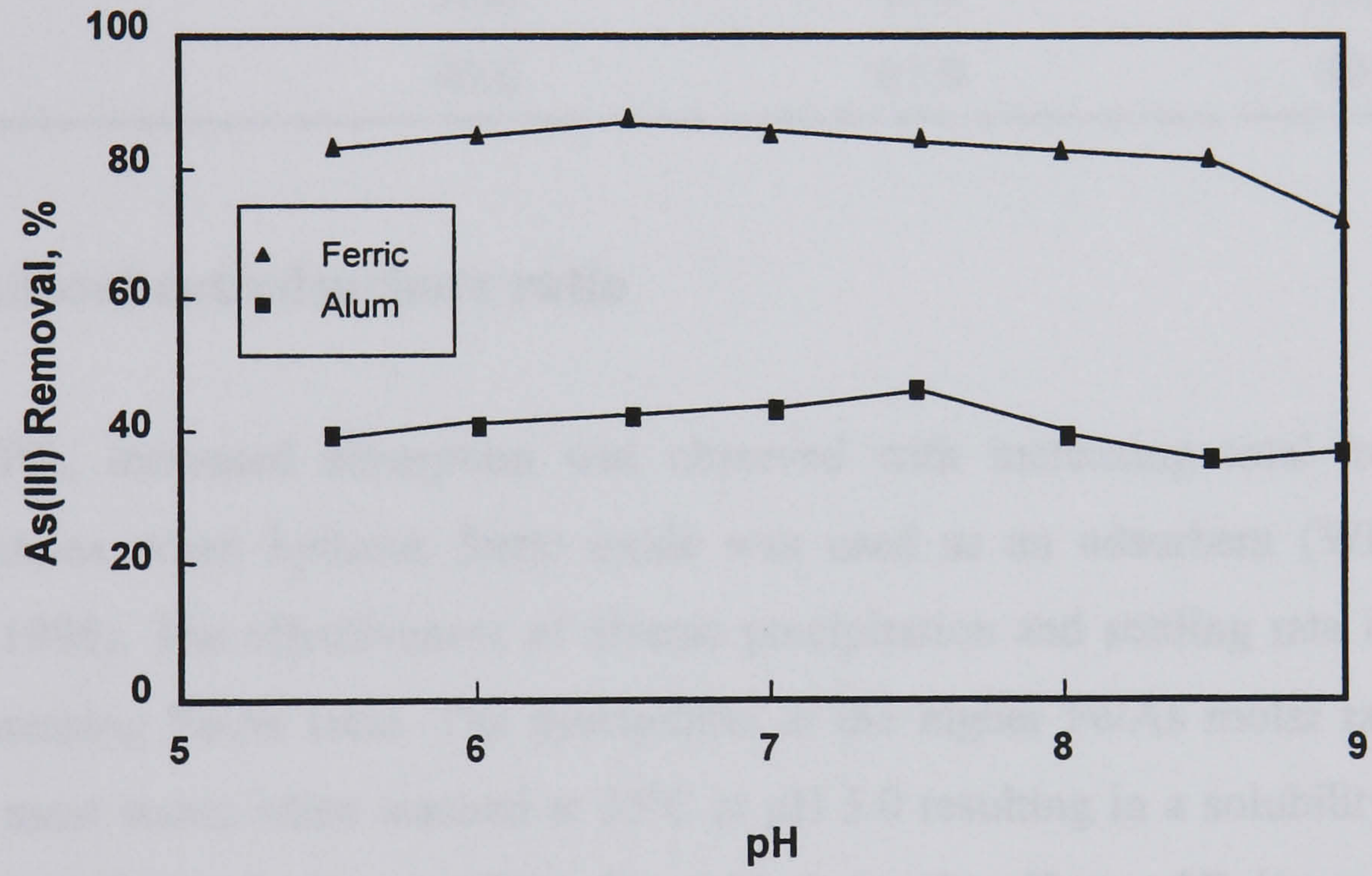


Fig 3.20 As(III) removal as a function of pH for alum and ferric coagulants with coagulant dose of 90 μM (formed insitu) and initial As(III) concentration of 300 μg/l (Beltran, 1993)

It has been shown that the removal rate increases with increasing dosage of coagulants (Gulledge and O'Conor 1973; Scott *et al*, 1995; and Hering *et al*, 1996). Table 3.6 shows removal of As(V) achieved at different coagulant dosages for a given pH value.

From Table 3.6, it is evident that removal is directly related to the coagulant dosage. The reason is probably that the higher the amount of coagulant, the greater is the mass of hydroxide, thus facilitating the coprecipitation and adsorption.

Table 3.6 As(V) removal at different coagulant dosages followed by sedimentation and sand filtration (Gulledge and O'Conor, 1973)

pH	Coagulant dosage, mg/l	As(V) removal, %	
		by Alum	by Ferric sulphate
7.0	10.0	65.0	94.0
	20.0	82.0	97.0
	30.0	84.0	98.0
	40.0	91.0	99.0

3.8.4 Adsorbent/adsorbate ratio

For As(III), increased adsorption was observed with increasing total iron/ total arsenic ratios when hydrous ferric oxide was used as an adsorbent (Wilkie and Hering, 1996). The effectiveness of arsenic precipitation and settling rate increased with increasing Fe/As ratio. The precipitates at the higher Fe/As molar ratio were also the most stable when leached at 25°C at pH 5.0 resulting in a solubility of 0.05 mg/l arsenic (Papassiopi *et al*, 1996). Fig. 3.21 shows the effects of Fe/As molar ratio on the removal of As(V) at pH 5.0.

It is seen that the arsenic precipitation with Fe/As ratio (molar) 2 and 4 shows an increase of residual As(V) concentration in the solution by increasing pH while that with Fe/As ratio 8 show very low residual As(V) concentration (< 0.1 mg/l) over a wide range of pH 2-8 (Fig. 3.22). For effective removal of arsenic, it is essential to have a Fe/As molar ratio significantly greater than unity at all initial arsenic concentrations (Robins *et al*, 1988).

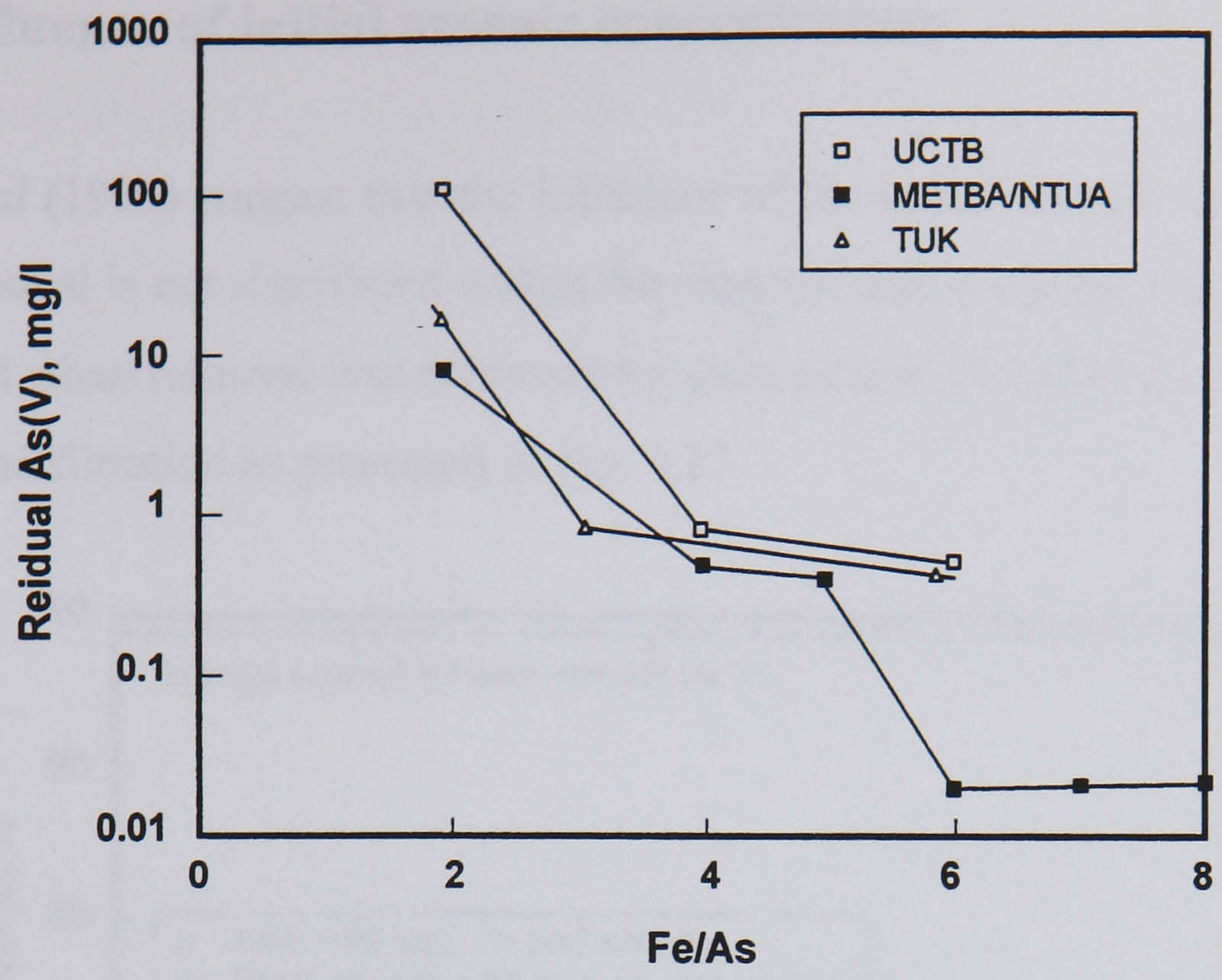


Fig 3.21 The effect of Fe/As ratio on the solubility of precipitates at pH 5 (Papassiopi *et al*, 1996)

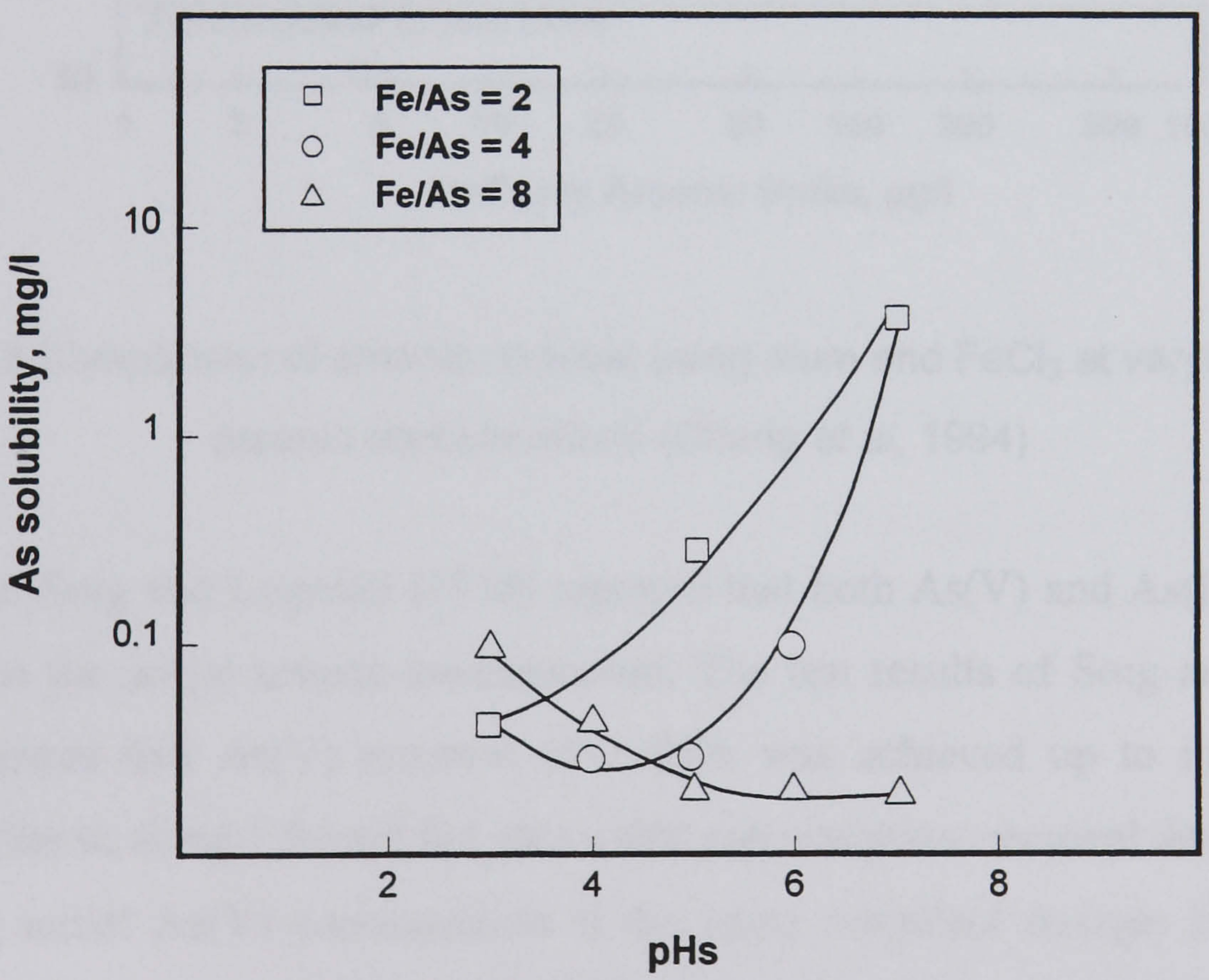


Fig 3.22 Solubility of arsenic as a function of pH with Fe/As ratios 2, 4 and 8 at 33°C (Papassiopi *et al*, 1987).

3.8.5 Influence of initial arsenic concentration

Cheng *et al* (1994) suggest that the influence of the initial arsenic concentration on As(V) removal is not significant within the range of initial arsenic concentration of 1 to 100 µg/l when removal was achieved by alum or iron coagulation using coagulant aid and sand filtration as presented in Fig. 3.23.

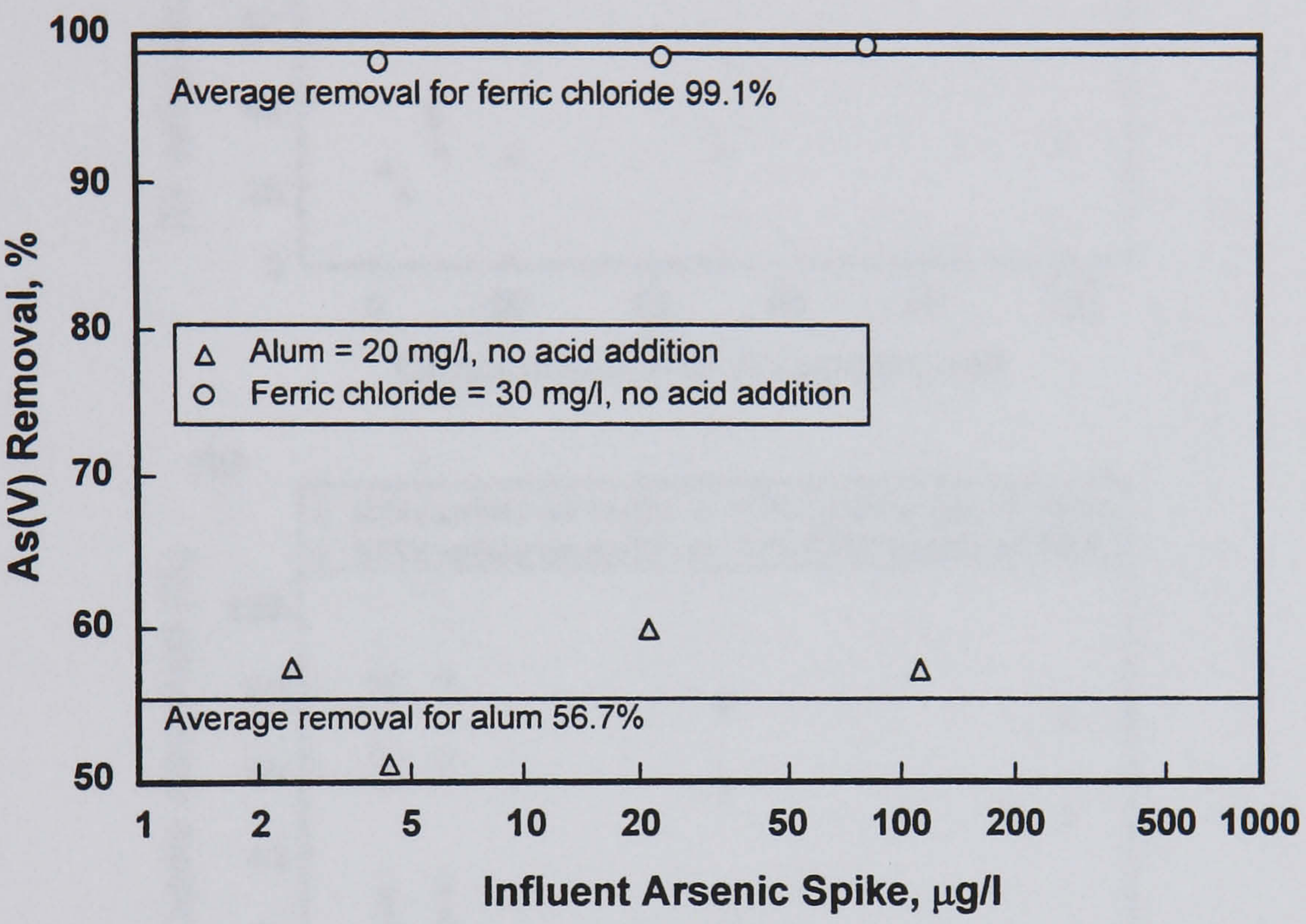


Fig 3.23 Comparison of arsenic removal using alum and $FeCl_3$ at varying initial arsenic concentrations (Cheng *et al*, 1994)

In contrast, Sorg and Logsdon (1978) reported that both As(V) and As(III) removal depends on the initial arsenic concentration. The test results of Sorg and Logsdon (1978) showed that As(V) removal of > 95% was achieved up to initial As(V) concentration to about 1.0 mg/l but above that concentration, removal decreases with increasing initial As(V) concentration at the same coagulant dosage. Hering *et al* (1997) stated that in coagulation with $FeCl_3$ (4.9 mg/l), As(V) removal is unaffected by initial arsenic concentration in the range of 1-100 µg/l but As(III) removal decreased slightly over the same range of initial arsenic concentration at same pH (Fig. 3.24a). Similar findings were obtained in case of As(V) adsorption with iron

(50 μm total iron) at pH 7.0, but As(III) removal by adsorption decreased greatly with increasing initial arsenic concentrations (Fig. 3.24b) (Hering *et al*, 1997).

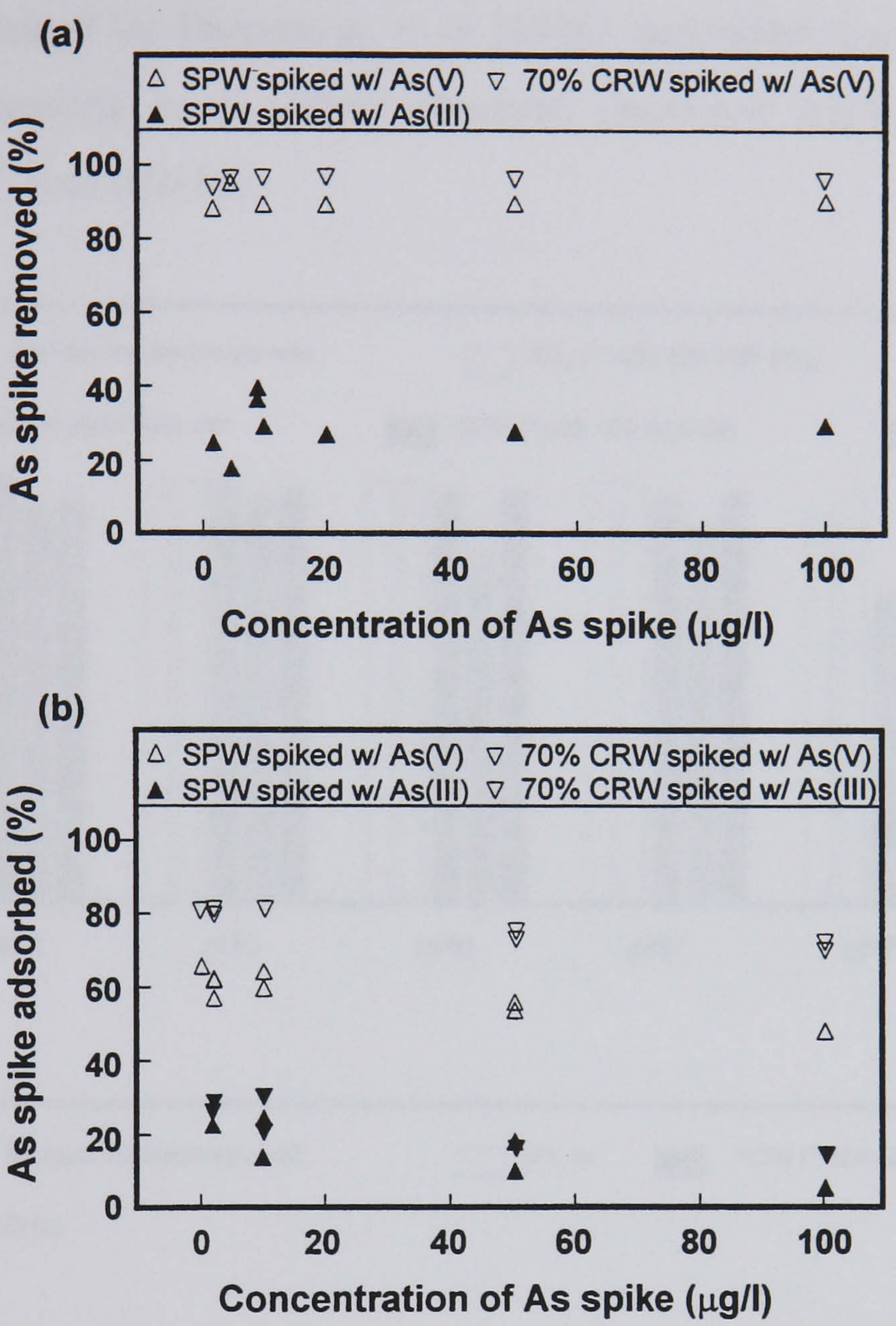


Fig. 3.24 Efficiency of (a) Arsenic removal by $FeCl_3$ (4.9 mg/l) and (b) adsorption onto preformed HFO (50 μm total iron) at pH 7.0 as function of concentration of As(III) or As(V) added to source waters (Hering *et al*, 1997).

3.8.6 Influence of co-occurring solutes and natural organic matter

Several studies were carried out to investigate the influence of different solutes in removal processes such as PO_4^{3-}, NO_3^-, SO_4^{2-} and Ca ions present in water together with arsenic (Hering *et al*, 1997; Papassiopi *et al*, 1996 and Peng and Di, 1994). Hering *et al* (1997) showed that the effect of sulphate on As(V) removal is not significant over the pH range of 4-9. But addition of sulphate (40 mg/l SO_4^{2-})

significantly depressed As(III) removal at pH 4.0 and 5.0 but no effect at higher pH values, which is consistent with the competitive adsorption of sulphate and As(III) as studied by Wilkie and Hering (1996) and Hering *et al* (1996) (Fig. 3.25). However the findings obtained by Papassiopi *et al* (1996) contradict those of Hering *et al* (1997) that Papassiopi *et al* (1996) observed decreased As(V) removal by the presence of SO_4^{2-} ions (0.6 M).

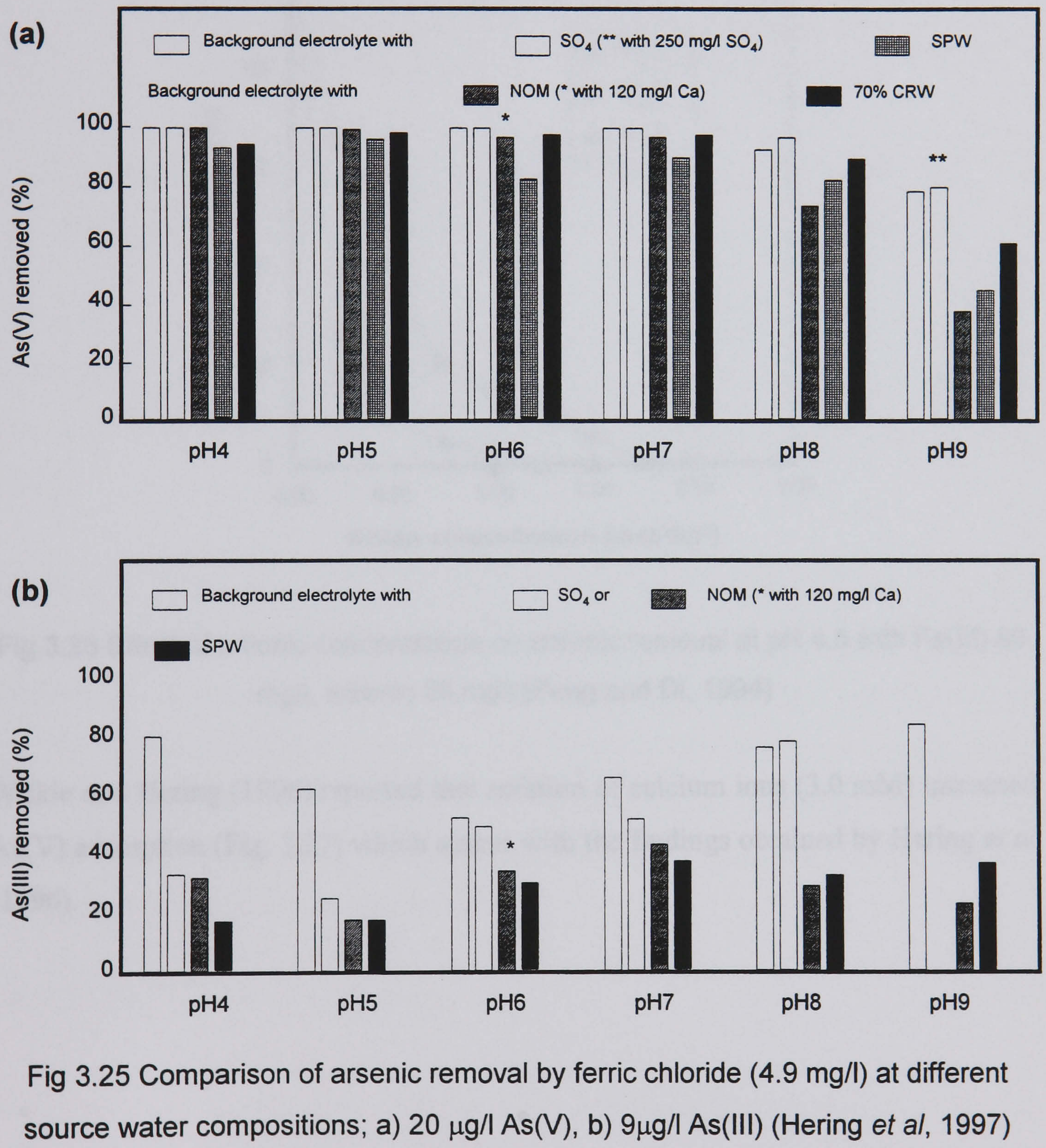


Fig 3.25 Comparison of arsenic removal by ferric chloride (4.9 mg/l) at different source water compositions; a) 20 μg/l As(V), b) 9μg/l As(III) (Hering *et al*, 1997)

According to Peng and Di (1994), the presence of sulphate and phosphate ions in the solution is found to reduce the efficiency of arsenic removal (As(V)) greatly. They explained the reason as follows: 1) competitive adsorption of SO_4^{2-} or PO_4^{3-} and arsenic ions on the positively charged ferric hydroxide surfaces or 2) the specific interaction with ferric hydroxide surfaces (Fig. 3.26). Peng and Di (1994) observed that the effect of NO_3^- is insignificant even when the concentration of NO_3^- is 0.04 mol/dm^3

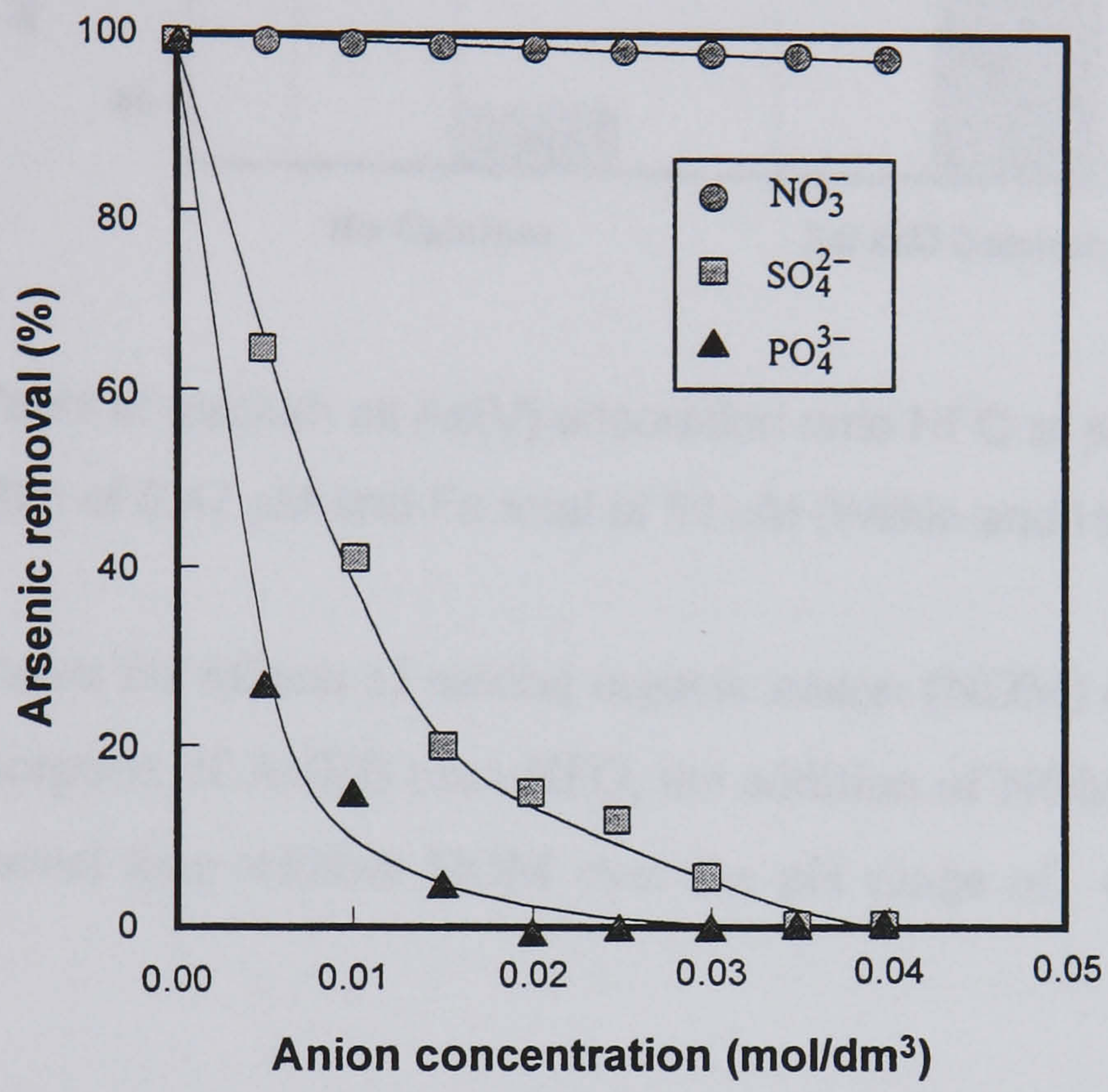


Fig 3.26 Effect of anionic concentration on arsenic removal at pH 4.5 with Fe(III) 80 mg/l, arsenic 35 mg/l (Peng and Di, 1994)

Wilkie and Hering (1996) reported that addition of calcium ions (3.0 mM) increased As(V) adsorption (Fig. 3.27) which agrees with the findings obtained by Hering *et al* (1996).

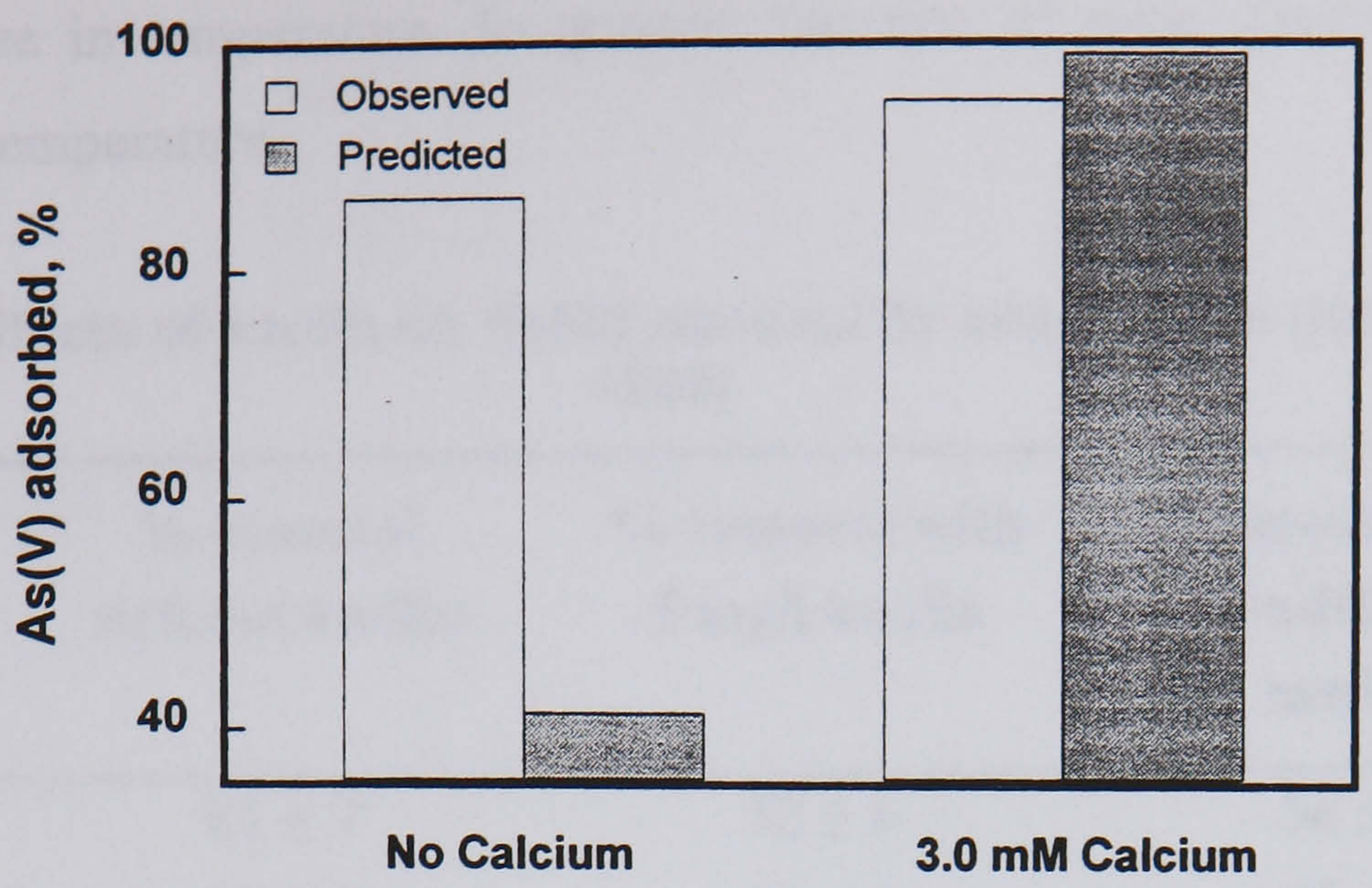


Fig. 3.27 Effects of calcium on As(V) adsorption onto HFO at pH 9 with As(V) concentration of 0.47 μM and Fe total of 50 μM (Wilkie and Herring, 1996)

Fig. 3.25 also shows the effects of natural organic matter (NOM) on As(V) removal by $FeCl_3$. In adsorption of As(III) onto HFO, the addition of NOM (4 mg/l) showed less arsenic removal than without NOM over the pH range of 4-7 (Hering *et al*, 1997).

Hering *et al* (1996) found that the addition of kaolin particles has no consistent effect on arsenic removal although the presence of background particulates is known to improve the efficiency of coagulation process (Amirtharajah and O'Melia, 1990). The decrease in As(III) removal in presence of 5 mg/l kaolin (with a corresponding turbidity of 8 NTU) was also observed when the background electrolyte was exposed to kaolin particles and kaolin was removed before the coagulation experiment (pre-conditioned media) as shown in Table 3.7.

3.8.7 Influence of temperature

Temperature is expected to influence the rate of chemical reactions and solubility of solids in liquids. The influence of temperature on solubility depends mainly upon the heat effects of the solution. If the reaction is endothermic, the solubility increases with increasing temperature and if the reaction is exothermic, the solubility decreases with an increase in temperature. In general, the rate of most chemical reactions increases with temperature.

Table 3.7 Effects of kaolin on As(III) removal by coagulation (Hering *et al*, 1996)

pH **± 0.1**	**% removal without kaolin**	**% removal with 5 mg/l kaolin**	**% removal in pre-conditioned media***
4.0	81 ± 7	52 ± 6	56 ± 1
5.0	64 ± 7	62 ± 3	63 ± 3
7.0	67 ± 3	59	58

Initial arsenic concentration: 6 μg/l
$FeCl_3$ dosage: 4.9 mg/l
*Preconditioned media: pH adjusted background electrolyte were pre-conditioned with 5 mg/l kaolin for 45 min with slow mixing at 45 rpm and filtered before use in coagulation.

There is little known about the temperature effect on arsenic removal. Prashad (1994) states that the rate of adsorption, k_{ads}, decreases with increase in temperature from 20 to 40 °C when As(V) adsorption is carried out onto hematite and feldspar (Table 3.8) which is expected for an exothermic adsorption process. This is an agreement with the findings reported by Singh *et al* (1998).

The effect of precipitation temperature was studied in the range of 33°C to 80°C by Papassiopi *et al* (1987). Ferric arsenate precipitation was formed by using ferric sulphate and $NaHAsO_4$ at pH 3 and 5 and it is found that by increasing temperature, the residual iron decreases and the residual arsenic decreases only at pH 3 but increases at pH 5 (Fig. 3.28).

Table 3.8 Variation in adsorption density and rate constant (k_{ads}) with temperature (Prashad, 1994).

System	Temperature °C	Maximum adsorption %	k_{ads} $*10^2$/ min
Arsenic-Hematite	20	81.41	11.6
	30	76.44	10.6
	40	70.18	10.4
Arsenic-Feldspar	20	76.14	6.3
	30	66.49	5.6
	40	61.28	3.2

Initial As(V) conc.: $1.3*10^{-4}$ mole/l and pH: 4.2

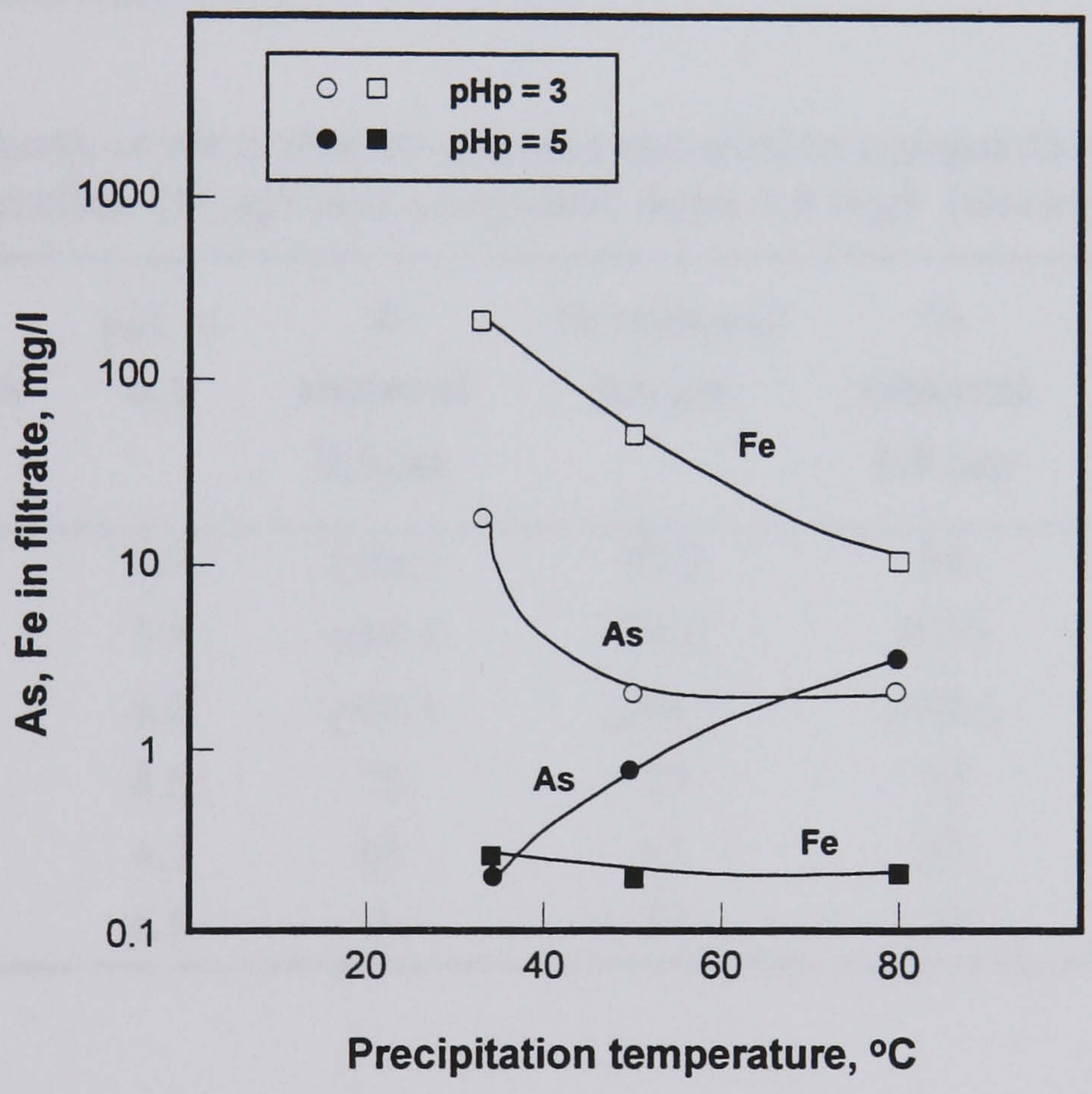


Fig 3.28 Variation of the residual As and Fe in the filtrate as a function of the precipitation temperature for pH 3 and 5, Fe/As ratio 4 (Papassiopi *et al*, 1987).

3.8.8 Influence of filtration

Effectiveness of arsenic removal depends on the efficiency of solid-liquid separation process. Greater efficiency of filter performance is necessary to prevent increased arsenic concentration in treated water caused by breakthrough of colloidal particles associated with arsenic. Studies carried out by Shen (1973) demonstrated that slow sand filtration gave higher removal than rapid sand filtration but the filtration run is very short.

Hering *et al* (1996) investigated the effects of filtration and filter size on arsenic removal in coagulation experiments (Table 3.9). Table 3.9 shows variations in filter size (from 0.1 to 1.0 μm) has only minor effects on As(V) and As(III) removal. Edwards (1994) reports a marked decrease (removal decreased by >40%) in arsenic removal efficiencies with unfiltered samples (Fig. 3.19). These decrease are particularly notable at low pH, indicating the formation of smaller, nonsettleable $Fe(OH)_3$ under these conditions.

Table 3.9 Effects of filter size on arsenic removal in coagulation at initial arsenic concentration 20 μg/l and coagulant dose 4.9 mg/l (Hering *et al*, 1996).

Arsenic oxidation state	pH ± 0.1	% removal 0.1μm	% removal 0.5 μm	% removal 1.0 μm	% removal without filtration
As(V)	4.0	≥99.5	99.0	96	
	5.0	≥99.5	96.0	97.0	
	6.0	≥99.5	≥99.5	≥99.5	
As(III)	4.0	76	73	72	54
	4.5	66	65	68	54
	6.0	5	51	54	51

3.9 OVERVIEW

The literature review has described the chemistry of arsenic together with its removal mechanisms and techniques. It was evident that most of them covered works on As(V) and there was a little information on As(III) removal and the factors influencing its removal.

It appears that coprecipitation and adsorption are the dominant mechanisms in coagulation-precipitation process in arsenic removal, but the literature review has shown a gap in the understanding of the exact mechanism involved in this process.

Furthermore, in spite of the existence of many studies on arsenic removal, it is not easy to compare the data because of different test conditions and procedures.

In view of the literature in this chapter, the arsenic removal mechanism by coprecipitation and adsorption using iron, arsenic adsorption capacity of different forms of carbon and the factors influencing As(III) removal such as Fe/As ratio, pH and presence of co-occurring solutes were taken into consideration in the experimental programme (chapter 4).

Chapter 4

EXPERIMENTAL PROGRAM AND RESULTS

4.1 INTRODUCTION

As noted in Chapter 1, the objective of the experimental program was to establish a practical method for removing arsenic at near zero cost. With this objective in view, two types of process were studied — first, the interaction with dissolved iron, this being a common water quality constraint in Bangladesh (Chapter 2) and second, the interaction of arsenic with charcoal because of its easy availability.

In the case of charcoal (as distinct from granular activated carbon, GAC), the aim was to see whether locally manufactured charcoal or that derived from burning of fuel wood had any benefit in removing arsenic.

In the case of iron, the method applied for removal of arsenic was adsorption and coprecipitation. There were several phases of the investigation. The initial phase aimed at identifying the optimum pH range for the formation of $Fe(OH)_3$ precipitates. The second phase focused on the factors influencing the removal of arsenic from water using iron. It also examined the effects of mixing and the mode of solid liquid separation. The third phase concentrated on the removal behaviour of arsenic using iron by simple mixing and settlement. In the fourth phase, appropriate arrangements for safe separation of the treated water from arsenic waste were studied. Table 4.1 summarises the tests undertaken in the experimental programme. For each test or group of tests, the primary objective is noted.

Values of the parameters such as As, pH and Fe/As ratio were chosen to be representative of the range found in Bangladesh. The exact form of arsenic found in groundwater in Bangladesh has not been confirmed yet. However, in reducing conditions (such as that normally found in groundwater) arsenic is more likely to be present in As(III) form and hence this form was used in the entire experimental investigation.

Table 4.1 List of the tests undertaken in the experimental programme

Objective	Test	Section
Investigation of adsorption capacity of charcoal and a comparison with other forms of carbon i.e. GAC and bone-char	Arsenic adsorption capacity of carbon	4.3
Identification of the optimum pH range for the formation of $Fe(OH)_3$	Mass of $Fe(OH)_3$ precipitates at different pH	4.4
Investigation of the factors influencing the removal of arsenic using iron	Influence of pH	4.5.1
	Sensitivity of Fe/As ratio	4.5.2
	Effects of mixing, filtration and settlement	4.5.3
	Effects of forms of Fe	4.5.4
	Effects of co-occurring solutes	4.5.5
	Effects of temperature	4.5.6
Investigation of arsenic removal behaviour using $FeCl_3$	Arsenic removal by $FeCl_3$ by simple mixing and settlement	4.6
Design of a suitable draw-off arrangements for collecting treated water	Draw-off arrangements	4.7.1
	Effects of flow-rate on draw-off arrangements	4.7.2

4.2 MATERIALS AND METHODS

4.2.1 Chemicals

Laboratory nano-pure water was the main source of water within the experiments, this embracing preparation of all the solutions and the sample water. The chemicals employed for the experiments were general purpose grade (GPR) and used without any purification. Solutions of arsenic (As(III)) were prepared from concentrated stock solution of arsenic trioxide, As_2O_3, (1 mg/ml) in 0.5 M/l HCl (BDH) for use in the tests. Iron presence was based on $FeCl_3$ solution obtained by dissolving solid $FeCl_3$ in nano-pure water. Background electrolyte was provided by 0.01 M/l $NaNO_3$ to fix the ionic strength and $NaHCO_3$ was added to provide alkalinity. pH was maintained by adding 0.1 M NaOH or 0.1 M HCl.

4.2.2 Measurement of Arsenic

In early parts of the study arsenic was measured by Electrothermal Atomic Absorption Spectrophotometer (ETAAS) (Unicam 929 model) method as stated in Standard Methods (APHA, AWWA and WEF, 1995). The arsenic detection range of the equipment was 2-60 μg/l. Samples containing arsenic greater than 60 μg/l, were diluted. Samples and standards contained the same concentration of $Ni(NO_3)_2$ as a modifier according to the specification in the Standard Method. In later part of this study (on availability of a new ICP-AES machine in Civil Eng. Dept.), arsenic was analysed by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) method. The minimum detection limit of this instrument for measuring arsenic was 10 μg/l. In the ICP-AES method, all samples and standards were acidified according to the standard methods (APHA, AWWA and WEF, 1995).

4.3 ADSORPTION CAPACITY OF CARBON IN REMOVING AS(III)

Three different forms of carbon were tested for adsorption in order to remove As(III) from water. These are granular activated carbon (GAC) (Norit, PK-1), non-activated animal granular charcoal (bone char) (BDH standard) and ordinary barbecue charcoal. Of these, GAC is the most expensive form of carbon and depends on sophisticated technology during its production, the ordinary untreated charcoal being the cheapest and easiest to produce. A comparison of the As(III) removal capacity of the three forms of carbon was made. Although GAC is known to be very effective in removing arsenic (Gupta and Chen, 1978), the objective was to assess the viability of using locally manufactured charcoal. Barbecue charcoal was an example of the type of charcoal, which was likely to be produced.

The characterisation of granular activated carbon used in this experiment is presented in Table 4.2.

Table 4.2 Characterisation of granular activated carbon (Norit PK-1)

Properties	Value
Bulk density (g/l)	255
Moisture (%)	2
Ash content (%)	7
Particle size	
> 0.84 mm (%)	4
> 0.5 mm (%)	52
> 0.25 mm (%)	98
Uniformity coefficient	1.5

4.3.1 Preparation of Carbon for Adsorption

To remove any impurities (oils, organic matter etc.) of carbon that might cause interference in adsorption experiments, all three types of carbon were washed as follows according to Huang and Fu (1984): 50 g of carbon was added to 1 litre of 0.1M HCl, mixed and shaken for 24 h in an orbital shaker (KL2). The acid wash was then followed by three consecutive rinse cycles, each using 1 litre of nano-pure water for 24 hrs. After rinsing, the carbon was dried overnight at 105°C and cooled to room temperature before use.

4.3.2 Adsorption Experiments

Batch adsorption tests were carried out to study the adsorption capacity of the three types of carbon described in Sec. 4.4 according to ASTM D 3860-89a (ASTM, 1993). Carbon was weighed out (in the range of 0.075- 6 g), placed into the isotherm bottles, and filled with 150 ml nano-pure water. As(III) solution was pipetted into each of the bottles according to the required initial As(III) concentration (100 μg/l). The bottle was then capped and agitated for a specific period of time at room temperature (18-19°C) in the orbital shaker KL2. pH of the samples were 5.1 to 5.4 without adding any acid or base. After a specified period of agitation (Tables 4.3, 4.4 and 4.5), samples were filtered through 0.45 μm filter papers and equilibrium arsenic concentration of the filtrate was measured by ETAAS method. Each of the tests was carried out four times.

Tables 4.3, 4.4 and 4.5 present the adsorption test results of As(III) onto GAC, charcoal and bone char and Figs. 4.1, 4.2 and 4.3 show the Freundlich adsorption isotherm of these three types of carbon.

Table 4.3 Test results of As(III) adsorption using granular activated carbon (GAC)

Test condition	**As(III) μg/l**	**GAC g/l**	**Avg. residual As(III) conc., μg/l**	**Avg. As(III) adsorbed, μg/l**	**Avg. As(III) adsorbed, μg/g of GAC**	**Avg. As(III) adsorbed, %**
Contact Time: 2 days pH: 5.1-5.4	100.0	0.5	57.9	42.1	84.2	42.1
		1.0	42.4	57.6	57.6	57.6
		3.0	31.8	68.2	22.7	68.2
		5.0	26.2	73.8	14.8	73.8
		7.0	21.4	78.6	11.2	78.6
		10.0	16.9	83.1	8.3	83.1
		20.0	11.7	85.1	5.7	85.1

Table 4.4 Test results of As(III) adsorption using charcoal

Test condition	As(III) µg/l	Char-coal g/l	Avg. residual As(III) conc., µg/l	Avg. As(III) adsorbed, µg/l	Avg. As(III) adsorbed, µg/g of charcoal	Avg. As(III) adsorbed, %
Contact	100.0	0.5	100.0	0	0	0
Time:		1.0	100.0	0	0	0
4 days		3.0	99.2	0.8	0.27	0.8
pH: 5.1-		5.0	96.7	3.3	0.66	3.3
5.4		7.0	95.4	4.6	0.65	4.6
		10.0	94.4	5.6	0.56	5.6
		20.0	92.1	7.9	0.40	7.9
		40.0	90.5	9.5	0.24	9.5

Table 4.5 Test results of As(III) adsorption using bone-char

Test condition	As(III) µg/l	Bone-Char g/l	Avg. residual As(III) conc., µg/l	Avg. As(III) adsorbed, µg/l	Avg. As(III) adsorbed, µg/g of bone char	Avg. As(III) adsorbed, %
Contact	100.0	1.0	98.6	6.6	2.2	6.6
Time:		3.0	93.4	6.6	2.2	6.6
2 h		5.0	91.4	8.6	1.7	8.6
pH: 5.1-		7.0	86.3	13.7	1.9	13.7
5.4		10.0	83.8	16.2	1.6	16.2
		20.0	77.8	22.2	1.1	22.2
		40.0	68.3	31.7	0.8	31.7

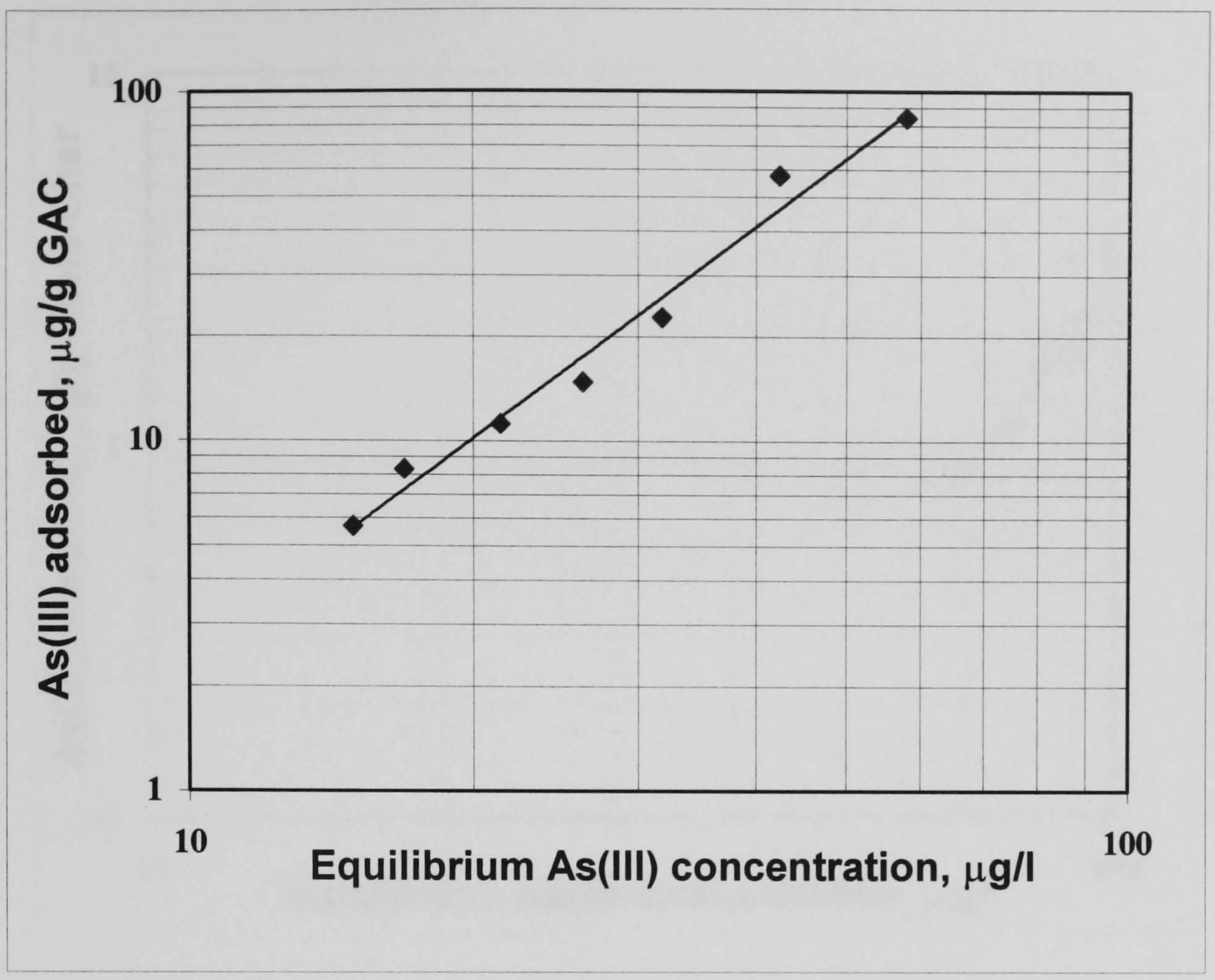


Fig. 4.1 Freundlich isotherm of As(III) using GAC

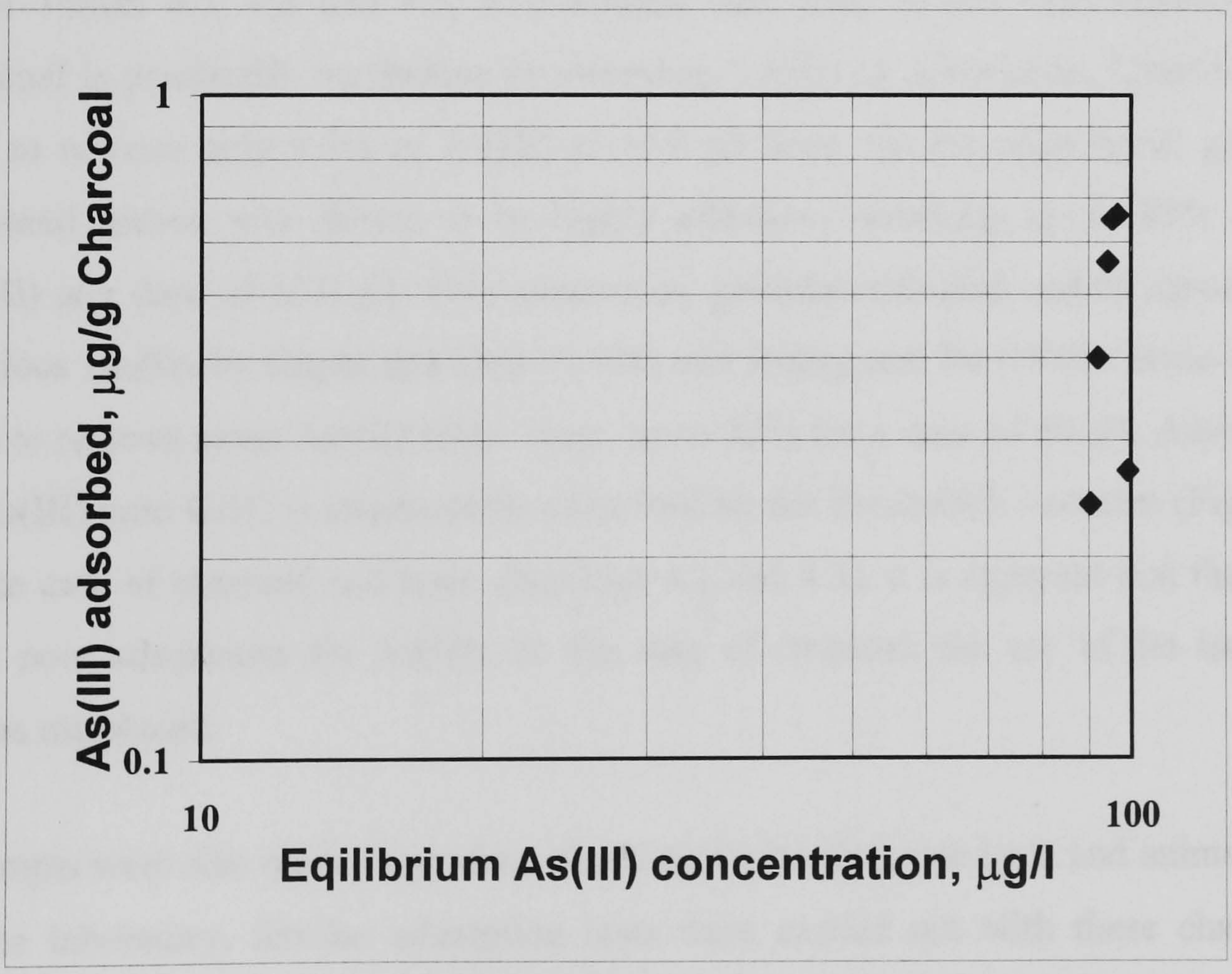


Fig. 4.2 Freundlich isotherm of As(III) using charcoal

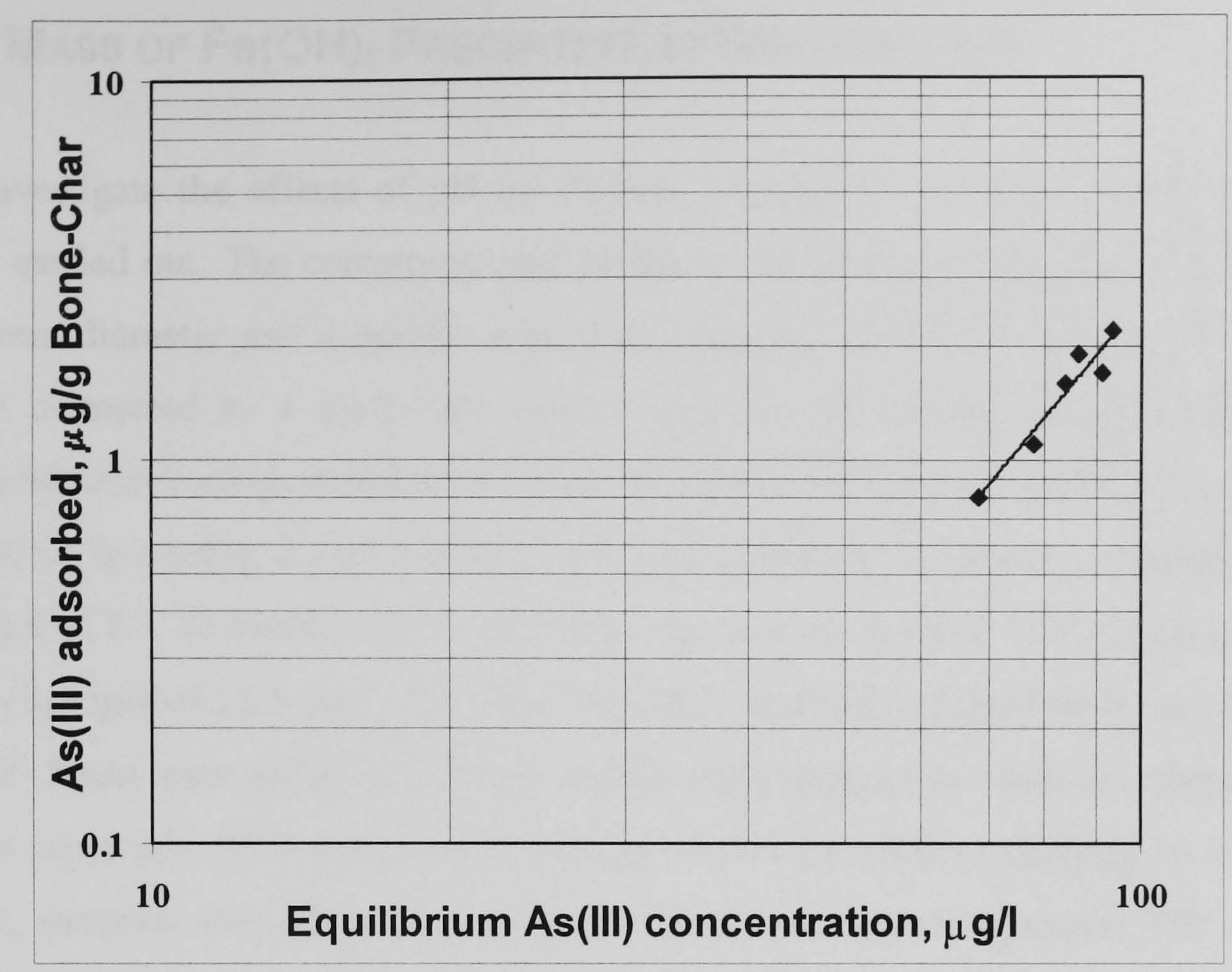


Fig. 4.3 Freundlich isotherm of As(III) using bone char

From Tables 4.3, 4.4 and 4.5, it is evident that GAC is the most effective and charcoal is practically ineffective in removing As(III) by adsorption. Charcoal was able to remove only 9.5% of As(III) at 40.0 g/l dose. On the other hand, granular activated carbon was shown to be highly effective, removing up to 85% of the As(III) at a dose of 20.0 g/l. This removal by granular activated carbon agrees with previous studies by Gupta and Chen (1978) and Huang and Fu (1984). Bone char is seen to remove some As(III) from water, up to 32% for a dose of 40 g/l. Adsorption of As(III) onto GAC is satisfactorily described by the Freundlich isotherm (Fig. 4.1). In the case of charcoal and bone char(Figs 4.2 and 4.3), it is apparent that these are very poor adsorbents for As(III). In the case of charcoal, the use of the isotherm seems misplaced.

Attempts were also made to produce charcoals by burning rice husk and animal bone in the laboratory. Similar adsorption tests were carried out with these charcoals. However, these procedures were not effective in producing charcoal. None was useful in removing arsenic.

4.4 MASS OF $Fe(OH)_3$ PRECIPITATE AT DIFFERENT PH

To investigate the effects of pH on $Fe(OH)_3$ precipitate, jar tests (AWWA, 1992) were carried out. The containers used in the jar tests were round plastic beakers of 150 mm diameter and a paddle with four impellers of 90 mm length and 32 mm width connected to a shaft was used to perform the mixing. Sample water was prepared with nano-pure water in which the alkalinity had been adjusted to 80 mg/l as $CaCO_3$ by adding 0.1 g/l $NaHCO_3$. pH was maintained by adding a predetermined amount of 0.1 M NaOH. $FeCl_3$ solution was used to produce $Fe(OH)_3$ precipitate. $FeCl_3$ dosages of 12.5 mg/l, 25.0 mg/l and 50.0 mg/l were applied over the pH range of 6-9. These were added to 1.0 litre sample water during the rapid mix phase. After 1 min rapid mix (200 rpm) and 19 min slow mix (20 rpm) (according to AWWA, 1992), samples were allowed to settle for 30 min at room temperature (18 - 19^0C). The precipitates were filtered through 0.45 μm filter papers by pressure filtration at 10.4 kN/m^2 pressure and dried for 24 h in an oven at 105°C. The weight of the filter paper was recorded before filtration and after drying. The experiments were repeated four times at each pH value and these results are shown in Table 4.6 and Fig. 4.4.

Table 4.6 Results of mass experiments

pH	**Average mass of $Fe(OH)_3$ precipitates (mg/l) at $FeCl_3$ dose of**		
	12.5 mg/l	**25.0 mg/l**	**50.0 mg/l**
6.0	3.78 ± 0.64 (SD)	9.87 ± 0.90	21.65 ± 0.8
6.5	3.95 ± 0.40 (SD)	10.13 ± 0.86	21.73 ± 1.1
7.0	4.85 ±0.61 (SD)	10.20 ± 0.3	23.98 ± 0.62
7.5	5.83 ± 0.1 (SD)	12.18 ± 0.38	24.38 ± 0.87
8.0	5.80 ± 0.25 (SD)	12.20 ± 1.25	24.36 ± 0.98
9.0	3.80 ± 0.3 (SD)	10.43 ± 0.60	21.64 ± 1.1

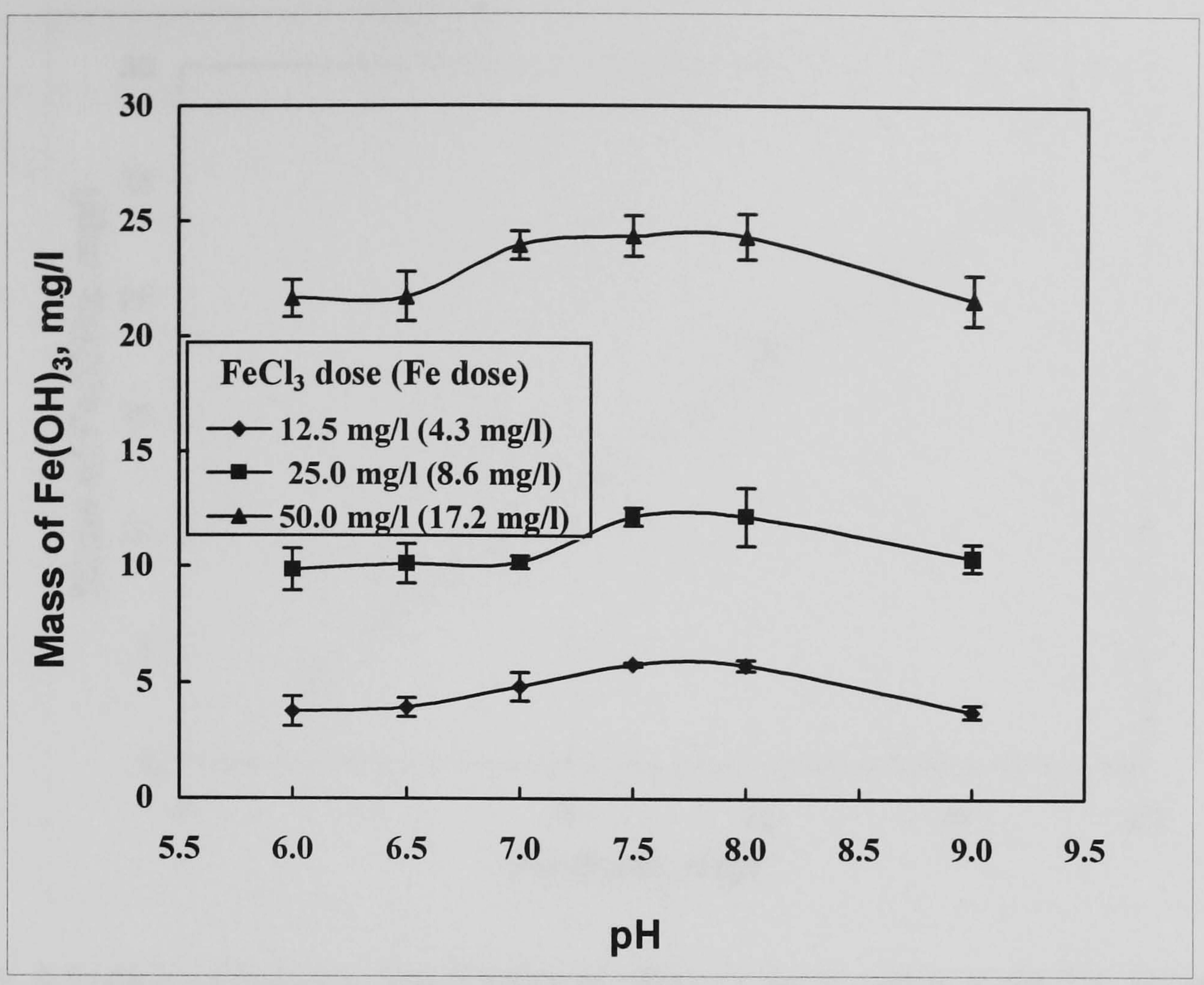


Fig. 4.4 Mass of $Fe(OH)_3$ precipitate at different pH and $FeCl_3$ dosages. Error bars refer to standard deviations.

From Fig. 4.4 it is seen that the amount of dry mass of $Fe(OH)_3$ precipitates increase over the pH range of 6.0 – 8.0 and decrease above pH 8.0 for each dosage of $FeCl_3$. This is consistent with the solubility of $Fe(OH)_3$, thus being least soluble at pH close to 8.0 (Ghosh and O'Conor, 1966).

Two more mass experiments with $FeCl_3$ dosages of 8.0 mg/l and 35.0 mg/l at pH 7.5 were carried out and the amounts of $Fe(OH)_3$ precipitates were again measured using the procedures described above. Fig. 4.5 shows the amount of dry mass of $Fe(OH)_3$ precipitates at different $FeCl_3$ dosage at pH of 7.5. It shows that the amount of $Fe(OH)_3$ precipitates is directly proportional to the dosages of $FeCl_3$ (i.e. amount of Fe) where the proportionality is as follows:

$$Fe(OH)_3\ (mg)/Fe\ (mg) = 1.43 \tag{4.1}$$

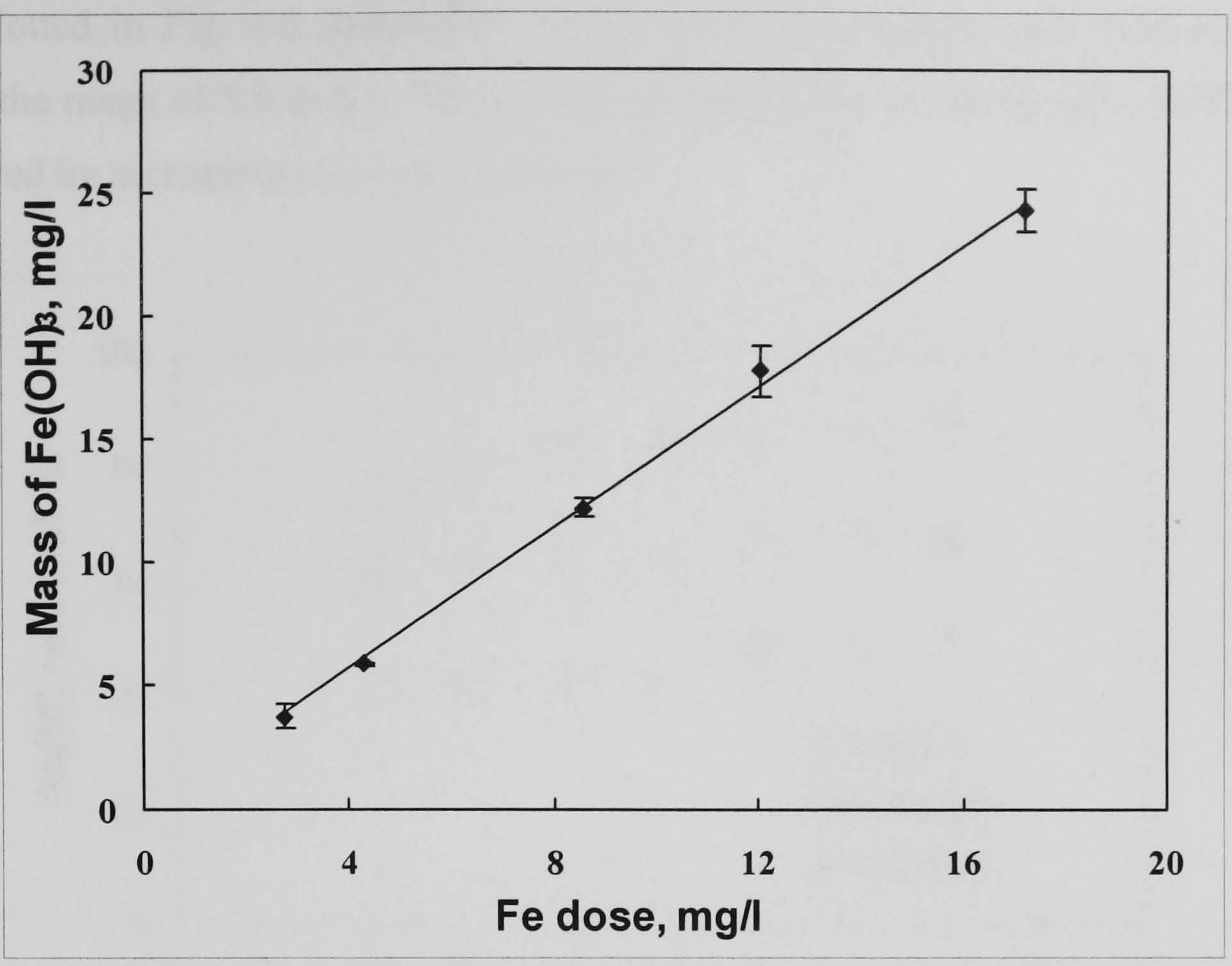


Fig. 4.5 Mass of $Fe(OH)_3$ precipitates at different Fe dosages at pH 7.5. Error bars denote standard deviations.

4.5 FACTORS INFLUENCING THE REMOVAL OF ARSENIC

4.5.1 Influence of pH

Jar tests were performed at three different Fe/As ratios (by weight) 5, 20 and 40 with a fixed dose of As(III) (0.5 mg/l). $FeCl_3$ was used to provide Fe at concentrations of 2.5, 10.0 and 20.0 mg/l respectively at pH values ranging from 5 to 8. pH of the 1.0 litre sample (containing 0.01M/l $NaNO_3$ and 0.1 g/l $NaHCO_3$) were adjusted to the target pH value by adding predetermined amounts of 0.1M HCl or 0.1M NaOH. On addition of the $FeCl_3$, the suspension was subjected to 1-min rapid mix (200 rpm), 19-min slow mix (20 rpm) followed by 30 min settling (AWWA, 1992). Samples of supernatant were then filtered through 0.45 μm cellulose nitrate filter paper and the filtrate was analysed for residual arsenic content. Each of the tests was carried out four times.

Data plotted in Fig. 4.6 shows that As(III) removal increases with increasing pH within the range of 5.0 to 8.0. The process of adsorption of As(III) onto $Fe(OH)_3$ is facilitated by increasing proportions of iron.

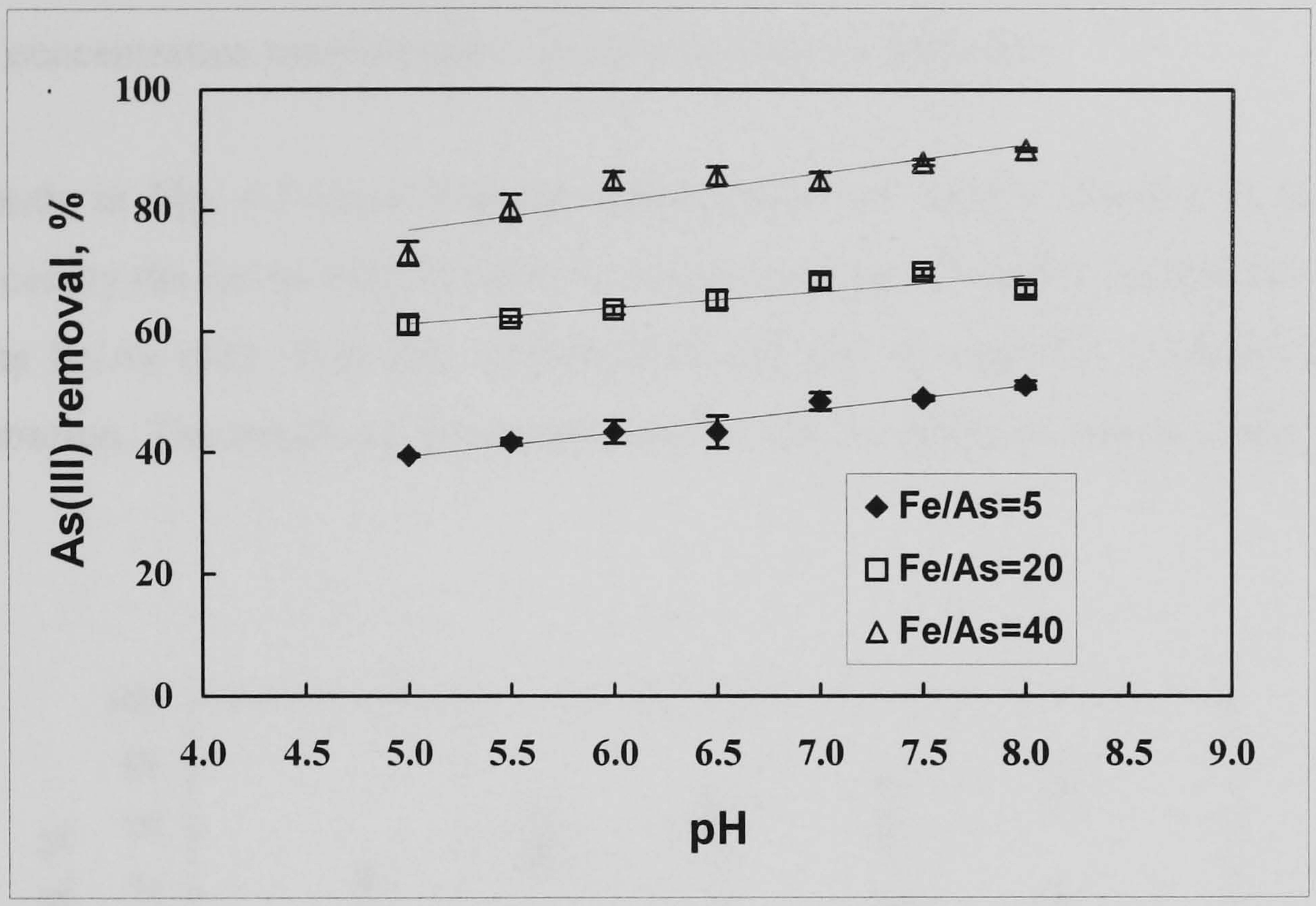


Fig. 4.6 Effects of pH on As(III) removal at different Fe/As ratios with initial As(III) 0.5 mg/l. Error bars refer to standard deviations.

4.5.2 Sensitivity of Fe/As Ratio

Experiments were conducted at Fe/As weight ratios of 5, 10, 20, 30 and 40 (corresponding to 6.7, 13.4, 26.9, 40.3 and 53.8 molar ratio respectively) with varying initial As(III) ranging from 0.1 mg/l to 0.5 mg/l. Each of the tests was based on 1 litre nano-pure water (with background electrolyte and alkalinity the same as described in the section 4.5.1) held in a conical glass flask to which required doses of arsenic and iron were added. A pH of 7.5 was maintained by adding predetermined amounts of 0.1M NaOH. The flask was then placed in the orbital shaker (KL2) and agitated at 410 rpm for 5 min and 100 rpm for 25 min followed by 60 min settling. The shaker was chosen to agitate the samples to form Fe-As complexes instead of using jar test apparatus because shaker was simpler equipment and was similar to manual shaking. The time and speed of agitation was chosen from experience — the flask was unstable and samples were about to spill at speed higher than 410 rpm, and 100 rpm was found to simulate slow mixing.

As with the pH tests, the samples were filtered through 0.45 μm filter paper prior to As(III) concentration measurement. Tests were done in triplicate.

The trends in Fig. 4.7 show that the effectiveness of As(III) removal is strongly influenced by the Fe/As ratio in solution, the percentage of As(III) removal increased with the Fe/As ratio. It is also evident that removal is sensitive to initial As(III) concentration. The trends are reasonably similar for the different values of the Fe/As ratio.

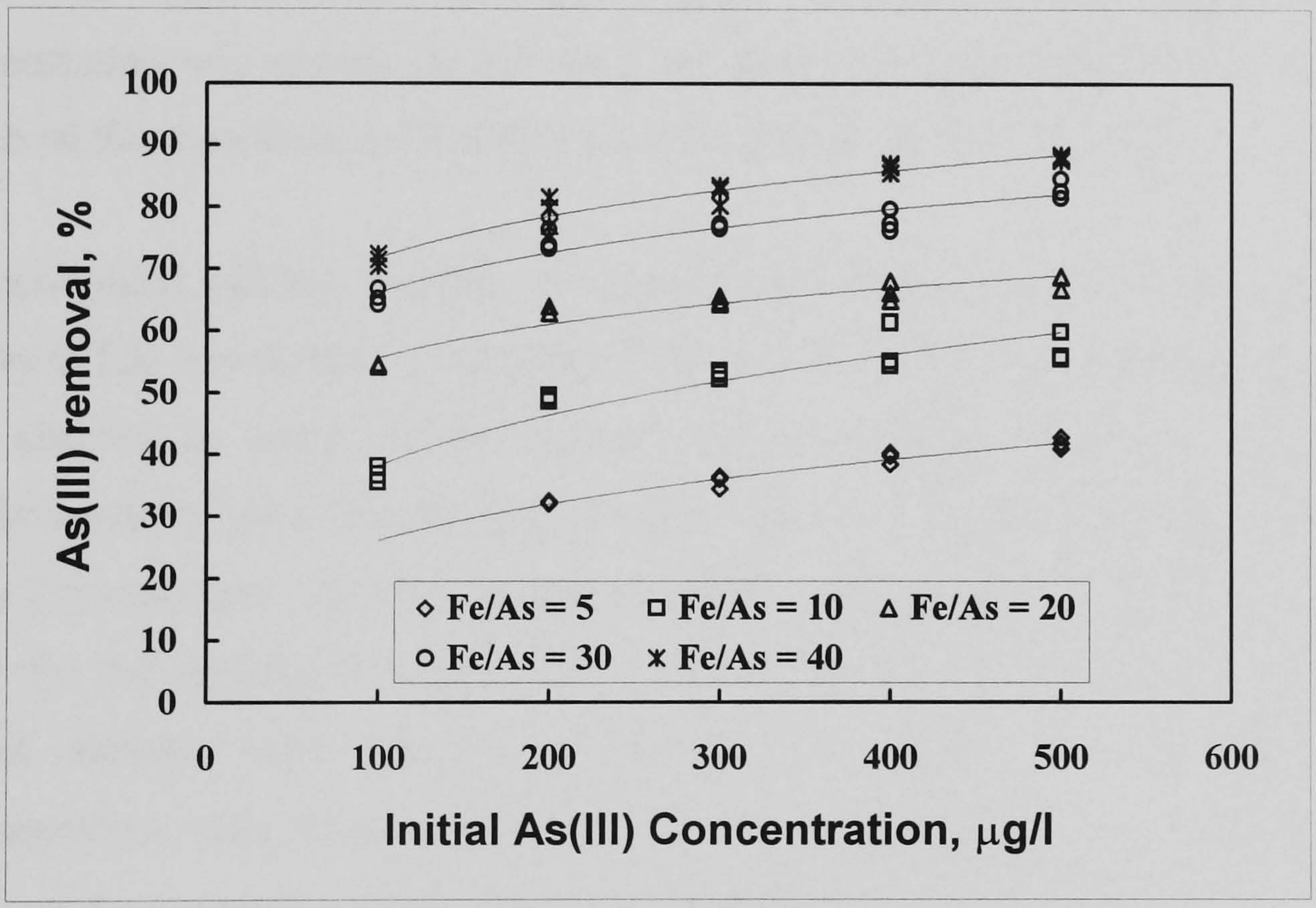


Fig. 4.7 Efficiency of As(III) removal (after filtration) at different Fe/As ratios and at varying initial As(III) concentration at pH 7.5.

4.5.3 Effects of Mixing, Filtration and Settlement

In the experiments described in Sec. 4.5.1 and 4.5.2, samples were subjected to prolonged and intense mixing. Such conditions are not realistically attainable in practice. Hence a further series of tests was carried out in order to investigate the influence of mixing type (mechanical and manual) and time, filtration and settlement on As(III) removal using iron.

4.5.3.1 Effects of mixing condition and filtration

Two types of mixing were studied; mechanical and manual. In both cases, initial As(III) concentration and Fe dosages were 0.2 mg/l and 4.0 mg/l respectively and pH was 7.5. The selection of the test parameters was based on the following considerations. From Fig. 2.1 it was evident that areas of arsenic concentration above 0.2 mg/l was not large and below that concentration, most of the areas were within Bangladesh limit. Again considering the Fe/As ratios (Figs. 2.1 and 2.2), most of the areas were within the ratio of 20 (by weight), therefore to maintain that ratio, iron concentration was chosen as 4.0 mg/l and finally pH was selected 7.5 as it was observed that formation of $Fe(OH)_3$ was maximum at pH 7.5 (Fig. 4.4).

In mechanical mixing, samples in conical glass flasks were mixed in an orbital shaker (KL2) at a rapid rate (410 rpm) for 5 min, at a slow rate (100 rpm) for 25 min and allowed to settle. In the manual mixing methods, samples were shaken continuously by hand over the time span of 15 s to 5 min and then allowed to settle. After 2 h settlement, the two sets of supernatant were collected at a depth of 20 mm from the top surface from each type of samples (both mechanical and manually mixed samples) and one set of sample was analysed for residual As(III) concentration with filtration through 0.45 μm filter paper and another set was analysed for the same without filtration. Each test was done in triplicate.

Table 4.7 and Fig. 4.8 present the effects of mixing condition and filtration on As(III) removal at different mixing time.

Table 4.7 As(III) removal at different mixing conditions of filtered and unfiltered samples after 2 h settlement

Test condition	Mean As(III) removal, %	
	Filtered	Unfiltered
Mechanical mixing	68.5	60.4
Manual mixing:		
15 s manual mixing	63.7	32.2
30 s manual mixing	63.6	45.4
1 min manual mixing	64.3	44.5
3 min manual mixing	64.0	49.3
5 min manual mixing	63.6	53.5

For the filtered samples, shown in Table 4.7, it is clear that the removal efficiency is insensitive to the state of mixing whereas for the unfiltered samples removal increases with mixing type and time. In the latter case the intensity of mixing possibly enhances flocculation (i.e. the promotion of larger aggregates), because it is likely that it is the larger particle sizes, which are responsible for the greater removal rates. Manually mixing for 5 min is almost as effective as mechanical mixing (Table 4.7).

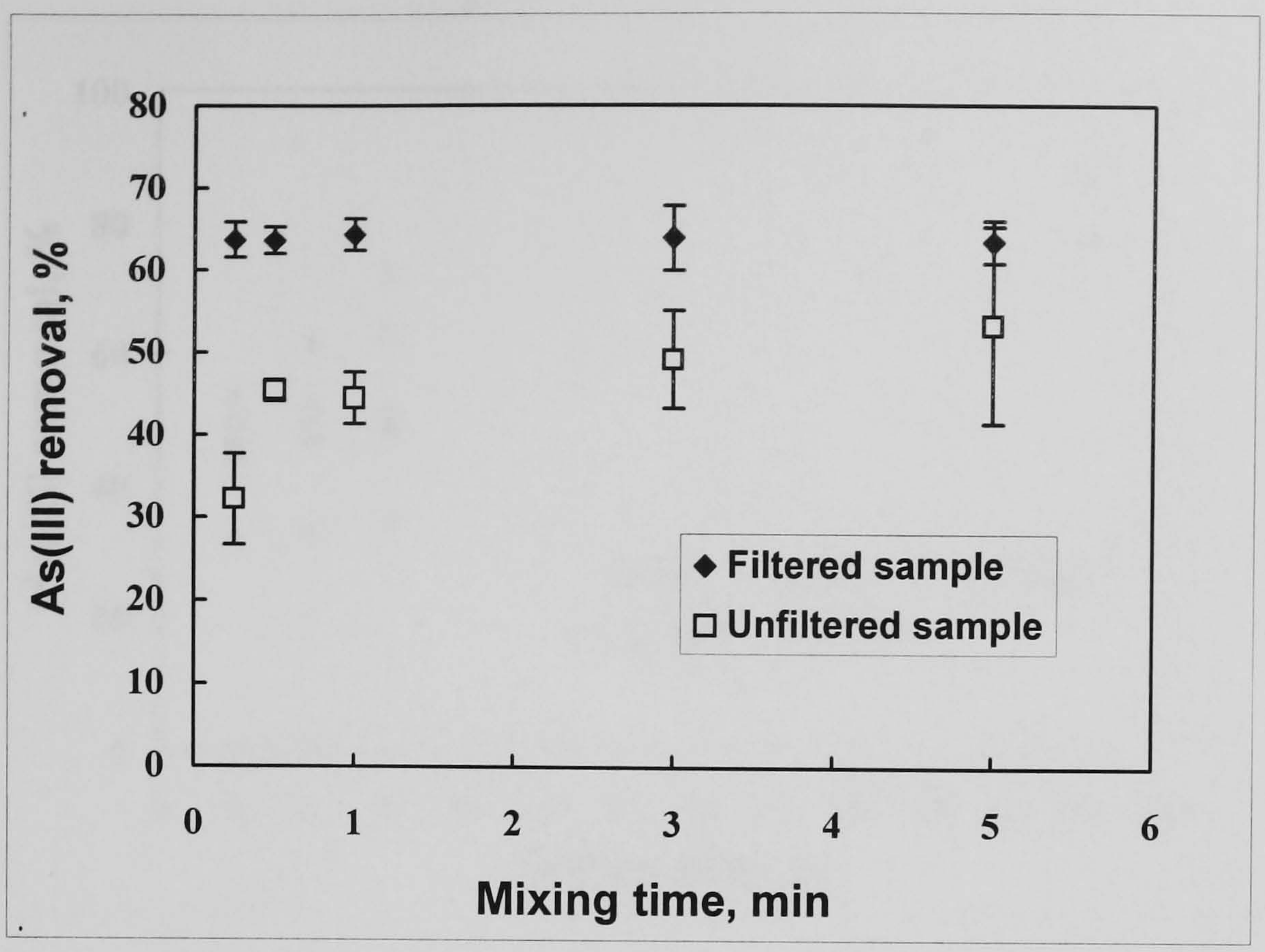


Fig. 4.8 Effects of filtration on As(III) removal at different mixing time of manually mixed samples after 2 h settlement at initial concentration of As(III) 0.2 mg/l, Fe dose 4.0 mg/l and pH 7.5. Error bars represent the standard deviation.

4.5.3.2 Effects of settlement

To investigate the effects of settlement on As(III) removal, samples of water containing 0.2 mg/l As(III) and 4.0 mg/l Fe at pH 7.5 were mixed manually in a conical glass flask over time spans of 15 s to 5 min following the same procedure described in Sec. 4.5.3.1 and were allowed to settle for 24 h. Supernatant was collected at specified time intervals, 2, 4, 6 and 24 h and analysed for residual As(III) concentration without filtration. Each test was carried out in triplicate.

Fig. 4.9 shows the effects of settling time on As(III) removal for manually mixed unfiltered samples at varying mixing times.

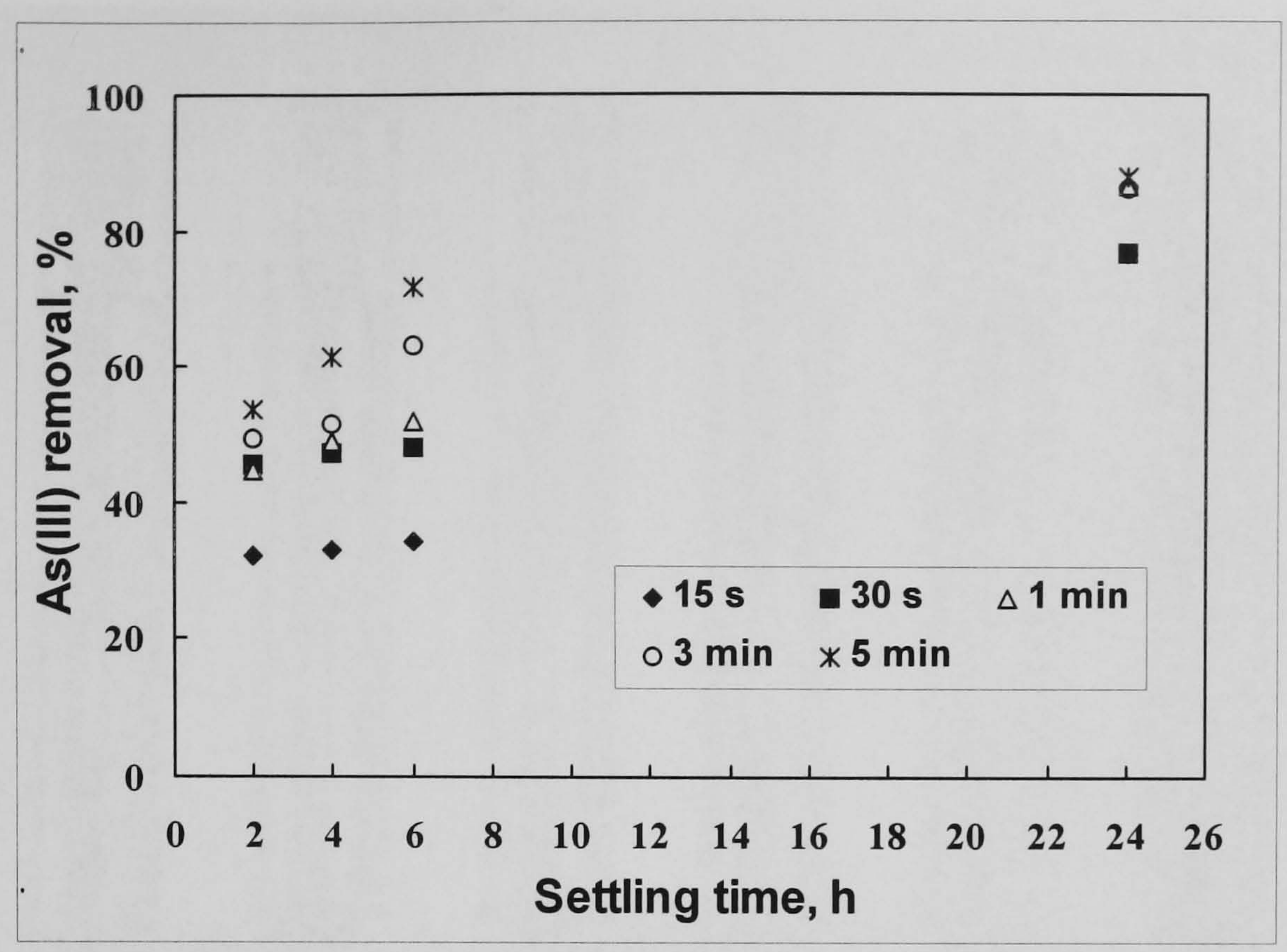


Fig. 4.9 Effects of settlement on As(III) removal for manually mixed unfiltered samples at varying mixing time with initial As(III) concentration of 0.2 mg/l, Fe 4.0 mg/l and pH 7.5.

From Fig. 4.9, it is seen that the overall removal becomes less sensitive to mixing time at longer settling times e.g. 24 h, whereas at shorter times, say 2-6 h, removal increases with increased mixing time.

Settling column tests were carried out in a long glass cylinder of 1.0 litre capacity (432 mm height) to test the influence of the liquid depth on the As(III) removal (Plate 4.1). Samples were prepared with initial As(III) concentration 0.2 mg/l, Fe 4.0 mg/l and pH 7.5. After shaking the sample manually for 1.0 min in a conical glass flask, it was transferred to the long cylinder and allowed to settle for several days. Samples of supernatant were taken from the top, middle and bottom of the cylinder at various day intervals to assess the influence of sample position and settling time on the removal process. Each of the tests was done in six times.

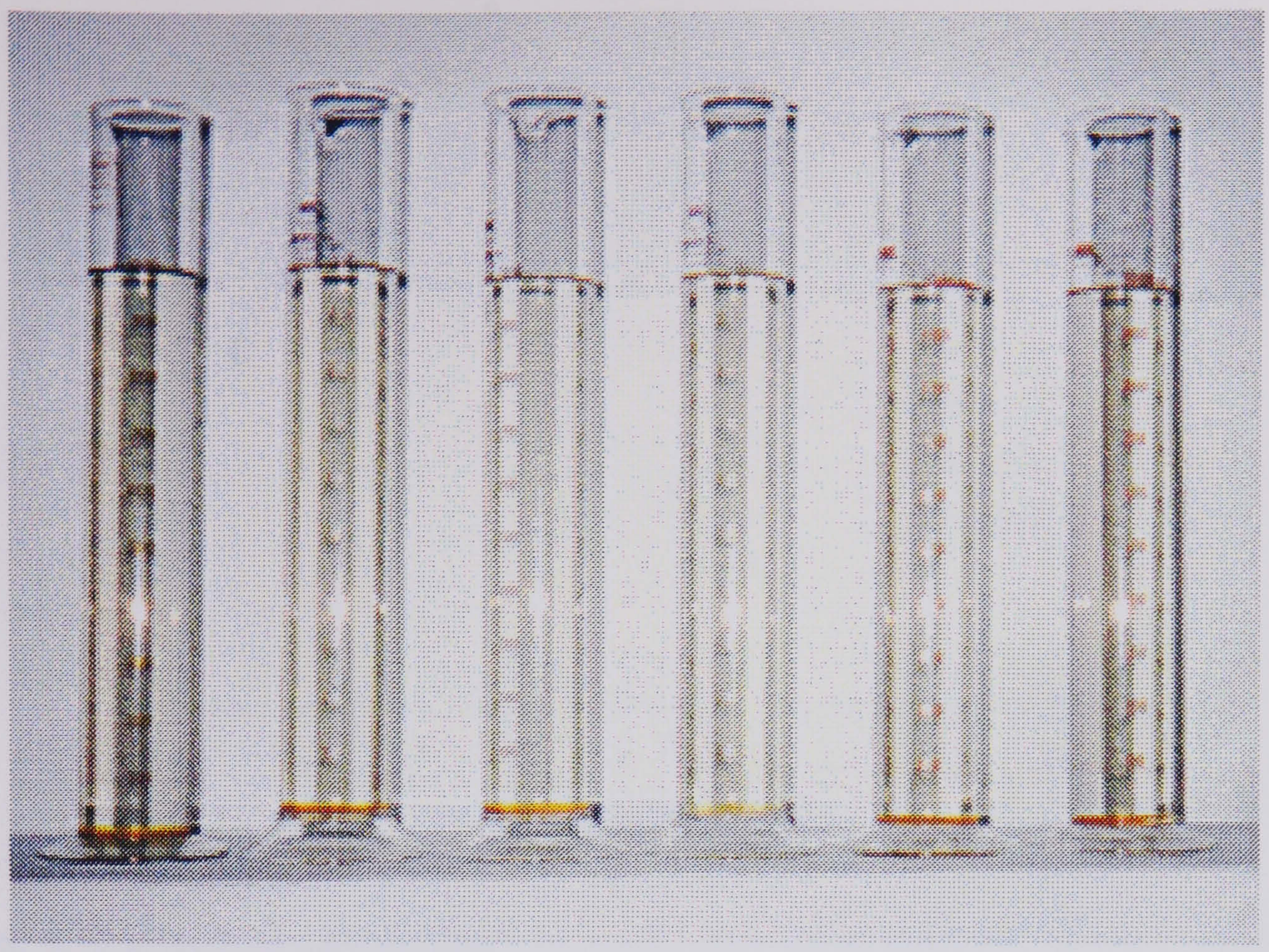


Plate 4.1 Settling column test.

The effects of sample position and settling time are presented in Fig. 4.10 and Fig. 4.11. Fig. 4.10 shows that the influence of sample depth is not significant on the overall removal. Fig. 4.11 emphasises the time dependence of the removal process. After 17 d settlement the final As(III) concentration is 16.2 μg/l, which corresponds a removal of 92%.

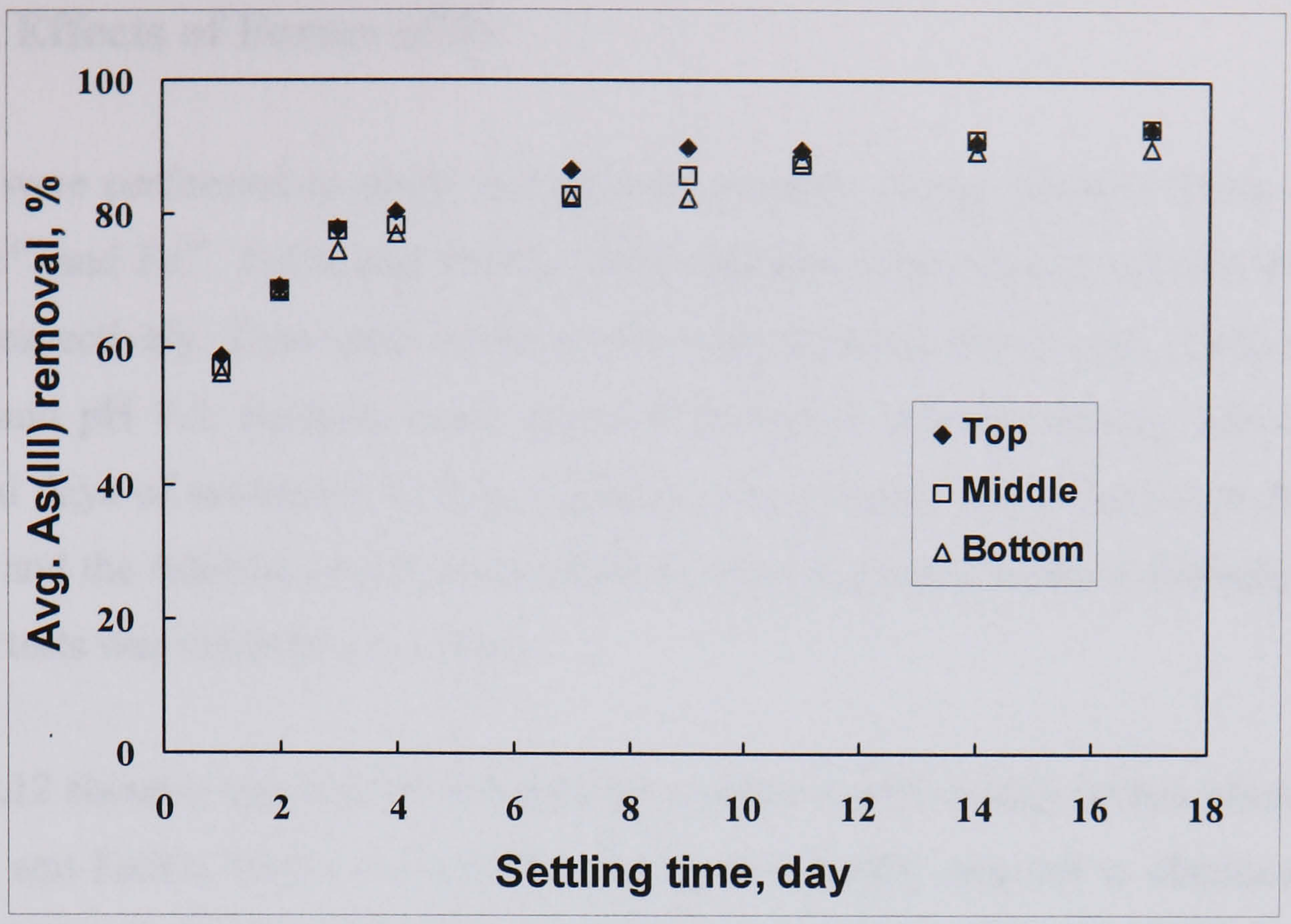


Fig. 4.10 Effects of sample depth on As(III) removal at different settling time with initial As(III) 0.2 mg/l, Fe 4.0 mg/l and pH 7.5.

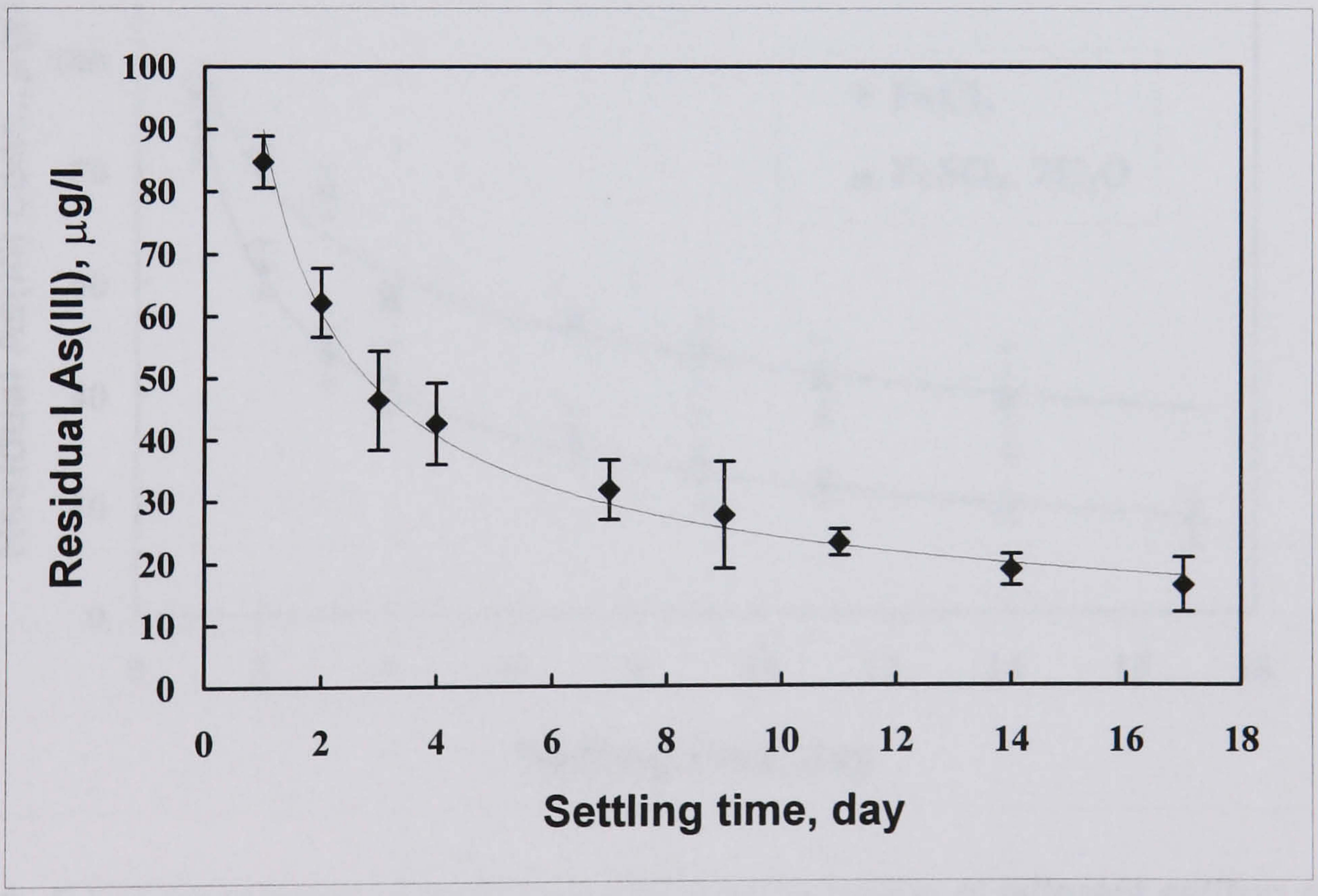


Fig. 4.11 Remaining As(III) concentration at different settling day from settling column test with initial As(III) concentration of 0.2 mg/l, Fe dose of 4.0 mg/l and pH 7.5. Error bars refer to standard deviations.

4.5.4 Effects of Forms of Fe

Tests were performed to study the removal capacity of two different forms of iron i.e. Fe^{2+} and Fe^{3+}. $FeCl_3$ and $FeSO_4.7H_2O$ solutions were used to provide Fe^{3+} and Fe^{2+} respectively. Tests were based on iron concentration of 4.0 mg/l, As(III) of 0.2 mg/l and pH 7.5. Samples were prepared by 1-min manual shaking followed by several days of settlement in long cylinders. Supernatant was collected at different times and the residual As(III) concentrations were measured without filtration. Each of the tests was conducted six times.

Fig. 4.12 shows a comparison between the residual As(III) concentration obtained by $FeCl_3$ and $FeSO_4.7H_2O$. It is evident that greater As(III) removal is obtained when using $FeCl_3$. It suggests that the particular form of Fe affects the removal process.

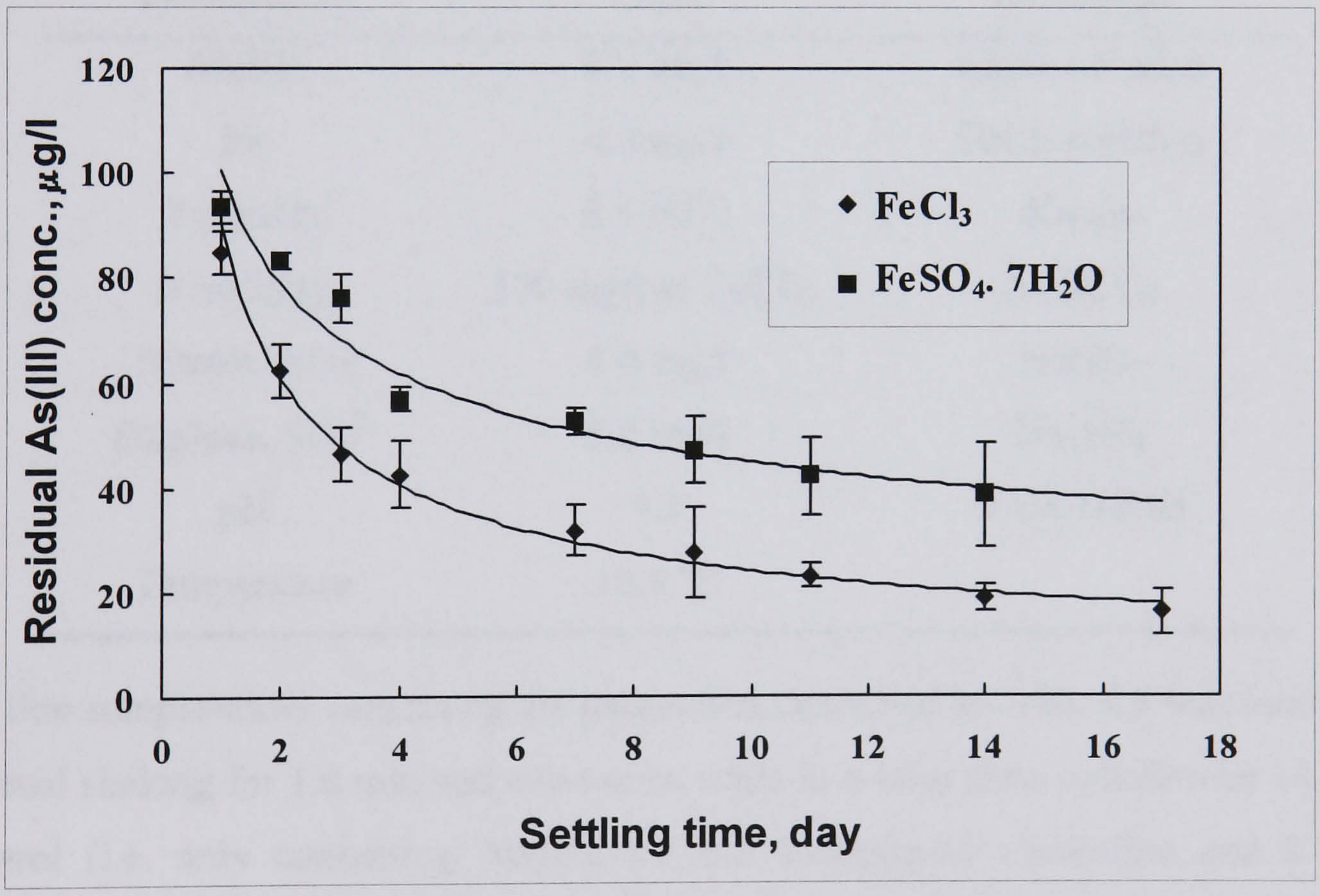


Fig. 4.12 Comparison of residual As(III) concentration at different settling day between $FeCl_3$ and $FeSO_4.7H_2O$ with initial As(III) 0.2 mg/l, Fe 4.0 mg/l and pH 7.5. Error bars refer to standard deviations.

4.5.5 Effects of Co-occurring Solutes

The influence of co-occurring solutes such as SO_4^{2-}, NO_3^-, turbidity and alkalinity present in natural water on arsenic removal process was examined. The concentration of these solutes was used as the values obtained by frequency analysis of these parameters found in the groundwater in Bangladesh (Appendix B).

Synthetic sample water was prepared by adding required amount of solutes in nano-pure water representing to simulate the conditions likely to be encountered in the groundwater of Bangladesh. The concentration of different parameters used in the synthetic water is summarised in Table 4.8.

Table 4.8 Concentrations of different parameters in synthetic water

Parameters	Value	Chemicals
As(III)	0.2 mg/l	As_2O_3 solution
Fe	4.0 mg/l	$FeCl_3$ solution
Turbidity	8.5 NTU	Kaolin
Alkalinity	190 mg/l as $CaCO_3$	$NaHCO_3$
Nitrate, NO_3	4.0 mg/l	$NaNO_3$
Sulphate, SO_4^{2-}	5.0 mg/l	Na_2SO_4
pH	7.5	0.1M NaOH
Temperature	18.9 °C	

1.0 litre sample water containing the parameters described in Table 4.8 was mixed by manual shaking for 1.0 min and allowed to settle in a long glass cylinder for 14 d. A control (i.e. only containing As(III), Fe and background electrolyte and 0.1 g/l $NaHCO_3$) was also prepared in the same way. Supernatant from the synthetic water and the control was collected at different day intervals from the mid depth of the cylinder. Residual As(III) concentrations were measured without filtration and are shown in Fig. 4.13.

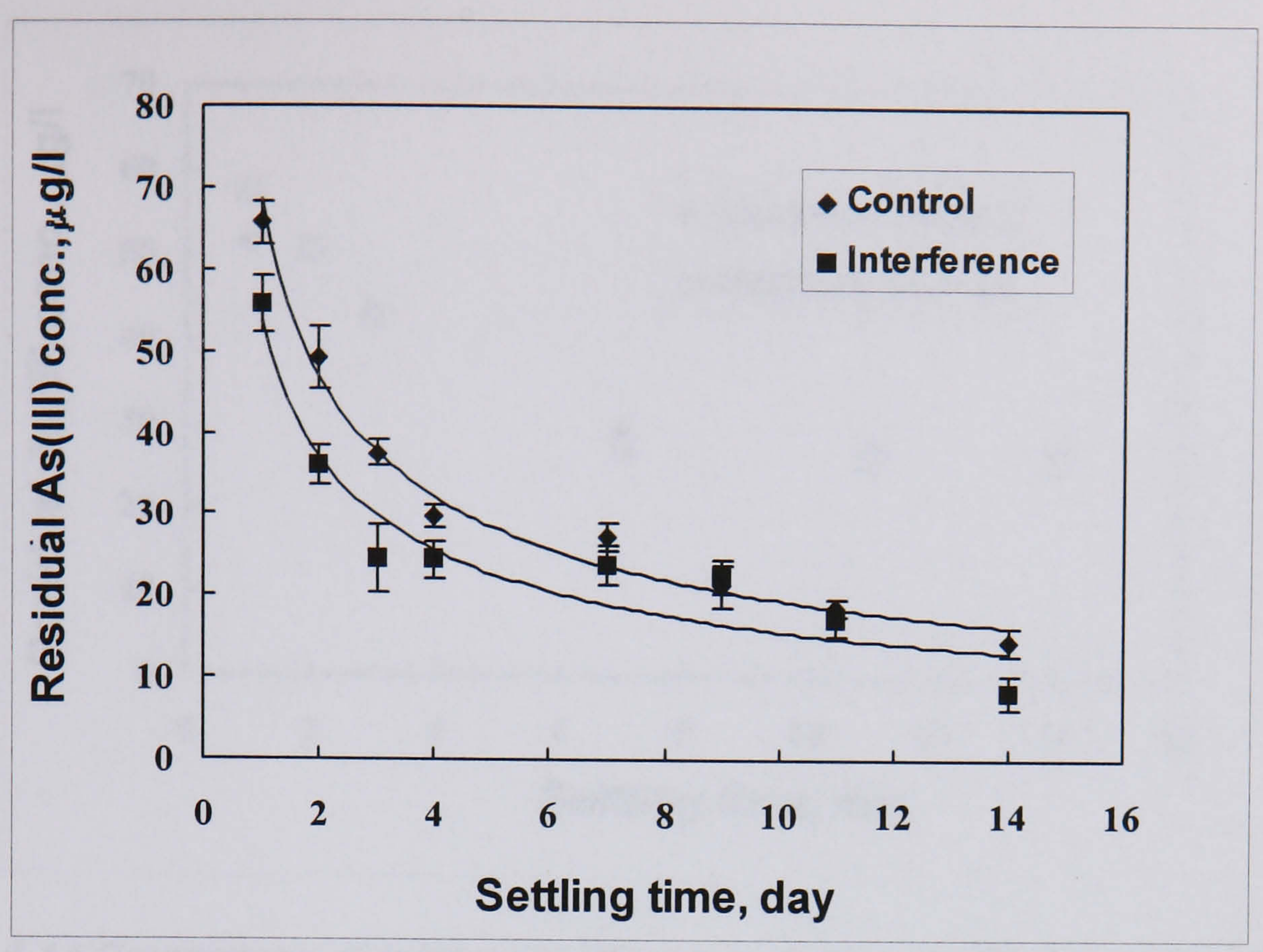


Fig. 4.13 Residual As(III) concentration at different settling time of control samples and samples containing interference with initial As(III) 0.2 mg/l Fe 4.0 mg/l and pH 7.5. Error bars denote standard deviations.

It is observed from Fig. 4.13 that higher removal of As(III) occurs in the synthetic water than in the control. Residual As(III) concentration comes down to 8.43 µg/l after 14 days settling for samples containing co-occurring solute whereas for the control samples, the mean residual As(III) concentration was around 14.6 µg/l at 14 days.

Tests were also conducted to study the individual effects of each solute such as turbidity, alkalinity and NO_3^-.

It is observed that there is no significant effect of alkalinity on As(III) removal as shown in Fig. 4.14. The residual As(III) concentration for low alkalinity (80.0 mg/l as $CaCO_3$) is almost same as with high alkalinity (190.0 mg/l as $CaCO_3$).

The effects of turbidity become insignificant on the removal process provided the settling time exceeds about 7 day (Fig. 4.15).

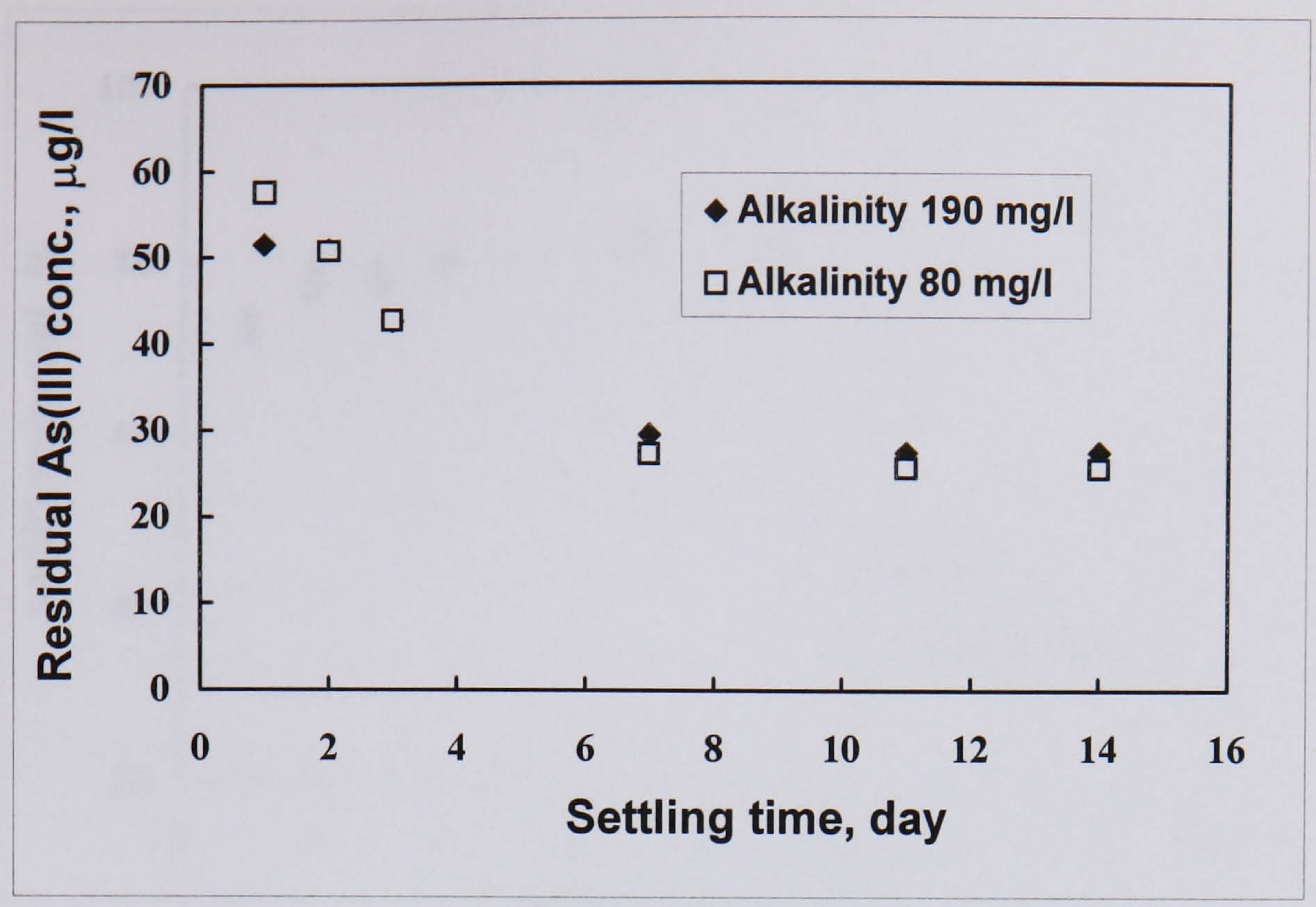


Fig. 4.14 Comparison of residual As(III) concentration at different settling time between samples containing high alkalinity and low alkalinity with initial As(III) 0.2 mg/l, Fe 4.0 mg/l and pH 7.5.

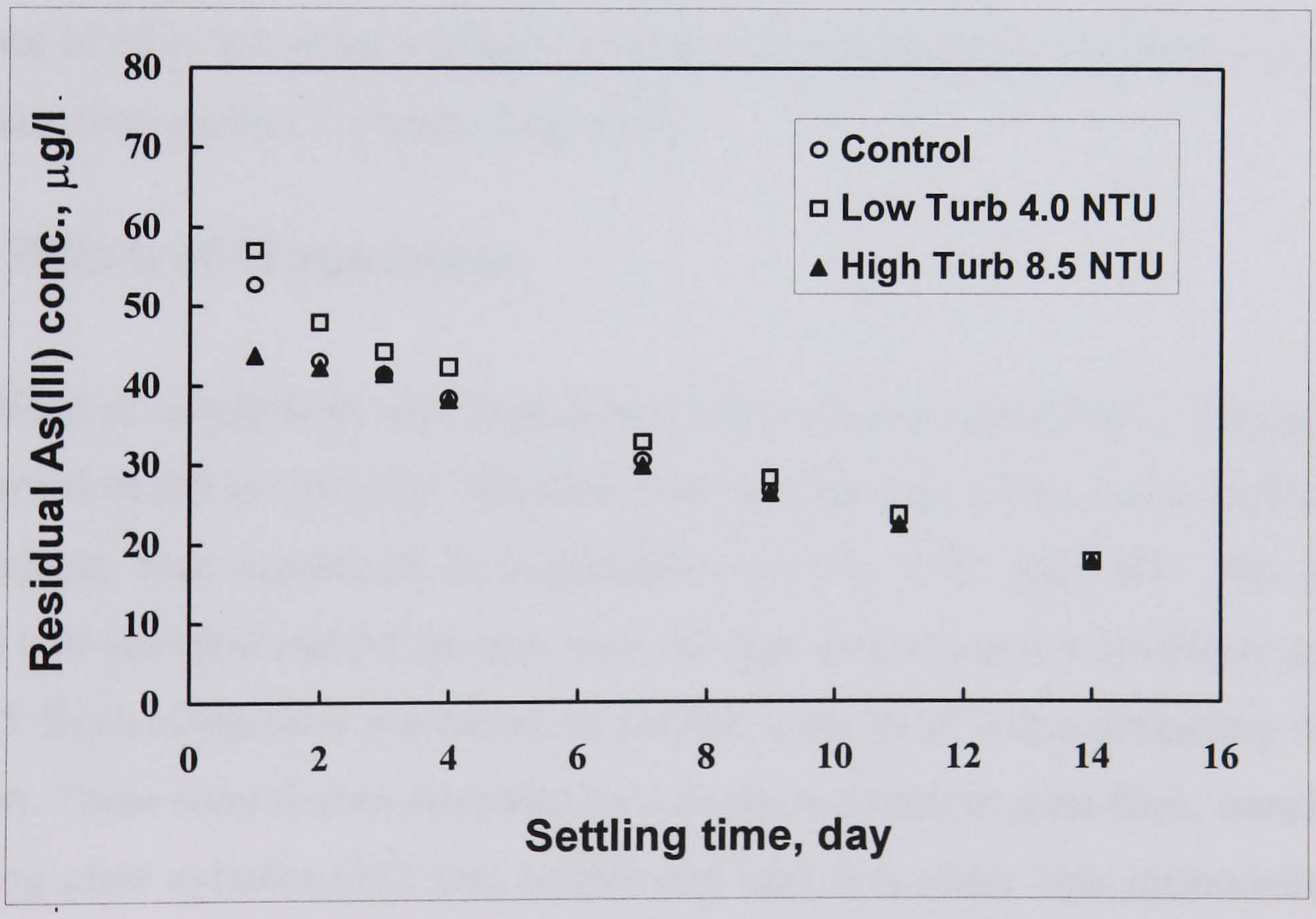


Fig. 4.15 Residual As(III) concentration of control sample and sample containing high turbidity and low turbidity with initial As(III) 0.2 mg/l, Fe 4.0 mg/l and pH 7.5.

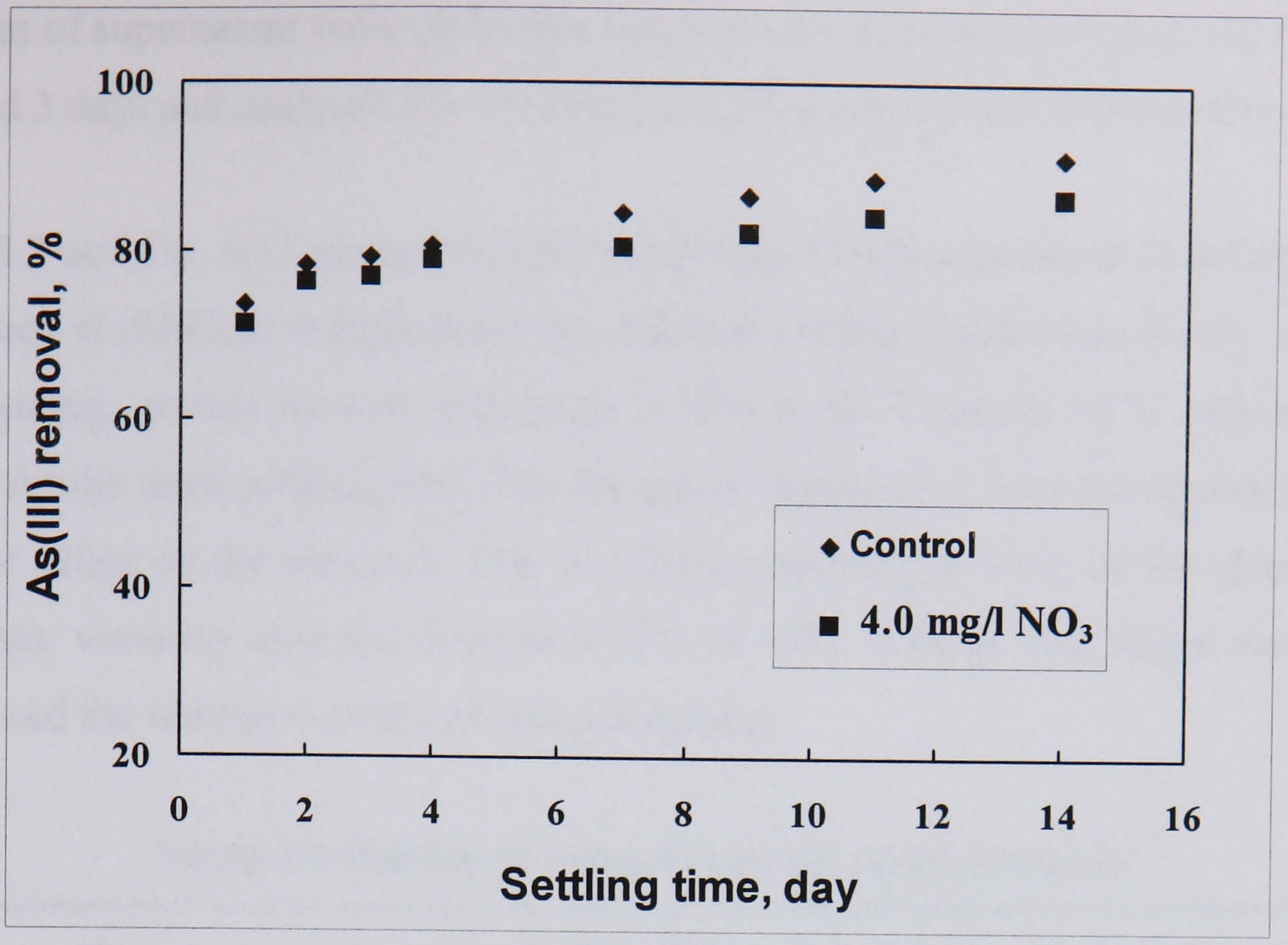


Fig. 4.16 Mean As(III) removal at different settling time of control sample and samples containing 4.0 mg/l NO_3^- with initial As(III) 0.2 mg/l, Fe 4.0 mg/l and pH 7.5.

Presence of NO_3^- has some influence on removal when samples are allowed to settle for a long time such as 7-14 days (Fig. 4.16).

4.5.6 Effects of Temperature

The effects of temperature was studied in As(III) removal using $FeCl_3$. Temperature is expected to affect viscosity, diffusion rates and kinetics of the Fe-As interaction. Experiments were conducted at temperatures of 5°C, 15°C and 30°C. The initial As(III) concentration and Fe dosages were 0.2 mg/l and 4.0 mg/l respectively and pH was 7.5. Each of the tests was based on 1.0 litre samples of water containing As(III) and iron. These were shaken manually for 1.0 min in a conical glass flask, transferred to a long glass cylinder (432 mm height) and kept in a water bath maintaining the desired temperature and allowed to settle there for three days. Each of the tests was performed in triplicate.

Samples of supernatant were taken from each set of temperatures at time intervals of 1, 2 and 3 days and analysed for remaining As(III) concentration without filtration.

Table 4.9 and Fig. 4.17 summarises the remaining As(III) concentration and removal efficiency at different temperatures for different settling times respectively. After 3 days settling, arsenic removal efficiency is 79% at 30 °C and at 15 °C efficiency is 74.8% for the same settling time. The change in temperature does not appear to have a major effect on the removal. This is a little surprising in view of the changes in kinematic viscosity over the interval of 5°C to 30°C, a factor that might well have influenced the settling velocity of fine precipitates.

Table 4.9 Effects of temperature on As(III) removal

Test temperature	Avg. residual As(III) concentration after settling, μg/l		
	1 day settling	2 day settling	3 day settling
5°C	60.7	50.1	49.3
15°C	63.3	51.6	50.4
30°C	54.2	44.7	41.5

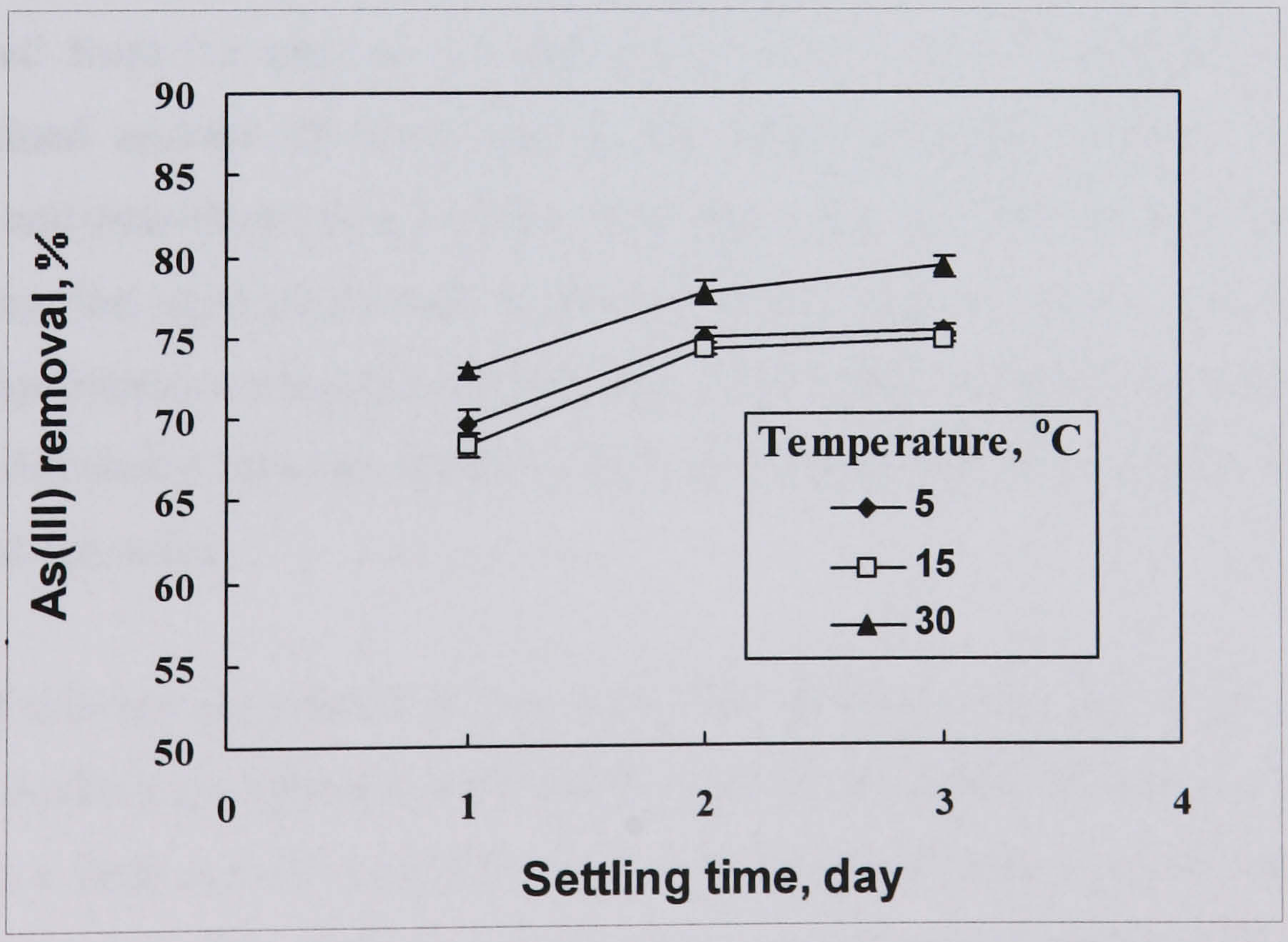


Fig. 4.17 As(III) removal at different temperatures with initial As(III) 0.2 mg/l, Fe 4.0 mg/l and pH 7.5. Error bars represent standard deviations.

4.6 ARSENIC REMOVAL USING $FeCl_3$ BY MANUAL MIXING AND SETTLEMENT

From experiments carried out in sections 4.5.3.1 and 4.5.3.2, it is evident that manual mixing and settlement can be a suitable low cost option for removing arsenic from water using iron. With this view in mind, further tests were carried out to investigate the removal behaviour of As(III) using iron, and the influence of Fe/As ratio and pH when samples are prepared manually and settlement is allowed for solid-liquid separation.

4.6.1 Removal behaviour of As(III) using Fe by manual mixing and settlement

A series of tests was carried out in order to study the removal characteristics of As(III) resulting from an interaction between As(III) and Fe(III). Each of the tests was based on 1.0 litre nano-pure water (with 0.01M $NaNO_3$ as background electrolyte and alkalinity of 100 mg/l as $CaCO_3$) held in a 2 litre conical glass flask. Fe dosage was based on $FeCl_3$ and kept constant at 4.0 mg/l and As(III) dosages were varied from 0.1 mg/l to 7.5 mg/l. A pH of 7.5 was maintained by adding predetermined amount of 0.1M NaOH. The flask was then shaken for 1 min manually and transferred to a 1.0 litre long measuring cylinder to settle for 1 day. After 1 day, the supernatant was collected and the residual arsenic was measured without any filtration using ICP-AES method. The removed As(III) was determined from the difference between As(III) added and residual As(III) measured. Each test was carried out twice.

Results of this test are plotted in Fig. 4.18. This trend is discussed in Section 6.3. When the As/Fe ratio approximately 0.6, it appears that a removal density of As(III) approaches a limit of 0.15 mg/mg Fe. However further increase of As/Fe ratio leads to higher removals. This perhaps suggests that an additional removal mechanism be activated in higher As/Fe ratios.

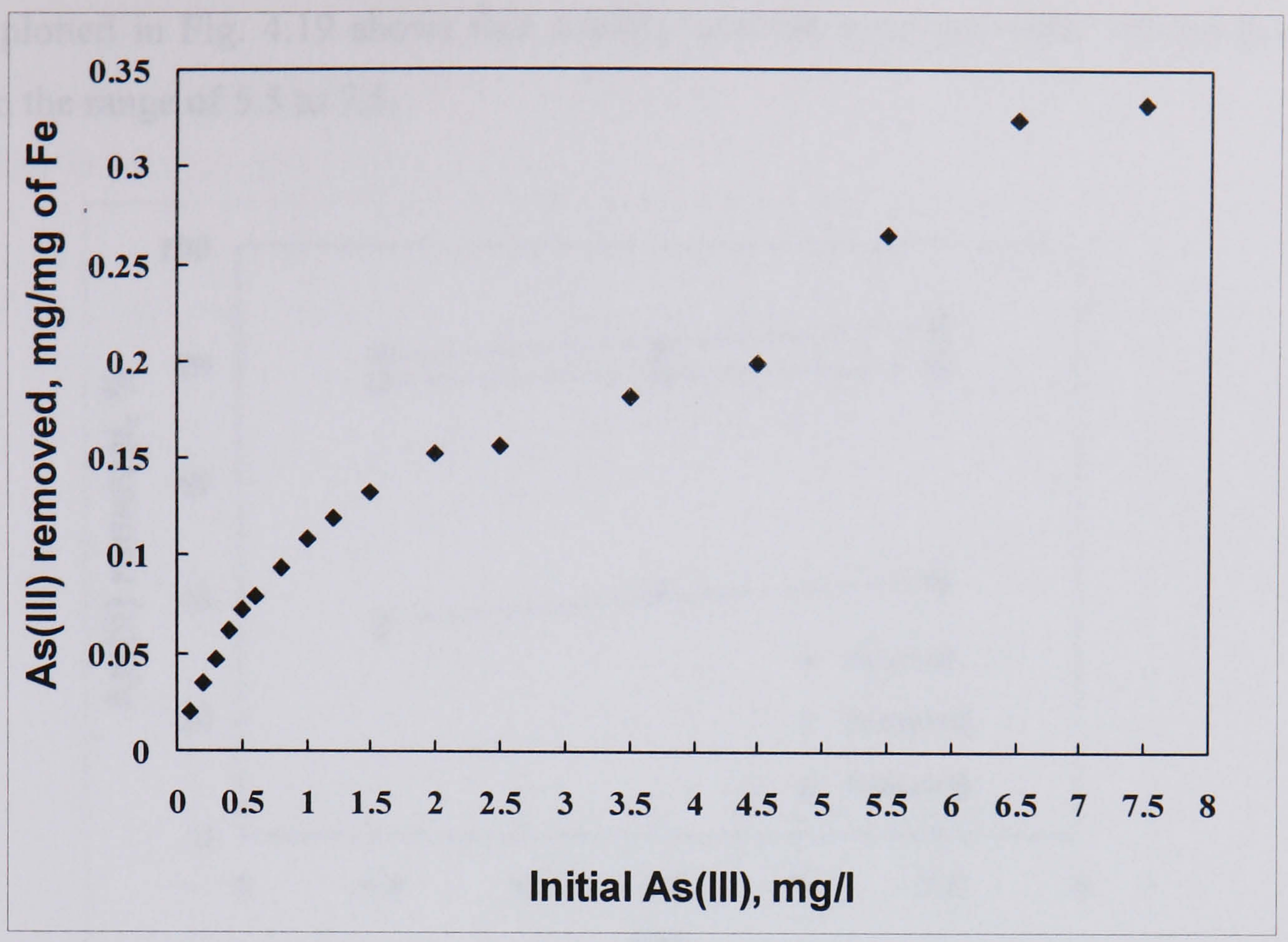


Fig. 4.18 Removal density of As(III) using $FeCl_3$ by 1 min manual mixing and 1 day settlement with initial As(III) concentration over the range of 0.1 – 7.5 mg/l, Fe 4.0 mg/l and pH 7.5.

4.6.2 Influence of pH

Tests were performed at three different Fe/As ratios (by weight) 5, 20 and 40 with a fixed dose of As(III) (0.3 mg/l). $FeCl_3$ was used to provide Fe at concentrations of 1.5, 6.0 and 12.0 mg/l respectively at pH values ranging from 5.5 to 7.5. Each of the tests was based on 1 litre nano-pure water (containing 0.01M/l $NaNO_3$ and 0.1 g/l $NaHCO_3$) held in a conical glass flask to which required doses of arsenic and iron were added. A pH of 7.5 was maintained by adding predetermined amounts of 0.1M NaOH. The sample was then mixed manually for 1.0 min and transferred to a 1.0 litre capacity long glass cylinder (432 mm height) to settle for 3 d. After 3 d settling, the supernatant was collected and the residual arsenic was measured without any filtration. Test were done in triplicate.

Data plotted in Fig. 4.19 shows that As(III) removal increases with increasing pH within the range of 5.5 to 7.5.

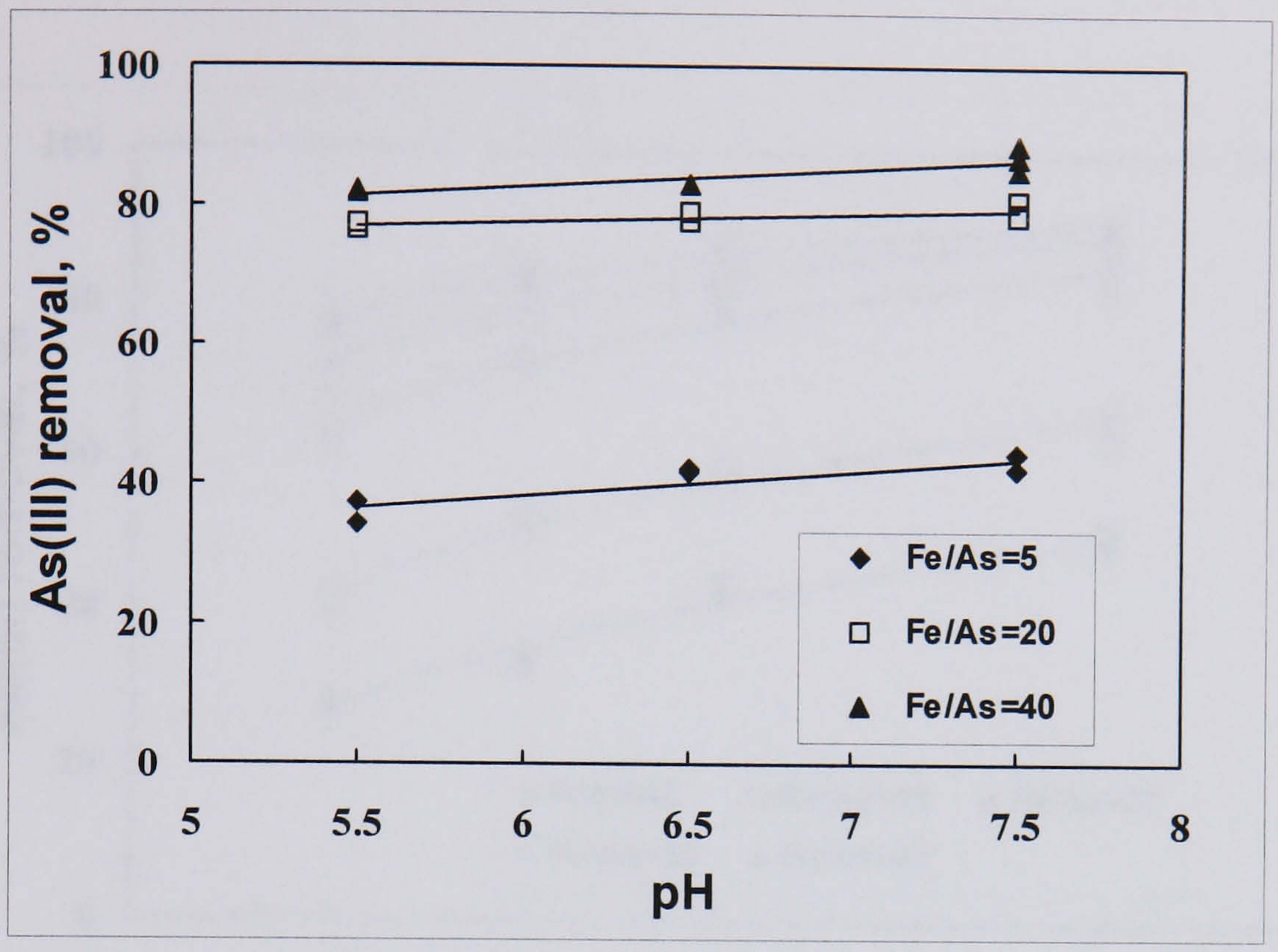


Fig. 4.19 Effects of pH on As(III) removal at different Fe/As ratios after 3 day settlement with initial As(III) concentration of 0.3 mg/l.

4.6.3 Influence of Fe/As ratio

Experiments were conducted at Fe/As weight ratios of 5, 10, 20, 30 and 40 (corresponding to 6.7, 13.4, 26.9, 40.3 and 53.8 molar ratio respectively) with varying initial As(III) ranging from 0.1 mg/l to 0.5 mg/l. Each of the tests was based on 1 litre nano-pure water (with background electrolyte and alkalinity are the same as described in the section 4.6.1) held in a conical glass flask to which required doses of arsenic and iron were added. A pH of 7.5 was maintained by adding predetermined amounts of 0.1M NaOH. The sample was then mixed for 1.0 min manually and transferred to a 1.0 litre capacity long glass cylinder to settle for 3 days. After 3 day settling, the supernatant was collected and the residual arsenic was measured without any filtration. Tests were done in triplicate.

The influence of Fe/As ratio on the As(III) removal is presented in Fig. 4.20. The trend is similar as obtained by mechanical mixing and filtration (Fig. 4.7) only the removal efficiency is higher in this case than that for the same Fe/As ratio and initial As(III) concentration. These trends will be discussed further in section 6.5.1, but are similar in form to data shown in Fig. 4.7.

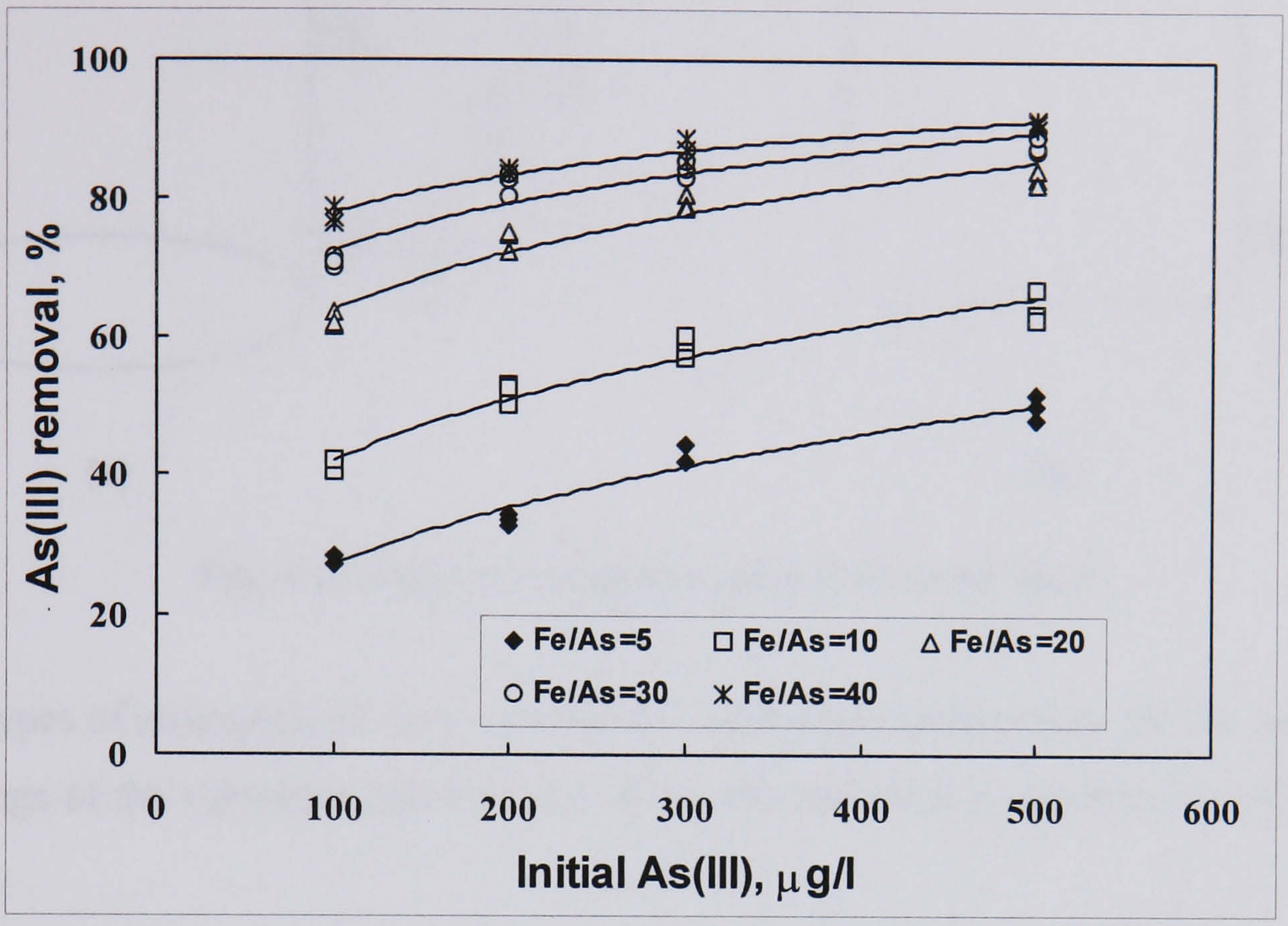
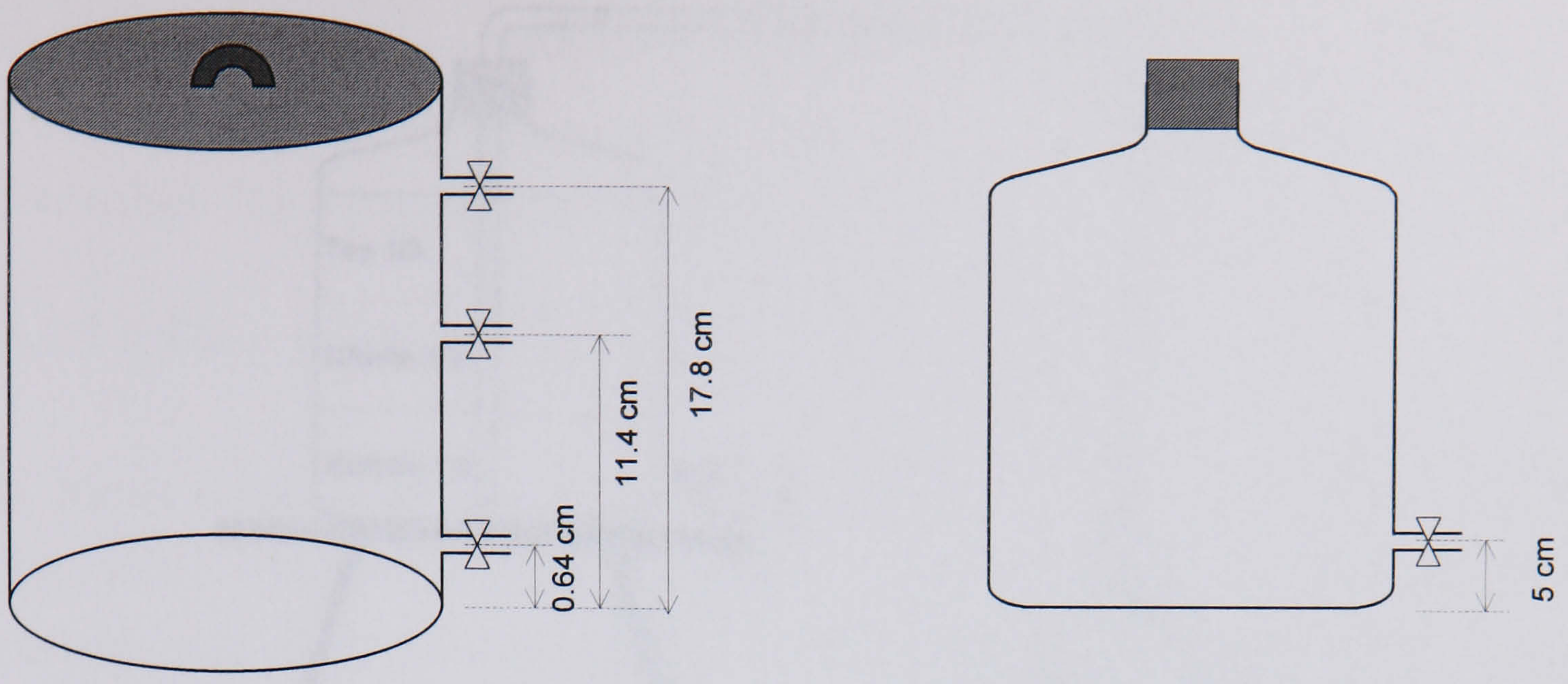


Fig. 4.20 Effects of As(III) removal at different Fe/As ratios and initial As(III) concentration at pH 7.5 after 3 day settlement.

4.7 DRAW-OFF ARRANGEMENT

As discussed in the previous sections, if water containing iron and arsenic is allowed to settle for several days, arsenic coprecipitates and adsorbs on iron and accumulates as precipitate. This process was seen to significantly reduce the concentration of arsenic. However, the problem of separating the precipitate from water remains and there is always a possibility of the precipitate being resuspended if the water is disturbed during separation. As a possible solution to this problem, a draw-off arrangement was studied.

Different types of container and arrangements were tested for collecting the treated water as shown in Fig. 4.21a and 4.21b.



(a) **(b)**

Fig. 4.21 Type of containers used in draw-off tests

Two types of arrangements were studied for collecting treated water: one through the openings of the container and the other from one container to another by siphoning action.

4.7.1 Experiments on Draw-off Arrangements

Sample water was prepared with 7.0 litre nano-pure water containing 0.1 g/l $NaHCO_3$ to provide alkalinity of 80.0 mg/l as $CaCO_3$ and 0.01 M/l $NaNO_3$ as background electrolyte. Initial As(III) concentration was 0.2 mg/l and Fe dosage was 4.0 mg/l and pH 7.2. Sample was mixed for 1.0 min in a plastic container and then transferred to the container as presented in Fig. 4.19a and 4.19b and allowed to settle for 3 days. Each test was done in triplicate.

The supernatants from the sample of arrangement shown in Fig. 4.21a were taken out through the three openings after 1, 2 and 3 d and analysed for residual iron concentration.

For the arrangements shown in Fig. 4.21b, supernatant was collected from top, middle and bottom of the container by siphoning as shown in Fig. 4.22

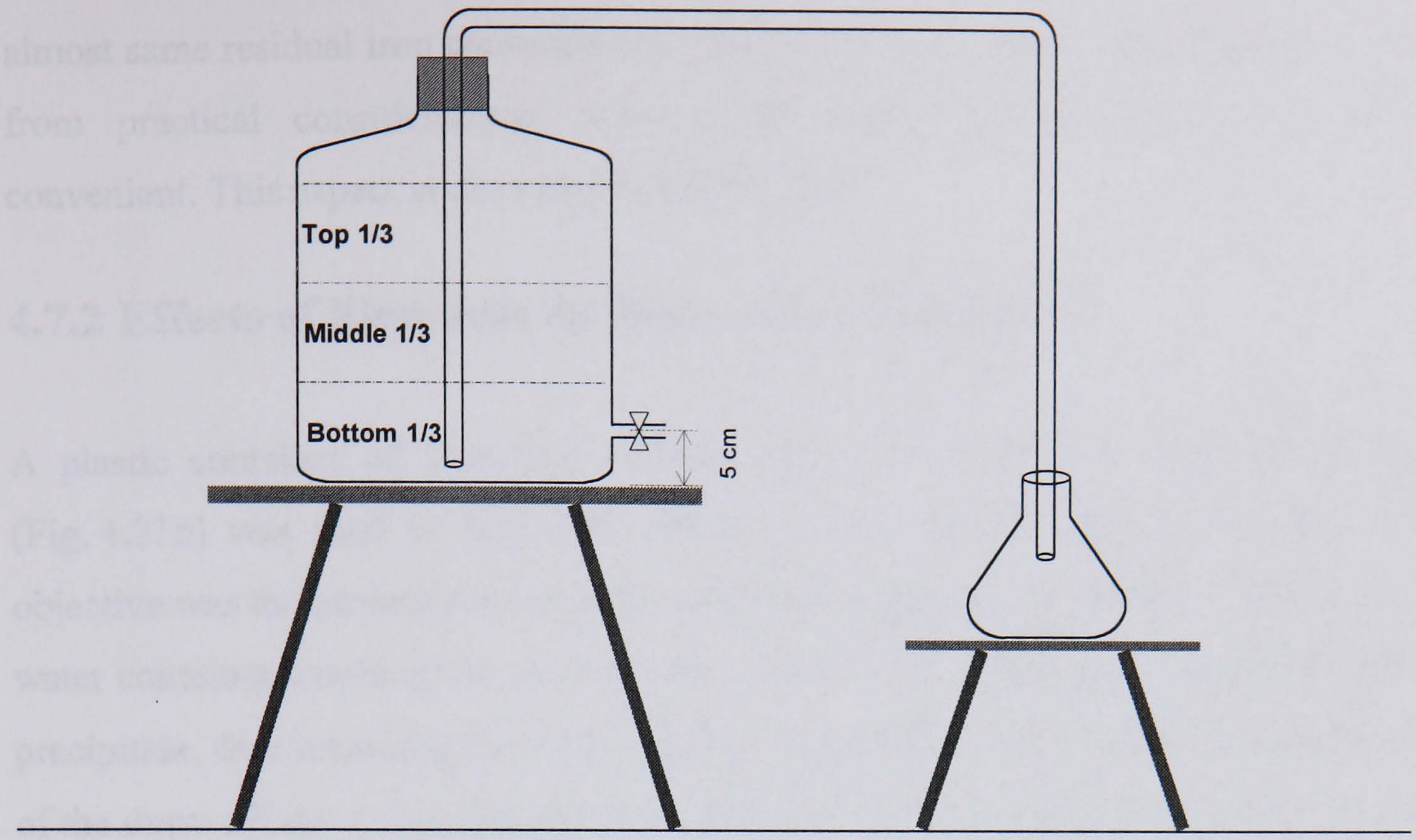


Fig. 4.22 Collecting samples by siphoning

Table 4.10 Residual iron concentration at different settling time from different drawing-off arrangement

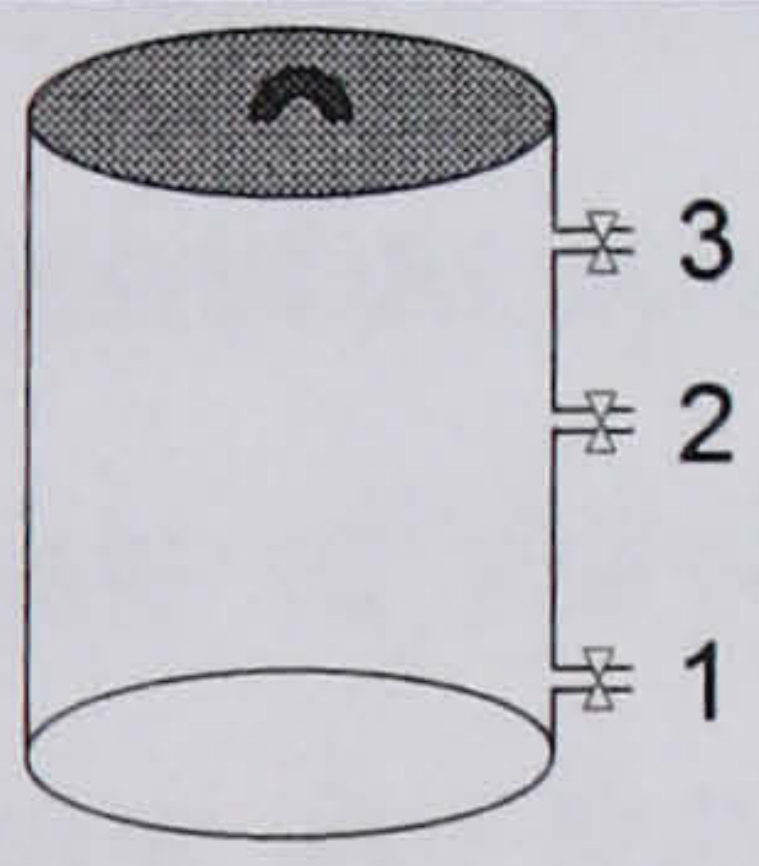
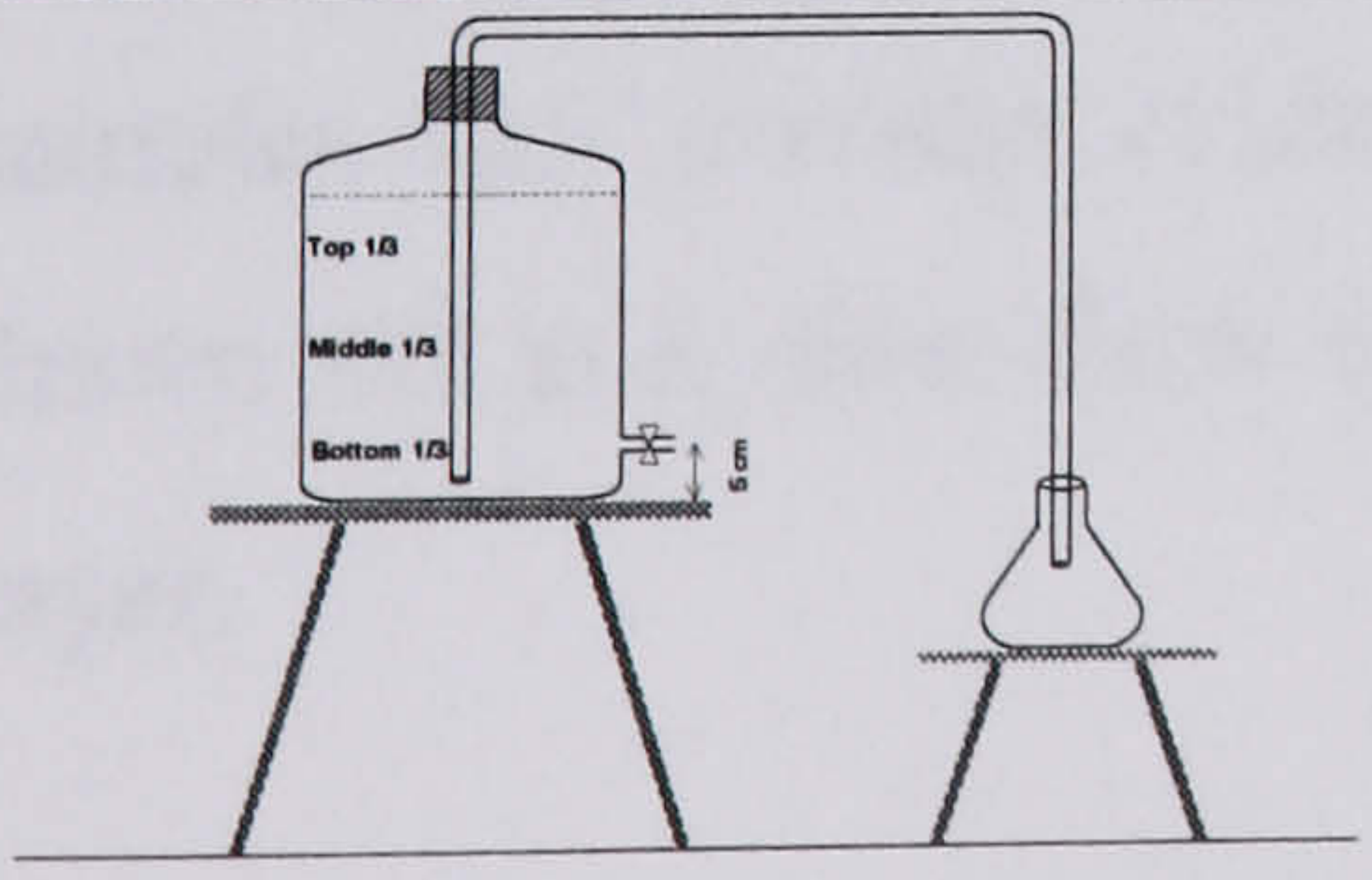
Draw-off arrangement	Initial Fe, mg/l	Sampling position	Residual Fe concentration after settling, mg/l		
			1 day settling	2 day settling	3 day settling
	4.0	Opening# 3	0.43	0.33	0.27
		Opening# 2	0.44	0.38	0.30
		Opening# 1	0.63	0.43	0.31
	4.0	Top	0.70	0.40	0.25
		Middle	2.6	0.41	0.26
		Bottom	1.4	0.51	0.27

Table 4.10 presents the residual concentration of Fe for two different draw-off arrangements. From this table it is observed that both the arrangements showed

almost same residual iron concentration (mean 0.28 mg/l) after 3 days settlement but from practical considerations, drawing off water through opening is more convenient. This aspect is discussed in Section 6.6.

4.7.2 Effects of Flow-rate on Draw-off Arrangement

A plastic container of 10.0 litre volume with a tap at 5.0 cm from the bottom (Fig. 4.21b) was used to study the effects of flow-rate on draw-off system. The objective was to determine whether the particular design of a commonly used type of water container would allow treated water to be drawn-off without resuspending the precipitate, thus impairing the water quality. A particular concern was the magnitude of the draw-off rate (from the tap) since this controls the extent of disturbance on the settled solids.

To achieve this, the container was filled with 7.0 litre of sample water containing 0.2 mg/l As(III), 4.0 mg/l Fe at pH 7.2. This was mixed manually for one minute and allowed to settle for three days. At the end of this period, one third of the sample was drawn off through the tap at its maximum opening and the flow rate was measured. Thereafter second and last one third of the sample were also drawn off immediately through the tap at its maximum opening. The residual Fe and As(III) concentrations were measured in each of these samples. The sampling procedure was also repeated with minimum opening of the tap. Each test was repeated 5 times. Fig. 4.23 shows the effects of flow rate on the Fe and As(III) concentrations of the samples. This shows that the flow rate has an influence on the levels of Fe and As(III) found in samples and provides evidence of resuspension. It implies that the sample must be drawn off at a slow flow rate (< 0.5 l/min) in order to avoid disturbing the settled layer.

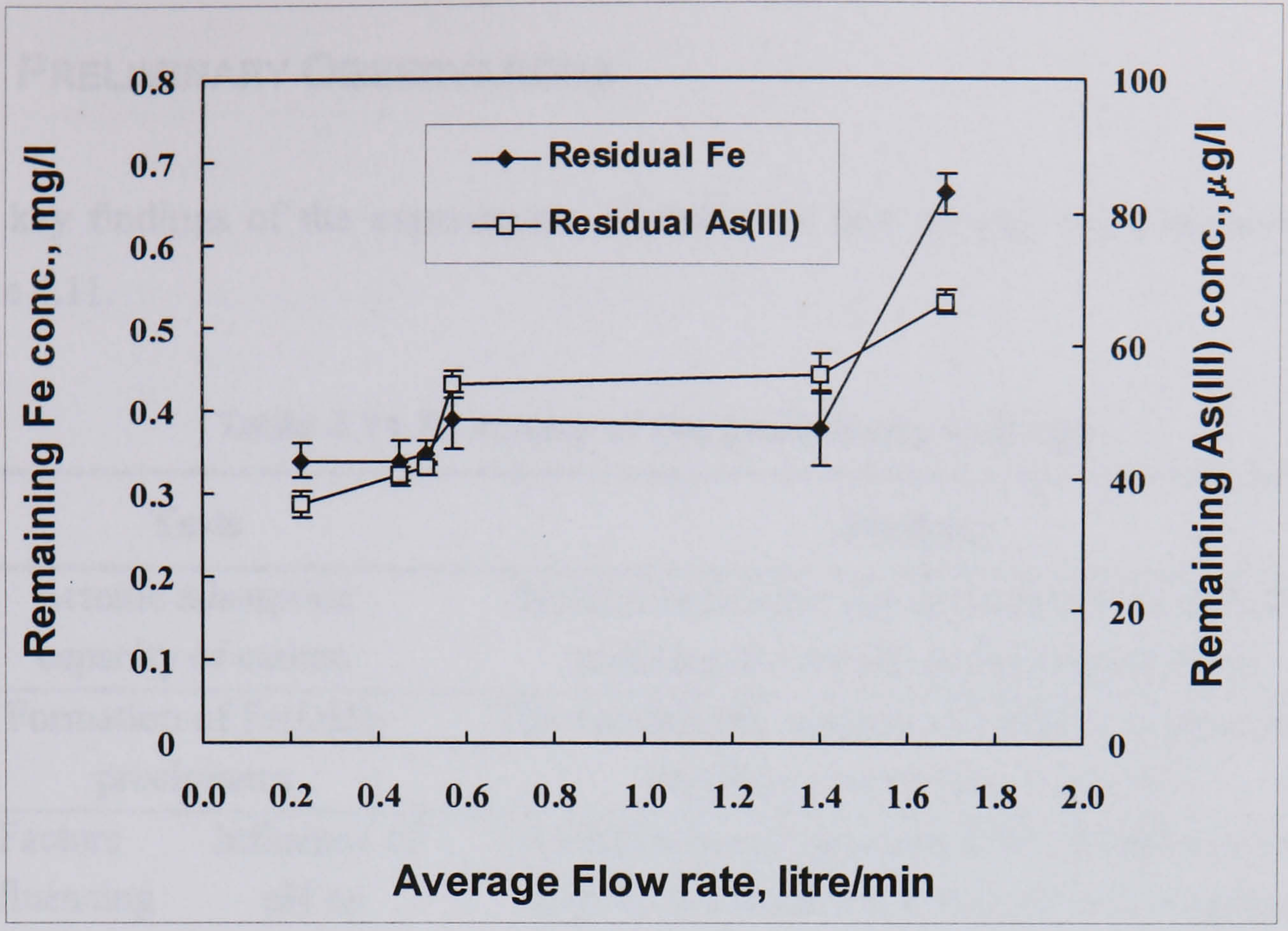


Fig. 4.23 Remaining Fe and As(III) concentration at different flow rate after 3 days settling with initial As(III) 0.2 mg/l, Fe 4.0 mg/l and pH 7.2. Error bars refer to standard deviations.

4.8 PRELIMINARY OBSERVATIONS

The key findings of the experiments discussed in this chapter are summarised in Table 4.11.

Table 4.11 Summary of the preliminary findings

Tests		Findings
Arsenic adsorption capacity of carbon		Neither bone-char nor charcoal are suitable for reducing the As(III) to the desired levels
Formation of $Fe(OH)_3$ precipitates		The suitable pH range for formation of maximum $Fe(OH)_3$ precipitate is 7.5 to 8.0
Factors influencing As(III) removal	Influence of pH on As(III) removal	As(III) removal increases with the pH over the range of 5-8 when $FeCl_3$ is used as a coagulant.
	Sensitivity of Fe/As ratio	Fe/As ratio (by weight) has significant influence on the removal of As(III). It is seen that removal of As(III) increases with increasing Fe/As ratio. The removal also increases with increasing initial As(III) concentration at the same Fe/As ratio.
	Effects of mixing, filtration and settlement	Arsenic removal by settlement can exceed the removals achieved by filtration. Over prolonged period of settlement (≥ 24 h), the removal becomes insensitive to the early mixing conditions.
	Effects of forms of Fe	Forms of Fe play a major role in removing arsenic from water. The higher As(III) removal was obtained by Fe^{3+} than Fe^{2+}
	Effects of temperature	Temperature did not exhibit any marked effect on the As(III) removal
	Effects of co-occurring solutes	The presence of co-occurring solutes have no significant effects on the As(III) removal.

(Continued)

Table 4.11 Summary of the preliminary findings (continued)

Tests	Findings
Arsenic removal by $FeCl_3$ by simple mixing and settlement	Removal of As(III) by $FeCl_3$ did not provide any indication that removal capacity approaches a saturation (maximum) stage.
Draw-off arrangements	Of the two arrangements tested, drawing of treated water through the opening of the container located at the bottom is proved better than that of siphoning action.
Effects of flow-rate on draw-off arrangements	Flow rate has significant influence on sample disturbance. It is seen that water may be drawn off (with only minimum impairment of its quality) using a particular container with a tap located 5 cm from the bottom, provided the draw off rate does not exceed of 0.5 l/min.

Chapter 5

DATA GENERALISATION AND POTENTIAL EFFECTS

5.1 INTRODUCTION

This chapter outlines a statistical analysis of the data and yields empirical equations, which can be used to estimate the potential removal of arsenic in Bangladesh. An analysis of this nature was carried out and is presented in the form of maps.

5.2 DATA ANALYSIS AND POTENTIAL FOR THE REMOVAL OF ARSENIC FROM GROUNDWATER IN BANGLADESH

5.2.1 Data Analysis

Experimental results showed that for filtered samples and settled samples, As(III) removal depends mainly on three factors: Fe/As ratio, pH and initial As(III) concentration (sections 4.5.1, 4.5.2 and 4.6.2, 4.6.3).

The sensitivity of the trends shown in Figs. 4.6, 4.7, 4.19 and 4.20 suggests that the data can be collapsed to a general form. This was assessed based on the test function

$$\text{As(III) Removal(\%)} = C\left(\text{Initial As(III)}\right)^m \left(\text{Fe/As}\right)^n \left(\text{pH}\right)^p \tag{5.1}$$

In which C, m, n and p are empirical constants to be evaluated through regression analysis.

Results of such analysis are summarized in Table 5.1. The correspondence between the observed and predicted removals based on eqn. 5.1 are shown in Figs. 5.1 and 5.2.

Table 5.1 Values of the constants in eqn. 5.1

Coefficients	Filtration	Settlement
C	4.44	3.98
m	0.17 ± 0.01	0.22 ± 0.02
n	0.34 ± 0.01	0.39 ± 0.01
p	0.33 ± 0.04	0.24 ± 0.12
r^2	0.95	0.93

Note: Units of constants are consistent with As(III) in μg/l and Fe/As ratio on a mg/mg basis. Error limits refer to standard errors at 95% confidence level.
r stands for regression coefficient.

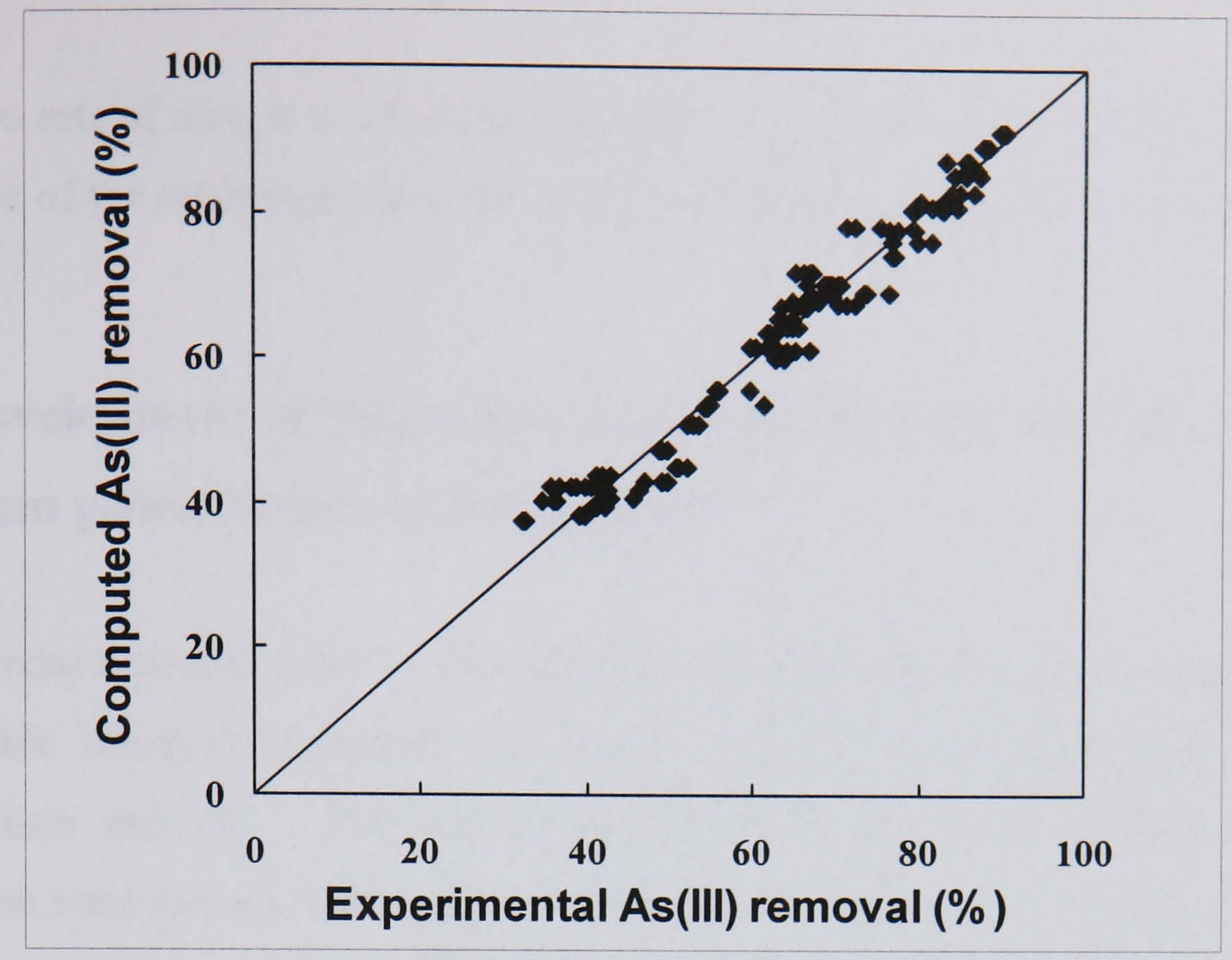


Fig. 5.1 Comparison of experimental and computed As(III) removal filtration data

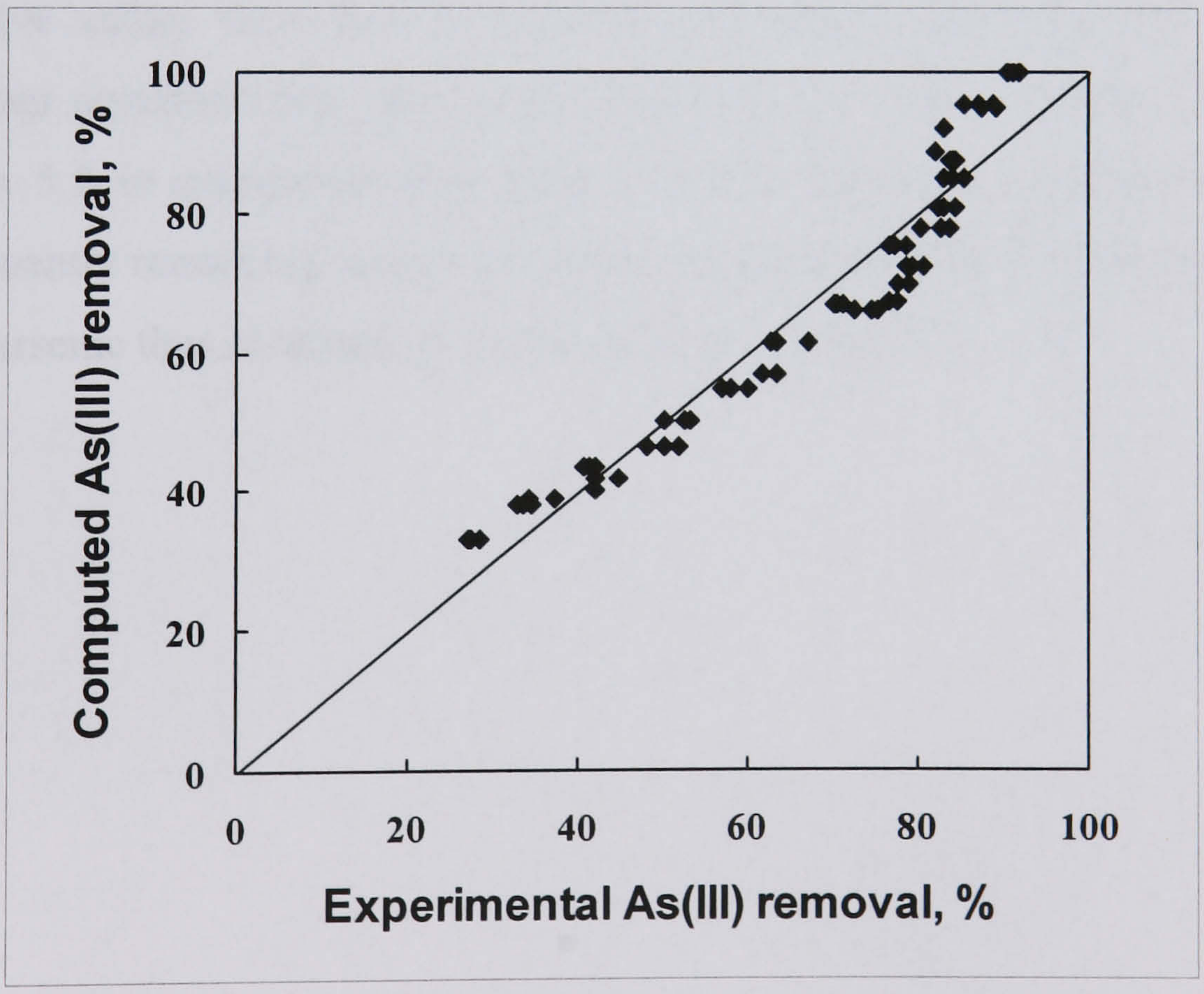


Fig. 5.2 Comparison of experimental and computed As(III) removal using 3 day settlement data

Of the two sets of data, it is clear that the better fit is obtained by the filtration data. In the case of the settlement data, the largest deviations occur at the highest removal rates.

5.2.2 Development of maps showing potential removal of arsenic from groundwater in Bangladesh

The empirical equation (eqn. 5.1) developed in this chapter allows the estimation of the possible removal of arsenic for given values of Fe/As ratio, initial As(III) concentration and pH. The natural distributions of As, Fe and pH all over Bangladesh have already been reported in Chapter 2 as Figs. 2.1, 2.2 and 2.3. These maps show various zones of different ranges (i.e. minimum and maximum) of concentration for a given parameter. The mean value of the minimum and maximum of a given zone was considered as representative of that particular zone for all three parameters (Fe, As and pH). These maps (As, Fe and pH) containing only the representative values were then overlaid on each other using GIS Software. The resulting map contained data on all these parameters at every location. They were used in eqn. 5.1, in conjunction with Table 5.1, to estimate the potential removal of, and subsequently remaining arsenic by filtration and settlement. The distributions of remaining arsenic thus obtained are shown in Figs. 5.3 and 5.4.

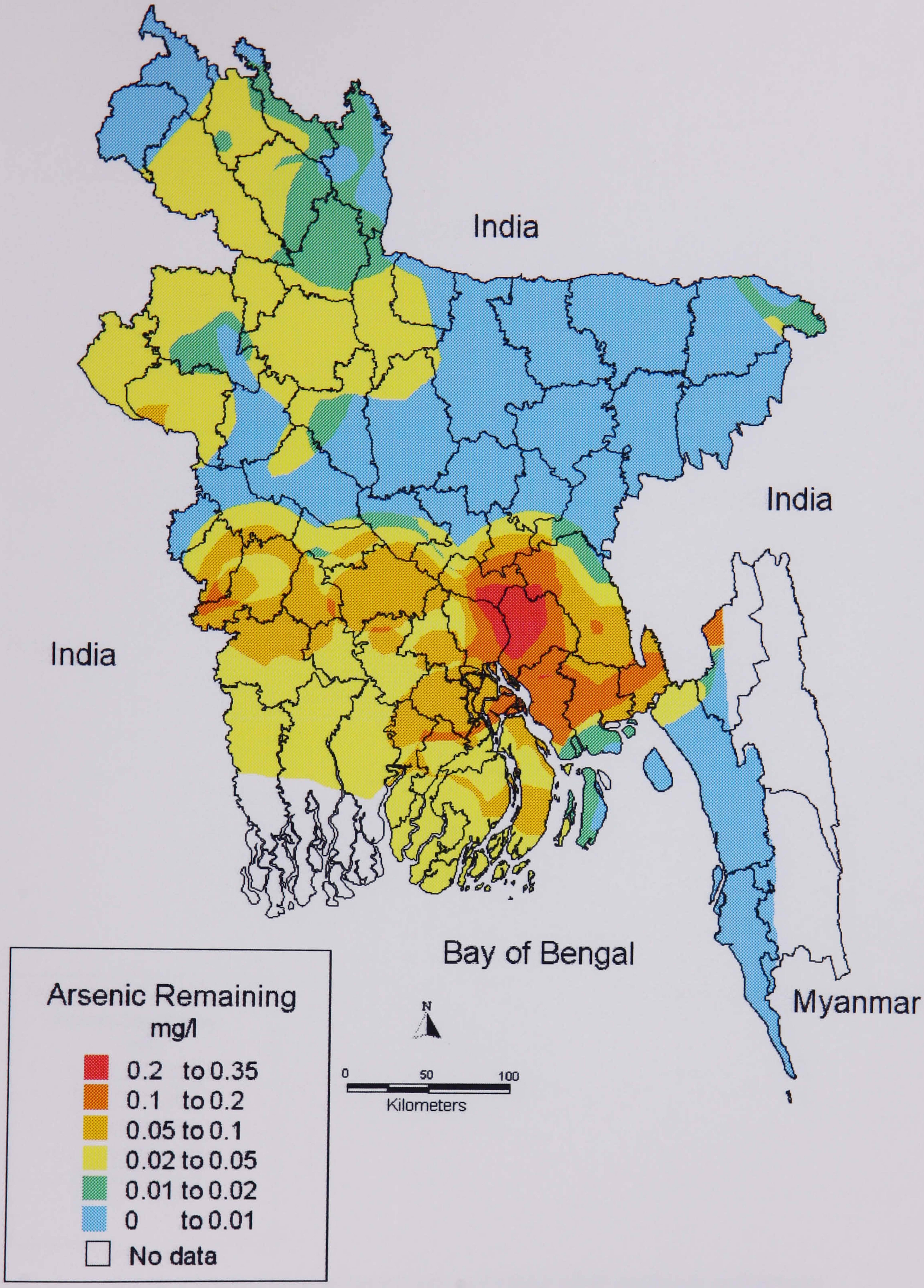


Fig 5.3 Remaining arsenic concentration after applying filtration

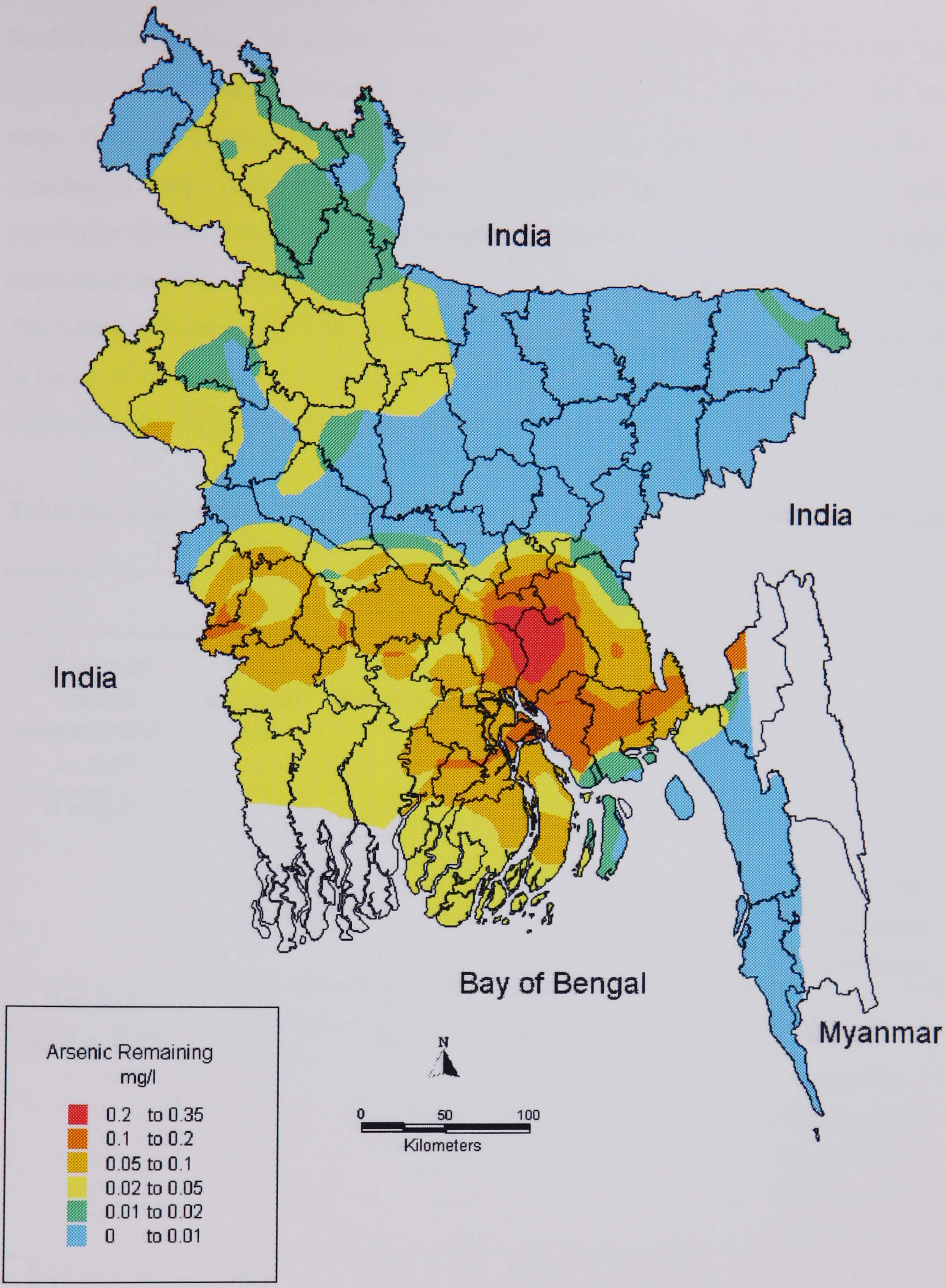


Fig 5.4 Remaining arsenic concentration after applying settlement

Further investigation was carried out to estimate the population to be benefited from the removal methods described in sections 4.5.1, 4.5.2, 4.6.2 and 4.6.3, using the maps showing arsenic concentrations (Figs. 2.1, 5.3 and 5.4) and population distribution map (Fig. 5.5). Arsenic concentration maps were overlaid with population distribution map. From these, population within different zones of As(III) concentration (both before and after treatment) were estimated (Tables 5.2 and 5.3). The tables indicate a significant reduction in the extent of arsenic contamination both in terms of area and the proportion of population affected if the levels of removal achieved in laboratory are representative of the field situation.

Table 5.2 Comparison of the extent of arsenic contamination between existing state and after treatment applying filtration

	Present status		**After treatment**		**Comment**
Range of arsenic concentration, mg/l	**% of mapped area**	**% of population**	**% of mapped area**	**% of population**	
0 to 0.01	—	—	35.1	34	34% of population complies with WHO standard after treatment
0 to 0.02	34.8	34	42.0	41	
0.02 to 0.05	28.3	27	30.4	28	69% population complies with Bangladesh standard after treatment
0.05 to 0.10	20.9	14	11.0	12	
0.10 to 0.20	8.3	10	4.2	5	
0.20 to 0.50	2.5	3	1.0	1	

Mapped area for arsenic concentration: 138,122 km^2
Total population: 121,367,603 (EGIS, 1997)

Table 5.3 Comparison of the extent of arsenic contamination between existing state and after treatment applying settlement

	Present status		After treatment		Comment
Range of arsenic concentration, mg/l	**% of mapped area**	**% of population**	**% of mapped area**	**% of population**	
0 to 0.01	—	—	35.1	34	34% of population complies with WHO standard after treatment
0 to 0.02	34.8	34	42.6	41	
0.02 to 0.05	28.3	27	28.9	26	67% population complies with Bangladesh standard after treatment
0.05 to 0.10	15.1	14	12.0	13	
0.10 to 0.20	8.3	10	4.2	5	
0.20 to 0.50	2.5	3	1.0	1	

Mapped area for arsenic concentration: 138,122 km^2
Total population: 121,367,603 (EGIS, 1997)

The residual levels of arsenic as shown in Figs. 5.3 and 5.4 after treatment reflect for the range of As, Fe and pH commonly found in Bangladesh (Figs. 2.1, 2.2 and 2.3). However, it does not take into account of possible interference, arising from the other salts present in natural water or the precise form of the iron present in groundwater. It is emphasized that these figures indicate the potential levels of arsenic remaining in the water after treatment.

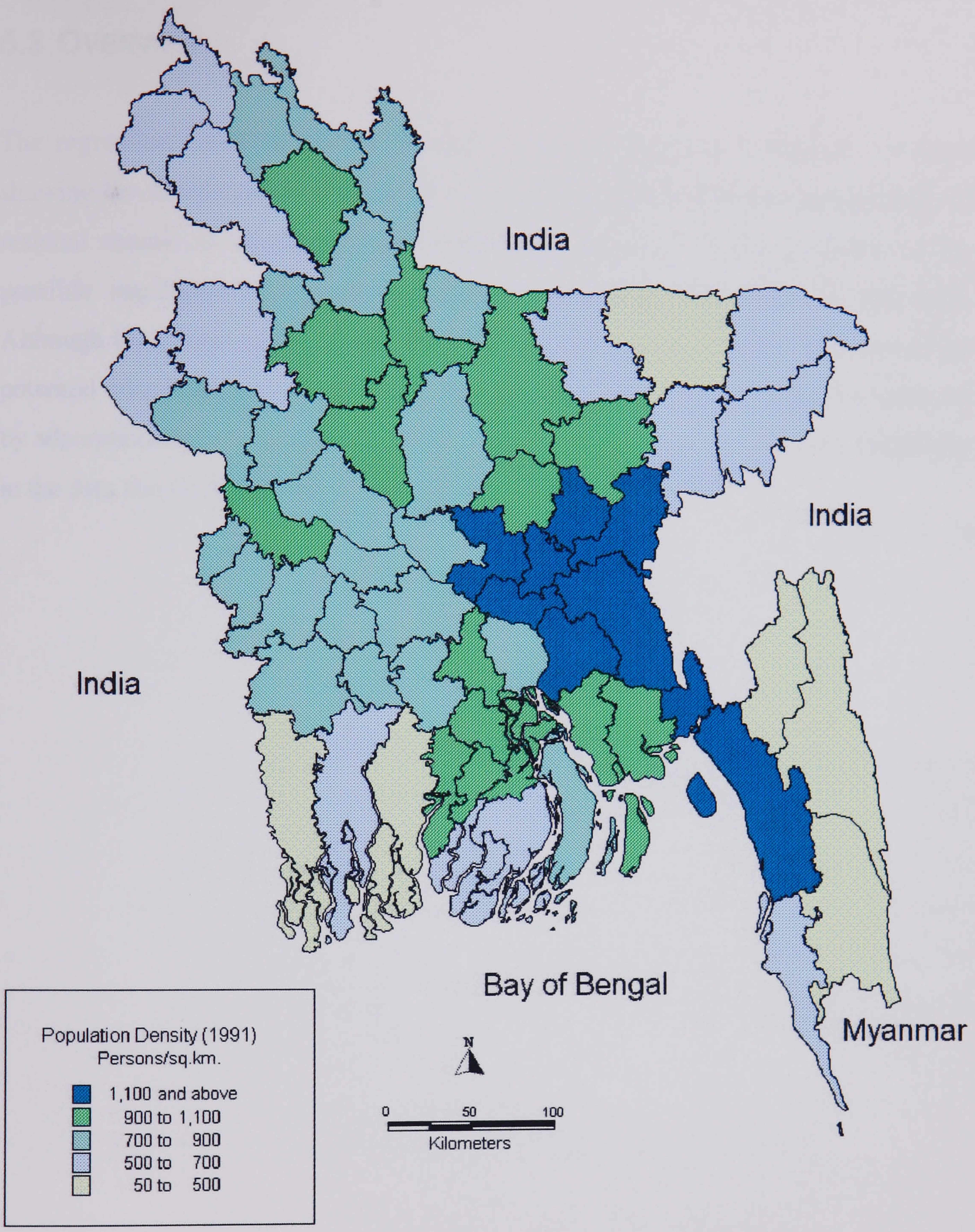


Fig 5.5 Distribution of population density in Bangladesh (EGIS, 1997)

5.3 OVERVIEW

The regression equation derived in this chapter (5.2.1) and availability of maps showing the distribution of arsenic, iron and pH (chapter 2) allowed development of residual arsenic maps (sec 5.2.2). These maps provide a broad overview of the possible implications of implementing the laboratory techniques in the field. Although the interpretation of the laboratory scale data has limitations in terms of the potential consequences of field level, they are indicative of what might be achieved by adsorption and coprecipitation. Here, it is noted that there is very little difference in the data shown in Tables 5.2 and 5.3.

Chapter 6

DISCUSSION

6.1 INTRODUCTION

This chapter focuses on the interaction of arsenic with iron and adds a detailed discussion on the removal mechanisms. Although unsuccessful, the outcome of the experimental investigation dealing with charcoal (section 4.3) is also discussed. The effects of different factors, which contribute to the removal of arsenic and the draw off arrangements, are also examined. The chapter concludes with a critical review of the implications of the technology developed in this study as shown in encapsulated maps (section 5.2.2).

6.2 PERFORMANCE OF CHARCOAL IN REMOVING ARSENIC

From data reported in section 4.3, a comparison of adsorption capacity of the three types of carbon (GAC, charcoal and bone char) was performed and is presented in Fig. 6.1. Fig. 6.1 demonstrates that charcoal is a very poor adsorbent in removing As(III) compared to other forms of carbon tested. The poor adsorbing capacity of ordinary untreated charcoal can probably be attributed to the following: adsorption depends mainly on accessible surface area and presence of active sites and particle size of the carbon. GAC is prepared at high temperature and pressure i.e. in a controlled environment, the activation process increases the internal surface area and thereby the number of sites available for adsorption. On the other hand, there is no activation and control of particle sizes in ordinary charcoal, as used in the study. Lumps of charcoal were simply crushed into particle form before using them in the tests.

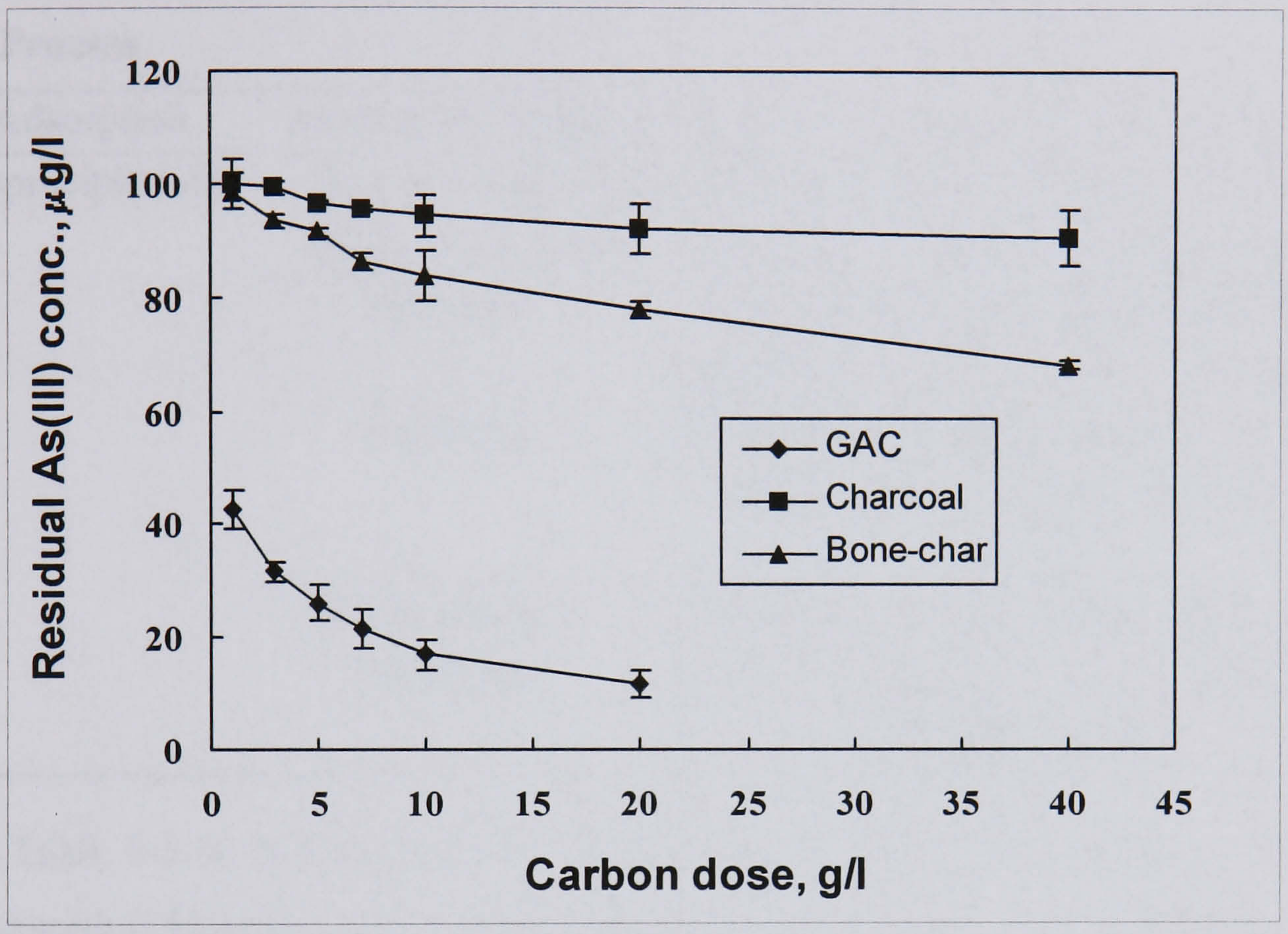


Fig. 6.1 A comparison of adsorption capacity of three different types of carbon in removing As(III) at initial As(III) concentration of 100 µg/l. Error bars refer to standard deviations.

6.3 As(III) Removal Mechanisms

Experimental data reported in sections 4.5.1, 4.5.2, 4.6.2 and 4.6.3 showed that the As(III) removal is strongly influenced by the factors pH, As(III) and Fe/As ratio (by weight) and this correlation is represented by eqn. 5.1. It is evident from Fig. 4.7 that the Fe concentration is the dominant factor in removing arsenic provided the pH between 6.0 to 8.0 as it is seen from Fig. 4.4 that amount of ferric hydroxide precipitates is dependent on pH.

In terms of trying to understand the mechanisms involved in the removal of As(III) (section 4.6.1), it seemed likely that the removal was influenced by the following processes noted in Table 6.1.

Table 6.1 Process involved in the removal of As(III) using iron in the current study

Process	Mechanism	
Adsorption	Association of dissolved arsenic with the surface of $Fe(OH)_3$	
Coprecipitation	Incorporation of soluble arsenic into a growing hydroxide phase via inclusion, occlusion or solid-solution formation	
	Inclusion	Mechanical entrapment of soluble arsenic inside the growing precipitates
	Occlusion	Entrapment of adsorbed arsenic in the interior of the growing hydroxide particles
	Solid-solution formation	Incorporation of arsenic into the bulk phase rather than only onto the surface of the precipitates

From Table 6.1, it is clear that the removal process has different stages. From the tests described in section 4.6.1, the overall removal appears to be accomplished by a multi step process — contact between Fe and As (influenced by molecular diffusion), floc formation (via shaking) and by sedimentation (over a period of time).

Much of the previous research reported in the literature has focused on arsenic removal using coagulation with ferric salts or adsorption onto preformed $Fe(OH)_3$ (Jekel, 1986; Cheng *et al*, 1994; Scott *et al*, 1995; and Hering *et al*, 1996). In the present study, no standard procedure of coagulation or adsorption process was followed, because simple techniques such as manual shaking and settlement were employed. An additional complication in terms of comparing with other studies is the time dependence of the removal process such as illustrated in Figs. 4.9 and 4.10. Therefore, it is difficult to make direct comparisons with other studies.

In order to gain a deeper insight into the data corresponding to removal at 24 h (section 4.6.1), these were plotted in the form of an adsorption isotherm even though it is recognised that there exists a combination of processes (as noted in Table 6.1) controlling the shape. This type of plot has the benefit of identifying the mg/g corresponding to the residual concentration, which (in practice) has to comply with target water quality standards. These are presented in Figs. 6.2a and 6.2b for two different ranges of initial As(III) concentrations. These figures also show adsorption data from Pierce and Moore (1982) study. Pierce and Moore (1982) investigated the behaviour of As(III) removal by purely adsorption onto preformed $Fe(OH)_3$. They found that for a certain range of initial As(III) concentration (0.05–1.0 mg/l), the adsorption reaches a saturation point. At higher initial As(III) concentration (2.5–50 mg/l), the adsorption of As(III) per unit mass of adsorbent increased linearly with increasing equilibrium concentration.

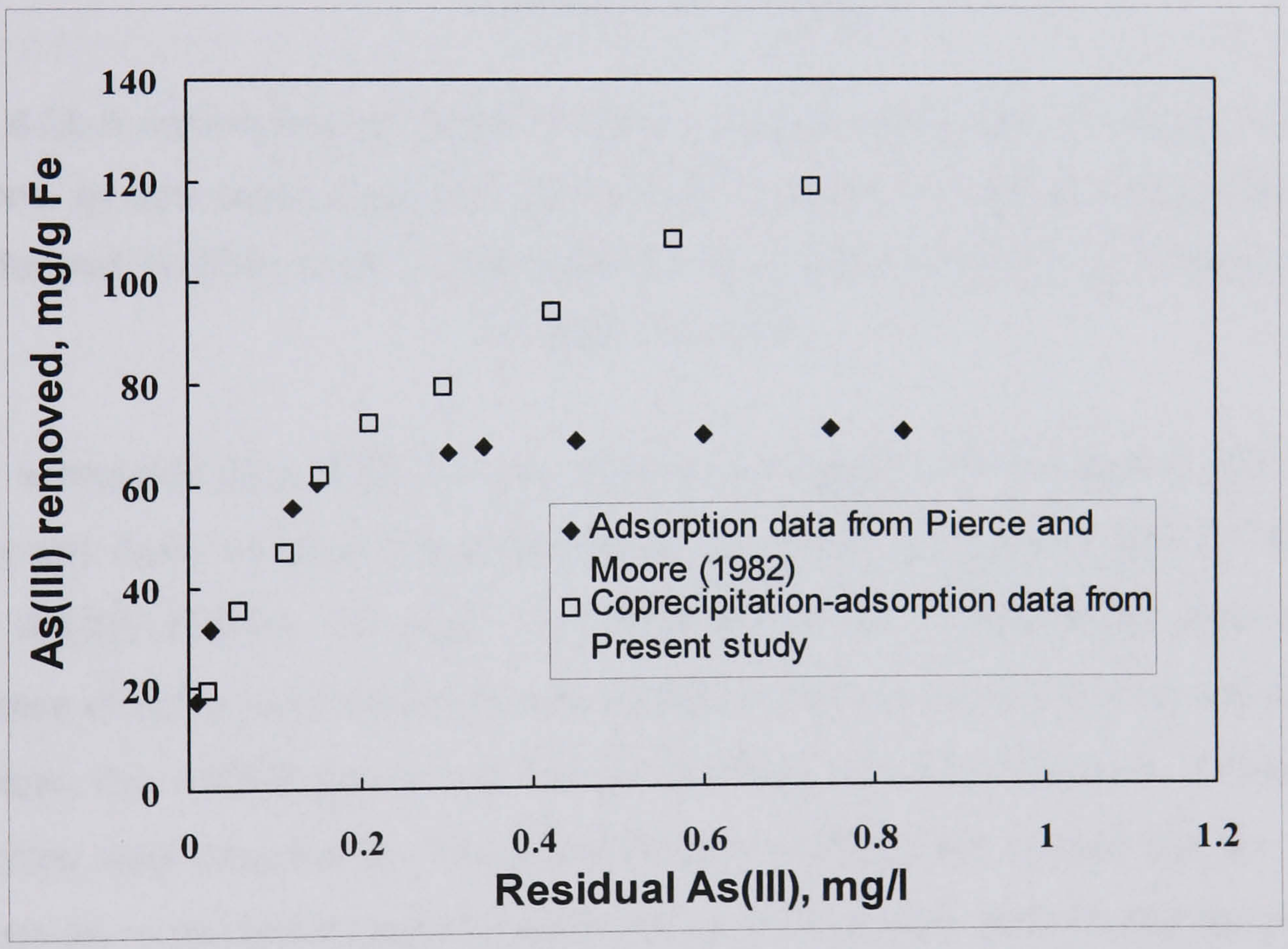


Fig. 6.2a A comparison of As(III) removal density as a function of residual As(III) concentration by adsorption-coprecipitation with $FeCl_3$ at pH 7.5 and adsorption onto preformed $Fe(OH)_3$ at pH 7.0 for initial As(III) concentration of 0.05-1.0 mg/l and contact time 24 h

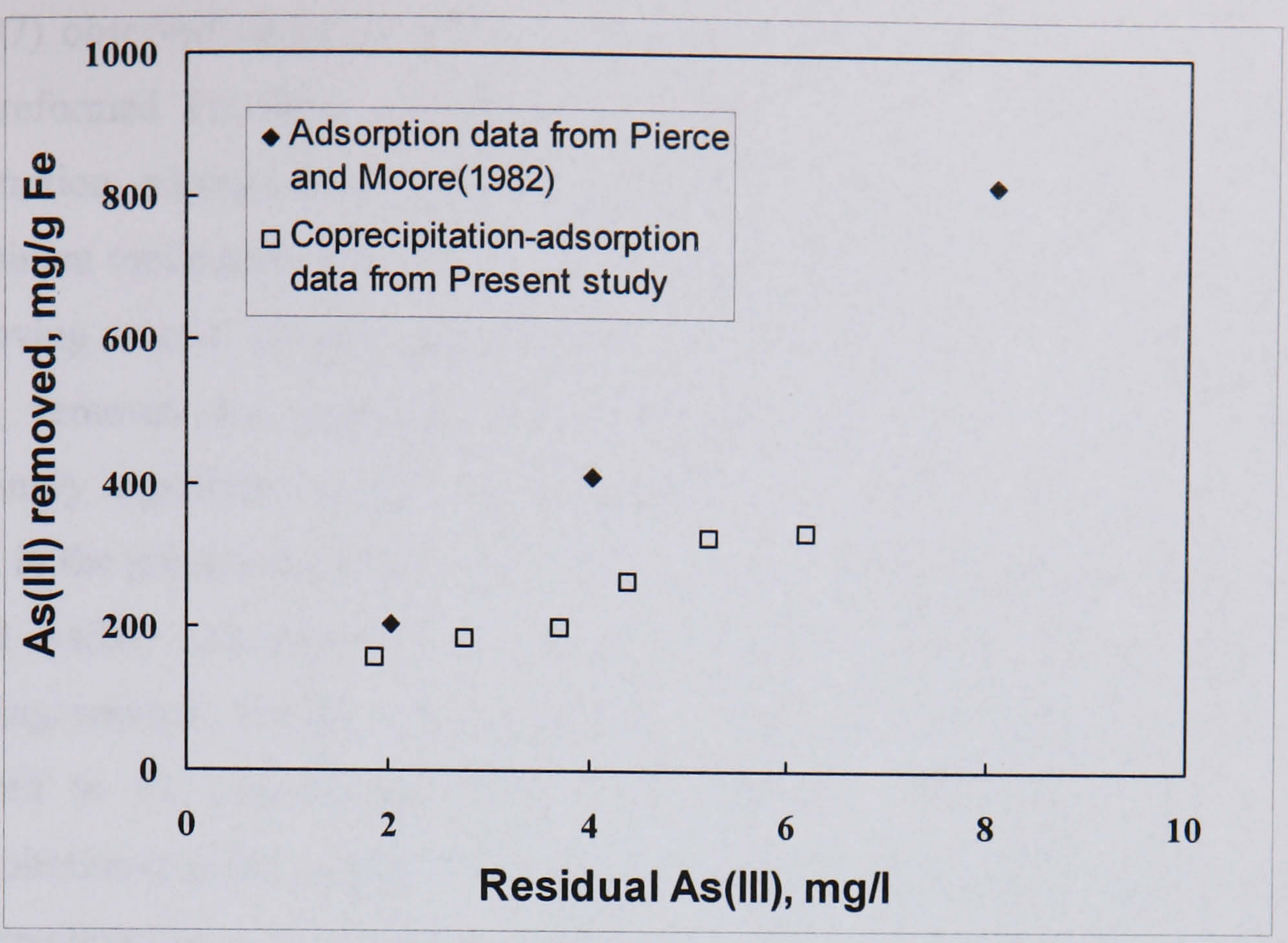


Fig. 6.2b A comparison of As(III) removal density as a function of residual As(III) conc. by adsorption-coprecipitation with $FeCl_3$ at pH 7.5 and adsorption onto preformed $Fe(OH)_3$ at pH 7.0 for initial As(III) concentration of 2.5 - 10 mg/l and contact time 24 h

Pierce adsorption data of pH 7.0 was chosen to compare with the data of pH 7.5 of the present study as they found maximum adsorption occurred at pH 7.0 for the initial As(III) of 0.05- 1.0 mg/l. The difference of the values of the data due to difference of pH is not considered to be significant as it is known that around neutral pH range, the As(III) removal is largely unaffected by pH (Edwards, 1994). The adsorption tests reported by Pierce and Moore (1982) were carried out for 24 h, supernatants were centrifuged and analysed for arsenic concentration and the present work was also carried out for 24 h settlement, supernatants were analysed for residual arsenic concentration without filtration. From Fig. 6.2a it is seen that removal density gained from the present study exceeds the adsorption density onto preformed $Fe(OH)_3$ when the removal density exceeds 60 mg/g. This is probably due to settlement. Comparative studies of arsenic (As(V) and As(III)) adsorption and coprecipitation reported that higher removal can be achieved by coprecipitation than by adsorption (Fuller *et al*, 1993; Edwards, 1994; and Hering *et al*, 1997). Hering *et* *al* (1997) observed more efficient As(III) removal by coagulation than adsorption onto preformed $Fe(OH)_3$. According to Edwards (1994), at low initial arsenic concentration, adsorption of arsenic to the precipitated $Fe(OH)_3$ is likely to be the predominant mechanism and at high arsenic concentration coprecipitation dominates in removing arsenic. He also suggested that the difference between the efficiency of arsenic removal by coprecipitation-adsorption and only adsorption become increasingly significant at high initial arsenic concentrations. This appears to be evident in the present study (Fig. 6.2a). The removal density are quite similar at low residual As(III) concentration of the two studies and difference increases with increasing residual As(III) concentration i.e. greater initial As(III) concentration compared to Fe concentration (Fig. 6.2a). Edwards (1994) suggested that in coprecipitation process, higher surface area formed than in preformed adsorption or that coprecipitation is an operative removal mechanism which is consistent with the results of previous research (Fuller *et al*, 1993).

Fig. 6.2b displays a very different form of behaviour. Removal density obtained by adsorption of Pierce's study is higher than those obtained by the present study for the stated range of initial As(III) concentration (Fig. 6.2b). The different nature of the removal density of the present study might possibly due to the differences in experimental procedure. Pierce's work was carried out by introducing preformed ferric hydroxide to the solution and not by neutralising an acid solution that contains both Fe and As, whereas the latter procedure was adopted in the present study.

Furthermore, from Fig. 4.18 it is evident that removal density did not reach a saturation point over the range of initial As(III) concentration used in the test (0.1 mg/l – 7.5 mg/l). A possible explanation of this anomalous behaviour of As(III) removal is as follows: at higher initial dosage of As(III) (≥ 2.5 mg/l), a large amount of 0.1M NaOH was required to maintain pH 7.5 constant and it is conceivable that the NaOH might change or reorder the internal properties of adsorption surface sites. It is, therefore, far from saturation and removal continued up to the highest initial concentration (7.5 mg/l) used in the test. Clearly this aspect requires further investigation.

6.4 REMOVAL OF AS(III) BY FILTRATION AND SETTLEMENT

From the tests described in sections 4.5.3.1 and 4.5.3.2, a comparison was made between the extent of As(III) removal obtained from filtration and settlement as shown in Table 6.2. Higher removals were achieved when samples were allowed to settle for 24 h instead of being filtered for the same test conditions. As an example, the data in Table 6.2 shows that the average removal of As(III) from a 5 min manually mixed sample after 24 h settlement was 88%, which exceeds the 64% removal achieved by filtration following 2 h settlement. Thus, settlement appears to offer excellent prospects as a simple solid-liquid separation technique.

Table 6.2 Comparison of filtration effects and settlement on As(III) removal

Test condition	**Mean As(III) removal at varying manual mixing time (%)**				
	15 s	**30 s**	**1 min**	**3 min**	**5 min**
Filtered sample after 2 h settlement	63.7	63.6	64.3	64.0	63.6
Unfiltered sample after 24 h settlement	76.9	76.7	86.7	86.3	87.9

Figs. 6.3a and 6.3b shows a comparison of As(III) removal obtained by settlement and filtration for the same test parameters (same Fe/As ratio, initial As(III) and pH) from the tests described in sections 4.5.1, 4.5.2, 4.6.2 and 4.6.3. Fig. 6.3a shows the removal obtained by different Fe/As ratios and different initial As(III) concentration at pH 7.5 when tests were carried out in long glass cylinders (432 mm height) and allowed to settle for 3 day (sections 4.6.2 and 4.6.3). Fig. 6.3b presents the filtered As(III) removal at the same Fe/As and initial concentration when tests were performed in a conical glass flask using mechanical mixing (sections 4.5.1 and 4.5.2). From these figures, it appears that removal by 3 days sedimentation is higher than removal by filtration for the values of As and Fe/As tested.

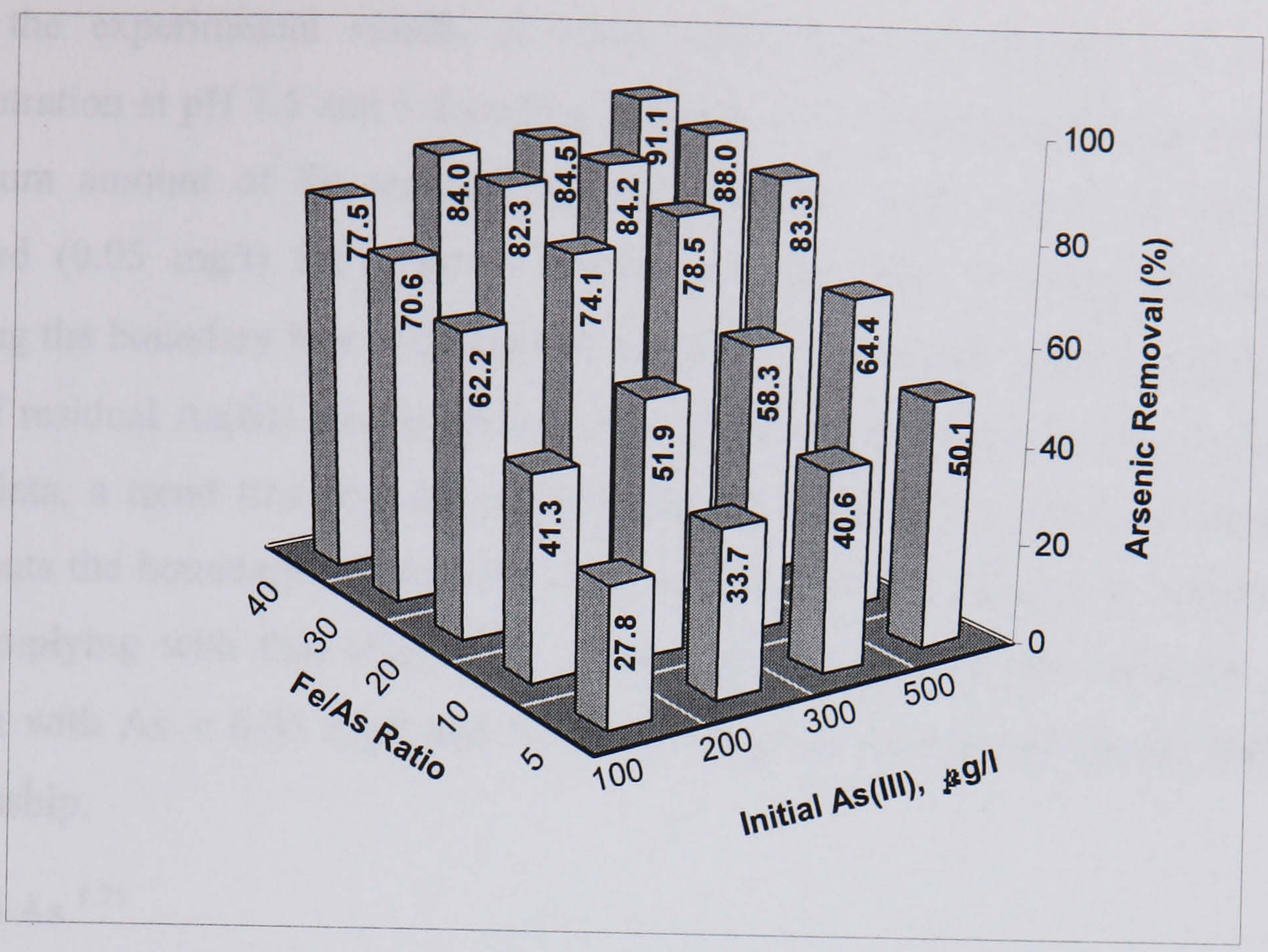


Fig. 6.3a: As(III) removal at different Fe/As ratio and initial As(III) concentration at pH 7.5 after 3 day settlement

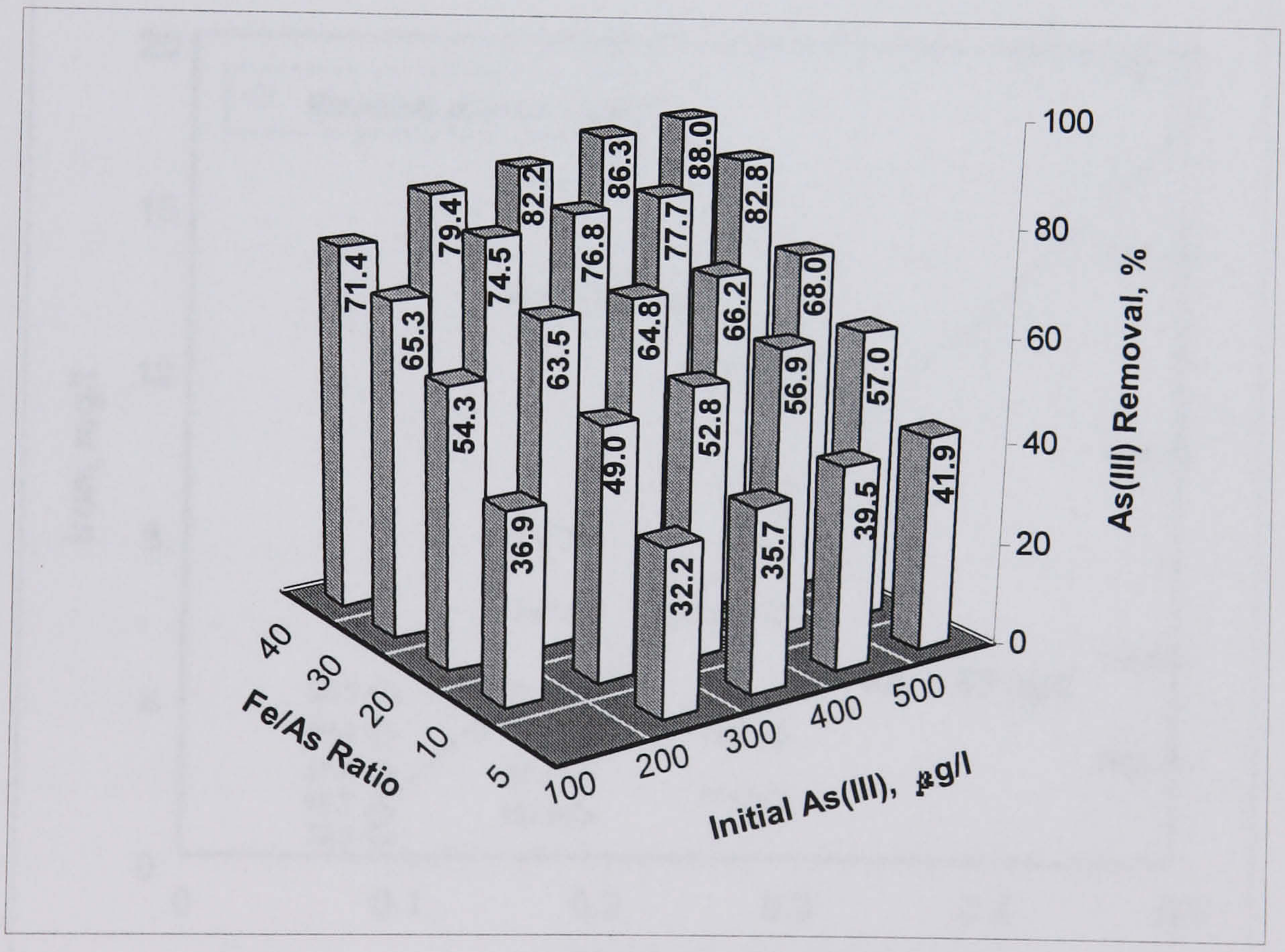


Fig. 6.3b Filtered As(III) removal at different Fe/As ratio and initial As(III) concentration at pH 7.5

From the experimental results of Fe/As ratio tests at different initial As(III) concentration at pH 7.5 and 3 d settling (section 4.6.3), it is possible to calculate the minimum amount of Fe required for reducing the arsenic level to Bangladesh standard (0.05 mg/l) for a given As(III) concentration. A graph was prepared showing the boundary line of 50 μg/l of residual arsenic along with the experimental data of residual As(III) concentration for a given set of As and Fe (Fig. 6.4). From these data, a trend line was drawn by performing regression analysis, which also represents the boundary between the zone complying with Bangladesh standard and not complying with that (Fig. 6.5). The trend line making the boundary of the domain with As < 0.05 mg/l and As > 0.05 mg/l is represented by the following relationship.

$$Fe = 66\,As^{1.75} \tag{6.1}$$

where, Fe and As concentrations are in mg/l.

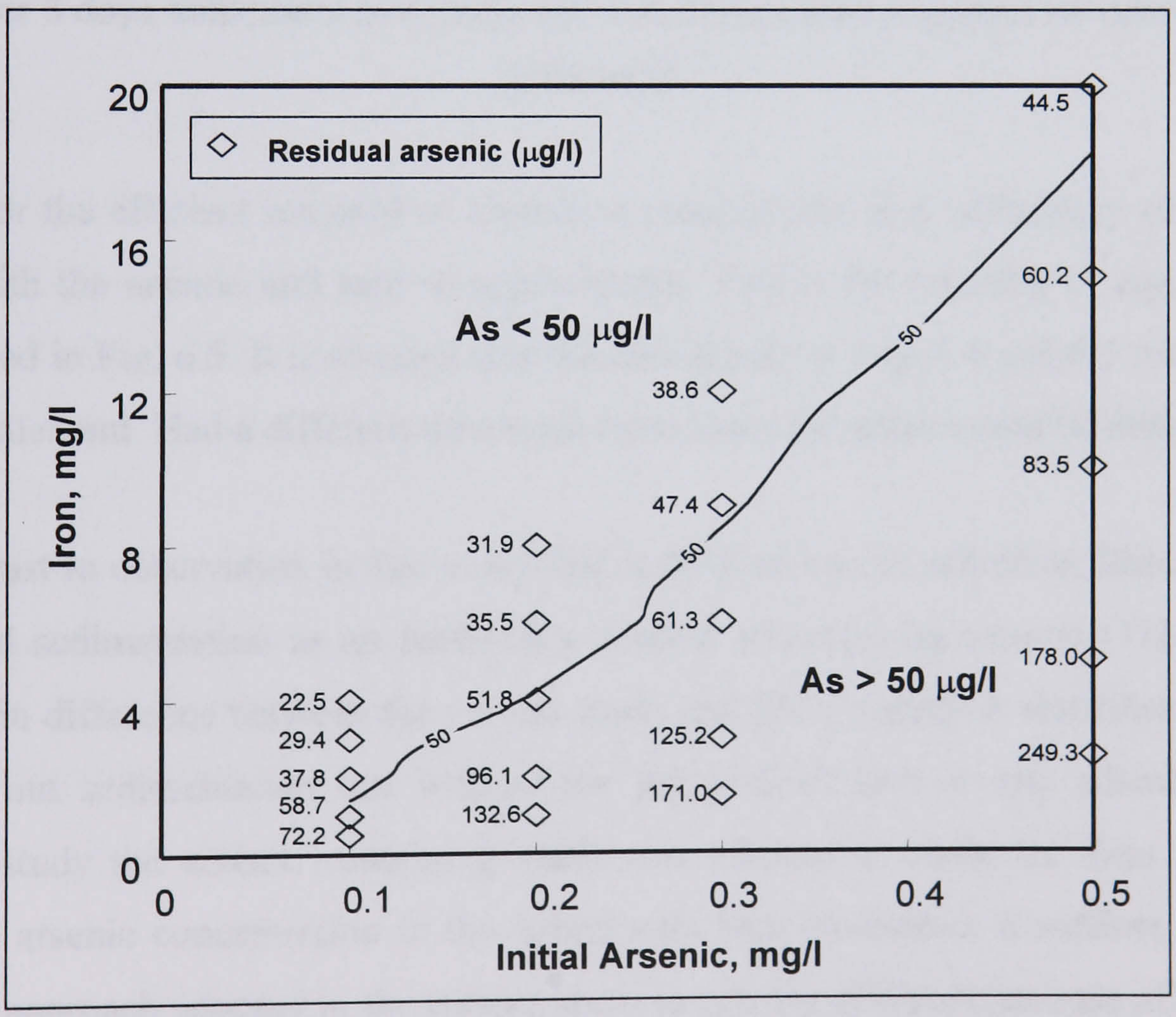


Fig. 6.4 Contour line showing the boundary of the zone complying with Bangladesh standard (50 μg/l) for residual arsenic concentration at pH 7.5 after 3 day settlement.

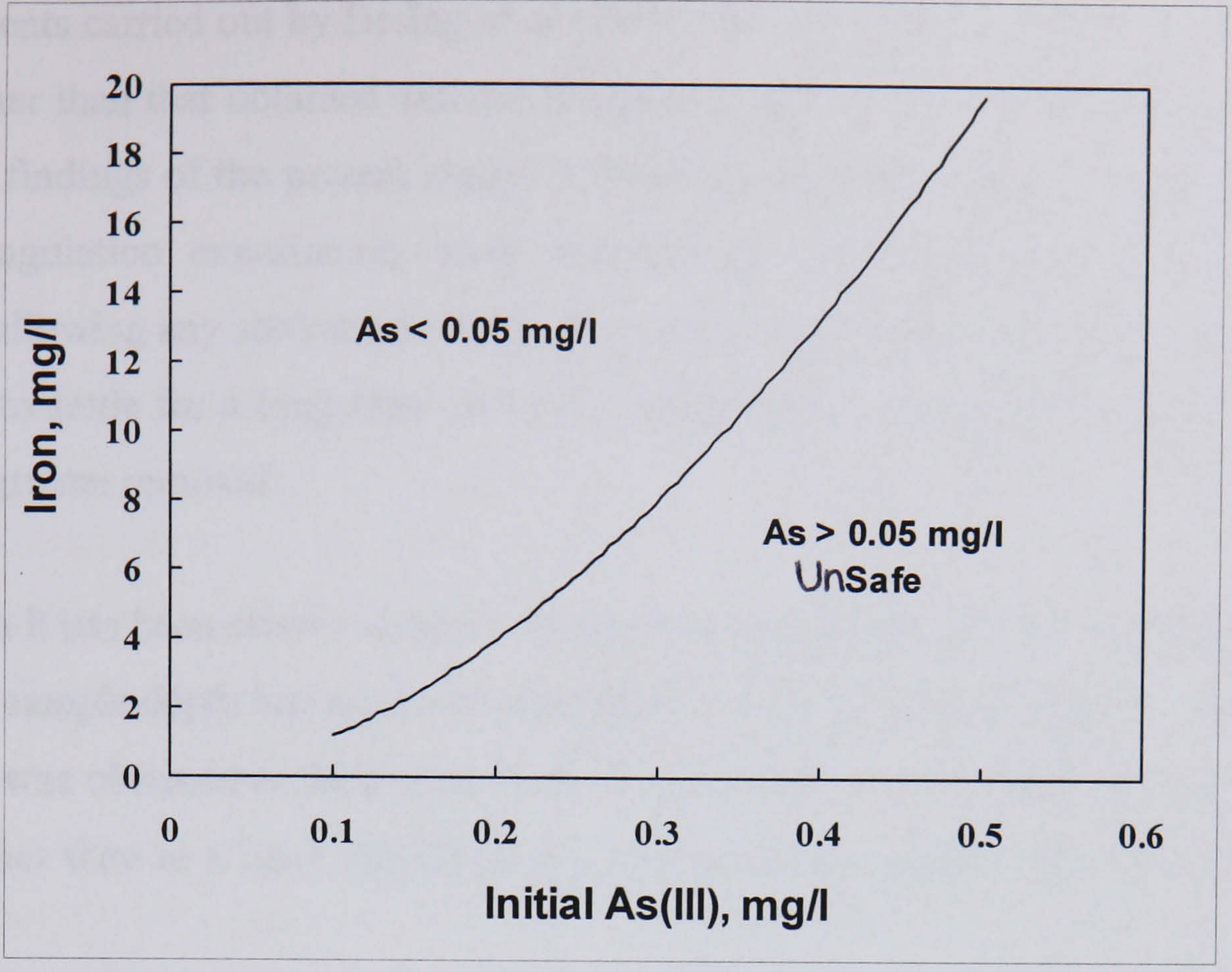


Fig. 6.5 Amount of minimum Fe required for a given arsenic concentration at pH 7.5 after 3 days settlement to comply with the Bangladesh standard for arsenic (0.05 mg/l).

Thus, for the efficient removal of arsenic, a precondition is a sufficiency of iron to react with the arsenic and lead to coprecipitate. This is the meaning of eqn. 6.1 as illustrated in Fig. 6.5. It is stressed that the data shown in Fig. 6.4 and 6.5 refers to 3 days settlement. Had a different time scale been used, the trend would be different.

In contrast to observation in this study that settlement can be effective, Shen (1973) regarded sedimentation as an ineffective method of removing arsenic (Table 3.4). The main difference between the current study and Shen's study is that Shen (1973) carried out sedimentation test *without* the presence of iron or any adsorbent. In Shen's study the arsenic containing water was allowed to settle for days and the residual arsenic concentration in the supernatant was monitored. It suffices to state that the approach adopted in the current study is entirely different because of the role of the iron precipitates.

Experiments carried out by Hering *et al* (1996) showed that the removal by filtration was higher than that obtained without filtration (Table 3.8) which is a disagreement with the findings of the present study. In Hering's case, supernatants of the samples from coagulation experiments were analysed for residual arsenic concentration without allowing any settlement. But in the present study, after mixing, samples were allowed to settle for a long time (at least 24 h) so that longer duration of settlement permits greater removal.

Although it has been observed from settling column test that over the settling time of 17 days, sample depth has no significant effect on As(III) removal (Fig. 4.10), higher removal was obtained at 24 h when tests were carried out in a shallow conical glass flask rather than in a long cylindrical glass container as used in the settling column test.

Table 6.2 shows that 24 h settlement gave about 20% higher removal than filtration for 1 min manually mixed samples when tests were carried out in a conical glass flask. But when settling column tests (using long cylinders) were carried out at the same test conditions, the removal after 24 h settling was same as that of filtration. About 10% higher removal was obtained by settlement than that of filtration when samples were allowed to settle in settling columns for three days. Therefore, it can be said that extent of arsenic removal also depends on the shape of the container. If samples were allowed to settle for 24 h in a long cylinder, the removal achieved was almost the same by both filtration and settlement. However, for longer periods of settlement, removal was higher by settlement (Figs. 6.3a and 6.3b).

6.5 COMMENTARY ON THE FACTORS INFLUENCING THE AS(III) REMOVAL

One of the objectives of this research work has been the investigation of the factors influencing the removal of As(III) using iron. Although there is sufficient information on the factors affecting arsenic removal (section 3.8), there appears to be very few studies on As(III) removal. The present study involved a separate series of tests (section 4.5) to investigate the influence of different factors on the removal of As(III). The conditions in these tests were representative of those prevailing in the groundwater of Bangladesh. In this section, the results of these tests have been discussed.

6.5.1 Effects of pH, Fe/As ratio and initial As(III) concentration

From analysis of the experimental results it is apparent that the removal of As(III) in association with Fe is influenced significantly by three factors; pH, Fe/As ratio and the initial As(III) concentration (section 4.5.1 and 4.5.2).

As(III) removal increased over the pH range of 5.0 – 8.0 (Fig. 4.6) which is an agreement with the findings of Sorg and Logsdon (1978). In this study, the possible mechanism of arsenic removal is coprecipitation and adsorption. The formation of $Fe(OH)_3$ increases over pH 5.0 –8.0 (Section 4.4; Ghosh and O'Conor, 1966) and facilitates the removal of arsenic over that pH range. According to Hingston *et al* (1967), adsorption occurred provided the energy of adsorption is sufficiently large to dissociate the arsenous acid (H_3AsO_3) which is a neutral molecule up to its first dissociation constant (pK_1) of 9.2. They, therefore, suggested that maximum adsorption should occur at pH 9.2.

There is a dearth of literature on the effects of Fe/As ratio on removal of arsenic in water. However, there are studies addressing this aspect with respect to As(V) (Papassiopi *et al*, 1996; Robins *et al*, 1988). As the present study deals principally with As(III), it is difficult to make meaningful comparisons with previous works tied to the effects of Fe/As ratio with As in form of As(V). Wilkie and Hering (1996) reported that As(III) removal increased with increasing Fe/As ratio when preformed hydrous ferric oxide was used as an adsorbent. The same trends were evident in this study (see Fig. 4.7). Robins *et al* (1988) worked on removal of As(V) at different Fe/As molar ratios and reported increased removal with increasing Fe/As molar ratio within the range of 1.5 to 10. They also suggested that for effective arsenic removal, Fe/As molar ratio should be significantly greater than unity for any initial arsenic concentration. According to Fig. 4.7, it is evident that removal of As(III) increased with increasing initial concentration at the same Fe/As ratio (by weight) and for all values of initial As(III) concentrations, Fe/As molar ratios were greater than unity (section 4.5.2). However, in ideal adsorption situation, removal should be the same at same Fe/As ratio irrespective of initial arsenic concentration. Since the removal mechanism here is adsorption-coprecipitation rather than purely adsorption, therefore, there might be a slight dependence on initial concentration of As(III) removal.

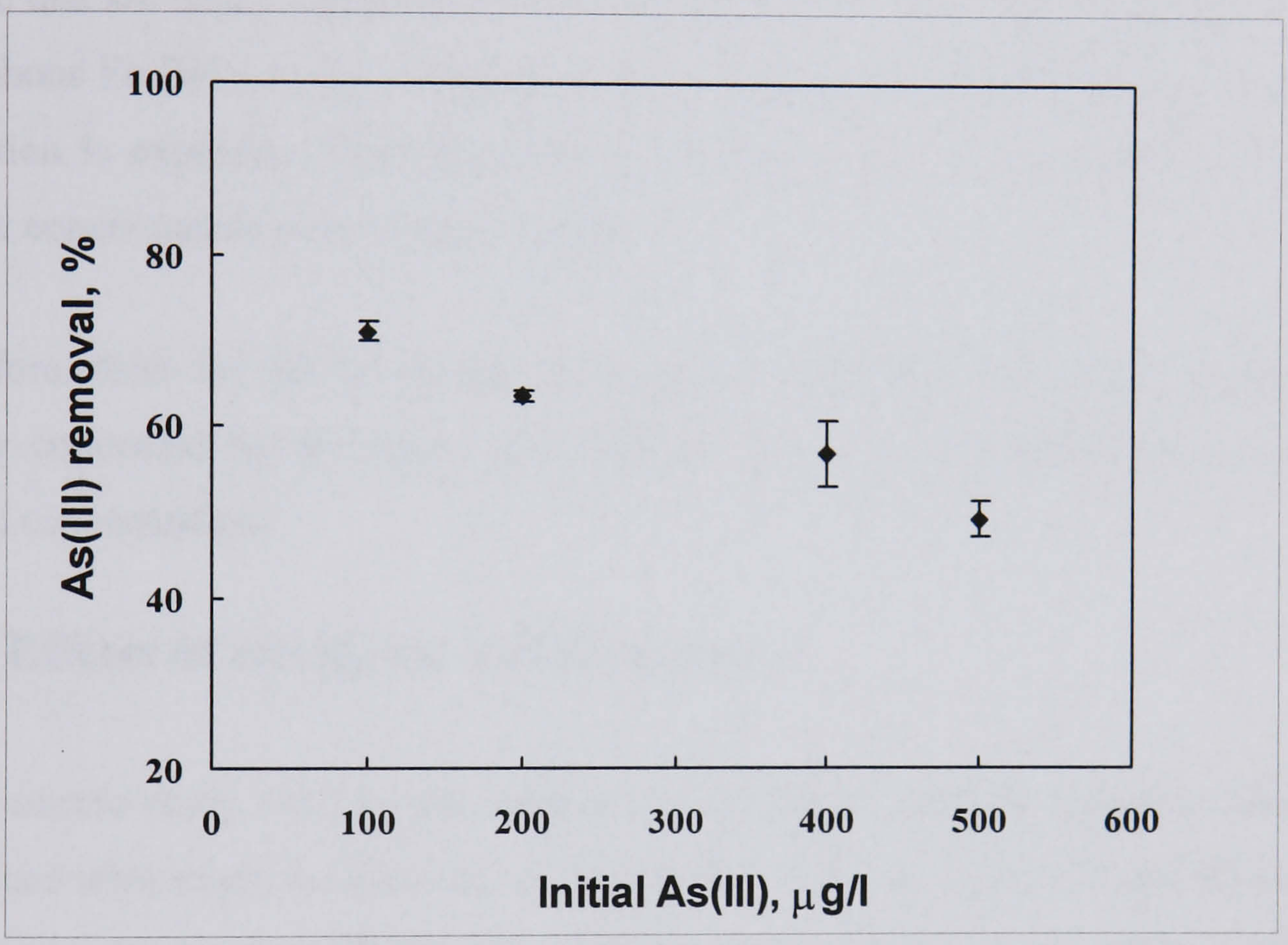


Fig. 6.6 Effect of initial As(III) concentration on As(III) removal at pH 7.5 and Fe 4.0 mg/l. Error bars denote standard deviation

Fig. 6.6 illustrates the effect of initial As(III) concentration on As(III) removal at pH 7.5 and Fe dosage of 4.0 mg/l. It shows that As(III) removal decreases with increasing initial As(III) concentration. Increased As(III) removal was observed at low initial concentrations. Similar findings were obtained by Wilkie and Hering (1996) and Hering *et al* (1997) (Fig. 3.24b). According to them this effect might be attributable to oxidation of As(III) at the HFO surface (Vitre *et al*, 1991) or preferential adsorption of As(III) to strong binding sites on the HFO surface. On the other hand, Hering *et al* (1997) found that removal efficiencies during coagulation with $FeCl_3$ were independent of initial As(III) concentration over the range of 0- 100 μg/l (Fig. 3.24a). Cheng *et al* (1994) also observed insignificant influence of initial arsenic concentration on As(V) removal over the range of 1- 100 μg/l (Fig. 3.23) but Sorg and Logsdon (1978) found a significant decreasing effect of As(V) removal when initial As(V) concentration is above 1.0 mg/l for the same coagulant dosage. Hering *et al* (1997) explained the lack of dependence on arsenic removal on initial arsenic over a limited range of concentration as follows: at low concentration of arsenic that are small compared with the concentration of adsorbent surface sites i.e. amorphous $Fe(OH)_3$ or the comparable solid formed in coagulation experiments, no saturation is expected. Thus the removal is expected to be independent of initial arsenic concentration over a limited range.

Therefore, from the above discussion, it can be concluded that arsenic removal is largely controlled by the Fe/As ratio and pH with a slight dependence on initial As(III) concentration.

6.5.2 Effects of mixing on As(III) removal

In the current study, mixing was achieved by manual shaking the intention being to reproduce what might be achieved at village level. It is, of course, recognised that its impact can not be quantified in the ways normally adopted by chemical engineers e.g. in terms of the mean velocity gradient (Weber, 1972). The purpose of the agitation was to enhance floc formation. From test results (Table 4.7) it has been found that the duration of shaking has no significant effect on the removal of arsenic over the mixing time of ≥ 30 s to 5 min. This can be explained as follows: the particles formed by manual shaking over this time period might be of ≤ 1 μm and hence perikinetic flocculation occurs due to Brownian movement. This might be the reason for getting almost similar removal irrespective of mixing type and time.

For unfiltered samples, it is seen that the removal is independent of shaking time for 24 h settlement but dependent on shaking time over the settling period of 2 to 6 h

(Fig. 4.9). The reason might be that for a shorter settling time (2-6 h), the particles are too small to settle down by gravity but for longer settling time, they have more time to flocculate by relative sedimentation, this resulting in enhanced settlement.

6.5.3 Effects of form of Fe

From work noted in section 4.5.4, it is observed that the As(III) removal capacity using the ferrous form of iron (as $FeSO_4.\ 7H_2O$) is less than ferric form of iron (as $FeCl_3$). From the literature, it is also found that less As(III) removal was obtained by ferrous iron than ferric iron (Table 3.5). In groundwater, iron is generally found as soluble ferrous form. Therefore, the successful transformation of the ferrous form into ferric form by aeration should be the first and principal step in the removal process of arsenic using the naturally occurring iron provided the pH and alkalinity of the water should be in the suitable range (section 3.5.2).

6.5.4 Effects of co-occurring solutes in water on As(III) removal

When tests were conducted with co-occurring solutes i.e. 8.5 NTU turbidity, 190.0 mg/l alkalinity as $CaCO_3$, 4.0 mg/l NO_3^- and 5.0 mg/l SO_4^{2-}, they gave higher removal than samples without these solutes (control sample) (Fig. 4.13). Tests with individual solutes did not show any significant effect on As(III) removal (Figs. 4.14, 4.15 and 4.16). The reason for this may be as follows. When all the solutes are present in water, they all help the precipitates to settle down faster by a form of enmeshment process. But the role of the individual solutes is much smaller compared to their combined effect and thus they do not show any significant effect on As(III) removal.

Previous studies (Peng and Di, 1994; Hering *et al*, 1997; and Papassiopi *et al*, 1996) showed that presence of SO_4^{2-} and PO_4^{3-} decreased arsenic removal. Most of these works were carried out for As(V) removal. Only Hering *et al* (1997) conducted tests with As(III) and found that addition of SO_4^{2-} significantly decreased As(III) removal at pH 4.0 and 5.0. But there was no effect at higher pH values even with SO_4^{2-}

concentration as high as 40 mg/l (Fig. 3.25). In Bangladesh groundwater, average concentration of SO_4^{2-} is 5.0 mg/l (Appendix B) (which is quite low) and hence no test was conducted to see its effect on arsenic removal. Furthermore, because of limited data, an effect of PO_4^{3-} was not investigated.

The effect of NO_3^- was found to be insignificant (Fig. 4.16), which agrees with the findings obtained by Peng and Di (1994).

Effects of turbidity (by adding kaolin particles) showed no effect on As(III) removal (Fig. 4.15) whereas Hering *et al* (1996) found reduced As(III) removal using kaolin. The findings from the present study and from Hering *et al* (1996) do not match with the findings of Amirtharajah and O'Melia (1990) who have been found that the presence of background particulates (like kaolin) improves the efficiency of the coagulation process. Therefore, the effect of kaolin particles appeared to be associated with changes in solution composition rather than the presence of the particles per se.

6.5.5 Effects of temperature

Tests conducted to observe the temperature effect showed that it did not exhibit any marked influence on As(III) removal (Fig. 4.17).

Test results described in Section 4.5.3.2 gave rise to lower As(III) removal (after 24 h avg. 60% removal) than tests described in Section 4.5.5 (after 24h, 67% avg. removal) for the same test conditions but at different ambient temperatures. Tests in section 4.5.3.2 were performed in winter and no temperature control was maintained. In the laboratory, temperature varied over a wide range of 5°C to 18°C in winter season. On the other hand, the tests described in section 4.5.5 were performed in summer time when laboratory temperature varied from 10°C to 22°C. Therefore, to investigate the effect of temperature, tests were conducted at varying temperature in a controlled manner (section 4.5.6). However the test did not provide any significant evidence that temperature was a major factor influencing As(III) removal. Results showed that only 4% higher removal was achieved for 25°C increase in temperature (Fig. 4.17).

Temperature influences viscosity, diffusion and the kinetics of Fe-As reaction. It was therefore, expected to influence removal of arsenic. However this was not the case and suggests that the different influences must counter-act each other.

6.6 SEPARATION OF TREATED WATER

The two methods studied for separating the precipitates from the treated water i.e. drawing of treated water through openings and by siphoning produced similar results after three days of settlement (Table 4.10). However, siphoning was not very easy to implement, as there was some disturbance and resuspension of the precipitates during placement of the pipe.

It was apparent that the flow rate in the sample draw off arrangement has a significant influence on sample disturbance. It was seen that (Fig. 4.23) for flow rates below 0.5 l/min, concentration of As(III) in treated water after separation from precipitates varies from 36 to 41 μg/l. Whereas, for higher flow rates (1.6 l/min) the concentration of As(III) was much higher (67 μg/l).

The aspect described for separation of treated water (section 4.7) is critical to the harvesting of the treated water and deserves greater attention. This provides scope for future work.

6.7 DISCUSSION ON POTENTIAL REMOVAL OF ARSENIC FROM GROUNDWATER IN BANGLADESH AND LIMITATIONS OF THE MAPS

The maps shown in Figs. 5.3 and 5.4 of remaining arsenic concentration applying filtration and settlement techniques have several limitations.

The existing distributions of As, Fe and pH show various zones of different ranges (i.e. minimum and maximum) of concentration. However, for eqn. 5.1, a single value was required for every location that was taken as the mean value of the minimum and maximum of the relevant zone. Although this was considered as representative of that particular zone, this approach introduced a significant approximation, as the ranges used in maps of existing As, Fe and pH are quite broad.

Experimental results showed that removal of arsenic by 3-day settlement is higher than that by filtration. However, when the likely benefits to be obtained applying the two techniques (Tables 5.2 and 5.3) of arsenic removal is compared in Table 6.3, they appeared to be fairly close. This phenomenon can be explained as follows.

Although settlement is found to produce higher removal compared to filtration, the difference is not significant at the lower Fe/As ratios i.e. 5 and 10. This phenomenon is understandable, as higher removal by settlement is caused by a prolonged Fe-As interaction and when there is insufficient Fe, the reaction quickly reaches a saturation point making removal by the two methods quite close. The maps were developed by estimating the removal of arsenic deploying the empirical relation (eqn. 5.1) obtained by regression analysis of filtration and settlement data. Such empirical relations are only estimates of the potential As removal under specific conditions of Fe/As ratio, pH and initial As(III). From the field data of As and Fe (Figs. 2.1 and 2.2), the Fe/As ratio was found to be quite low (below 15) in many areas. The estimated removal by settlement in such areas was seen to be lower from the filtration equation. But in areas having higher Fe/As ratios, the opposite was seen to occur. The result of factors is that one almost nullifies the other. In addition spatial distribution of Fe, As and pH in this study was taken from maps that used broad classification ranges to show their distribution over the country. Such ranges made only minor differences in the conclusions obtained from the two methods, and were barely detectable.

Table 6.3 Comparison of the extent of arsenic contamination between existing state and after treatment

	Present Status	After treatment	
		Filtration technique	Settlement technique
Percent area complying with WHO limit	—	35.1	35.1
Percent area complying with Bangladesh standard	63	72.4	71.5
Percent population complying with WHO limits	—	34	34
Percent population complying with Bangladesh standard	61	69	67

It is important to note that the distribution of iron concentration in Bangladesh as reported by EGIS (1997) (chapter 2) has limitations. As stated above, EGIS has produced a map (Fig. 2.2) showing different regions having a given range (minimum and maximum) of iron concentration. According to this map iron concentration in the groundwater vary from 0.25 to more than 2 mg/l. On analysis of the data collected from BUET (section 2.4 and Appendix B) it was found that about 200 out of 384 samples had iron concentration less than or equal to 1 mg/l. However, in 40 cases, high values (10 mg/l or greater) were found. This shows that the map produced by EGIS understates iron concentration. But since BUET data does not contain any locational information, it is not possible to identify the region or determine the extent of such underestimation. Consequently, maps showing the potential for removal of arsenic based on the iron map of EGIS will be on the conservative side. This has an important consequence because the evidence presented in this study shows that with a higher level of Fe, the Fe/As ratio is higher and this leads to a higher level of removal (see Figs. 4.7 and 4.20). In the empirical relation (eqn. 5.1), the power of Fe/As ratio are 0.34 and 0.39 for filtration and settlement approaches respectively. This means that a two-fold increase in iron concentration will increase the stated removals by 1.26 and 1.30 times for the respective approaches. Thus it is suggested that the maps showing the residual arsenic (Figs. 5.3 and 5.4) and the consequences of potable water (see Table 6.3) are regarded as conservative.

6.8 ARSENIC REMOVAL AT VILLAGE LEVEL

A simple and practical method that can be adopted at village level for reducing the level of arsenic in contaminated groundwater in Bangladesh is described below. This method applies to water in, which there is a sufficient iron concentration to form iron-arsenic precipitates.

For iron concentration between 1.0 and 20.0 mg/l and arsenic concentration between 0.1 to 0.5 mg/l, there is a reasonable expectation that after following the procedure described below, the water will comply with the Bangladesh Water Quality Standard for arsenic (0.05 mg/l).

Procedure:

- Fill a clean container of 10 litre capacity (Fig. 6.7) with about 7 litre water to be treated leaving an air space
- Shake the container for 1 minute
- Allow 3 days for particle settling
- Take out treated water through the tap, not exceeding a flow-rate of 0.5 litre/min

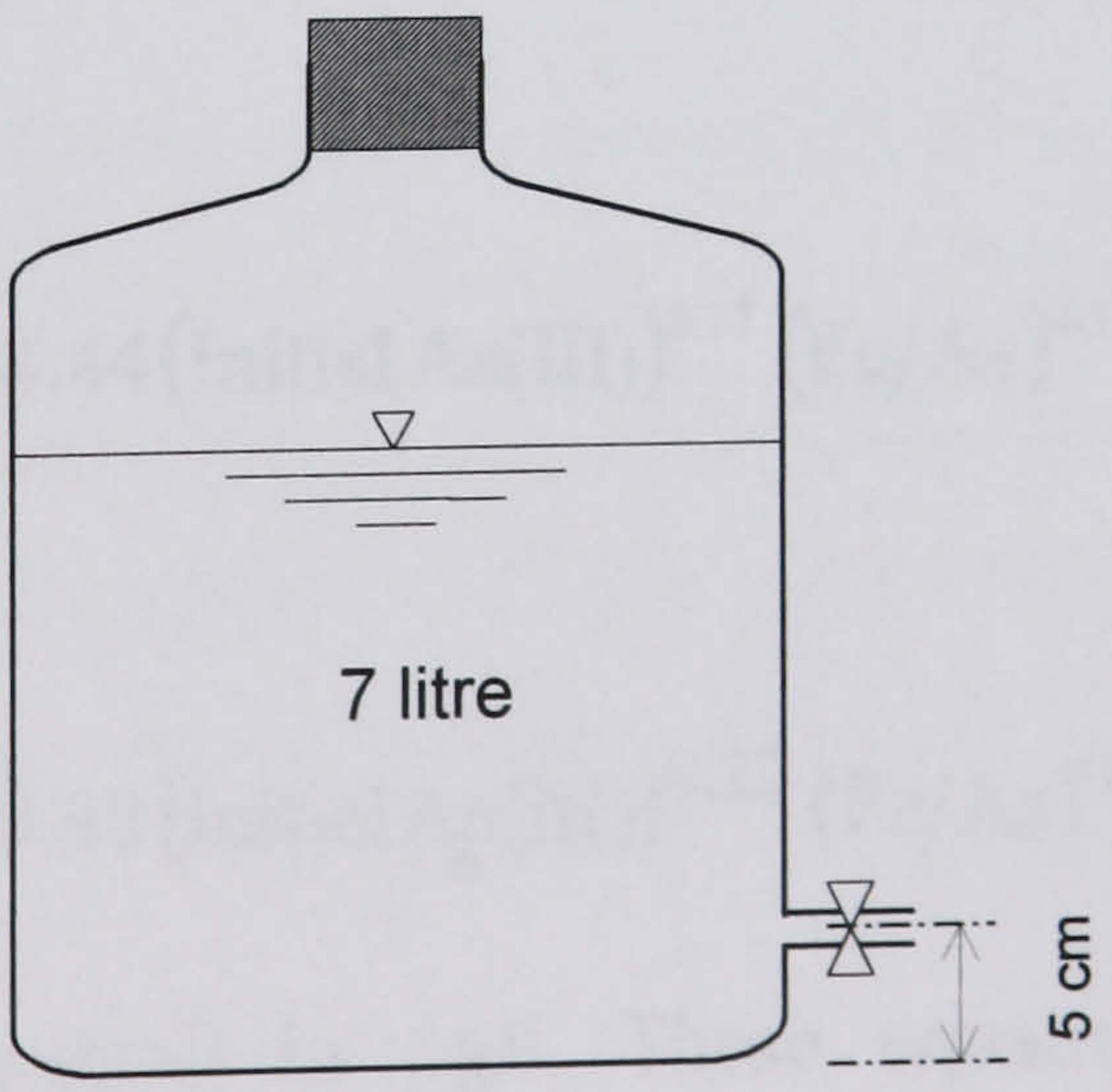


Fig. 6.7 Container to be used for arsenic removal.

Chapter 7

CONCLUSIONS

7.1 CONCLUSIONS

The principal conclusions drawn from this study are as follows:

1. Arsenic present in groundwater can be removed to a large extent by coprecipitation and adsorption with iron. It was found that As(III) removal was influenced strongly by the Fe/As ratio and pH and to some extent by the initial As(III) concentration. A combination of these factors led to the following relationships for describing the removal.

   Filtration

   $$\mathrm{As(III)\,Removal(\%)} = 4.44\left(\mathrm{Initial\,As(III)}\right)^{0.17}\left(\mathrm{Fe/As}\right)^{0.34}\left(\mathrm{pH}\right)^{0.33} \qquad (7.1)$$

   3-day settlement

   $$\mathrm{As(III)\,Removal(\%)} = 3.98\left(\mathrm{Initial\,As(III)}\right)^{0.22}\left(\mathrm{Fe/As}\right)^{0.39}\left(\mathrm{pH}\right)^{0.24} \qquad (7.2)$$

   where As(III) is expressed in µg/l. These equations are valid for As(III) concentration of 0.1 to 0.5 mg/l, Fe/As ratio (by weight) 5 to 40 and pH 5 to 8.

2. Following prolonged settlement, it was found that arsenic removal could exceed the removal achieved by filtration through a 0.45 μm filter paper. The experiments demonstrated that about 77% arsenic removal could be achieved from water containing 0.2 mg/l As(III), 4.0 mg/l Fe at pH 7.5 by 1 min manual mixing and 3 days settlement and after 17 days settlement removal could reach up to 92% for the same test conditions.

3. The potential for removing arsenic by the naturally occurring iron in Bangladesh has been investigated using data on existing distributions of arsenic, iron and pH from EGIS. The results of this investigation have been presented in the form of two maps (Figs. 5.3 and 5.4), one for settlement (using eqn. 7.1) and one for filtration (using eqn. 7.2) respectively. However, on comparison with BUET data it was found that EGIS iron map underestimates its concentration. Therefore, the maps prepared using EGIS data will be on the conservative side.

4. A relationship was established (Fig. 6.5 and eqn. 6.1) to show the implications of iron concentration on reducing the level of arsenic contamination corresponding to 3 days settlement. From a practical point, this is important because it shows the minimum amount of iron requirement for a given arsenic concentration to achieve Bangladesh standard of arsenic for drinking water. For example, when the arsenic level is 0.10 mg/l, the minimum amount of iron requirement is 1.2 mg/l at pH 7.5 to attain the Bangladesh limit (0.05 mg/l).

5. If the coprecipitation-adsorption and settlement technique is applied in the field, it is estimated that further 8% of the total area of Bangladesh would comply with the Bangladesh standard for arsenic in drinking water freeing an additional 7 million from arsenic contamination at near zero cost. As far as WHO standard is concerned, 34% of the population over 35% of the total area will be free from arsenic contamination.

6. Of the range of the interference tested, these enhanced higher arsenic removal. However, it was shown that the individual presence of interference did not exhibit any marked effect on arsenic removal.

7. After settling, the treated water may be drawn-off (with only minimum impairment of its quality) using a particular container with a tap located 5 cm from the bottom provided the draw-off rate does not exceed about 0.5 l/min.

8. It was evident that charcoal was ineffective in removing arsenic from water.

7.2 SCOPE OF FUTURE WORK

The following recommendations are made to extend the present study:

1. The present study was based on synthetic samples. It is recommended that this is supported by extensive field trial i.e. the naturally occurring form of iron and arsenic in groundwater together with other co-occurring solutes.

2. The removal behaviour of arsenic by coprecipitation-adsorption and settlement at higher initial arsenic concentration deserves investigation because of uncertainty concerning the saturation of removal density.

3. Further work is required on draw off arrangements and disposal of the arsenic waste.

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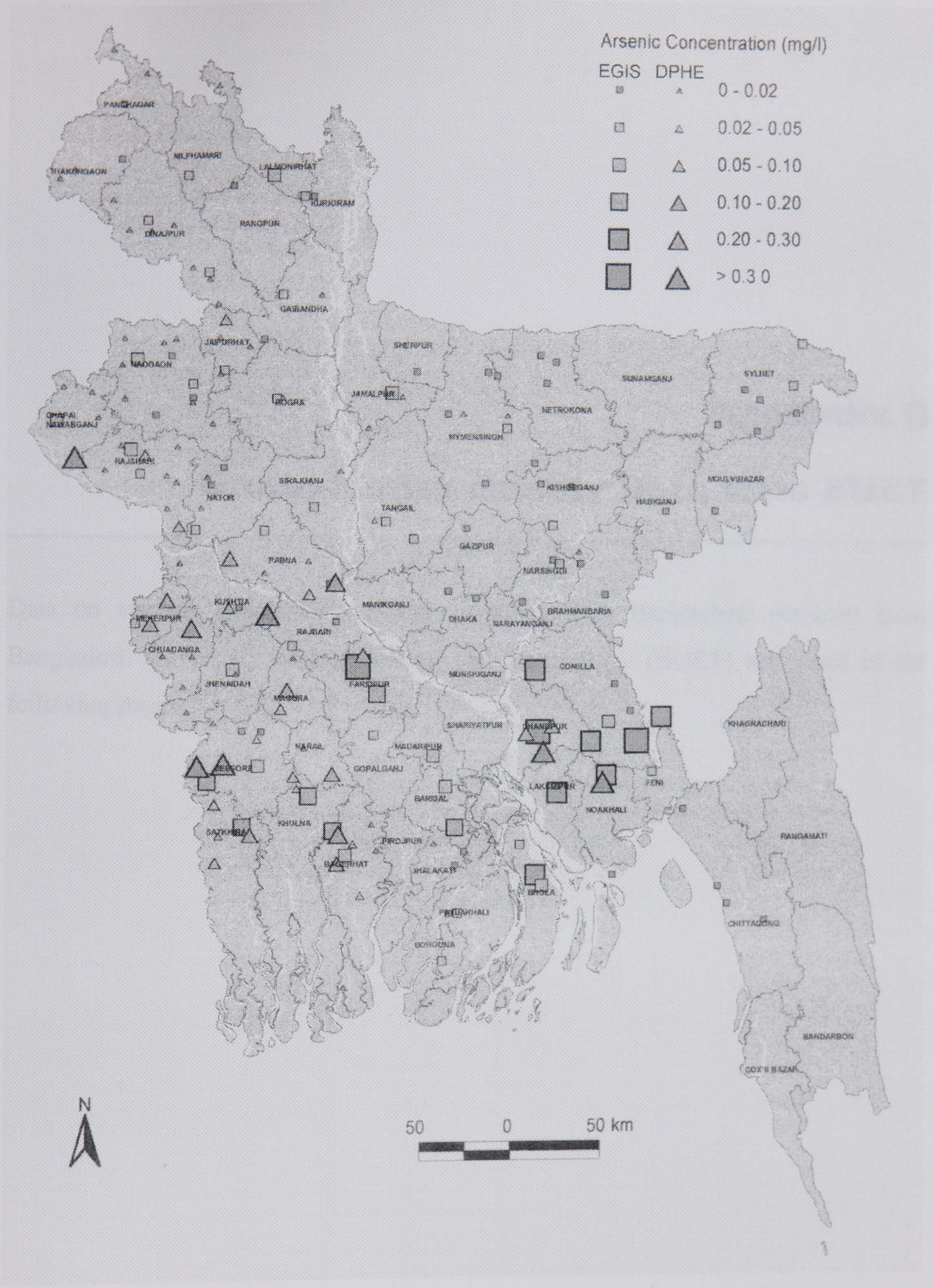
Appendix A

Comparison of Data on Arsenic from DPHE and EGIS

A comparison on the data on arsenic from Department of Public Health Engineering, Bangladesh and EGIS is reproduced in the following page.



Comparison of arsenic concentrations in groundwater in Bangladesh obtained from EGIS and DPHE (EGIS, 1997)

Appendix B

Groundwater Quality Data from BUET

Data on various groundwater quality parameters in Bangladesh obtained from Bangladesh University of Engineering and Technology (BUET) are listed in the following pages.

Division	Chloride mg/l	Alkalinity mg/l	Hardness mg/l	Magnesium mg/l	Manganese mg/l	Nitrate mg/l	Sulphate mg/l	Turbidity NTU	pH	Iron mg/l
Dhaka	36	150	96	14	0	3	4	10	7.3	1.6
Dhaka	24	123	95	8	0.3	4.5	3	19	7.4	8
Dhaka	32	389	320	18	0	3.5	0	3.5	7.1	18
Dhaka	19	136	100	7	0	3.5	1	4.8	7.2	7
Dhaka	20	102	65	0	0	0	0	6	6.7	0
Dhaka	148	153	190	10	0.3	4	12	13.8	7.1	10
Dhaka	20	194	117	9	0.75	4.5	5	52	6.7	9
Dhaka	24	91	82	6	0	2.5	0	5	7.5	6
Dhaka	20	188	110	7	0.2	1.5	3	27	7	7
Dhaka	19	120	75	8	0.1	2	1	10	7.1	8
Dhaka	16	110	65	4	0	0	1	3.4	7.9	4
Dhaka	22	276	185	12	0	1	2	0.77	6.7	12
Dhaka	480	86	215	11	0.4	12	21	78	7.2	11.4
Dhaka	755	194	66	0.8	0.1	6	13	27	6.9	0.82
Dhaka	130	116	103	4	0	4.5	9	2	6.9	4
Dhaka	28	156	55	19	0.45	11	8	0	7.1	19
Dhaka	37	89	97	14	0.2	15.5	42	17	7.1	14
Dhaka	18	142	100	6	0.1	3.8	37	48	6.9	6
Dhaka	20	145	40	2	0	0	12	38	6.9	2.4
Dhaka	18	93	104	9	0.4	4.2	0	100	6.6	9
Dhaka	22	0	80	8	0	10	0	0		8
Dhaka	0	154	50	2	0	7	11	11	7.1	2
Dhaka	21	57	344	2	0.1	8	0	128	7.3	2
Dhaka	18	81	66	14	0.4	7	0	2.5	7.1	14.6
Dhaka	60	201	38	1	0.2	8	0	0.1	6.8	1
Dhaka	205	85	220	19	0	0	0	2.1	6.6	19
Dhaka	17	63	140	20	0	0	624	0.5	7.2	20
Dhaka	15	610	40	0	0	0	672	42	7.3	0
Dhaka	190	750	180	11.7	0.35	1.5	0	66	10.2	11.7
Dhaka	260	64	78	9.7	0.4	0.5	19	0	6.6	9.72
Dhaka	0	249	72				56	1	6	1.37
Dhaka	27	131	106					1.53	7	0.2
Dhaka	28	153	110					12	7.6	0.1
Dhaka	14							8.2	7.2	0.8
Dhaka	31	92	64	5.6	0.8	0.01	103.7	3.7	7.2	0.34
Dhaka	18	96	120	26	0	0	0	4.9	7.6	0
Dhaka	14	35	108	17	0	0	0	14.2	9.4	7
Dhaka	17	90	48	2.4	0	0	303	0	7.4	4
Dhaka	0	414	195	0	0	11	0	0	7.2	4
Dhaka	95	155	400	25	0.8	0.01	23	50	6.9	0.6
Dhaka	28	286	400	0	0.3	0	25	3.8	7.1	4.5
Dhaka	100	286	96	30	0	0	2	25	9.1	0.01
Dhaka	100	102	288	23	0	0	3	25	7.2	0.05
Dhaka	22	100	322	0	0	4.5	7	0.2	7.2	0.03
Dhaka	95	505	47	0	0	4	1	2	7.1	0.4
Dhaka	41	488	56	0	1.2	3.5	2	6	7	4.5
Dhaka	22	64	221	3	0.2	3.5	2	101	6.8	1
Dhaka	25	96	3	3	0	3	5	0	7.4	0.4
Dhaka	123	485	43	3	0.15	0	2	0	7.9	0.5
Dhaka	19	54	45	15	0	2.5	0	0	8.5	0.5
Dhaka	34	83	135	4	0	3.2	3	11.5	6.7	0.1
Dhaka	33	84	55	0	0	0.35	23	25	7.1	0
Dhaka	23	199	50	7	0	0.4	11	10.5	7.2	0.1
Dhaka	21	85	95	7	0	0	298	3.4	7.2	0.5
Dhaka	23	96	100	2	0	1.1	0	9.5	6.7	0.4
Dhaka	15	218	21	4	0.8	0.5	0	0		1
Dhaka	39	107	56	2.5	0	0.5	0	7.5	8.1	10
Dhaka	11	347	6	7.5	0.34	0.8	11.6	0.17	6.9	0.05
Dhaka	17	102	54	0	0	0.8	0	6	6.5	0.05
Dhaka	95	14	220	20	0.4	0.3	17.6	0	6.2	16
Dhaka	50	98	44	23	0.35		23	26	6.3	2
Dhaka	12	0	100	6.7	0.35			148	6.8	0.2
Dhaka	0	236	168	0	0.2			0	6.9	2.3
Dhaka	12	239	76	0				2.1	6.9	8
Dhaka	36	151	224	31				122	7.4	3
Dhaka	21	150	112					12.9	6.6	1.65
Dhaka	97	69						10	6.8	2

Division	Chloride mg/l	Alkalinity mg/l	Hardness mg/l	Magnesium mg/l	Manganese mg/l	Nitrate mg/l	Sulphate mg/l	Turbidity NTU	pH	Iron mg/l
Dhaka	18	460						5.6	6.9	2
Dhaka								71	6.7	8
Dhaka	15	170	128	0	0.25	0.5	18.2	22	7	2
Dhaka	55	180	116	8.7	0.15	8	11.5	18.7	6.8	0
Dhaka	18	61	200	9	0.15	11	0	34	6.9	8
Dhaka	27	216	218	23	0.3	0	76	40	8	8
Dhaka	17	200	242	0	0.6	0	0	106	8	1.5
Dhaka	53	254	0	0	0.3	0	0	0	7.3	2.8
Dhaka	234	0	230	0	0	4.5	0	0	7.1	13
Dhaka	0	0	188	13	1.5	4.5	0	85	7	2.5
Dhaka	0	338	188	13	1.5	1	0	85		3
Dhaka	15	289	155	8	0.2	2	0	31	7.8	0.6
Dhaka	15	289	180	12	0.2	3	0	0.3	7.1	0.6
Dhaka	29	297	185	9	1.9	0.2	10	163	7.1	0.6
Dhaka	25	287	174	15	0.45	1	2	37	7.1	12
Dhaka	50	321	185	140	0.5	3.5	0	38	7.5	3
Dhaka	86	168	1125	140	0.1	3.5	0	4.6	7.4	0.3
Dhaka	280	223	1125	51	0.1	5.2	0	4.6	7.4	2
Dhaka	700	355	385	99	1	5.6	0	177	6.9	0.3
Dhaka	1450	358	800	47	3.5	4.5	0	146	7.2	6
Dhaka	650	539	350	7	0.6	2	0	60	7.2	1
Dhaka	16	526	100	14	0	3	0	2.4	6.9	0.7
Dhaka	12	485	212	12	0.2	11.5	0	21	6.7	0.8
Dhaka	13	160	700	0	0	35.5	11.5	4	7	0
Dhaka	11	240	76	34	0.05	0.1	59.5	11	7.3	4.5
Dhaka	9	351	148	7	0.2	0.1	0	7.8	7.23	10
Dhaka	2	99	128	15	0.2	3	24	4.5	7.3	30
Dhaka	150	138	244	24	0.2	9.8	0	8.9	7.7	0.6
Dhaka	70	213	115	20	0	10	0	0.25	7.5	1
Dhaka	245	185	218	21.5	0.5	18	0	50	7.1	0.6
Dhaka	128	131	192	20	1.5	0.6	62	140	6.9	0.6
Dhaka	240	147	202	0	1.1	0.6	0	390	6.6	0.4
Dhaka	73	182	186	26.2	1.8	0	14.4	9	7	3
Dhaka	64	153	148		0.3	0.8		15	6.8	1.8
Dhaka	73	163	186		1.8			9	6.8	18
Dhaka	120	172	170		0.3			14.5	7	2
Dhaka		158						0	7	3
Dhaka		172						2.5	6.8	10
Dhaka		145						22	7	1.1
Dhaka								118	6.8	2
Dhaka	0	0	140	0	0	0	0	26	7.7	3
Dhaka	250	163	158	34	1.2	0.5	13	71	7.7	0.5
Dhaka	88	238	90	0	0.4	0.04	0	0	6.7	0.8
Dhaka	175	137	212	58	0.5	0.18	71	20	6.6	0.3
Dhaka	110	124	228	0	0	0	26	12.5	6.8	13
Dhaka	22	132	134	0	0.2	0	0	20	7	36
Dhaka	0	0	0	17	0	3.5	5	0	6.9	14.7
Dhaka	41	173	142	17	0.6	3.5	0	46	6.9	7
Dhaka	168	153	130	11	0	3	4	23	6.8	0.19
Dhaka	63	17	160	0	0.1	0	0	168	8.1	0.2
Dhaka	0	0	0	8	0	2.5	3	132	6.9	3.6
Dhaka	22	166	155	8	0.7	2	3	145	6.8	1.5
Dhaka	24	175	120	36	2	1	4	66	6.6	4
Dhaka	245	132	210	26	2.5	3.5	0	12.8	7.2	0.88
Dhaka	430	137	400	12	0.4	4	0	3.1	7.3	5.6
Dhaka	29	270	176	10	0	2	0	49	7.2	0
Dhaka	115	180	155	14	0	2	3	30	6.6	0
Dhaka	265	182	210	9	1.2	4	27	12.3	7.2	8
Dhaka	30	86	92	0	0	0	50	56	6.4	5.2
Dhaka	26	126	150	0	0	0	11	0	6.8	1.25
Dhaka	48	228	140	0.75	0.75	3.2	0	0	7.1	0.1
Dhaka	20	210	120	0.3	0.3	1.5	10	130	6.8	0
Dhaka	19	155	130	0.2	0.2	2	10	77	7.1	0
Dhaka	20	345	0	0	0	0	2	7.3	7.1	0.28
Dhaka	19	345	0				0	1.35	6.9	
Dhaka	14	396	0.6				2	0.3	7.1	
Dhaka	20	354	0.3				0	0.23	7.2	

Division	Chloride mg/l	Alkalinity mg/l	Hardness mg/l	Magnesium mg/l	Manganese mg/l	Nitrate mg/l	Sulphate mg/l	Turbidity NTU	pH	Iron mg/l
Dhaka	14	110	0.4				2	7.8	6.7	
Dhaka	0	0	0				0	8.6	7	
Dhaka	35	200	0				14.4	60	6.9	
Dhaka	45	212	0.28				16	52	6.7	
Dhaka	5	190					18	77	7.1	
Chittagong	65	69	36	3	0.5	7	28.8	26	6.5	0.35
Chittagong	28	163	128	9.7	0.2	48	17.3	27	6.7	2.2
Chittagong	110	111	96	9.7	0.1	0.25	0.46	66	6.8	0.37
Chittagong	130	134	128	8.7	0.85	0.3	5.76	34	6.9	0.65
Chittagong	65	124	106	9	0.2	0.5	6	56	6.9	0.35
Chittagong	14	121	120	9	0	2	5	1.55	7	1
Chittagong	9	146	82	10	0.5	2.5	8	72	6.7	2
Chittagong	145	113	96	13	0.2	3	8	95	7.3	3.2
Chittagong	213	173	210	13	0	5	5	25	6.6	3.5
Chittagong	110	238	270	17	0.05	5	24.96	176	6.9	4
Chittagong	59	200	140	17.5	0.65	0.25	12.5	1.2	6.9	0.4
Chittagong	620	134	105	16	0.65	4.5	24	95	6.3	5.5
Chittagong	21	114	96	8	2	3	60	1.55	7.8	5
Chittagong	21	114	96	13	0.1	3		2.5	6.5	5
Chittagong	730	113	235	8	1.5	3		1.48	7.2	12
Chittagong	15	186	138	0.2	0	0		4.2	7.5	0.3
Chittagong	740	95	240	2	0	0.05		0.31	7.6	10
Chittagong	150	89	100	9	0	3		22	6.5	0.3
Chittagong	620	82	190	17.5	0.1	2		5.1	7.1	0.4
Chittagong	155	88	105	21.4	0	0.3		33	5.5	0.3
Chittagong	17	147	48	18	0	0.3		3	5.9	2.6
Chittagong	12	28	66	5	0.7	2		74	7.4	2.53
Chittagong	59	37	73	0	0.2	2		0.5	7.4	0
Chittagong	21	148	20	10	0.5	3		2.6	6.7	0.2
Chittagong	36	116	18	8	0.5	2		71	7.3	0.3
Chittagong	20	172	20	2	0.2	11.5		82	7.3	5
Chittagong	235	105	135		0.35			5.7	7	0.02
Chittagong	22	141	43		1.5			8	7	3
Chittagong	450	32	180		0			45	7.5	0.05
Chittagong	10	230	86		0.25			38	6.9	0.4
Chittagong	21	205	85					30	6.7	10
Chittagong	8	123	44					57	6.7	6
Chittagong	600	68	160					66	6.92	0.3
Chittagong	25		160					3.5	6.7	0.9
Chittagong	50		54					0.5	6.8	5
Chittagong	14		29					41	3.6	3.5
Chittagong								124	7.5	2
Chittagong	275	153	188	19	0.2	12	11	34	8.2	5.5
Chittagong	19	89	54	11	0.2	4.2	11	23	7.7	3.5
Chittagong	20	97	58	7	0.5	0.4	9	75	8	1.1
Chittagong	21	112	78	22.5	0.45	0.2	9	2.1	7.8	0
Chittagong	975	0	334	43.7	0	9	12	2.8	7.1	3.7
Chittagong	110	231	110	7	0	1	3	441	6.7	5.8
Chittagong	136	254	60	4	1.5	2	4	3.5	7.5	2.25
Chittagong	108	239	512	46	0.24	4.2	18	2	7.1	0.5
Chittagong	110	207	245	16	0.2	3	19		7.3	0.55
Chittagong	55	175	584	80.7	0.25	1.4	5		7.3	0.65
Chittagong	20	110	370	20	1.2		7		7.2	0.6
Chittagong	660	136	8	5.8	0	1			7.1	0.65
Chittagong	260	118							6.8	1.15
Chittagong	22	411							7.4	0.6
Chittagong	16	87							7.2	0.6
Chittagong	17	103							8	0.8
Chittagong	37	479							7.2	0.8
Chittagong	37	163							7.1	0.35
Chittagong	56	9							7.4	0.35
Chittagong	45	679							7.1	1.4
Chittagong	41	769							7.3	7
Chittagong	71	254							7	0.1
Chittagong	51	181							7.1	0.15
Chittagong	40								7.1	0.03

Division	Chloride mg/l	Alkalinity mg/l	Hardness mg/l	Magnesium mg/l	Manganese mg/l	Nitrate mg/l	Sulphate mg/l	Turbidity NTU	pH	Iron mg/l
Chittagong	40								6.9	0.03
Chittagong	410								7	0.02
Chittagong	61								8	0.05
Chittagong	49								8	0.05
Chittagong	47								7.9	0.05
Chittagong	66								8.1	0.03
Chittagong	57								8.1	0.05
Chittagong	260								7.8	0.07
Chittagong	280								7.5	3.2
Chittagong	300								7.6	0.1
Chittagong	310								7	0.05
Chittagong	330								7.3	0.3
Chittagong	350								7.2	0.35
Chittagong	1120								7.3	0.38
Chittagong	141								7.1	0.42
Chittagong	250								7.1	0.44
Chittagong	82								7	0.42
Chittagong	32								7	0.05
Chittagong	285								7.1	0.01
Chittagong	275								6.8	
Chittagong	310								8	
Chittagong	340									
Chittagong	30									
Chittagong	320									
Chittagong	55									
Chittagong	28									
Rajshahi	35	214	208	11	0.9	24	58	19.3	6.8	1.25
Rajshahi	85	207	176	3	1.5	4.5	3	12	7.2	1
Rajshahi	51	175	150	2	0.2	3.5	1	81	6.8	9
Rajshahi	34	222	145	0.65	0	2.5	35	14.8	7.6	0.8
Rajshahi	33	220	143	24.9	0	0.2	22.5	3.9	7.6	0.6
Rajshahi	15	65	35	21	0.3	0.01	47	1.78	9.55	0.15
Rajshahi	33	200	140	22	0.25	0.01	58	5	6.9	0.2
Rajshahi	62	110	10	1	0.25	0.01	14.4	1	6.9	0.01
Rajshahi	10	58	46	3	0.1	4	18.2	2.8	6.8	1.5
Rajshahi	8	92	52	1	1.2	4.5	20	12	6.6	0.18
Rajshahi	10	111	68	9	0	3.5	0	130	9	0.3
Rajshahi	14	40	20	8	0.1	3.5	0	1.59	6.7	0.8
Rajshahi	79	95	35	0	0.1	3.5	0	35	6.4	6
Rajshahi	15	24	15	11.5	0.45	0.16	0	5	7.1	0.03
Rajshahi	13	109	108	18.5	0.45	0.9	14.5	9.8	7.2	8
Rajshahi	26	141	115	30.1	0.45	11	82.5	33	6.9	
Rajshahi	23	149	110	0.97	0.5	15	57.6	11	6.9	
Rajshahi	21	107	118	2	0.3	0.18	21	6	7	2
Rajshahi	30	47	54	0	0.25	8	24	6	7.1	0.26
Rajshahi	26	57	56	0	0.2	4		7	7.2	0.2
Rajshahi	9	68	58	3	0.25	0		9	7.1	1.6
Rajshahi	16	72	74	73	0.09	1		0.72	7	1
Rajshahi	16	60	74	12	0.1	0.2		1.21	7.2	0.6
Rajshahi	95	459	604	12	0.05	3		0.29	7.1	0
Rajshahi	24	475	574	2.9	0	3		1.03	7.2	3.2
Rajshahi	40	471	328		0.4	0.5		0.85	7.1	3.2
Rajshahi	12	446	306		1.1			34	7.3	0.18
Rajshahi	19	509	380		0.8			0.65	6.9	0.1
Rajshahi	16	130	60		1.2			8	7.1	0.05
Rajshahi	14	482	388		0			6.4	7.5	0.2
Rajshahi	30	45	18		1.3			2.1	6.5	0.22
Rajshahi	38	477	230		0.15			3	7.1	0.16
Rajshahi	12	478	292					3	7.1	0.5
Rajshahi	30	464	248					2.5	7.1	0.5
Rajshahi	38	453	250					14	7.2	1
Rajshahi	37	93	72					78	6.7	12
Rajshahi	14	82	62					11.2	6.6	8
Rajshahi		112	98					0.36	7	0
Rajshahi		118	102					116	6.9	3

Division	Chloride mg/l	Alkalinity mg/l	Hardness mg/l	Magnesium mg/l	Manganese mg/l	Nitrate mg/l	Sulphate mg/l	Turbidity NTU	pH	Iron mg/l
Rajshahi		68	84					6.1	6.9	11
Rajshahi		166	130						6.9	0.35
Rajshahi		156	134						6.9	
Rajshahi		200	160						7.8	
Rajshahi		210	150						7.5	
Rajshahi		194	20.7						7.5	
Rajshahi		41							7.1	
Khulna	26	433	345	25	0.5	6	0	38	7	2.5
Khulna	260	444	350	26	1.2	7	0	75	7.1	6
Khulna	22	415	192	25.3	0.1	7.5	0	1	7.7	0.14
Khulna	23	209	255	17	0.2	4	0	8.4	7.6	1.75
Khulna	15	468	225	15	0.5	2	3	28	7.2	3
Khulna	180	285	252	7.8	0.15	0.86	0	3.5	7	0.75
Khulna	100	348	280	0	0.3	0.3	10.6	55	7	2.8
Khulna	80	350	54	8.7	0.15	9	22	35	6.9	5.2
Khulna	16	348	146	19	0	2	0	9.5	7.2	0.6
Khulna	30	153	285	0.6	0.5	2	11.5	4.5	7	0.08
Khulna	120	333	444	25.9	26.2	18	0.8	4	7.3	0.4
Khulna	39	518	170	5.8	0.3	0.01	0	11.6	7.3	1
Khulna	23	145	154		0.2	1.3	0	14.5	6.8	0.44
Khulna	14	408	184		0.35	3	14.4	6.5	7	2
Khulna		376	300					18	7.7	0.5
Khulna		317						6.7	6.8	
Sylhet	13	141	125	16	2.5	4.5	1	142	6.5	26
Sylhet	14	148	131	17	0	4	1	25	7.1	0.24
Sylhet	17	126	78	5	0	3	16.3	1.18	7.9	0.2
Sylhet	24	183	155	9	0	2	15.4	56	7.1	4
Sylhet	47	153	135	9	0	2	6.7	11.5	6.7	1.3
Sylhet	58	154	160	10	0	2	56	5	6.9	0.5
Sylhet	28	145	110	14	0	4	14.4	8	6.9	0.12
Sylhet	20	150	98	6	0	3	31	11.8	7.3	0.4
Sylhet	22	71	45	4	0	3	31.7	0.45	6.9	0.05
Sylhet	32	145	100	7	0	2		22	7.3	4
Sylhet	33	140	75	5	0	2		3.5	6.9	0.1
Sylhet	19	72	35	2	1.5	3		56	6.5	8
Sylhet	19	70	32	2	1.7	2		109	6.5	10
Sylhet	28	58	45	12.8	0.3	1		4.2	6.5	0.2
Sylhet	16	75	6	12.6	0	5.2		33	7.4	0.5
Sylhet	17	70	192	1	0.1	1		33	7.4	0.25
Sylhet	17	22	208	39.4	0	1		6.5	6.4	0.2
Sylhet	22	397	18	12	0.15	0.2		0.43	7	7
Sylhet	32	280	28	4	0.35	11.5		0.25	7.4	2.4
Sylhet	8	38	22	17	1	0.5		1	6.6	0.6
Sylhet	35	43	12	12	0.25	0.75		2.5	6.6	0
Sylhet	4	40	186	7	0.05	1.3		170	6.7	0
Sylhet	0.6	33	72	4	0.2	1.4		33	7.1	0
Sylhet	17	21	142	23	0.2	19		3	6.5	0.2
Sylhet	16	90	58		0.9	6		22	6.7	17
Sylhet	90	258	58		0.1			504	7.4	7
Sylhet	60	136	60					25	7.9	0.1
Sylhet	60	178	122						7	3.5
Sylhet	140	298							7.1	1.5
Sylhet	44	297							7.1	1.75
Sylhet		64							6.3	48
Sylhet		144							7.4	1.5
Barisal	20	86	40	2	0	0	0	4	6.8	0.25
Barisal	215	0	130	0	0	2	2	0	7.7	0.02
Barisal	545	0	160	0	0	1.5	3	0	7.8	0.05
Barisal	200	318	40	8	0.1	0.6	0	0.3	7.8	0
Barisal	60	192	138	30	0.12	4	82	1.2	6.9	1.7
Barisal		462	380					7.5	7.6	0.55

Division	Chloride mg/l	Alkalinity mg/l	Hardness mg/l	Magnesium mg/l	Manganese mg/l	Nitrate mg/l	Sulphate mg/l	Turbidity NTU	pH	Iron mg/l
Unknown	7	88	46	6	0.1	15.8	0.24	185	6.7	20
Unknown	2	198	140	0.3	32	31	31	85	7.2	3
Unknown	46	130	236	2.8	16	8	33	1.3	6.9	0
Unknown	60	130	244	2.8	0	2	6.7	25	7.1	2
Unknown	54	306	24	10.6	0	3	23	2.5	6.9	0.23
Unknown	56	80	0.78	2.4	0	1.5	21	7.5	6.9	0.05
Unknown	160	277	124	2.5	7	2	13	133	7.6	0.55
Unknown	20	102	126	2.6	6	3.2	9	5.1	7.7	12
Unknown	14	360	188	2.6	5	12	8	7.7	5.9	14.5
Unknown	26	252	48	215	0.7	6	49	6.2	7	0.05
Unknown	27	293	14	66	0	19	12.5	0.2	7.3	0.3
Unknown	16	274	65	103	0.45	3.5	22	44	6.7	3.2
Unknown	32	255	276	60	0.12	16	8	7.2	7	0.2
Unknown	35	347		20	0.9	12	4	2	7.3	0.67
Unknown	11	86	104	126	0.15	10	0	97	7.3	0.9
Unknown	480	194	85	4	0.6	4.5	5	200	7.2	0.08
Unknown	755	114	83	18	0.45	12	0	275	7.6	6
Unknown	730	155	21	16	45	1	2	19	7.1	1.3
Unknown	130	64	215	104	67	1.2	3	7.9	7.1	1.5
Unknown	28	368	66	86	0.7	0.5	2	0.37	6.3	2
Unknown	37	169	103	2	0	2	2	34	3.6	1
Unknown	140	173	60	11.4	0.2	5		7.8	6.6	0.4
Unknown	21	300	20	0.82	0.5	3		0.3	6.8	0.05
Unknown	63	462	126	4	0.6	3.5		3.1	7.8	5
Unknown	15	34	118	2	0.25	3		2.7	7	24
Unknown	140	75	0.93	19	0	3		60	6.9	60
Unknown	220	608	164	9.7	0.6	4		39	6.5	4
Unknown	70	292	130	0.5	0	5		117	7.6	2
Unknown	71	122	516	47	0.12	3		78	7.3	0.8
Unknown	9	185	196	31	2.5	2		27	7.9	0
Unknown	18	600	134	8	0	3.5		2	7.3	5.5
Unknown	170	81	22	0.61	30	0		504	7.4	0.1
Unknown	15	139	44	2.3	0	3.5		8.3	7.2	0.5
Unknown	19	90	90	7.7	0.09	3		7	7.6	0.15
Unknown	17	220	64	5	0	19		30	6.8	0.02
Unknown	34	178	40	16	1	4.2		44	7.1	0.12
Unknown	140	251	176	32	0	2		26	6.9	0.35
Unknown	40	150	48	16	9	2		0	7	0.1
Unknown	0	172	125	11	0.9	1		129	6.5	15
Unknown	35	462	240	30	1.3	2		15.1	6.7	0.9
Unknown	33	350	115	19	0.1	2		126	7.2	14
Unknown	20	616	130	2	0	2		1.12	7.3	18
Unknown	81	246	380	5	0	2		16	6.9	3.6
Unknown	2	37	260	2.46	0.8	2		4.7	7.1	0.1
Unknown	40	190	395	0	0			4	6.3	9.5
Unknown	20	124	235	10	0			7.8	7.6	4.2
Unknown	32	31	20	5	0			3.8	7	9.2
Unknown	630	205	60	38				2.5	6.7	0.03
Unknown	760	166	80	17				0.3	6.9	48
Unknown	275	187	4	5				31	7.6	0.4
Unknown	24	215	136	4.55				0.4	7.1	0.15
Unknown	15	110	70	9				9	6.2	2.2
Unknown	21	114	120	9				3.5	6.7	7
Unknown	26	16	220	3				50	7.3	2
Unknown	21	181	75	8					7.6	0.7
Unknown	37	118	605	6					6.9	0.12
Unknown	43	164	280						7.6	10.6
Unknown	19	160	80						6.5	1.5
Unknown	35	70	70						5.9	0.2
Unknown		199	145						6.9	3.04
Unknown		230	150						11.2	1.4
Unknown		170	45						7.6	0.46
Unknown		116	115						6.8	0.3
Unknown			85						7	0.7
Unknown									7.2	0.3

Division	Chloride mg/l	Alkalinity mg/l	Hardness mg/l	Magnesium mg/l	Manganese mg/l	Nitrate mg/l	Sulphate mg/l	Turbidity NTU	pH	Iron mg/l
Unknown									6.8	0.35
Unknown									7.4	0
Unknown									7.4	25
Unknown									7.1	0.01
Unknown									7.6	2.87
Unknown									7.2	0.08
Unknown									6.9	0.5
Unknown									7.6	3
Unknown									7.5	0.4
Unknown									7.4	0.02