REMOVAL OF ARSENIC FROM WATER BY FERRIC CHLORIDE

NIBEDITA CHOWDHURY

OCTOBER, 1999

Bangladesh University of Engineering and Technology
Dhaka

REMOVAL OF ARSENIC FROM WATER
BY
FERRIC CHLORIDE

BY
NIBEDITA CHOWDHURY

A thesis submitted to the Department of Civil Engineering of
Bangladesh University of Engineering and Technology, Dhaka, in partial fulfillment
of the requirements for the degree
of

MASTER OF SCIENCE IN CIVIL ENGINEERING

25th OCTOBER, 1999

REMOVAL OF ARSENIC FROM WATER
BY
FERRIC CHLORIDE

BY
NIBEDITA CHOWDHURY

A thesis approved as to style and content
for the degree of M.Sc, Engg (Civil):

Dr. M. Ashraf Ali **Associate Professor** **Dept. of Civil Engineering, BUET** **Dhaka-1000**	**Chairman** **(Supervisor)**
Dr. Md. Humayun Kabir **Professor & Head** **Dept. of Civil Engineering, BUET** **Dhaka-1000**	**Member**
Dr. Md. Delwar Hossain **Professor** **Dept. of Civil Engineering, BUET** **Dhaka-1000**	**Member**
Dr. Noor M. Kazi **Water Supply Sector Specialist** **Bangladesh Arsenic Mitigation Water Supply Project** **Mohakhali, Dhaka**	**Member**

25th October, 1999

DECLARATION

I hereby certify that the research work reported in this thesis has been performed by me and this work has not been submitted elsewhere for any other purpose (except for publication).

October, 1999

Nibedita Chowdhury

Nibedita Chowdhury

ACKNOWLEDGEMENT

The author wishes to express her deepest gratitude to Dr. M. Ashraf Ali, Associate Professor, Department of Civil Engineering, BUET for his continuous guidance and affectionate encouragement at every stage of this research work.

The author also acknowledges the services of Mr. Abdur Rahman and Mr. Abbas of the Environmental Engineering laboratory.

ABSTRACT

Widespread arsenic contamination of groundwater has become a major public health concern in Bangladesh, where water supply is heavily dependent on groundwater. The present study focused on removal of arsenic from groundwater by coagulation with ferric chloride. Removal of both As(V) and As(III) was found to increase with increasing coagulant (ferric chloride) dose. For higher coagulant (ferric chloride) doses, removal efficiencies appear to be independent of initial arsenic concentration. Removal efficiency of As(III) by ferric chloride was found to be significantly lower than that of As(V). For example, 25 mg/L of ferric chloride could bring down As(V) concentration to less than 10 μg/L from an initial concentration of 0.25 mg/L; whereas in case of As(III) a ferric chloride dose as high as 125 mg/L resulted in a residual arsenic concentration of about 55 μg/L, higher than the drinking water standard (50 μg/L) set by the Bangladesh EQS. It was found that removal efficiency of As(III) pre-oxidized with bleaching powder was almost identical to that of As(V). For a sorbate/sorbent ratio (expressed as μg As/mg Fe) of about 50 or less, removal efficiencies exceeding 95 percent could be achieved, irrespective of the initial arsenic concentration. This can serve as a guideline value or thumb rule in determining required dose of ferric chloride for arsenic removal. A maximum adsorption density of about 353 μg As/mg Fe was achieved with a As(III) (pre-oxidized) concentration of 2.0 mg/L and ferric chloride concentration of 25 mg/L. However, at optimum sorbate/sorbent ratios (i.e., 50 or less) maximum adsorption density achieved was much less, about 50 μg As/L permg/L Fe.

Since significant fraction of arsenic in the groundwater of Bangladesh can exist as As(III), it appears that arsenic removal technology based on ferric chloride coagulation must involve a pre-oxidation step for converting As(III) to As(V). In this study, good removal of As(III) was achieved in jar tests using a chlorine (bleaching powder) dose 3 to 4 times that calculated from stoichiometric consideration. However, the unstable nature of bleaching powder is a cause of concern in its use as an oxidant. Results obtained from this study enabled determination of ferric chloride dose required for achieving a particular removal goal for arsenic present at different initial concentrations. It was found that ferric chloride requirement for satisfying the WHO standard (10 μg/L) was significantly higher than that required for satisfying the Bangladesh standard of 50 μg/L. Thus, the cost of arsenic removal by ferric chloride would depend on the water quality standard it is designed for. This is important in view of the possible revision of the drinking water standard for arsenic in many countries. In Bangladesh, arsenic removal by coagulated flocs of ferric hydroxide could be a very effective technique, particularly in view of the presence of elevated levels of iron in many regions of the country.

Removal of As(V) appears to be maximum in the neutral pH range and slightly depressed at higher pH values, exceeding 8. Since pH of groundwater usually falls between 6 and 8 in Bangladesh, pH is not likely to play a major role in determining the removal of arsenic from groundwater by ferric chloride. Although pH has a more pronounced effect on As(III) removal, this may not be an important consideration for arsenic removal by ferric chloride involving pre-oxidation. Phosphate appears to have a dramatic effect on arsenic removal from groundwater. Removal of arsenic present at an initial concentration of 0.10 mg/L (and treated with 10 mg/L of ferric chloride) came down from 92 percent (in the absence of phosphate) to about 46 percent in the presence of 2 mg/L of phosphate. Relatively high concentrations of phosphate, reaching as high as 5.8 mg/L, have been found in some places of Bangladesh and it appears that ferric chloride doses determined from laboratory batch studies (without the presence of phosphate) can significantly underestimate the actual dose requirement. Effect of phosphate on arsenic removal by ferric chloride also suggest that phosphate ions can play an important role in the release of arsenic in the groundwater environment in Bangladesh.

CONTENTS

Page No.

Declaration iii
Acknowledgement iv
Abstract v
List of Figures ix
List of Tables xii

Chapter 1: INTRODUCTION

1.1 General 1
1.2 Objectives of The Present Research 4
1.3 Scope of the Research 5
1.4 Methodology 5
1.5 Organisation of the Thesis 7

Chapter 2: LITERATURE REVIEW

2.1 Introduction 9
2.2 Historical Review 9
2.3 Occurrence of Arsenic 10

2.4 Uses of Arsenic

2.4.1 Historical Uses 12
2.4.2 Modern Uses of Arsenic 14

2.5 Sources of Arsenic

2.5.1 Natural Sources of Arsenic 15
2.5.2 Anthropogenic Sources 17

2.6 Chemistry of Arsenic

2.6.1 Chemical Properties 18
2.6.2 Some Principal Compounds of Arsenic 18
2.6.3 Chemistry of Arsenic in Water 21
2.6.4 Oxidation of Arsenic 24
2.6.5 Analysis of Arsenic 27

2.7 Health Implications of Arsenic in Drinking Water

2.7.1 Arsenic Uptake and Distribution 27
2.7.2 Acute Toxicity in Humans 30
2.7.3 Arsenic Carcinogenesis 32
2.8 Drinking Water Standards for Arsenic 34

2.9Arsenic Mobilization in the Environment

2.9.1 Arsenic in the Atmosphere 35
2.9.2 Arsenic in the Aquatic Systems 36
2.9.3 Arsenic in the Soil 40

Chapter 3: ARSENIC CONTAMINATION IN BANGLADESH AND ARSENIC REMOVAL TECHNOLOGIES

3.1 Introduction 42
3.2 Arsenic Contamination in Bangladesh 43
3.3 Arsenic Contamination in Other Countries 46

3.4 Arsenic Removal Techniques

3.4.1 General 49

3.4.2 Coagulation, Adsorption and Co-precipitation

3.4.2 .1 Coagulation by Alum and Ferric Salts 51
3.4.2.2 Lime Softening 54
3.4.2.3 Fe-Mn Oxidation 55
3.4.2.4 Naturally Occurring Iron in GroundWater of Bangladesh 56

3.4.3 Adsorption Techniques

3.4.3.1 Activated Alumina 56
3.4.3.2 Activated Carbon 57
3.4.3.3 Iron Oxide Coated Sand 58
3.4.3.4 Other Adsorptive Processes 58
3.4.4 Ion Exchange 59
3.4.5 Membrane Techniques 60
3.4.6 Microbial Process 61
3.5 Comparative Merits and Demerits of Arsenic Removal Technologies 61

Chapter 4: REMOVAL OF ARSENITE AND ARSENATE BY FERRIC CHLORIDE

4.1 Introduction 64

4.2 Materials and Methods 65

4.3 Results and Discussion 67

4.3.1 Effects of Coagulant Dose and Initial Arsenic Concentration 68

4.3.2 Effects of Pre-Oxidation on Removal Efficiency of As(III) 71

4.3.3 Effects of Adsorption Density 77

4.3.4 Requirement of Ferric Chloride 83

4.4 Conclusions 86

Chapter 5: EFFECT OF SOURCE WATER COMPOSITION ON ARSENIC REMOVAL

5.1 Introduction 92

5.2 Materials and Methods 96

5.3 Results and Discussion 98

5.3.1 Effects of pH 99

5.3.2 Effects of phosphate 103

5.4 Conclusions 107

Chapter 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 General 109

6.2 Conclusions 109

6.3 Recommendations 112

Reference:

Appendix A

LIST OF FIGURES

Page no.

Figure 2.1 A simplified comprehensive cyclic of transfer of arsenic 11

Figure 2.2 Predominance diagram of As(III) and As(V) as a function of pH 23

Figure 2.3 Eh-pH diagram of inorganic arsenic species 23

Figure 2.4 Rate of catalytic oxidation of As(III) in a linearized plot 25

Figure 2.5 Solubility diagram of Iron

Figure 2.6 Arsenic reactions in aquatic regimes 37

Figure 2.7 Chemical forms of arsenic and their transformation in soils 38

Figure 3.1 Map showing levels of arsenic contamination in Bangladesh 44

Figure 3.2 Arsenic removal from ground water by ferric ion precipitation without and with pre-chlorination to oxidize As(III) 52

Figure 3.3 Solubility Diagram of Ferric Hydroxide 53

Figure 4.1a Removal of As(V) as a function of ferric chloride dose for three different initial As(V) concentrations 69

Figure 4.1b Removal of As(V) as a function of iron concentration for three different initial As(V) concentrations 70

Figure 4.2 Comparison of removal of As(V) and As(III) as a function of iron dose (added as ferric chloride) for an initial arsenic concentration of 0.25 mg/L 72

Figure 4.3 Comparison of removal of As(V) and As(III) and pre-oxidized As(III) as a function of iron dose (added as ferric chloride) for an initial arsenic concentration of 0.25 mg/L 74

Figure 4.4 Comparison of removal of As(V) and and pre-oxidized As(III) as a function of iron dose (added as ferric chloride) for an initial arsenic concentration of 0.50 mg/L 75

Figure 4.5 Removal of pre-oxidized As(III) as a function of ferric chloride dose for different initial As(III) concentrations 76

Figure 4.6 Removal of As(V) as a function of Sorbate/Sorbent ratio 78

Figure 4.7 Removal of As(III) as a function of Sorbate/Sorbent ratio 79

Figure 4.8 Calculated adsorption density as a function of iron dose for three different initial As(V) concentrations 80

Figure 4.9 Calculated adsorption density as a function of iron dose for four different initial As(III) concentrations 81

Figure 4.10 Comparison of adsorption densities of As(V) and pre oxidized As(III) 82

Figure 4.11 Residual arsenic concentration as a function of iron dose for three different initial As(V) concentrations 84

Figure 4.12 Residual arsenic concentration as a function of iron dose for four different initial As(III) concentrations (pre-oxidized) 85

Figure 4.13 Requirement of Ferric Chloride to bring down residual arsenic conc. below 0.050 mg/L for different initial arsenic concentration 87

Figure 4.14 Requirement of Ferric Chloride to bring down residual arsenic conc. below 0.01 mg/L for different initial arsenic concentration 88

Figure 5.1 Effect of pH on removal of As(V) at an initial concentration of 0.25 mg/L during coagulation with 25 mg/L ferric chloride 100

Figure 5.2 Effect of pH on removal of As(V) at an initial concentration of 0.25 mg/L during coagulation with 100 mg/L ferric chloride 101

Figure 5.3 Effect of phosphate on removal of As(V) at an initial concentration of 0.10 mg/L during coagulation with 10 mg/L ferric chloride 104

Figure 5.4 Effect of phosphate on removal of As(V) at an initial concentration of 0.25 mg/L during coagulation with 10 mg/L ferric chloride 105

LIST OF TABLES

Table 2.1 Arsenic concentration in rocks 13
Table 2.2 Principal modern uses of arsenic compounds 15
Table 2.3 Naturally occurring minerals containing arsenic 16
Table 2.4 Calculated ratios of arsenic concentrations in natural reservoirs with respect to soil 16
Table 2.5 Calculated arsenic rates of transfer 17
Table 2.6 Production rates of the main arsenical compounds 17
Table 2.7 Chemical properties of arsenic 19
Table 2.8 Arsenic compounds and species and their environmental and toxicological importance in water 21
Table 2.9 Chemical equilibria of arsenic and arsenious acid 22
Table 2.10 Simplified overview of analysis methods for testing of arsenic 28
Table 2.11 Maximum Concentration of arsenic found in ground water 29
Table 2.12 Arsenic concentration of natural water 30
Table 2.13 Arsenic poisoning from drinking water 31
Table 2.14 Preliminary USPEA health advisory values estimated to prevent diseases 31
Table 2.15 Case history of chronic arsenic intoxication from ingestion of arsenic 33
Table 2.16 Epidemiology of arsenic ingestion related to chronic toxicity and cancer 34
Table 2.17 Solubility products of various solid metal arsenates 40
Table 3.1 Arsenic contamination scenario in Bangladesh 45
Table 3.2 Overview of dearsenzation methods and their advantages and disadvantages 62
Table 4.1 Composition of ground water used in this study 68
Table 5.1 Composition of ground water used in this study 99

Chapter 1

INTRODUCTION

1.1 GENERAL

Access to safe drinking water in sufficient quantity is a basic requirement for human life. Safe drinking water is rarely found in the nature. In Bangladesh, there are two sources of water - surface water and groundwater. The surface water often contains pathogenic microorganisms responsible for waterborne diseases. Pathogenic contamination of water is the primary reason behind the prevalence of diarrheal diseases in Bangladesh, particularly in rural areas. The water supply in Bangladesh, particularly the rural water supply, is almost entirely based on groundwater which is extracted primarily by shallow tubewell. There are an estimated four million tubewells in rural Bangladesh. People have become accustomed to drinking tubewell water which is free from bacteriological contamination. Besides, people have become very familiar with the hand pump technology and can maintain their own tubewell water supply with minimum support from outside.

In recent years widespread arsenic contamination of groundwater has become a major concern for the hand tubewell based drinking water supply, particularly in the rural areas. Awareness about the presence of arsenic has been growing since late 1993 when arsenic was first detected in the district of Chapai Nawabgonj bordering the West-Bengal district of India. Since then higher levels of arsenic (exceeding the WHO standard of 0.01 mg/L and Bangladesh standard of 0.05 mg/L) have been detected in many regions of the country (Ahmed et al., 1997; Khan et al., 1998; Talukder et al., 1998; Safiullah et al., 1998; Tanabe et al., 1998; Ahmed and Ali, 1998). Affected areas and estimates of affected population are being updated as more data are becoming available. Out of 64 administrative districts of Bangladesh, arsenic contamination has so far been reported in 61 districts and an estimated 40 million people are at risk of arsenic toxicity. In a recent study by the National Institute of Preventive and Social Medicine (NIPSOM), arsenic related diseases (arsenicosis) have been identified in 37 districts (Ahmad et al., 1998). A total of 6000 cases were identified in 162 villages in the 37 districts, mostly in the rural areas. Among the identified patients, 53% were male, 47% female, and the most affected age group was found to be 20 - 40 years.

Arsenic toxicity has no known effective medicine for treatment, but drinking of arsenic free water can help the arsenic affected people to get rid of the symptoms of arsenic toxicity. There is an urgent need to ensure supply of arsenic free drinking water to the millions of arsenic affected people in Bangladesh. The options that are commonly suggested as possible alternatives to arsenic affected groundwater include: (1) Arsenic free deep tubewell water, (2) Surface water, (3) Rainwater harvesting, and (4) Treatment of groundwater for arsenic removal. While arsenic-free deep aquifers have been identified in some places, this option appears to be too expensive for large scale use in rural areas. The principal problem with surface water is bacteriological contamination. In addition availability of surface water is not uniform throughout the year. Rainwater harvesting can be a probable alternative. But seasonal variation in rainfall pattern, proper storage of rainwater and public acceptance are some of the issues that need to be adequately addressed. Groundwater treated for arsenic removal is another very promising option to provide arsenic-free water to the rural population. Since people are already accustomed to using groundwater and millions of tubewells are already there in the rural areas, this option can make use this available infrastructure. It should be noted that only water used for drinking and cooking purposes need to be treated; so volume of water that need to be treated would not be very high.

Various technologies have been used for removing arsenic from groundwater. The most commonly used technologies include co-precipitation with alum or iron; adsorptive filtration (e.g., using activated alumina); ion exchange; microbial process and membrane processes such as reverse osmosis. Ion exchange and membrane techniques appear to be too expensive for large scale use in Bangladesh. Apart from cost, both ion exchange and membrane techniques would require higher levels of technical expertise on the part of the user for operation and maintenance. Presence of high concentrations of iron in the groundwater, which precipitates as ferric hydroxide solids after extraction, would definitely interfere with the efficiency of membranes. Microbial processes are still at a development stage.

Arsenic removal by coagulation-adsorption- coprecipitation and by adsorption appear to be the most promising techniques for use in Bangladesh. However, recent experiences with adsorptive filtration devices designed for arsenic removal suggest that high iron concentration in groundwater of Bangladesh, which clogs the filter media, is a particular concern for such systems. Co-precipitation based systems can be developed with simple and easily available chemicals and may be cost-effective for use in Bangladesh. Coagulation with ferric chloride has been found to be an effective means of removing arsenic from water both at bench scale and pilot scale tests (Hering et al., 1996; Cheng et al., 1994; McNeill and Edwards, 1995; Scott et al., 1995; Edwards, 1994; Hering et al., 1997). In coagulation with ferric chloride, freshly precipitated amorphous ferric hydroxide, $Fe(OH)_3$ (am) is formed upon addition of the coagulant. Arsenic is primarily removed by adsorption onto the surface of $Fe(OH)_3$ (am) and subsequent co-precipitation. In general, ferric chloride has been found to be more effective in removing arsenic than alum on a weight basis and As(V) has been found to be more effectively removed than As(III). However, majority of the reported work used low initial arsenic concentrations (often less than 0.10 mg/l) in determining effectiveness of ferric chloride for its removal. In many studies synthetic water, rather than actual groundwater, was used. In view of the reported higher concentration of arsenic in Bangladesh, effectiveness of ferric chloride in removing arsenic from groundwater need to be tested for arsenic concentrations typical of those reported in Bangladesh. The level of treatment achievable with higher initial arsenic concentration is also important since the World Health Organization (WHO) has already reduced its recommended limit for arsenic in drinking water from 0.05 mg/l to 0.01 mg/l and the limit is currently under review in a number of other countries. Such a revision of arsenic standard may also be forthcoming in Bangladesh. Effects of source water composition (e.g., pH, SO_4, PO_4) on arsenic removal by ferric chloride also need to be evaluated keeping in view the typical composition of groundwater in Bangladesh. In

Bangladesh, arsenic removal by adsorption and co-precipitation onto coagulated flocs of ferric hydroxide could be a very effective technique, particularly in view of the presence of elevated levels of iron in many regions of the country. Water from hand-pump tubewells in about 65% of the country contains dissolved iron in excess of 2 mg/l and in many areas dissolved iron concentration is as high as 15 mg/l (Hossain and Huda, 1997). Arsenic has often been found to be associated with high iron concentrations. Naturally present iron, which forms ferric hydroxide flocs upon extraction, therefore, can play an important role in removing arsenic from groundwater.

1.2 OBJECTIVES OF THE PRESENT RESEARCH

The major objectives of this research work were:

- To evaluate the removal efficiency of arsenate [As(V)] and arsenite [As(III)] by coagulation with ferric chloride;
- To evaluate the effects of various parameters (i.e., initial arsenic concentration, sorbate/sorbent ratio) on removal efficiency;
- To evaluate the effect of pre-oxidation of arsenite (to arsenate) on its removal efficiency from groundwater;
- To evaluate the need for pre-oxidation in arsenic removal by ferric chloride in Bangladesh;
- To determine the doses of ferric chloride (and oxidizing agent) required for removal of arsenic present at different initial concentrations;
- To evaluate the effect of source water composition, especially effect of pH and phosphate, on arsenic removal by ferric chloride.

1.3 SCOPE OF THE STUDY

This study evaluates the removal efficiency of arsenic from groundwater by adsorption onto coagulated flocs of ferric hydroxide upon addition of ferric chloride. The natural groundwater used in this study was spiked with required quantity of As(V) and As(III) stock solutions to achieve the required concentration of arsenic . Ferric chloride solution was added to achieve the required concentration of iron to form the ferric hydroxide flocs. No attempt was made to adjust pH. In this study, effects of pre-oxidation of arsenite on its removal efficiency from groundwater also evaluated. To study the effect of pre-oxidation on removal efficiency of arsenite, groundwater spiked with As(III) was first treated with required dosages of commercial bleaching powder before addition of ferric chloride. The needs for pre-oxidation in arsenic removal from groundwater of Bangladesh were also evaluated. This study was conducted under the laboratory condition where mixing was conducted mechanically duration of mixing ,time of settling of flocs were same for different tests. Effects of mixing energy on arsenic removal was not evaluated in this study. The important parameters such as initial concentration of arsenic, sorbate/sorbent ratio, the effects of source water composition, especially effects of phosphate and pH were also evaluated in this study.

1.4 METHODOLOGY

Efficiency of $FeCl_3$ in removing As(V) and As(III) from groundwater was evaluated in a series of jar tests. All jar tests were conducted in 1 L glass beakers using arsenic-free groundwater spiked with As(V) and As(III) standard solutions. The arsenic-free groundwater was collected from the groundwater supply at Bangladesh University of Engineering and Technology (BUET), Dhaka. Groundwater is extracted using a number of deep tubewells at the BUET premises and is supplied directly to different academic and administrative buildings through a distribution system. Groundwater samples collected from a tap at the Environmental Engineering Laboratory of the Department of Civil Engineering, BUET were found to be free from arsenic. This arsenic free tap water was used in all jar tests. Groundwater collected from the tap was analyzed for detailed characterization a number of times during the course of the study. As(V) stock solution was prepared by dissolving its sodium salt $Na_2HAsO_4.7H_2O$ in distilled water, while As(III) stock solution was prepared by dissolving arsenic trioxide (As_2O_3) in distilled water containing sodium hydroxide (NaOH). Required quantity of As(V) or As(III) stock was added to the beakers to achieve the desired initial arsenic concentrations. Ferric chloride stock solution (prepared by dissolving $FeCl_3.6H_2O$ to distilled water) was then added to the beakers to achieve iron concentration ranging from 1 to 25 mg/L. No attempt was made to adjust pH of the samples. The beakers were then subjected to 1 minute of rapid mixing with 45rpm, 15 minutes of slow mixing with 15rpm, and the flocs were then allowed to settle for 30 minutes. Clear supernatant samples were then collected using a pipette from about 2 cm below the liquid surface. The supernatant samples were analysed for arsenic and iron concentrations. In all cases 200 ml samples were collected for arsenic analysis; 10 to 50 ml samples were collected for iron analysis. In the jar tests, initial pH of groundwater and final pH after coagulation were recorded.

To evaluate the effects of pH, pH adjustments were made with sodium hydroxide (NaOH) or hydrochloric acid (HCl) solutions. In each beaker, pH of the supernatant was measured with a pH meter. Effect of phosphate (PO_4) on arsenic [As(V)] removal also evaluated in similar experiments where the beakers were spiked with standard solution of potassium dihydrogen phosphate (KH_2PO_4) to attain desired phosphate concentration. Residual phosphate concentration in the supernatant after coagulation was also determined for a limited number of experiments.

In all cases, removal of arsenic was calculated by subtracting arsenic concentration in the clear supernatant from the initial concentration. Concentration of iron present as ferric hydroxide flocs was calculated by subtracting the residual iron present in the supernatant solution from the iron added to water as ferric chloride.

All chemicals, except bleaching powder, used in this study were of reagent grade. Commercial bleaching powder available in the market was used in this study. Arsenic concentrations in this study were determined using Silver Diethyldithiocarbamate Method (Standard Methods, 1985). In all cases 200 ml samples were collected for analysis of arsenic and volume (200 ml) of the samples were reduced to about 35 - 40 ml in an water bath before analysis. Detection limit of arsenic for the Silver Diethyldithiocarbamate Method is about 1 μg and 200 ml samples were collected to detect lower concentrations of arsenic. With a detection limit of 1 μg and an initial sample volume of 200 ml, the lowest detectable concentration was therefore 5 μg/l or 0.005 mg/l. Iron concentrations were determined by colorimetric method (potassium thiocynate method). Detailed characterization of groundwater used in this was carried out by analyzing it for pH, conductivity, alkalinity, hardness, chloride, phosphate, nitrate, sulphate, iron, manganese, calcium, magnesium, sodium and potassium.

1.5 ORGANIZATION OF THE THESIS

Apart from this chapter, the remainder of the thesis has been divided into five chapters. Chapter 2 presents literature review concerning occurrence of arsenic, sources of arsenic, uses of arsenic and behavior of arsenic in the environment. This chapter emphasizes the chemistry of arsenic and oxidation of arsenic. The effect of arsenic on health is also discussed in this chapter.

Chapter 3 briefly reviews the status of arsenic contamination in Bangladesh, and a short overview of arsenic contamination of drinking water in other countries. A detailed review of arsenic removal technologies and the relative merits and demerits of the different technologies have been discussed.

Chapter 4 represents the results of arsenic (both arsenate and arsenite) removal from groundwater by coagulation with ferric chloride. The effects of initial arsenic concentration, coagulant dose, and the effects of pre-oxidation of arsenite to arsenate are also discussed. In addition, effects of sorbate/sorbent ratio and adsorption density on arsenic removal have been discussed. Requirement of ferric chloride doses for arsenic removal is also presented in this chapter.

Chapter 5 represents the effects of source water composition on removal of arsenic from water during coagulation with ferric chloride. This chapter provides a detailed discussion on the effects of various constituents of water on arsenic removal. This chapter mainly emphasized the effects of phosphate and pH on removal and presents experimental results on the effects of pH and PO_4 on arsenic removal. Possible implications of high concentration of phosphate in the groundwater environment have been discussed in details in this chapter.

Finally, chapter 6 presents major conclusions of the study and also provides recommendations for future study.

Chapter 2

LITERATURE REVIEW

2.1 INTRODUCTION

Arsenic is a naturally occurring element. Pure arsenic is a gray metal which is usually found in the environment combined with other elements such as oxygen , sulfur and iron. Arsenic may be found in organic form when it is combined with carbon and hydrogen. Arsenic and arsenical compounds are extremely toxic. Sometimes arsenic occurs naturally scattered in the soil, from where it leaches into ground water. Sometimes it may be found in effluents of different industries. This chapter presents a review of literature concerning occurrence, source, chemistry and health effects of arsenic and its behavior in the environment.

2.2 HISTORICAL REVIEW

Arsenic is derived from the Greek word for orpiment (Forbes, 1964). In the forth century B.C., Aristotle named arsenic sulfide as sandarach (Nriagu,1994). The name is probably connected with the root sand- or sard-, meaning red. Ancient Indian cultures valued arsenic compounds during the age of Buddha. The magnitude of names for white arsenic in Sanskrit (Sankh and Sabala Kshara), Hindi (Sanbul-Khar, Sammal khar, Sankhyia sanbul, and Sankyhia), and Bengali (Sanka or Senko) suggest general familiarity and extensive use of this compound presumably in some nefarious ways (Bagachi,1969).

The discovery of elemental arsenic is generally credited to the German Dominican scholar and alchemist Albertus Magnus (1193-1280) (Nriagu,1994). His description of a substance (De Rebus Metallicis) in arsenic compounds is supposedly the first reference to the metallic form of arsenic (Nriagu,1994). According to Berthelot (1893), metallic arsenic was first mentioned in the third or forth century by Zosimus, who referred to it as a second mercury that burns up to the "soul of the color" or white oxide. Geber (Jabir ibn-Haiyan), an Arabian alchemist of the eight century, apparently produced arsenic from its sulfides, but his product was not recognized a metal (Parr, !958). In 1641, Schorder, in his pharmacopoeia, divulged a procedure for obtaining elemental arsenic through the reduction of arsenious oxide with charcoal (Aitchinson, 1960). Meyer postulated that arsenic was first prepared by western alchemists in the thirteenth century. Later, in 1675, Leery obtained a regales, a metallic arsenic, by heating arsine's oxide with soap and potash (Aitchinson,1960). Brand, in 1733, carried out the first accurate experiments on the chemical nature of arsenic and showed that white arsenic was the clax or oxide of the element (Hunter,1978).

2.3 OCCURRENCE OF ARSENIC

Arsenic ranks 20th in abundance in the earth's crust. It is associated with igneous and sedimentary rocks, particularly with sulfidic ores. Natural phenomena such as weathering, biological activity and volcanic activity, together with anthropgenic inputs are responsible for the emission of arsenic into the atmosphere, from where it is redistributed on the earth's surface by rain and dry fallout. Arsenic is also mobilized by dissolution in water, with aquatic and soil sediment concentrations being controlled by a variety of input and removal mechanisms (Cullen and Reimer, 1989) . There is general agreement that most anthropogenic atmospheric input is due to smelting operations and fossil fuel combustion, but still unresolved is the extent to which man's activities contribute to the overall arsenic cycle (Edlestein,1985). Fig 2.1 shows a simplified, comprehensive cyclic of transfer of arsenic (after Bhumbla and Keefer, 1994). Because both natural and anthropogenic inputs vary geographically, environmental substrates show wide ranges of arsenic concentration. Even crustal levels, which are often quoted as 3 ppm, display values from 0.1 to several hundred ppm , depending on the types of rocks being considered (Cullen and Reimer, 1989). The natural content of arsenic in soils is usually 5 ppm (Vinogrador,1959; Backer and Chesnin ,1975) to 6 ppm (Bowen, 1979). The levels of arsenic may be much higher in soils contaminated by human activities (Huang Yan-chu, 1994). In nature, arsenic goes through the reactions of oxidation - reduction, precipitation- dissolution, adsorption - desorption and organic and biochemical methylation. All of these reactions control the mobilization and bio-accumulation of arsenic in the environment (Bhumbla and Keefer, 1994) .

The presence of arsenic in igneous, metamorphic and sedimentary rocks generally results in its presence of in the water phase. In Table 2.1 arsenic concentrations in different rocks are presented. Arsenic concentrate in some minerals, for instance, arsenic readily substitutes silicon, iron(III), and aluminium in crystal lattices of silicate minerals (Onishi and Sandell, 1955). Concentration of arsenic tends to be high in volcanic glass, aluminisilicate minerals and igneous rocks containing iron oxide. Sedimentary rocks, generally contain higher

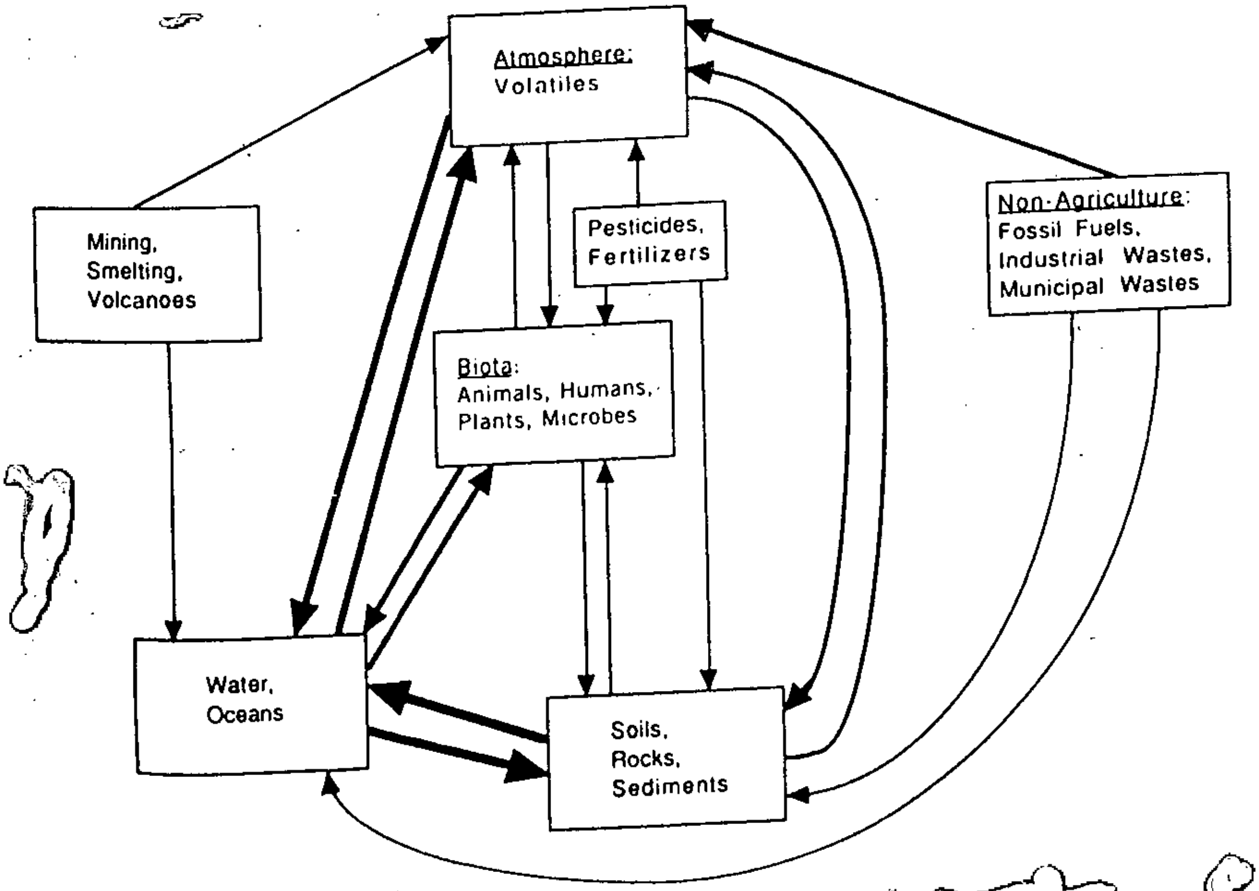

Figure 2.1 A simplified comprehensive cyclic of transfer of arsenic (after Bhumbla and Keefer, 1994)

concentration of arsenic than igneous and metamorphic rocks. Arsenic in non-marine shales /clays has been adsorbed by clay minerals, whereas arsenic associated with marine shales/clay is present in pyrites and organic matter (Tourtelot, 1964). High arsenic concentrations in phosphorite have been positively correlated with the organic and the iron content (Stow, 1969) of the rock. The capacity of a sediment to retain and concentrate arsenic is primarily controlled by grain size (Horowitz, 1984), because a finer grain size results in a greater surface area so a greater adsorption capacity per unit weight. Any retention of arsenic by soils would occur by adsorption, especially if the soils contained iron or aluminum oxides (Livesey and Huang, 1980).

2.4 USES OF ARSENIC

2.4.1 Historical Uses

The use of arsenic is recorded 2000-3000 years ago in the orient. Orpiment and realger are occasionally cited in Akkadian texts as ingredients of paints and for ornamental or cosmetic purposes (Forbes, 1964). The yellow sulfide of arsenic was known to the classical painters as *aurpigmentum* and was a common ingredient in most of the colors used in the Middle Ages for painting, and also for writing and in imitation of gold (Thompson, 1956). Arsenic bronzes were made by the Egyptians, who used it with copper and tin in making metal mirrors (Derry and Williams, 1961). Arsenic was also used in the third millennium to produce a silvery surface effect on mirrors and animal statuettes and as one of the fluxing ingredients in the manufacture of glass (Coghlan, 1975). Arsenic is cited in the first treatises on glasses as one of the fluxing ingredients in glass manufacture (Nriagu, 1994). Its effects are produced by crystallization during the cooling of the glass (Singer et al., 1957).

The main uses of arsenic compounds in antiquity were pharmaceutical and medicinal. At the beginning of the sixteenth century, the revolutionary Paracelcus designated arsenic, along with opium, mercury, lead, and copper sulfate as part of the modern pharmacopoeia (Hunter, 1978). Some arsenic compounds, mainly arsenate of potash, which was prepared by fusing the trioxide with salpeter, seemed to be greatly favored as a medicine by Paracelcus, who named it *arsenicum fixum* (Meyer,1975).

Table 2.1 Arsenic Concentration in Rocks

Type of rock	Arsenic (mg/kg)
Igneous (Boyle and Jonasson, 1973)	
- *Ultrabasic:*	
Peridotite,dunite, Serpentinite	0.30-15.8
- *Basic:*	
Basalt(extrusive)	0.18-113
Gabbro(Intrusive)	0.06-28
- *Intermediate*:	
Latite,andesite, trachyte(extrusive)	0.50-5.8
Diorite,granodiorite, syenite(intrusive)	0.09-13.4
-*Acidic:*	
Rhyolite(extrusive)	3.20-5.4
Granite(intrusive)	0.18-15
Metamorphic rocks (Boyle and Jonasson,1973)	
Quartize	2.20-7.6
Slate/phylite	0.50-143
schist/gneiss	0.0-18.5
Sedimentary rocks (Onishi,1978)	
- *Marine:*	
shale/claystone(near shore)	4.0-25
shale/claystone (off shore)	3.0-490
Carbonates	0.1-20.1
Phosphates	0.4-188
Sandstone	0.6-9
- *Nonmarine:*	
Shales	3.0-12
ClayStone	3.0-10

Until the nineteenth century, arsenic (As_2O_3) was the preferred poison of most homicidal practitioners, to the point where laws were passed against possession of it (Emsley, 1985). Despite this, Flower's solution (1% potassium arsenate, discovered in 1786) became the most widely used medication for a variety of illness for 150 years (Frost, 1984). Donovan's solution (arsenic iodide) and deValagin's solution (arsenic trichloride) were also recommended to treat rheumatism, arthritis, asthma, malaria, trypanosome infections, tuberculosis, and diabetes (Leonard, 1991). Several poisoning cases have been reported from the historical use of arsenical pigments for coloring artificial flowers, toys, wallpaper, and wrapping papers (Nriagu, 1994). A vast literature exists regarding the hypothesis that arsenic poisoning was the cause of Napoleon's death, due to its presence in the green pigments of the wallpaper (Jones, 1982; Richardson, 1974). White arsenic sublimes on heating and it has been claimed that candles with poisoned wicks were used to poison Leopold I of Austria in 1970 (Nriagu,1994). In fact, death lamps in which oil and wax impregnated with arsenic and other substances are burned have been used to poison victims slowly (Gimlette and Desmond, 1981).

2.4.2 Modern Uses of Arsenic

Elemental arsenic has few uses, one of which is to impart more nearly spherical shape in the manufacture of lead shot. It is also used in certain alloys to increase strength at elevated temperatures, in bronzing and in pyrotechniqes. All naturally occurring arsenic consists of the stable isotope arsenic-75; the radioactive isotopes arsenic-72,-74, and -76 have been used in medical diagnostic procedure. Arsenic oxides is utilized in pesticides and serves as a decolorizer in the manufacture of glasses and a preservatives for hides. Arsenic pentoxides comprises a major ingredient of insecticides, herbicides, and metal adhesive. Arsine (AsH_3) has been used as a doping agent for semi-conductor and as a military poison gas. The arsenic sulfides are used as pigments and in pyrotechnics. $NaH_2AsO_4.H_2O$ on heating forms a variety of condensed oxo-anions, such as $Na_2H_2As_2O_7$, $Na_2H2As_3O_{10}$, and $(NaAsO_3)_n$. Some salts such as lead arsenate and calcium arsenate are useful for sterilizing soils and controlling pests, respectively. The dihydrogen arsenic itself is used in medicine as are several other arsenic compounds. Most of the medicinal uses of arsenic compounds depend on their toxic nature. From the 1860s until the introduction of DDT and other organic pesticides in the 1940s, inorganic compounds of arsenic remained the dominant insecticides available to farmers and fruit growers (Nriagu and Azcue,1990).

The major use of arsenic, about 75% of the total consumption, still is in the agricultural field in the form of monosodium methylarsonate (MSMA), di-sodium methylarsonate (DSMA), dimethylarsinic acid (Cacodylic acid), and arsenic acid (Nriagu and Azcue, 1994). Arsenic acid is used in the formation of wood preservative salts and sodium arsenate solutions are used for debarking trees, in cattle and sheep dips, and in aquatic weed control. Minor additions of arsenic (0.02-o.5%) to copper and copper alloys raise the re-crystalization temperature and improve corrosion resistance (Carapella, 1978). Main modern uses of arsenic are shown in Table 2.2.

Table 2.2 Principal Modern Uses of Arsenic Compounds

Sector	Uses
Agriculture	Pesticides, Insecticides, defoliants, wood preservatives, debarking trees, soil steriliant
Livestock	Feed additives, disease prevention (swine dysentry, heartworn infection), cattle and sheep dips, algaccides
Medicine	Antisyphylitic, drugs, treatment of trypanosomiasis, amebiasis, sleeping sickness
Electronics	solar cells, optoelectronic devices, semiconductor applications, light-emitting diodes (digital watches).
Industry	Glassware, electrophotography, catalysts, pyrotechnics, antifouling paints, dyes and soaps, ceramics, pharmaceutical substance
Metallurgy	Alloys(automotive body solder and radiators), battery plates (hardening).

2.5 SOURCES OF ARSENIC

2.5.1 Natural Sources of Arsenic

Arsenic is a component of more than 245 minerals (Fredrick et al., 1994). These are mostly ores containing sulfide, along with copper, nickel, lead, cobalt or other metals. The most important ores are arsenopyrites or mispickel (FeS), realger (As_4S4), orpiment (As_4S_6), cludite, Iolligngite ($FeAs_2$), nicoliote (NiAs), cobalt glance (CoAsS), Gersdroffite (NiAsS) and smaltite ($CoAs_2$). Within these minerals, arsenopyrite is probably the most common mineral . Table 2.3 shows some naturally occurring minerals containing arsenic. Arsenic and its compounds are mobile in the environment. Weathering of rocks converts arsenic sulfides to arsenic trioxide, which enters the arsenic as dust or by dissolution in rain, rivers or groundwater (Clifford and Zhang, 1993). Volatile forms of arsenic e.g., arsine (AsH_3) and trimethyl arsine [$(CH_3)_3As$] enter the atmosphere from land and water, are returned by rain and atmospheric fallout. The oxidized forms of arsenic are converted back to sulfides by anaerobic processes occurring on land and water sediments (Tamaki, 1992). The concentration of arsenic in natural reservoir with respect to soils have been shown in Table 2.4. The rates of transfer of fluxes among the individual reservoirs are shown in Table 2.5. Soils and oceans are the remaining major reservoirs that have much more inherent arsenic than do biota (plants, animals, man, and microbes) and the atmosphere. The average concentration of arsenic in soils of the world is 7.2 ppm (Anoonymous, 1978). Arsenic in the natural environment occurs in soils at an average concentration of about 5 to 6 mg/kg, but this varies among geographic regions (Peterson et al., 1981).

Table 2.3 Naturally Occurring Minerals Containing Arsenic (NRCC, 1978)

Endogenous	**Formula**	**Supergeneous**	**Formula**
Arsenite	As	Arsenolite	As_2O_3
Antimony arsenide	$AsSb$	Mutite	$Pb_5(PO_4,AsO_4)_3Cl$
Realger	AsS	Adamite	$Zn_2AsO_4(OH)$
Orpiment	As_2S_3	Erythrite	$Co_3AsO_4.8H_2O$
Arsenopyrite	$FeAsS$	Annabergite	$N_{13}(AsO_4)_2.8H_2O$
Nicolite	$NiAsS$	Scorodite	$(Fe.Al)AsO_4.2H_2O$
Gersdorffite	$CoAsS$	Pharmacosiderite	$Fe_3(AsO_4)_2OH_3$
Cobaltite	$CoAsS$	Olivenite	$Cu_2(AsO_4)OH$
Smaltite	$(Co,Ni)\ As_x$	Beaudanite	$PbFe_3(AsO_4)SO_4$
Skutteridite	$(Co,Ni)As_x$		
Loellingite	$(FeAs_2)$		
Tennantite	$(Cu_{12}As_4S_{13})$		
Jordanite	$(Pb,Ti)_{13}As_7S_{23}$		
Pearcite	$Ag_{16}As_2S_{12}$		
Proustite	Ag_2AsS_3		
Energite	Cu_3AsS_4		
Rathite	$Pb_3As_5S_{10}$		

Table 2.4 Calculated Ratios of Arsenic Concentrations in Natural Reservoirs With Respect to Soil (Mackenzie et al., 1979)

Reservoir	**Approximate ratios with respect to soil**
Rocks	25,000
Oceans	4
Soil	1
Biota	0.0005
Atmosphere	0.000001

Table 2.5 Calculated Arsenic Rates of Transfer (Mackenzie et al., 1979)

From:	**To:**	**Approximate Amount ($\times 10^8$ g/yr)**
Land	Oceans	3,000
	Atmosphere	1,000
	Biota	300
Atmosphere	Oceans	2,000
	Land	1,000
Oceans	Sediments	2,500
	Biota	1,300
	Dissolved	1,000
Sediments	Land	2,400
Mining, Smelting Terrestrial biota	Land	300
Volcanoes	Land	54
	Sediments	40
	Atmosphere	3

2.5.2 Anthropogenic Sources

Recent estimates have placed the ratio of natural to anthropogenic inputs of arsenic at 60:40 (Chilvers et al., 1985). The global production rates of arsenic compounds, determined in a recent surveys are shown in Table 2.6.

Table 2.6 Production rates of the main arsenical compounds (Alloway, 1990)

Compound	**Production (tons As/year)**
Herbicides	8,000
Cotton desiccant	12,000
Wood preservatives	16,000

The anthropogenic influence on the level of arsenic in soils depends on the human activity, the distance from the pollution sources, and the pollution dispersion pattern (Yan-Chu, 1994).

Arsenic may accumulate in soil through use of arsenical pesticides, application of fertilizers, irrigation, dust from the burning fuels, and disposal of industrial and animal wastes (Sandberg and Allen, 1975). It is a natural contaminant in lead, zinc, gold and copper ores and can be released during the smelting process (Crecelious et al., 1974; Ragaini et al., 1977; O'Toole et al., 1971; Rosehart and Lee, 1973). The stack dust and flue gases from smelters often contaminate soils with arsenic downwind from the operation (Crecelcious et al., 1974; Ragaini et al., 1977). Arsenic is also commonly associated with phosphate minerals, in an average concentration of 7.7 μg/l (Alloway, 1990).

2.6 CHEMISTRY OF ARSENIC

2.6.1 Chemical Properties

Arsenic is a chemical element in the nitrogen family (group VA of the periodic table), existing in both gray and yellow crystalline forms. It is widely distributed in nature, and occasionally found un-combined, usually in association with such metals as antimony and silver. It also occurs combined in its sulfides realger and orpiment; as arsenic oxide; and as a constituent of various metallic sulfides, of which arsenopyrite is the most abundant. Although some forms of arsenic are metal-like, it is best classified as non-metal (Encyclopaedia Britannica, 1994). There are three polymorphic modifications of arsenic. The cubic α- form is made by condensing the vapor at very low temperatures, is metastable, is soluble in CS_2, and consists of tetrahedral As_4 units. The black β-polymorph is isostructural with black phosphorous(II), also metastable, and both of these modifications revert to the stable γ form, gray or metallic, rhombohedral arsenic, on heating or exposure to light. Gray or metallic arsenic, which is more stable and more common than the softer yellow form, is very brittle, tarnishes in air, and sublimes when heated strongly i.e., it passes directly into a vapor without melting and reverts to the crystalline solid without liquefying upon cooling the vapor (Encyclopedia Britannica, 1994). The chemical properties are given in Table 2.7.

2.6.2 Some Principal Compounds of Arsenic

Because arsenic has a range of oxidation states from -3 to +5, it can form a variety of different kinds of compounds. Among the most important commercial compounds are the oxides, the principal forms of which are arsenious oxide (As_2O_3) and arsenic pentoxide (As_2O_5). Arsenious oxide, commonly known as white oxide, is the material most widely used for the synthesis of arsenic compounds. It is produced as a by-product of the nonferrous

Table 2.7 Chemical Properties of Arsenic (Encyclopedia Britannica, 1994)

Parameter	Value
Atomic number	33
Atomic weight	74.92158
Melting point (gray form)	814°C (1,497°F) at 36 atmospheres pressure
Density (gray form) (yellow form)	5.73 g/cc at 14°C (57°F) 2.03g/cc at 18°C (64°F)
Boiling point	616°C (1141°F) (sublimes)
Specific gravity(α,β,γ)	2.026, 4.7, 5.727
Oxidation number	-3, 0, +3 , +5
Electronic configuration	2-8-18-5 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
Electrical resistivity	33.3μohm cm (273 K)
Covalent radius	121 pm
Ionic radius (As^{3+})	69 pm
Metallic radius	139 pm
Toxicity level	0.5 mg.m^{-3} of air

metal industry, primarily from the smelting of copper ores. Naturally occurring metal arsenides, realgar, and orpiment also convert to the trivalent oxide when roasted in air. The formation of the trioxide by the roasting of a sulfidic ore is illustrated in Eq. 2-1.

$$2\,FeAsS + 5\,O_2 \rightarrow Fe_2O_3 + As_2O_3 + 2\,SO_2 \qquad (2\text{-}1)$$

Elemental arsenic undergoes reaction with oxygen to yield the trioxide as follows:

$$4\,As + 3\,O_2 \rightarrow 2\,As_2O_3 \qquad (2\text{-}2)$$

The direct reaction between the elements yields the trioxide most exclusively. The reaction in air proceeds very slowly, but the rate increases rapidly with increasing temperature, decreasing particle size, and the presence of moisture. The trioxide is moderately soluble in water, but dissolves easily in aqueous alkali to produce a solution of arsenic, AsO^{2-}. It is slightly soluble in polar organic solvents such as alcohols and ethers and insoluble in benzene. The most useful reagent for the synthesis of pentoxide (As_2O_5) is concentrated nitric acid. The reaction between elemental arsenic and nitric acid gives H_3AsO_4 . The controlled dehydration of this acid (Eq. 2-3) gives the pentoxide.

$$4\,H_3AsO_4 \rightarrow 6\,H_2O + As_4O_{10} \qquad (2\text{-}3)$$

Hypochlorous, chloric and perchloric acids also oxidize the metal or As_2O_3 , to the pentavalent state. Arsenic pentoxide dissolves readily in water to produce arsenic acid, H_3AsO_4.

Arsine (AsH_3) is the best known of the hydrides of arsenic. It is a colorless poisonous gas composed of arsenic and hydrogen. The gas also called arsenic hydride, is produced by the hydrolysis of metal arsenides and by the reduction by metals of arsenic compounds in acidic solutions. Other hydrides of arsenic are diarsine (As_2H_4), diarsine dihydride (As_2H_2), and polymeric diarsine monohydride $(As_2H)_x$.

Arsenic pentoxide, the anhydride of arsenic acid, H_3AsO_4, is very soluble in cold water and dissolves to form a solution of arsenic acid. The free acid can be obtained as a hydrate, $H_3AsO_4.0.5\ H_2O$, by the evaporation of a cold aqueous solution. Arsenic acid is strong as H_3PO_4. Arsenic trioxide is the anhydride of arsenious acid. The solubility of arsenic trioxide in water at 25°C is 21.6 g L^{-1}. The rate of dissolution of trioxide in water is painstakingly slow, sometimes requiring up to 50 h of continuous agitation. The free acid has never been isolated. The solubility of arsenic trioxide increases greatly and occurs much more rapidly in both acid and alkaline media. Metal salts containing orthoarsenate, AsO_4^{3-}, monohydroarsenate, $HAsO_4^{2-}$, and dihydrogen arsenate, $H_2\ AsO_4^-$ are known. Diarsenic disulfide, As_2S_2, but more properly written as As_4S_4, exists in nature as mineral realgar. As_4S_4 is normally prepared as an impure material and must be purified by sublimation under an atmosphere of CO_2. Diarsenic trisulfide, As_2S_3, is found in nature as orpiment, has been referred to yellow arsenic sulfide. Diarsenic pentasulfide As_2S_5, has been described a brownish- yellow, glassy, amorphous, and highly refractive. When suspended in water and heated, it decomposes into the thermodynamically more stable As_2S_3 and free sulfur. Two binary As-P compounds has been reported . They are As_2P and AsP. Diarsenic phophide is a black and lustrous and turning brown on exposure to air. AsP is described as a lustrous and red brown powder.

Arsenic also forms numerous organic compounds, as for example, tetramethyldiarsine, $(CH_3)_2As\text{-}As\ (CH_3)_2$, used in preparing the common desiccant cacodylic acid. Several complex organic compounds of arsenic have been employed in the treatment of certain diseases, such as amebic dysentry, caused by microorganism. Some of the most important compounds and species are shown in Table 2.8.

Table 2.8 Arsenic Compounds and Species and Their Environmental and Toxicological Importance in Water (Data from Stuart et al., 1996; Kartinen & Martin, 1995; WHO,1996)

Compounds	**Example**	**Aquatic environment**	**Toxicity**
Arsine	As^{3-}	Minor importance	Most toxic arsenic species
Elemental Arsenic	As	Minor importance	Least toxic As species
Trivalent Arsenic Arsenite Inorganic	As(III) H_3AsO_3 $H_3AsO_3^-$ $HAsO_3^{2-}$ AsO_3^{3-}	Anaerobic pH=0-9 pH=10-12 pH=13 pH=14	10× more than As(V)
MMAs(III) DMAs(III) TMAs(III) Organo-As(III)	$CH_3As(III)O_2^{2-}$ $(CH_3)_2As(III)O^{1-}$ $(CH_3)_3As(III)$	Several fungi & bacteria can methylate As(III)	Less than inorganic As(III)
Pentavalent arsenic Arsenate Inorganic	As(V) H_3AsO_4 $H_2AsO_4^{1-}$ $HAsO_4^{2-}$ AsO_4^{3-}	Aerobic pH=0-2 pH=3-6 pH=7-11 pH=12-14	10× less than As(III)
MMAs(V) DMAs(V) TMAs(V) Organo As(V)	$CH_3As(V)O_3^{2-}$ $(CH_3)_2As(V)O_2^{1-}$ $(CH_3)_3As(V)O$	Methylation through reduction of As(V) to As(III) minor importance	Less than inorganic As(V)

2.6.3 Chemistry of Arsenic in Water

Arsenic is stable in four oxidation states (+5, +3, 0, -3). The oxidation state is closely related to the arsenic immobilization and hence the release of arsenic from its geological formations into the water bodies and biosphere (Dahi,1997). Both the oxidation state and the release are determined by the soil and water pH, the redox potential, the in excess occurrence of sulfide, the occurrence of other ions as well as solids of especially iron and manganese (Dahi, 1997).

The oxides of both arsenic (III) and arsenic (V) are soluble in water. In reducing waters, arsenic is found primarily in the trivalent form [As(III)] and forms arsenious acid. Arsenic(V) forms arsenic acid. Arsenic acid and arsenious acid dissociate to form respectively arsenite and arsenate ions. Table 2.9 shows the reactions that governs the speciation of arsenic and their equilibrium constants. Figure 2.2 shows the predominance diagram of arsenic species as a function of pH.

Table 2.9 Chemical equilibria of arsenic and arsenious acid (Cherry et al., 1979)

Arsenic acid:

$H_3AsO_4 + H_2O = H_2AsO_4^- + H_3O^+$ pKa = 2.20

$H_2AsO_4^- + H_2O = H\,AsO_4^{2-} + H_3O^+$ pKa = 6.97

$H\,AsO_4^{2-} + H_2O = AsO_4^{3-} + H_3O^+$ pKa = 11.53

Arsenious acid:

$H_3AsO_3 + H_2O = H_2AsO_3^- + H_3O^+$ pKa = 9.22

$H_2AsO_3^- + H_2O = H\,AsO_3^{2-} + H_3O^+$ pKa = 12.13

$H\,AsO_3^{2-} + H_2O = AsO_3^{3-} + H_3O^+$ pKa = 13.40

From Fig 2.2, it is seen that arsenic acid is a more strong acid than arsenious acid. Within the range of natural waters, where pH is between 6 and 9, the trivalent inorganic arsenic is found as non-dissociated arsenious acid, while the pentavalent arsenic is primarily found as the ionised di-hydrogen arsenate and mono-hydrogen arsenate. The valency in which arsenic exists is related to both pH and the oxidation reduction potentials, Eh. The hypothetical electron activity at equilibrium, pE, is used interchangeably with Eh. These parameters are simply related by pE = (F/2.3 RT) Eh, where T is the absolute temperature, and F and R are the Faraday and gas constants, respectively (Cherry et al., 1979). Thus at 25°C, 2.3RT/F = 0.058 V mol^{-1} and pE= Eh/0.059. The equation linking arsenic speciation to pH and pE are readily available, but Eh versus pH diagrams (Fig 2.3), which indicate the predominant soluble species and relevant solids, are the most concise way of presenting this information (Cherry et al., 1979). The Eh-pH diagram for arsenic (total concentration 10^{-5} mol/l) in a system including oxygen, H_2O and sulfur (total concentration 10^{-3} mol/l) showing the predominant soluble species and the solids with solubilities low enough to occur this system is illustrated in Fig 2.3.

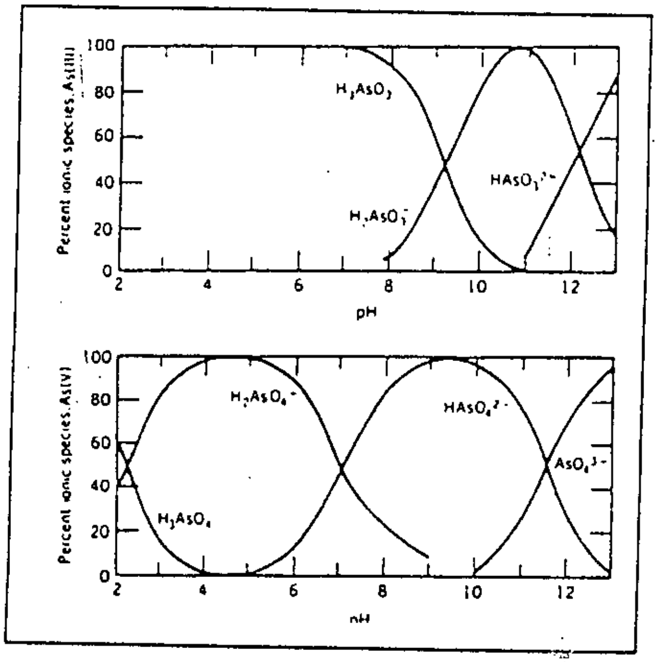

Figure 2.2 Predominance diagram of As(III) and As(V) as a function of pH (Gupta and Chen,1978)

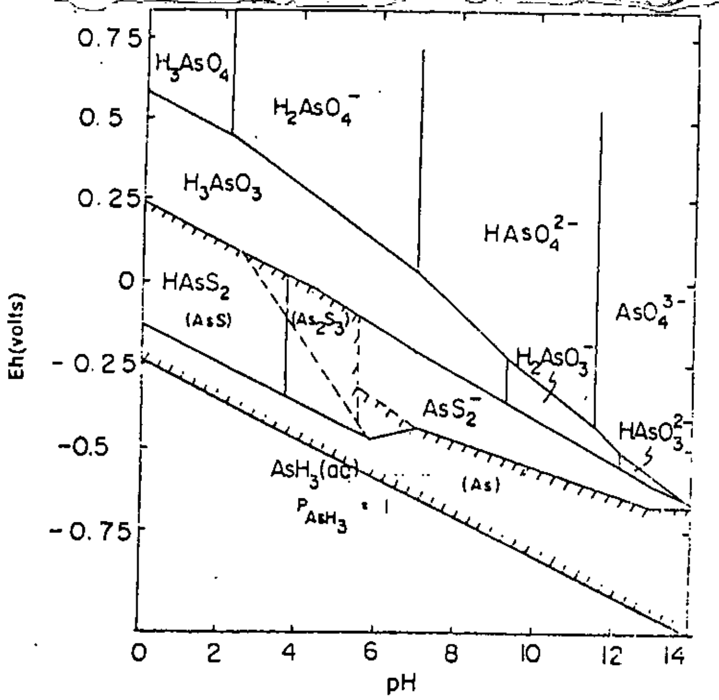

Figure 2.3 Eh-pH diagram of inorganic arsenic species (Ferguson et al., 1972)

The pE range for aquatic systems is restricted by the stability of water and extends (for pH 4 - 10) from approximately 17 to -10; beyond these limits water is oxidized to O_2 or reduced to H_2, respectively (Stumm and Morgan, 1981). Turner et al. (1979), proposed a simple equation, pE = 20.6 - pH, for the calculation of the electron activity in oxic systems. Regardless of the specific pE, it is apparent that in oxygenated waters (high Eh) such as surface water and shallow ground water, arsenic is found in the arsenic acid species of (in order of increasing pH) H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}. At moderate Eh conditions (i.e., generally deeper ground water) arsenic occurs as arsenious acid species of H_3AsO_3 , $H_2AsO_3^-$ and $H\ AsO_3^{2-}$. .At strongly reducing conditions (low Eh) arsenic will occur as As(III) . The pH -Eh diagram in Fig. 2.3 gives the specific conditions under which each of these species occur. By determining the pH and Eh of a solution it is possible to determine which species of arsenic will be prevalent. Speciation of arsenic samples into arsenite and arsenate is a reasonable method to determine the redox potential of natural waters (Cherry et al., 1979).

2.6.4 Oxidation of Arsenic

The effective removal of arsenic from water requires the complete oxidation of As(III), especially if the drinking water standard is low (Jekel and Van Dyck-Jekel, 1989). There are various means of oxidation available, but in drinking water treatment there are important considerations such as the limited list of chemicals, the residuals of oxidants, oxidation by-products and the oxidation of other inorganic and organic compounds. In oxygenated waters, As(V) is dominant, existing in anionic forms of either $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} over the pH range typically encountered in water treatment (pH 5 - 12). Under anoxic conditions, As(III) is stable, with nonionic (H_3AsO_3) and anionic ($H_2AsO_3^-$) species dominant below and above pH 9.22 (Edwards, 1994).

Although thermodynamics can provide an accurate prediction of possible changes in a given non equilibrium condition, they give no insight to the rate at which those changes will be occur (Edwards, 1994). In general As(III) and As(V) acid-base reactions can be assumed to occur instantaneously, whereas changes between oxidation states require indeterminate time periods in natural waters. For instance, the conversion of As(III) to As(V) in oxygenated water is thermodynamically favored, yet the transformation takes days, weeks, months depending on the specific conditions. Strongly acidic or alkaline solutions, the presence of copper salts, carbon, unknown catalysts and higher temperatures can increase the oxidation rate (Ferguson, 1972, and Johnson et al., 1972). Some technical and operational problems are to be expected where chemicals are added continuously to water in small-scale treatment plants and operators are not available all the time. In view of this some catalytic oxidation is done. Catalytic oxidation can be achieved by powered active carbon and dissolved oxygen in stirred reactors. The rate of oxidation can be described by a first-order equation, as demonstrated by the results in Fig 2.4, plotted in a semi-logarithmic diagram. The rate equation can be expressed for As(III) as follows:

$$C(As_t)/C(As_0) = \exp(-kt) \tag{2-4}$$

where C is concentration , t is time, and k is A constant.

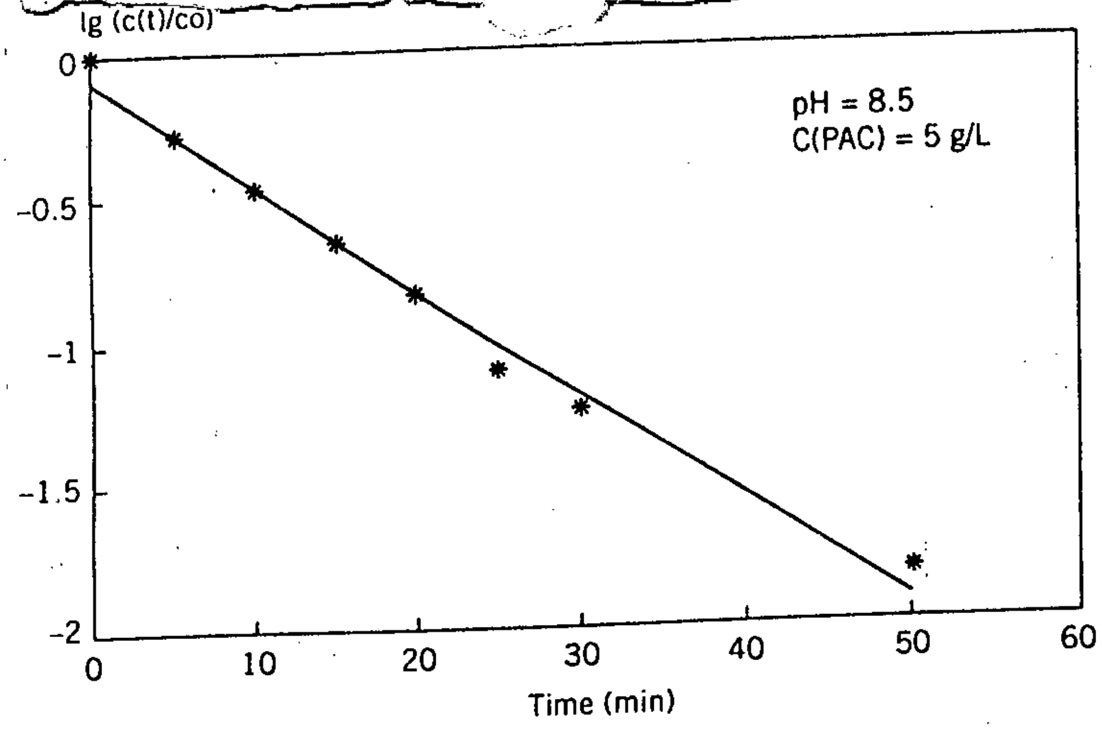

Figure 2.4 Rate of catalytic oxidation of As(III) in a linearized Plot According to a First-order Rate Equation. Experimental conditions: pH = 8.5; 5 g/L powdered active carbon; initial As(III): 40 ppb (Gottschalk et al., 1992).

Tests with varying conditions and chemical compositions of the water showed that the rate constant is proportional to the square root of the OH^- concentration (pH range 6-10). The rates of oxidation are not fast enough and high concentrations (5-10 g/L) of powdered active carbon are required to oxidized more than 90% of As(III) in 20 to 30 minutes (Jekel, 1994). For use in a treatment plant, this technique is not yet feasible, as the carbon must be removed again to residual concentrations of less than 1 ppm. The main problem appears to be the simultaneous adsorption of As(III) and oxygen on the solid surface in the first step of catalysis.

UV irradiation for As(III) oxidation requires high-pressure mercury lamps with an emission spectrum between 190 and 254 nm; low -pressure mercury lamps, with their main line at 254 nm, are ineffective. The rate of oxidation can also be described by a first order rate equation, but the rate constants are considerably higher compared to the activated carbon catalysis. Nearly complete oxidation can be achieved within 30 to 60 seconds but with a high-energy input of 3 to 4 kWh/m^3 treated water (Jekel, 1994).

In the oxidation processes with dosing of chemicals, effective oxidants are free chlorine, hypochlorite, ozone, permanganate, and hydrogen per oxide/Fe^{2+} (Fenton's reagent), but not the chloramines (Frank and Clifford,1986). These oxidants can directly transform As(III) to As(V) in the absence of oxygen (Frank et al., 1986; Lauf et al., 1993; and Oscarson et al., 1983). Chlorine is widely used for oxidation purpose, but may lead to chlorinated by-products, namely trihelomethenes (THMs), form reactions with natural organic matter. Ozone, widely used in surface water treatment for oxidation and disinfection, is quite effective but is not feasible for a specific application with As(III) oxidation. The most feasible oxidants to date are potassium permanganate and Fenton's reagent (H_2O_2/Fe^{2+}) for the removal of As(V) by precipitation-coagulation and rapid filtration (Jekel, 1994). Permanganate (a weak oxidant) oxidizes As(III), ferrous and manganese ions specifically and quickly. The manganese (IV) hydroxide which is formed must be filtered out afterwards, together with the precipitated As(V). Chlorine and permanganate are able to oxidize arsenic (III) to (V) within very short time, e.g., 1/2 an hour or even few minutes (Dahi, 1997).

Unexpectedly, As(III) oxidation has been observed to be independent of oxygen concentration in sea water (Johnson et al., 1972).

Arsenious acid oxidation by most common oxidants may be stated as follows (Dahi, 1997):

$$H_3AsO_3 + 1/2\,O_2 = H_2AsO_4^- + 2\,H^+ \quad (2\text{-}5)$$
$$H_3AsO_3 + HClO = H_2AsO_4^- + 2\,H^+ \quad (2\text{-}6)$$
$$H_3AsO_3 + 2/3\,MnO_4^- = H_2AsO_4^- + 1/3\,H^+ + 2/3\,MnO_2 \quad (2\text{-}7)$$

According to Jekel's study, of all the oxidation processes, the preferred means is potassium per manganate in cases with a subsequent precipitation/filtration step, and chlorine or hypochlorite where legally possible. If, however, an efficient catalytic procedure in a fixed bed reactor can be developed, oxidation by dissolved oxygen would be preferable, especially for small -scale plants. The reduction of As(V) to As(III) in the absence of oxygen is chemically slow and require and require bacterial medication (McBride et al., 1971).

2.6.5 Analysis of Arsenic

There is no shortage of analytical procedures for total arsenic determinations (Irgolic, 1983). Inorganic arsenic in water is commonly analyzed by means of colorimetric methods utilizing colored complexes formed with diethyldithiocarbamide or molybdate (APHA, AWWA, and WEF, 1995). Arsenic can be detected at very low concentration using a hydride generation inductively coupled plasma mass spectrometry (ICPMS) method (detection limit 0.02 μg/L), inductively coupled plasma (ICP) mass spectrometer(detection limit 0.4 μg/L), and atomic adsorption spectrometer with graphite furnace etc. As(III) and total inorganic arsenic can also be determined separately by using on-line pre-treatment in hydride generation atomic absorption spectrometry (Wolfgang et al., 1992). Table 2.10 shows the simplified overview of analysis methods for testing arsenic.

2.7 HEALTH IMPLICATIONS OF ARSENIC IN DRINKING WATER

2.7.1 Arsenic uptake and distribution

Human beings are exposed to arsenic in many different ways: by ingestion of contaminated water and food; by ingestion of contaminated water and food; by ingestion of arsenic containing medicinal preparations; by homicidal and suicidal ingestion of arsenic compound; by inhalation of arsenic containing dust or volatile arsenic compounds; and by adsorption

Table 2.10 Simplified Overview of Analysis Methods for Testing Arsenic (Dahi, 1998)

Methods	Advantages	Disadvantages
Flow Injection – Hydride generation-Atomic absorption spectrometry	-most sensitive, down to1-4 µg/L -least interference -most reproducible	-very high cost investment -very high cost of O&M -Dependency of foreign company specific parts -Dependency of imported chemicals -dependency on expert technicians
Hydride Generation – Scraper – Spectrophotometry	-medium sensitivity,e.g. 10-30µg/L -Medium reproducibility -normally low interference -relatively low cost of investment ,apart from spectrophotometer	-high cost of investment -high cost of O&M -dependency on imported chemicals -dependency on trained technicians
Hydride Generation – scraper –Indicator paper field kit	-relatively easy to use to field -Low investment costs -low chemical costs -easy to train on use	-quantitative indication of occurrence -low sensitivity -low reproducibility -risk of false negative response -high interference (solar irradiation) -Dependency on imported chemicals -dependency on trained technicians -Not yet tested and standardised

through skin and mucous membranes during the handling of arsenic compounds or through prolonged therapeutic usage of arsenic containing preparations (Luh et al., 1973). The concentration of arsenic in air is usually only a few ng As/m^3; the average national exposure in the united states has been estimated at 0.006 µg/L (USEPA,1988). Exposures may be higher in polluted areas for example, the concentration of arsenic in air may reach 1 µg/L As /m^3 near smelters or power plants that burn oil with a high arsenic content (Fredrick et al., 1994). Adsorption of inhaled arsenic ranges between 30 to 80 percent, depending on the relative portions of vapor and particulate matter. Food is a significant source of arsenic. Regional and individual eating habits greatly affect inorganic arsenic intake because some foods are relatively high in arsenic. For example, marine crabs, lobster, shrimp, and cod typically constain 10-40 mg As/kg based on fresh weight (Fredrick et al., 1994). In comparison, pickerel, catfish, coho salmon and other fresh water fish, along with pork and beef, typically contain < 1 mg As/kg. Studies indicate that the arsenic content of many foods is mainly inorganic arsenic, typically 65-75 percent (Weiler, 1987; Dabeka et al., 1993). However, fish, fruits, and vegetables primarily contain organic arsenic; less than 10 percent of the arsenic in these foods exists in the inorganic form. USEPA estimates that, overall, about 20 percent of total dietary arsenic intake is in an inorganic form. This estimate is important because inorganic arsenic intake is of primary concern; organic arsenic in foods is less toxic than inorganic forms and most is exerted rapidly. Organic forms of arsenic sea food, for example, are trimethylated, and most are excreted unchanged.

Ingestion of drinking water is an important source of arsenic exposure, and concentrations are generally highest in ground water, especially where geochemical conditions favor arsenic dissolution (Fredrick et al., 1994). In certain countries such as Taiwan, Chile, the United States, Germany, India and Bangladesh, there are numerous cases of arsenic existing in significant concentrations. Table 2.11 shows the typical arsenic concentration in ground water of different countries of the world.

Table 2.11 Maximum Concentration of arsenic found in ground water (after Pontious et al., 1994)

Country	Concentration of Arsenic (mg/L)
Taiwan	upto 1.82
Hungary	> 0.1
India	> 0.05
Mexico	> 0.4
USA	> 0.1
Chile	0.43
Bangladesh	> 0.5
China	> 0.2

Concentrations of arsenic surface water, although generally low, also may be high enough for concern under certain geological conditions. Table 2.12 shows the arsenic concentration in surface water of different countries .

Table 2.12 Arsenic concentration of natural water (after Wedephol, 1969)

Fresh water	**Concentration, μg/l**
Lakes in Greece	1.1-54.5
Lakes in Japan	0.16-1.9
Lakes in Wisconsin, USA	2-56
Rivers and lakes ,USA	10-1100
Rivers in Sweden	0.2-0.4
Rivers in Japan	0.25-7.7
Elbe River,Germany	20-25
Columbia River,USA	1.6

2.7.2 Acute Toxicity in Humans

Acute arsenic exposures (high concentrations ingested over a short time period) can cause a variety of adverse effect (Frederick et al., 1994). The severity of the effect depends primarily on the level of exposure. Acute high-dose oral exposure to arsenic typically leads to gastrointestinal irritation accompanied by difficulty in swallowing, thirst, abnormally low blood pressure and convulsions. Death may occur from cardiovascular collapse.

The respiratory tract, nervous system, and skin may be considered as the critical targets of prolonged arsenic exposures. Arsenic level in tissues and excreta are of limited importance on diagonsing chronic arsenic poisoning. The lethal dose (LD_{50}) to humans is estimated at 1-4 mg As/kg for an adult (Vallee et al., 1960, Winship, 1984). Short-term exposure to doses of greater than 500μg As/kg/d can cause serious blood, nervous system, gastro-intestinal, and other ill effects and also may lead to short death (USEPA, 1993). Short-term intake of doses from 30 to 300 μg As/kg/d has not caused serious effects in most people, but some may experience relatively mild effects (USEPA, 1993). Prolonged arsenic toxication results are shown in the Table 2.13.

USEPA recently presented preliminary calculations of the concentration of arsenic that can be ingested in drinking water over a one day, 10-day, and longer - term period without adverse health effects (other than cancer). These values are known as health advisories (HAs), summarized in Table 2.14. They conclude that short- term (1-90 days) or longer-term (2-3 years) intake of 50 µg As/kg/d can lead to gastrointestinal, liver, nervous system, and/or dermal effects. The values in Table 2.14 were calculated assuming 10 kg body weight for an adult, 1-L/d water consumption for a child, 2-L/d water consumption for an adult, and a uncertainty factor of 10.

Table 2.13 Arsenic Poisoning From Drinking Water

Sl. No.	Main organ	Effects	Reference
1	Nervous system disorders	Ataxia, paralysis, peripheral neuropathy	Valle et al., 1960
2	Respiratory system distress	Nasal septum perforation, bronchitis and cancer	Luh et al., 1973
3	Skin changes	Melanosis,dermatitises, hyperkeratosis and cancer	Ott et al., 1974;
4	Heart	Heart and occlusive arterial disease	Yeh, 1963; Hindmarsh et al., 1977
5	Liver	Liver cirrhoses and cancer	Zadivar,1977

Table 2.14 Preliminary USEPA health advisory values estimated to prevent adverse effects (other than cancer) from arsenic ingestion (USEPA, 1993)

Population	Exposure Duration	Health Advisory Value mg/L	Basis
Child	One day	0.05	A 1904 published report on the use of Flower's solution
Child	Ten day	0.05	1956 report on effects observed in adults exposed to arsenic in soya sauce
Child	Longer term	0.05	A 1975 report on effects observed in adults subchronically exposed to arsenic in medicinals
Adult	Longer term	0.05	Same as long term advisory for a child

Chronic exposure to low concentrations of arsenic are of primary interest when the health significance of arsenic in drinking water is evaluated (Frederick et al., 1994). The most common signs of long-term, low level arsenic exposure from drinking water are dermal changes, these include variations in skin pigments, hyperkeratoses and ulcerations (Tseng et al., 1968; Chen et al., 1988). Vascular effects are also associated with chronic arsenic exposure (Tseng,1977; Borgono et al., 1977). A small area on the southwest coast of Taiwan where Blackfoot disease, a peripheral vascular disease is endemic has been studied extensively (Tseng et al., 1968). Studies of Canada (Hindmarch et al., 1977) and the United States (Southwick et al., 1983) report neurological effects after chronic exposure from drinking water containing arsenic. Enlargement of the liver was observed in populations in India that were exposed to arsenic in drinking water (Abernathy and Ohanian, 1993).

Chronic arsenic poisoning resulted from chronic ingestion as little as 0.15- 3.3 mg As/day in drinking water and food prepared with water (Hindmarsh et al., 1977). Table 2.15 describes case histories of chronic arsenic intoxication. Table 2.15 shows that children are more sensitive to arsenic toxicity: a dose of 0.08 g/kg-body resulted in arsenic intoxication in an adult (Morris et al., 1974) whereas a 80 times less dose produced similar toxicity in a child (Kobayashi and Ohbe, 1971).

2.7.3 Arsenic Carcinogenesis

Arsenic is a known human carcinogen and has been classified as such by a number of carcinogen assessment groups including the U.S. Environmental protection Agency and the International Agency for Research on Cancers (Gibb, 1995). A carcinogenic risk of ingested arsenic has been reported in various populations throughout the world including populations of Taiwan, Mexico, Japan, Chile, Argentina, The United Kingdom, Germany. On the basis of current evidence, it appears that ingested inorganic arsenic increases the risk of cancers of the liver, kidney, and bladder, and possibly other internal sites (Bates et al., 1992). Inhaled arsenic has been shown to be associated with increased lung cancer risks in smelter worker populations in the United states, Sweden, and Japan. An increased skin cancer risk was also observed among the sheep dip workers. Table 2.16 presents the best evidence available regarding the possible carcinogenic of arsenic in the human body .

Studies indicate that an increased risk of cancer is evident even at low as 0.1- 158 $\mu g/m^3$ (Hill and Fanning, 1948). Dobson and Pinto (1966) suggested that a life time cumulative exposure of less than 1 g of arsenic is capable of effecting symptoms of chronic arsenic intoxication and an increased incidence of cancer. The frequency and severity of chronic arsenic intoxication correlate with the incidence of skin cancer. Yeh et al. (1968) studied the area of Taiwan where the incidence of Black-foot disease was high. They found that 89.7% of the patients with skin cancer, compared with 18.4% in a control group from another area, had hyper-pigmentation, and 71.7% had keratoses compared with 7.1% in a control group.

Table 2.15 Case History of Chronic Arsenic Intoxication From Ingestion of Arsenic

As dose (g/kg body weight)	Rate of exposure	Source of As	Subject to	Symptoms of toxicity	Incidence of Cancer	Latent period of cancer	Reference
0.001	0.12	Ingestion of arsenic tablets over 3 months	Child, female, 9 years	Diaarrhea, abdominal pain, hypoproteinemia, protein losing enterpathy,	No cancer	N.I.	Kobayashi and Ohbe ,1971
0.08	2.0	Ingestion of flower's solution over 3 years(age 50-53)	Adult male, 61 years	At 58 haematemesis, hyperjeratoses; at 61-pigmentation,liver andspleen enlarged,portal hypertension	N.I.	N.I.	Morris et al., 1974
0.11	2.6	ingestion of 1% As_2O_3 solution over 3 years (age 7-10)	Adult male, 36 years	N.I.	At 21- tongur carcinoma ; at 28 skin carcinoma on knee , palm , scrotum , lump nodes; at 29- Bowen's disease; at 36-epidermoid carcinoma metastasis	14	Minkowitz , 1964
0.30	1.8	ingestion of Flower's solution over 12 years(age 18-30)	Adult male,42 years	At 39- weakness , Melena, spleen palpable, non cirrhotic portal hypertension , keratoses	At 42- toungc carcinoma	21	Huet ct al., 1975
0.30	0.7	Ingestion of 1% As_2O_3 over 30 years age	Adult female	Keratoses, hyperpigmentation	Skin carcinoma	N.I.	Taub, 1970
0.40	1.2	Ingestion of Flower's solution over 22 years(age 35-57)	Adult male, 72 years	At 59-haematemasis, portal hypertension , at 72- keratoses	At 72- laryngeal and bronchial carcinomas	24	Morrish et al., 1974
0.20	1.0	Ingestion of Flower's solution over 3 years (age 22-37)	Adult male,43 years	At 43-melena, hyperkeratosis, hemoperitonium, enlarged liver	At 43- angiosarcoma of liver	21	Lender et al., 1975

Although arsenic may not act as a direct agent of visceral cancer, the literature provides cases of secondary carcinoma of internal organs, e.g., colon, bladder, gollbladder, pancreases, liver, ureter, prostate, lymph nodes and bronchia, as a consequence of metastases of primary skin cancer induced by arsenic exposure including ingestion, injection and inhalation (Jackson and Grainge, 1975; Rosset, 1958; Zaldivar, 1974). In the study by DeVilliers and Beker (1969) in Yellowknife, N.W.T., the incidence of leukemia was threefold greater in people exposed to arsenic than in the general Canadian population. The slow dose not reflect arsenic induced carcinoma until the latency period has been exceeded. No definite trend for the latent period of arsenic induced cancers and the level of arsenic exposure, although previous studies did find a negative correlation, i.e., a higher level of arsenic produced cancer with a shorter latent period (i.e., heavy exposure, 34 years; medium exposure, 39 years; light exposure, 41 years). Tseng et al. (1968) and Yeh (1973) observed that a minimum latency period also occurred with the classic symptoms of chronic arsenic poisoning, i.e.. 5 years for hyper-pigmentation and 4 - 15 years for keratoses.

Table 2.16 Epidemiology of Arsenic Ingestion Related to Chronic Toxicity and Cancer

Level of As exposure mg /L	**Sources of As**	**Subject**	**Age (yr)**	**Symptoms**	**% of incidence of cancer in exposed population**	**Reference**
0.00-0.29	Ingestion of As contaminated well water	Taiwan, Female	0-19 29-39 40-59 >60	Hyperpigmentation 17.6%, Keratoses 6.8%; Black foot disease 0.7%	Negligible 0.01 0.36 0.91	Tseng et al., 1968 Yeh. 1973
--	--	Taiwan, Male	0-19 20-39 40-59 >60	Hyperpigmentation 19.2%, Keratoses 7.5%; Black foot disease 0.9-1.2%	Negligible 0.15 0.65 4.81	Tseng et al., 1968 Yeh. 1973
>0.60	Ingestion of As contaminated well water	Taiwan, Female	0-19 20-39 40-59 >60	Hyperpigmentation 17.6%, Keratoses 6.8%; Black foot disease 0.7%	Negligible 0.35 4.80 11.00	Tseng et al., 1968 Yeh. 1973
--	--	Taiwan, Male	0-19 20-39 40-59 >60	Hyperpigmentation 19.2%, Keratoses 7.5%; Black foot disease 0.9-1.2%	Negligible 2.24 9.80 25.5	Tseng et al., 1968 Ych. 1973
0.01-1.82 (avg. 0.4-0.6)	Ingestion of As contaminated well water	Taiwan (China)	All ages	Hyperpigmentation 18.4%, Keratoses 7.1%; Black foot disease 0.89%, chronic arsenic 18.5%	1.06	Tseng et al., 1968 Yeh. 1973
--	--		>50	Hyperpigmentation 89.7-90.2%, Keratoses 79.7%;	100	Tseng ct al., 1968 Yeh. 1973
2.8-4.5	Ingestion of As contaminated well water	Coboda, Argentina	All ages	Chronic arsenicalism(Keratoses, liver and kidney ailments) 15%	High incidence	Jackson and Graingc, 1974 Zaldivar, 1974

2.8 DRINKING WATER STANDARDS FOR ARSENIC

The Tolerable Daily Intake, TDI, is an estimate of the amount of substance per kg of body weight that can be ingested daily over a life time without appreciable health risk. For a proven human carcinogen chemical like arsenic it is accepted that the threshold values, TDI, does not exist (Dahi, 1997). This is because, theoretically, there will always be a probability of harmful effect, i.e., risk at any level of exposure (Galal-Gorchev, 1997).

Estimated risks are normally based on 60 Kg person, drinking 2 L of water per day, for a life time of 70 years. The WHO guideline value for substances in drinking water is the concentration corresponding to an upper bound estimate of an excess lifetime cancer risk of 10^5. In other words GV is the concentration expected to give one additional cancer case per 100,000 people ingesting the water for 70 years .

On this basis the arsenic concentration for acceptable skin cancer risk is calculated to be 0.17µg /L. For practical limitation in available analysis methods, only a provisional guideline value of GV=10 µg /L is established (Dahi 1998). Thus the estimated excess lifetime skin cancer risk associated with exposure to 10 µg /L drinking water concentration for a lifetime of 70 years is : $P = (10\mu g /L. 10^{-5}) / o.17\mu g /L = 6.10^{-4}$; i.e., 6 additional skin cancer cases per 10,000 exposed.

For comparison the national standards adopted are 10µg /L in the European Union, 25µg /L in Canada and 50 µg /L in Bangladesh Standard (Galal – Gorchev, 1997).

2.9 ARSENIC MOBILIZATION IN THE ENVIRONMENT

2.9.1 Arsenic in the Atmosphere

Arsenic enters the atmosphere from natural sources that include volcanic activity, wind erosion, sea spray, forest fires, and low temperature volatilization (mainly biological formation of volatile arsenicals) (Cullen & Kenneth, 1989). Smelting operations and fossil fuel combustion contribute anthropogenic sources of arsenic (Edelstein, 1985). These inputs are balanced by removal processes such as dry deposition and rainfall (Cullen and Kenneth, 1989). Most anthropogenic emissions, such as smelting and fossil fuel combustion, consist of As_2O_3 (Pacyna, 1987). It was suggested that sea spray will mainly contribute arsenate

(Andreae, 1980) – the dominant species in seawater. However, arsenic speciation studies of rain and snow samples suggest that the ratio of inorganic oxidation states is not reflective of the arsenic source but is governed instead by redox changes in the atmospheric environment (Andreae, 1980). Using the lower arsenic content of rain , it is determined that 75% of the yearly global emissions of arsenic to the atmosphere were from pollution sources (Walsh et al., 1979).

It is estimated that the ratio of natural to anthropogenic inputs to atmosphere is 60:40 (Chilvers and Peterson, 1987). Natural sources of arsenic were largely comprised of low-temperature volatilization from soils (60%), with most of the remainder due to volcanic activity. Anthropogenic emissions are dominated by metal productions, especially copper smelting (40%) (Chilvers and Peterson, 1987).

Most of the of the arsenic in the atmosphere is in the form of particulate matter (Cullen and Kenneth, 1989). Less than 10% is present in the vapor phase or on particles smaller than 0.2 μm (Walsh, 1987; Mackenzie et al., 1979). Analysis of these solids has revealed that they are often considerably enriched (10-1000 times) in arsenic in comparison to the continental crust (Mackenzie et al., 1979). This is probably due to gas - particle reactions such as adsorption and/or complexation that capture volatile arsenicals (Johnson and Braman, 1975). It is common practice to trap these particles on filter paper but care must be taken in the subsequent extraction of adsorbed arsenic in order to preserve the speciation (Riggin et al., 1984) .

2.9.2. Arsenic in the Aquatic System

The range of water soluble inorganic arsenic compounds is quite limited and that pH is the major factor controlling the differences in aqueous arsenic speciation in the fresh water and the marine environments (Wagemann, 1978; Turner et al., 1981; Crecelius, 1986). Fresh water systems rarely exceed a pH range of 5-9 (Crecelisus et al., 1986) and the maximum pH distribution in sea water is even narrower (7.5- 8.3) (Broecker & Peng, 1982). Thus As(V) should strongly dominate over As(III) in oxygented waters. For example, As(V)/As(III) ratios of 10^{15}-10^{26} have been calculated for seawater (Andreae, 1979).

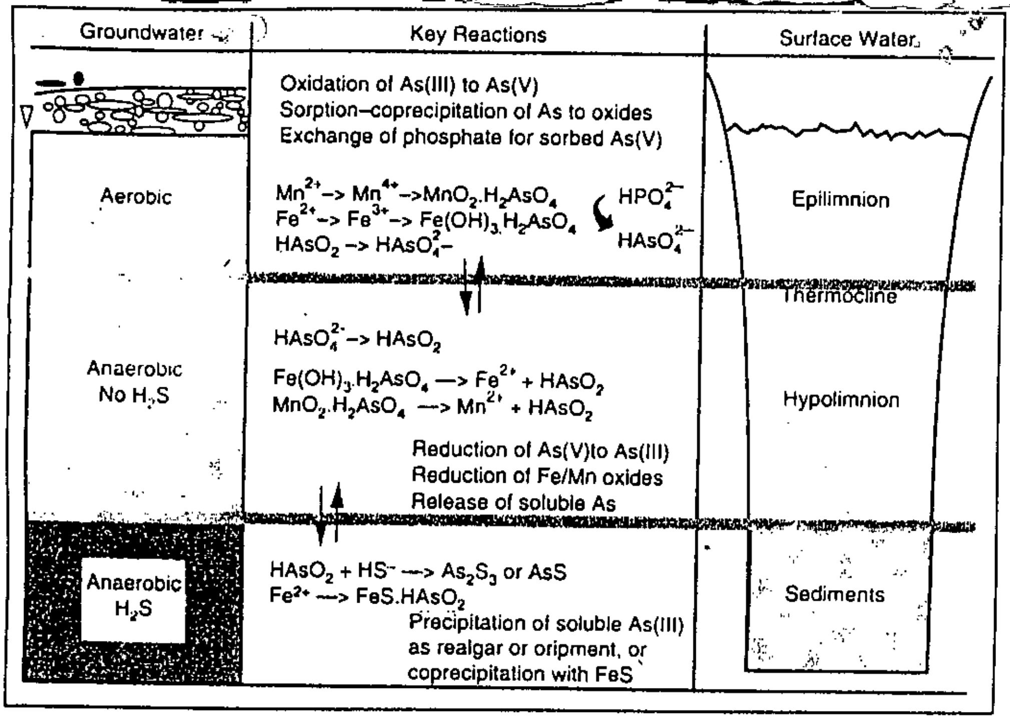

Figure 2.5 Arsenic Reactions in Aquatic Regimes (Edward, 1994)

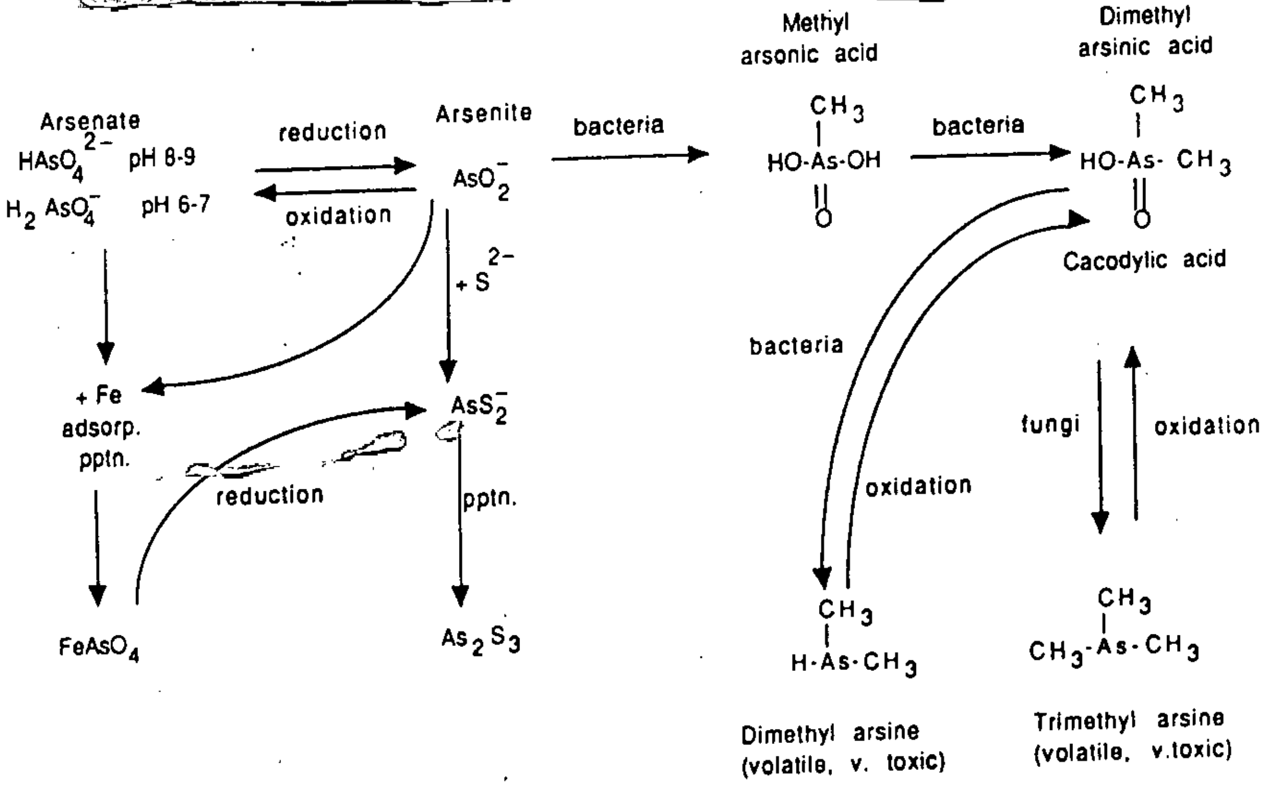

Figure 2.6 Chemical Forms of Arsenic and Their Transformation in Soils (Bhumbla and Keefer, 1994)

A cycle for arsenic in aquatic systems is illustrated in Fig 2.5. These reactions are generalized to a ground and surface water source and include transfers from solution to solid phases, and conversion from one oxidation state to another. For each water source, three distinct zones are demarcated; oxic, anoxic without sulfide and anoxic with sulfides (Edward, 1994). These zones might correspond to the eplimnion, hypolimnion and sediments within a strata, lake or analogously, to increasing depth with a ground water aquifer. In the aerobic epilimnetic water, reduced form of arsenic tends to be oxidized to arsenate which coprecipitates with ferric hydroxide (Ferguson et al., 1972). High concentration of orthophosphate may compete with arsenic for adsorption sites in this zone, increasing soluble arsenic concentration and mobility (Edward, 1994). Turbulent dispersion and convection transport some of the arsenate across the thermocline to the oxygen - depleted hypolimnion, where reduction to $HAsO_4$ and AsS_2^- take place, depending on the sulfur concentration and Eh (Ferguson et al., 1972). In anoxic regimes without sulphides, As(III) is stable and dissolved forms of iron and manganese are favored. Arsenic mobility (solubility) is highest in this zone because: (1) As(III) is believed to sorb strongly onto oxides than As(V) and (2) Coprecipitation-sorbed arsenic is released upon dissolution of arsenic-containing iron and manganese oxides (Edward, 1994). In anoxic zones with sulfides, As(III) becomes immobilized because of the formation of orpiment, realgar or is coprecipitated with iron pyrite.

Over 245 arsenic-containing minerals are known in nature and it is possible that the formation of such solids could limit environmental arsenic concentrations. Table2.17 summrizes the solubility products of several metal arsenates. Orpiment was found to be over saturated in the presence of sulfide at low Eh and low pH [$<2 \times 10^{-7}$ M at $\leq$ pH 7 as $HAsS_2$ (aq)] with slightly greater solubility [~ 1×10^{-5} M as AsS_2^- (aq)] at higher pH (Wagemann, 1978). Thus orpiment may provide a solubility control on dissolved arsenic at low pH and Eh and in the presence of high sulfide (0.1-10 μg/L, depending on the dissolved solids - i.e., other ion concentrations) (Wagemann,1978; Crecelius, 1986). However, sulfide activity may be limited by other element (Fe^{2+}) and arsenic sulfide may not reach saturation (Cherry et al., 1979). The conversion of orpiment to AsS_3^{3-} in neutral or alkaline solution will also increase arsenic solubility (Greenwood, 1951). $Ba_3(AsO_4)_2$ was over-saturated over a wide range of Eh, pH, and dissolved solid values (Wagemann, 1978; and Crecelius et al., 1986); but dissolved barium would be analytically undetectable even in waters with very low arsenic concentrations (Crecelius et al., 1986).

2.9.3 Arsenic in the Soil

Under reducing conditions, arsenite dominates in soils which is more mobile and soluble (Deuel and Swoboda, 1972), but elemental arsenic and arsine can also be present (Walsh and Keeny, 1975). Arsenate can be sorbed onto clays, especially kaolinite and montmolillonite (Frost and Griffin, 1977). The adsorption and retention of arsenic by soils control its persistence, activity, movement, transformation and ecological effects (Sieling, 1946; Dean and Rubins, 1947; Woolson et al., 1973b; Koyama, 1975). Arsenic adsorption is related to the pH, chemical and physical properties and cation exchange capacity of soils, and to the amount of arsenic in the soils (Norimoto and Osamu, 1982; Frost and Griffin, 1977; Zhou,1986; Xu et al., 1988).

Table 2.17 Solubility Products of Various Solid Metal Arsenates (Lenon et al., 1983)

Solid	Solubility Product
$AlAsO_4$	$1.6 * 10^{-16}$
$Ba_3(AsO_4)_2$	$7.7*10^{-51}$
$Ca_3(AsO_4)_2$	$6.8*10^{-19}$
$Cd_3(AsO_4)_2$	$2.2*10^{-33}$
$Co_3(AsO_4)_2$	$7.6*10^{-29}$
$Cu_3(AsO_4)_2$	$7.6*10^{-33}$
$CrAsO_4$	$7.8*10^{-21}$
$Fe AsO_4$	$5.7*10^{-20}$
$Mg_3(AsO_4)_2$	$2.1*10^{-20}$
$Mn_3(AsO_4)_2$	$1.9*10^{-29}$
$Ni_3(AsO_4)_2$	$3.1*10^{-26}$
$Pb_3(AsO_4)_2$	$4.1*10^{-36}$
$Sr_3(AsO_4)_2$	$8.1*10^{-19}$
$Zn_3(AsO_4)_2$	$4.0*10^{-28}$

In soils, arsenic forms solid with Fe, Al, Ca, Mg and Ni; however, there are no arsenic solids, other than As_2S_3, that have solubilities <0.05 mg/L (Gupta and Chen, 1978). Retardation of arsenic movement in soils is related to the concentration of phosphate present from fertilizers or wastes disposed on land, but is not related to variations in concentrations of Cl^- ,NO_3^-, or SO_4^{2-} (Livesey and Huang, 1981). Soluble arsenic concentrations are usually controlled by redox conditions, pH, biological activity, and adsorption reactions, but not by solubility equilibria (Bhumbla and Keefer, 1994). In both soil and water systems, arsenic species are subject to both chemically and microbiologically to oxidation and reduction (Walsh and Keeny, 1975). Soil components that contribute to sorption an retention of arsenic are oxides of Al, Fe, and Mn, soil mineralogy, and organic matter.

Chemical forms and their transformations in soils are illustrated in Fig 2.6. Oxidation, reduction, adsorption, dissolution, precipitation, and volatilization of arsenic reactions commonly occur. Some soil reactions are associated with bacterial and fungal microorganisms. Decomposition of any organic material added to soils (e.g., sewage sludge, sawdust, compost, manure, crop residues) yields organic substances that can adsorb arsenic (Bhumbla and Keefer, 1994).

The forms of arsenic present in soils depend on the type and amounts of sorbing components of the soil, pH, and the redox potential (Yan-Chu, 1994). The percentage of water - soluble arsenic is proportional to arsenic added to the soil , and inversely proportional to the iron and aluminum content (Woolson et al., 1973b). The water soluble fraction of arsenic was highest in soils with the lowest clay content and lowest in soils with highest clay content (Micheal and Russell, 1976).

Chapter 3

ARSENIC CONTAMINATIN IN BANGLADESH AND ARSENIC REMOVAL TECHNOLOGIES

3.1 INTRODUCTION

Arsenic contamination in Bangladesh has taken a serious turn in recent times with detection of arsenic in groundwater in almost all the administrative districts. Thousands of people are reported to have already shown symptoms of being poisoned by arsenic and several millions are at risk of arsenic toxicity from drinking arsenic contaminated tubewell water. The southern, south-western and north-eastern parts of Bangladesh appear to be the worst affected areas. An estimated 40 million people are exposed to arsenic concentrations above the current Bangladesh standard of 0.05 mg/L; the number would be much higher if the WHO guideline of 0.01 mg/L is adopted. Arsenic toxicity has no effective medicine for treatment, but drinking of arsenic free water is urgently needed to mitigate arsenic toxicity and protection of health and well being of rural people living in acute arsenic problem areas of Bangladesh. In Bangladesh, people are very accustomed to using groundwater which provided them with water free from bacteriological contamination for long. As a result people may not be very keen about the prospects of using alternative sources of water (e.g., surface water and rain-water). Suitable and affordable technology for removal of arsenic from well water would serve as a very effective means of combating the present arsenic calamity in Bangladesh.

This chapter briefly reviews the status of arsenic contamination in Bangladesh. It also provides a short overview of arsenic contamination of drinking water sources in other countries. A detailed review of arsenic removal technologies have been provided and the relative merits and demerits of the different technologies have been discussed with particular emphasis given to their suitability for application in Bangladesh.

3.2 ARSENIC CONTAMINATION IN BANGLADESH

Presence of high concentrations of arsenic in tubewell water in excess of acceptable limit has become a major concern in Bangladesh. Report on arsenic contamination of groundwater in the West Bengal state of India, adjacent to the western border of Bangladesh, was first published in 1983. The detection of arsenic in the bordering states of India prompted Bangladesh to investigate the presence of arsenic in its groundwater. Awareness about the presence of arsenic in Bangladesh has been growing since late 1993 when arsenic was first detected in Baroghoria union of Chapainawabgonj district bordering West Bengal, India. Since then a number of Govenment and Non-Government organizations, such as Department of Public Health and Engineering (DPHE), Atomic Energy Commission (AEC), Dhaka Community Hospital, NIPSOM, Dhaka University, Jahangirnagar University, and Bangladesh University of Engineering and Technology (BUET), have been conducting tests on tubewell water samples for detecting the presence of arsenic. From available data it is clear that unacceptable levels of arsenic in groundwater have been found in a vast majority of the districts of the country and a large number of patients are suffering from arsenocosis and its complications (DCH, 1998).

In a study conducted by the Dhaka Community Hospital during 1998, well water in 41 districts (out of 64) were found to have arsenic above 0.05 mg/L, the maximum permissible value recommended by Bangladesh EQS; and in 52 districts the arsenic concentration was more than 0.01 mg/L, the WHO recommended value for safe water (DCH, 1998). Although not all the tubewells in the 41 districts with an area of 89,186 sq km and a population of 76.9 million are contaminated, there are thousands of pockets of contaminated groundwater and a large number of people in these districts are at the risk of developing arsenic toxicity. In a more recent study, arsenic has been reported to be detected in 61 out of 64 administrative districts. Figure 3.1, developed by British Geological Survey (1999) based on available data on arsenic concentration in tubewell water, provides a picture of the present situation of arsenic contamination in Bangladesh. Figure 3.1 shows widespread arsenic contamination in Bangladesh. It shows that tubewells in large parts of Sylhet and Dhaka divisions, most of Chittagong division

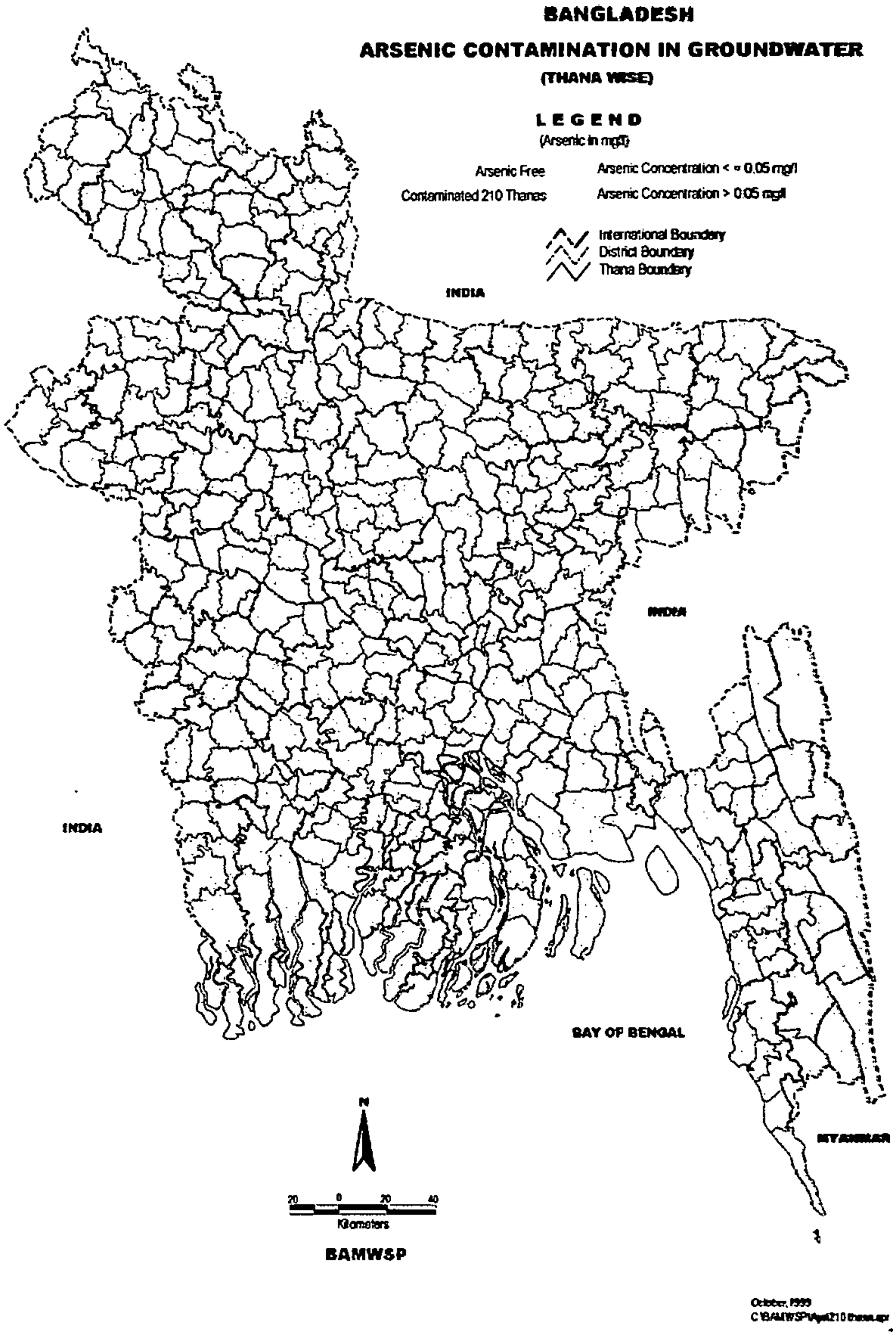

Figure 3.1 Map showing levels of arsenic contamination in Bangladesh (British Geological Survey, April' 1999)

except the Hill Tracts area, significant parts of Rajshahi division, and most parts of Khulna and Barisal divisions except the coastal areas are contaminated with arsenic. Highly affected districts include Sylhet, Sunamgonj, Comilla, B-Baria, Narayangonj, Chandpur, Laksmipur, Feni, Noakhali, Sariatpur, Munshiganj, Bagerhat, Satkhira, Jessore, Jhenaidah, Chuadanga, Nawabganj, Manikganj, Faridpur, and Gopalganj. Presence of arsenic in the coastal areas is low because most of the groundwater in this saline area is extracted from arsenic-free deep aquifer. Detailed investigation in the Chittagonj Hill Tracts area is yet to be done. Table 3.1 presents status of arsenic contamination in Bangladesh from a recent study (DPHE/DFID, 1998).

Table 3.1 Arsenic Contamination Scenario in Bangladesh (Source: DPHE/DFID, 1998)

Division	No. of Districts	No. of affected Districts	No. of Thanas	No. of affected Thanas	% of affected Thanas of the Divisions	% of affected Thanas against the Country
Dhaka	17	16	134	61	45	12
Chittagong	11	7	93	21	22	4
Rajshahi	16	16	127	35	27	7
Khulna	20	10	63	42	66	9
Barisal	6	6	38	18	47	4
Sylhet	4	4	35	34	97	7
6 Divisions	64	59	490	211	-	43

Note: Table represents affected Thanas, where As Concentrations in ground water is > 0.05 mg/L.

The number of patients showing symptoms of arsenic toxicity are increasing as results from recent studies are becoming available. In a recent study by the National Institute of Preventive and Social Medicine (NIPSOM), arsenic related diseases (arsenicosis) have been identified in 37 districts (Ahmad et al., 1998). A total of 6000 cases were identified in 162 villages in the 37 districts, mostly in the rural areas. Among the identified patients, 53% were male, 47% female, and the most affected age group was found to be 20 - 40 years. Three stages of manifestations of chronic arsenicosis were observed in the study (Ahmad et al., 1998), but most of the patients were found in the first and second stages. The most common presentations were melanosis, keratosis, hyperkeratosis and depigmentation. Cancers were found among 0.8% and actinic keratosis and Bowen's diseases were observed among 3.1% of the cases. It is important to note that the study found that the cases at initial and second stages of toxicity showed improvement when patients stopped taking arsenic contaminated water and increased intake of protein rich food, vitamin A, E and C. Dhaka Community Hospital and the School of Environmental Studies, Jadavpur University, conducted surveys for arsenicosis patients in 22 districts and found patients with arsenical skin lesion such as melanosis, leuco-melanosis, keratosis, hyper-keratosis, dorsum, non-petting oedema, gangrene, skin cancer, etc. in 21 districts (up to February, 1998). Arsenic patients were found in 93 villages in 21 districts (Mandal et al., 1998). 5664 people were examined in the affected villages and 33.6 percent of them were diagnosed as patients with arsenical skin manifestations. A total of 2167 hair samples, 2165 nail samples, 220 skin samples and 830 urine samples were analyzed and an average of 94 percent of them were found to have arsenic concentrations above normal limit. It is believed that systematic study covering all the arsenic affected districts would reveal many more arsenic affected patients in Bangladesh.

3.3 ARSENIC CONTAMINATION IN OTHER COUNTRIES

Besides Bangladesh, arsenic contamination of drinking water source has been reported for a number of countries world-wide. In fact detection of arsenic in groundwater of West Bengal state of India, bordering western Bangladesh prompted the investigation to determine the existence of arsenic in Bangladesh. The official report on arsenic study in West Bengal, India was first presented in 1983 based on a study on groundwater samples from six districts of the state. The study showed that groundwater samples of all 6 districts were contaminated with arsenic above the allowable limit for drinking water (i.e., 0.05 mg/L). To date, arsenic has been found in groundwater in eight districts of West Bengal covering an area of about 38,000 square km having about 38 million population (Mandal et al., 1998). An estimated 1.5 million people in 863 arsenic affected villages of the these districts are drinking arsenic contaminated water and among them more than 200,000 people are suffering from arsenic related diseases.

Besides Bangladesh and India, arsenic contamination of drinking water source, both surface and groundwater, has been reported in a number of Asian countries including China, Mongolia, Taiwan and Thailand (Dong et al., 1998; Fen et al., 1998; Chen, 1998; Chiou et al., 1998; Choprapawor, 1998; Dahi, 1998). In Mongolia, the first case of arsenic poisoning was discovered in 1990. Many of the arsenic affected areas are located in the arid region. In 1996, 15 villages of 3 counties were surveyed for pollution and health damage (Dahi, 1998). About 90% of the wells tested showed arsenic at levels higher than 50 µg /L. The highest concentration detected in the well water samples was 1088 µg/L. The arsenic contamination was found to be associated with high concentrations of fluoride. In the survey, 35 percent of 612 inhabitants tested had arsenic lesions. More serious effects were detected including high cancer mortality (Dahi, 1998). It was estimated that 655 villages of 11 counties are arsenic affected. Arsenicosis seemed to cause extreme sufferings to the inhabitation of the region.

The arsenic problem in Taiwan was first reported in 1968 and it was here that arsenicosis was given the name "Black Foot Disease". In a survey covering 83000 wells in Taiwan, 19% of the wells showed arsenic levels over 50µg /L (Dahi, 1998). It was reported that about 100,000 inhabitants used well water containing 10-1820µg /L of arsenic (on an average 500 µg /L) for over 40 years. Based on data from this study, dose–response relationships were established for the occurrence of bladder and lung cancer and for bladder cancer mortality (Dahi, 1998). In southern Thailand, arsenic was reported to occur in some shallow as well as deep wells in 1996; the concentrations were found to vary between 1 and 5100µg /L (Dahi, 1998).

Cases of arsenic contamination of water sources have also been found in Chile, Mexico, Argentina, Hungary, United Kingdom and the United States (Csanady et al., 1998; Leonardi et al., 1998; Hering, 1998; Dahi, 1998). In Chile, arsenic exposure is reported to be contained in one province, region II, extending over an area of 125,000 km^2 with a population of about 400,000. The region is very arid with limited water resources, even very deep wells are not reliable sources of water for the towns of the region. Antofagusta, the largest city of the region is inhibited by 2/3 of the regions population and its water supply comes from three rivers. The rivers originate from the Andes, and water is brought via aqueducts from upstream sites. In 1957, it was found that drinking water contained 800-1300 µg arsenic /L. In 1962, the first cases of arsenosis were reported. Different sorts of specific and nonspecific arsenic intoxications have been reported since. In 1970 a treatment plant was established which reduced arsenic concentrations to 40µg arsenic /L. It is estimated that 7% of the deaths from 1989-1993 are caused by previous exposure to arsenic (Dahi, 1998).

In Mexico, 11 counties in the Langunera region of northern Mexico have reported the arsenic problems. A populations of about 127,000 inhabitants have been drinking water containing 100-500 µg/L. Various pathological effects, including genotoxic effects of arsenic have been reported. In Argentina, the first notification of water borne arsenocosis were reported as early as the beginning of the century. The term 'Bell Ville disease' was used to describe arsenic caused skin manifestations. Several regions in eastern and central Argentina were affected by arsenic in groundwater. Arsenic levels above 100 µg/L were often found; even levels as high as 2000 µg/L have been reported (Dahi, 1998). The source of contamination was found to be natural due to the soil composition and thus polluting the shallow well waters. The deep well water and the surface water showed no or low levels of arsenic.

USA is the probably the only arsenic affected country which has carried out a nation wide survey of arsenic occurrence in drinking water. About 347,000 people had public water supply containing more than 50µg /L of arsenic and about 2.5 million people had public water supply containing more than 25µg /L of arsenic (Dahi, 1998). Arsenic concentration of 46 µg /L was found in one county in California and of 92 µg /L in two counties of Navada. Studies from 1972 to 1982 showed no correlation with specific skin alterations and neurological abnormalities. A recent case study has shown increased risk of bladder cancer at very low levels of arsenic exposure in some groups (Dahi, 1998).

Although arsenic contamination of drinking water sources has been reported in many countries, the present arsenic contamination scenario in Bangladesh appears to be the worst cases detected so far world-wide, both in terms of area and population affected.

3.4 ARSENIC REMOVAL TECHNIQUES

3.4.1 General

A variety of technologies has been used for removal of arsenic from water. The most common technologies to remove arsenic are precipitation/sedimentation, co-precipitation and adsorption onto coagulated floc, filtration, adsorption onto activated carbon, Fe-Mn oxidation, and lime softening. For all of these technologies (except reverse osmosis) adsorption is the fundamental process governing arsenic removal (Hering et al.,, 1996). The current advanced treatment options to remove arsenic include activated alumina, iron-oxide-coated sand, reverse osmosis, ion exchange, and electro-dialysis. The term "advanced" is used in the context that the technologies are not yet proven at full-scale treatment plants (at least for low-level arsenic removal) and their use generally requires an entirely new treatment step (Edwards, 1994). The following section briefly describes some of the arsenic removal technologies.

3.4.2 Coagulation, Adsorption and Co-precipitation

3.4.2.1 Coagulation by Alum and Ferric Salts

Arsenic can be effectively removed by coagulation using alum, ferric salts etc. (Hering et al., 1996; Edwards, 1994). Ferric salts have been found to be more effective in removig arsenic than alum on a weight basis and effective over a wider range of pH (Hering et al.,1996). In both cases, pentavalent arsenic (arsenate) can be more effectively removed than trivalent arsenic (arsenite). Both (aluminum and ferric) metal salts facilitates the conversion of soluble As(V) and As(III) species into insoluble products (Frank et al., 1986; Shen, 1973; and Pierce and Moore, 1982). These products might form through precipitation, co-precipitation or adsorption mechanisms (Edwards, 1994). Precipitation refers to the insolubilization of contaminants by exceeding a solubility product, in this case that of either $Fe(AsO_4)$ or $Al(AsO_4)$ solids (Dove,1985). Co-precipitation is defined as an incorporation of soluble arsenic species into a growing hydroxide phase via inclusion, occlusion, or adsorption. Finally, adsorption refers to formation of surface complexes between soluble arsenic and the solid oxyhydroxide surface site.

In the coagulation–flocculation process aluminum sulfate or ferric chloride or ferric sulfate is added and dissolved in water under efficient stirring for one to few minutes. Rapidly aluminum or ferric hydroxide micro flocs are formed. The water is then gently stirred for few minutes for agglomeration of micro flocs into larger easily settleable flocs. During this flocculation process all kinds of micro particles and negatively charged ions are attached to the flocs by electrostatic and chemical attachment. Arsenic is also adsorbed onto coagulated flocs. As trivalent arsenic occurs in non-ionized form, it is not subject to significant removal. Oxidation of As(III) to As(V) is thus required as a pretreatment step for efficient removal . This can be achieved by addition of bleaching powder (chlorine) or potassium permanganate. Adsorption of arsenic onto ferric oxyhydroxides can be expressed by the following equations (Edward, 1994):

$$\equiv \text{Fe-OH} + H_2AsO_4^- + H^+ \rightarrow \equiv \text{Fe-}H_2AsO_4 + H_2O \quad \text{(Arsenate adsorption)} \qquad (3\text{-}1)$$

$$\equiv \text{Fe-OH} + H_3AsO_3 \rightarrow \equiv \text{Fe-}H_3AsO_3 + H_2O \quad \text{(Arsenite adsorption)} \qquad (3\text{-}2)$$

where $\equiv$Fe-OH represents a surface site for adsorption.

Arsenic adsorbed on ferric hydroxide flocs as Fe-As complex is removed by sedimentation. Filtration may be required to ensure complete removal of all flocs. Similar reactions take place in case of alum with the formation of Al-As complex as an end product which is removed by the process of sedimentation and filtration.

Arsenic removal efficiency by the coagulation process is dependent on the types of coagulant, coagulant dosage, pH of the raw water and the valency of the compounds such as As(III) or As(V). According to Bellack (1971), Gulledge and O'Conner (1973), Shen (1973), Sorg and Logsdon (1978), and Jekel (1986), best removal is achieved with As(V) and ferric salts if the pH value is between 7.2 to 7.5. Under optimized conditions of Fe^{3+} dosage and pH, efficiencies approach 99% if the arsenic content of the raw water is in the range of 0.1 to 1 ppm. The residual arsenic concentration after solids removal is than below 0.01 ppm. As shown in Fig. 3.2, 1 to 2 ppm of Fe^{3+} are sufficient for removal of more than 95% arsenic (initial concentration of about 135 ppb) if pre-chlorination is used to oxidize As(III). The solids may than be removed by direct filtration without the settling step required for higher coagulant dosages (Jekel, 1994). Dependence of arsenic removal on pH values is related to the pH dependence of adsorption and the solubility of amorphous iron hydroxide, which is minimum at pH 8 and goes up above and below this pH value. Solubility curve of amorphous iron hydroxide is shown in figure 3.3.

3.4.2.2 Lime Softening

Water treatment by the addition of fresh calcined lime, or calcium oxide is an efficient process for As(V) removal (Jekel, 1994). The precipitated calcium hydroxide acts as sorbing flocculant for arsenic. Excess of lime would not be dissolved, but remains as a thickener and coagulant aid, which has to be removed along with the precipitated calcium hydroxide through a sedimentation/filtration process. The highest removals are achieved when the end pH of the water is as high as 10.6 to 11.4 (Dahi, 1997). Obviously this would require a secondary treatment in order to readjust the pH. Simple acidification may not be enough, buffering of the water may be required.

Sorg and Logsdon (1978) reported more than 90% removal of As(V) (initial concentration 0.4 ppm) if the pH is above 10.5. As(III) removal could be about 75% at pH values above 11.0. The mechanism of removal may be adsorption onto the calcium carbonate and magnesium hydroxide, or it may a direct precipitation of calcium arsenates, similar to the phosphate precipitation that occurs under similar condition (Jekel, 1994). Previous studies recommended lime addition for the removal of arsenic in gold mine waste waters as the most economical treatment, provided careful control of the oxidation of As(III) to As(V), pH > 12 and effective filtration of the precipitate is exercised. If arsenic levels below 0.5 mg/dm^3 are required, a modification of the method by phosphate addition must be considered.

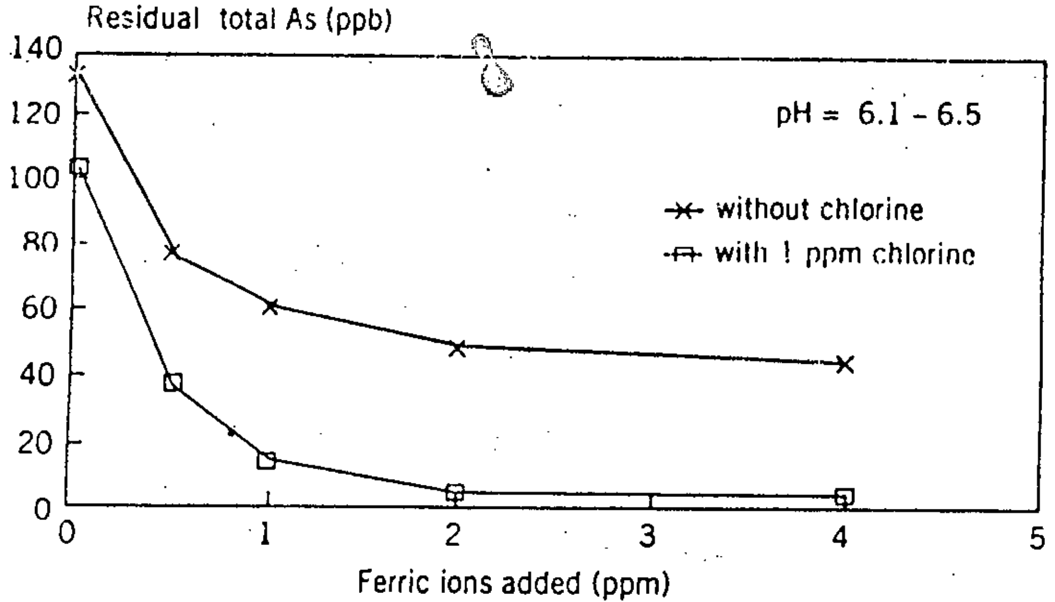

Figure 3.2 Arsenic removal from ground water by ferric ion precipitation without and with pre-chlorination to oxidize As(III). Initial total arsenic concentration: 135 ppb; initial As(III) concentration: 60 ppb (Jekel, 1986).

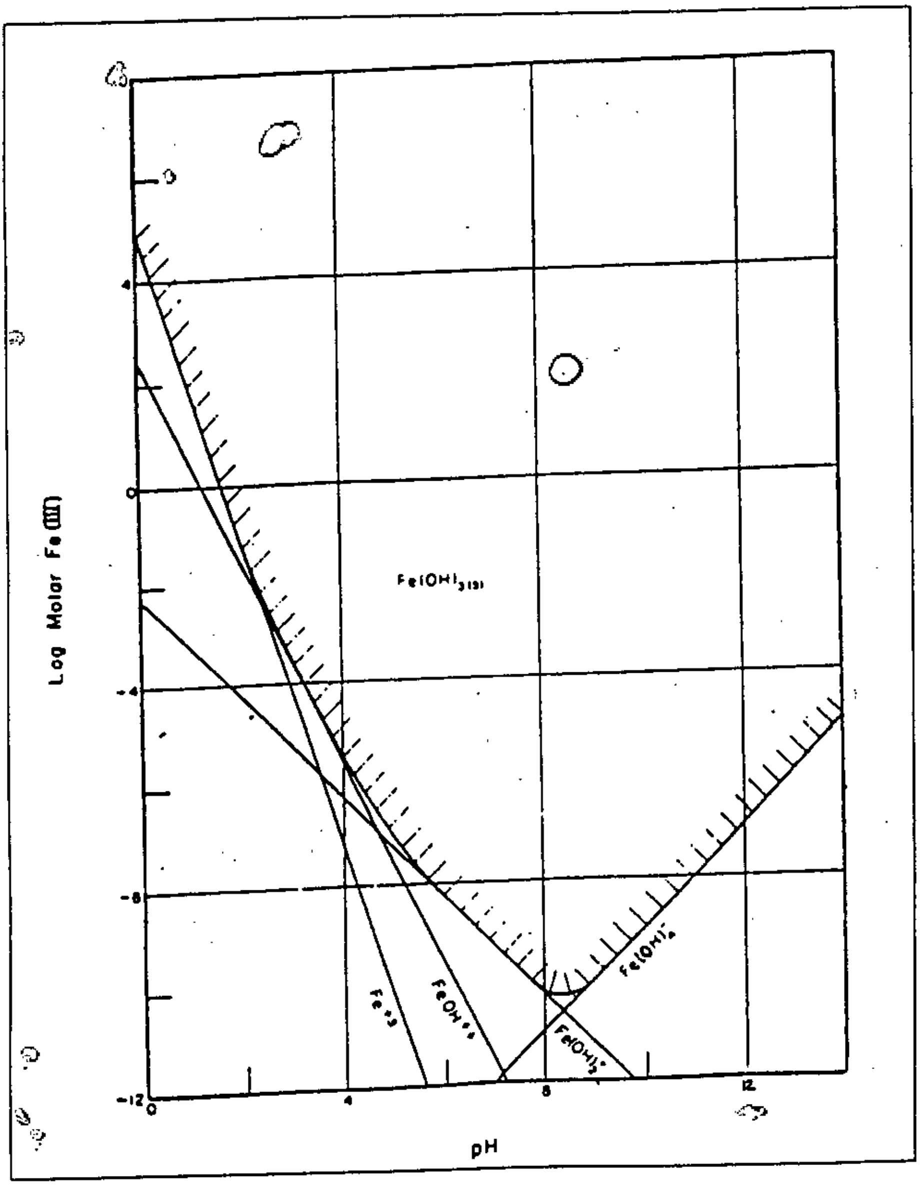

Figure 3.3 Solubility Diagram of Ferric Hydroxide (Ghosh et al., 1966)

According to Dutta and Choudhury (1991), As(III) could be removed from a concentration of 0.6 ppm to less than 0.05 ppm by lime softening (dose: 800 ppm) and using a powdered coal additive (dose: 2g/L). However, the chemical dosages were quite high and preoxidation would have been beneficial. In view of the high lime requirements of the process, its application may be limited to very hard waters, which need softening in a central treatment plant (Jekel, 1994). The precipitation processes described produce sludges with a considerable arsenic content of up to 10% by weight that must be disposed of safely as toxic waste. The lime softening can be used as a pre-treatment to be followed by e.g., iron coagulation (Dahi, 1997).

3.4.2.3 Fe-Mn Oxidation

According to Edwards (1994), high arsenic concentration are often correlated with high Fe(II)-Mn(II). Therefore, understanding behavior of arsenic during Fe(II)-Mn(II) removal is of particular interest. The removal mechanism involving oxidation to remove Fe(II) and Mn(II) leads to formation of hydroxides that remove soluble arsenic by co-precipitation and adsorption reactions. The production of oxidized Fe-Mn species and subsequent precipitation of hydroxides are analogous to an *in-situ* coagulant addition with the quantity of Fe on Mn removed translating into dose (Edwards, 1994).

Iron and manganese exert a strongly influence on arsenic concentrations in the environment. Though scorodite ($FeAsO_4.2H_2O$) is not observed to form at levels of arsenic typicall found in natural systems (Dove, 1985,; Waychunas, et al.), other solids such as Ca_3 (AsO_4), $Ba_3(AsO_4)_2$ and specially aresnopyrite (FeAsS) and $Mn_3(AsO_4)$ are believed to exert some control over arsenic solubility (Welch et al., 1988; Boyle et al., 1973; Korte, 1991). At lower concentrations, however, the coprecipitation - adsorption of arsenic with iron and manganese oxide solids are more important (Ferguson et al., 1972; Welch et al., 1988; Korte, 1991; Masscheleyn et al., 1991; Takamatsu et al., 1985). Arsenic can be immobilized through adsorption - coprecipitation with iron and manganese hydroxide, mobilized when such solids are dissolved under reducing conditions or released from the oxide surfaces in the event of competition (for sorptive surface sites) in the presence of orthophosphate and natural organic matter (Xu et al., 1991; Devenport and Peryea ,1991).

Based on conservative estimates of adsorption alone, arsenic removal during Fe(II) precipitation is expected to be fairly efficient. According to Edward (1994), when removal by both adsorption and coprecipitation are considered, removal of arsenic during manganese precipitation is relatively ineffective when compared with iron. For instance, precipitation of 1 mg/L Mn(II) is predicted to remove only 25% of 5 μg/L influent concentration. When much higher concentrations of Mn(II) are precipitated, removal can be more significant; precipitation of 3 mg/L Mn(II) is predicted to produce an effluent with 3.75μg/L arsenic when influent concentration is 12 μg/L influent. The pH of water is predicted to play an important role in arsenic removal via adsorption to iron hydroxide but the limited data collected for manganese suggest that pH is not significant in arsenic removal during manganese precipitation (Lauf and Wear, 1993).

3.4.2.4 Naturally Occurring Iron in groundwater of Bangladesh

Naturally occurring iron in groundwater of Bangladesh has the potential of playing an important role in the removal of arsenic by adsorption. It has been found that hand tubewell water in 65% of the area in Bangladesh contains iron excess of 2 mg/L and in many acute iron problem areas, the concentration of dissolved iron is higher than 15 mg/L. It has been found that in ground water iron and arsenic are coexist. Most of the tubewell water samples satisfying Bangladesh Drinking Water Standard for iron (1mg/L) also satisfy the standard for arsenic (50 μg/L), while higher arsenic concentrations are usually associated with higher iron contents (Hossain and Ali, 1997). The iron precipitates [$Fe(OH)_3$] formed by oxidation of dissolved iron present in groundwater acts as adsorption sites for arsenic. Only aeration and settling of tubewell water rich in dissolved iron has been found to remove significant arsenic from water (Ahmed et al., 1998). Experimental results show the effectiveness of added Al^{3+} and Fe^{3+} is higher than natural iron precipitates in removing arsenic, but the process involving naturally occurring iron flocs does not involve cost of chemicals.

3.4.3 Adsorption Techniques

3.4.3.1 Activated Alumina

Granular activated alumina is a pomising method for arsenic removal (Jekel, 1994). Activated alumina is porous alumina oxide, Al_2O_3, having sorptive surface. It has specific surfaces of 200 to 300 m^2/g that can be used for phosphate, floride and arsenic adsorption especially in the fixed bed technique. Activated alumina is an effective adsorbent for these anions and it can be regenerated periodically with diluted NaOH and sulfuric acid.

According to Dahi, (1997), when water passes through a packed column of activated alumina, pollutants and other components in the water are adsorbed to the surface of the grains. Eventually the column becomes saturated, first at the upstream zone. Later, as more water is passed through, the saturated zone moves downstream and, in the end, the column get totally saturated. The total saturation means that the concentration of the pollutant under consideration in the effluent water increases to the same value as the influent water. Different pollutants and components of the water get saturated at different times of operation, depending upon the specific sorption affinity of medium to the given component. The total saturation of column must be avoided. The column is only operated to a certain break point, where the concentration of arsenic is e.g., 50μg/L. The time between the start of operation and the break point of the column is presented by the volume of treated water V. When dividing V with the bulk volume of the activated alumina packed, a standard parameter is obtained which is the number of Empty Bed Volumes, EBV, or just Bed Volumes, BV. BV is an expression of the capacity of treatment before the column medium needs to be regenerated. It is an operational measurement of the specific sorption capacity of the given activated alumina towards arsenic.

When the alumina surface becomes saturated with arsenic then adequate removal cannot be possible. It is then necessary to regenerate the alumina. Regeneration of the saturated alumina is usually carried out by exposing the medium to 4% caustic soda (NaOH) either in batch or by flow through the column. After regeneration, residual caustic soda is washed out and the medium is neutralized with a 2% solution of sulfuric acid rinse. During this process about 5-10% of alumina are lost, and the capacity of residual medium is significantly reduced, approximately by 30-40%. After only 3 to 4 regenerations, the media has to be replaced. Alternatively, in order to avoid on site regeneration, the saturated alumina can be recycled to a dealer, who can take care of standardizing the capacity of the activated alumina using an appropriate mixture of fresh and regenerated media.

Activated alumina can be applied successfully if the pH is slightly acidic (pH 5.5-6.0) and if the competing anions (sulfate, phosphate and flouride) are present in small concentrations (Jekel, 1994). As(V) is removed far more efficiently than As(III) (Dahi, 1997). So pre-chlorination (i.e., pre-oxidation) often improves the column capacity. The principal advantage of activated alumina is its simple operation over one to three months before regeneration is required, making it more feasible for small-scale plants.

3.4.3.2 Activated Carbon

Removal of As(V) by adsorption onto activated carbon is more effective than that of As(III). Activated carbon is manufactured from carbonaceous material such as wood, coal, petroleum residue, etc. A char is made by burning the materials in the absence of air. The char is than oxidized at high temperature to create a very porous structures. Activated carbon is crushed into granules ranging from 0.1 to 2 mm in diameter or is pulverized to a very fine powder. Dissolved materials adsorbs to both exterior and interior surfaces of the carbon. When these surfaces become saturated with dissolved substances, the carbon must be regenerated. Design of granular-activated-carbon systems is based on flow rates and contact times. Carbon columns can be arranged in parallel to increase the capacity and in series to increase the contact time. The major problem associated with granular-activated-carbon-contact systems is plugging of the bed by suspended solids in the water. Provisions may be made in the design of the vessel for back-washing the bed in a fashion similar to filter back-washing. A method of pre-treating activated carbon by a ferrous salt to enhance As(V) removal was described by Huang and Vane (1989). They could increase the carbon capacity by a factor of 10, due primarily adsorption of Fe^{2+} arsenate complexes. The carbon could be regenerated with the ferrous salt solution.

Little is known about the adsorption mechanism of arsenic species on activated carbon. The arsenic adsorption mechanism cannot be solely explained in terms of molecule-surface interaction, electrostatic interaction, or occlusion. It is apparent that $H_2AsO_4^-$ is the major species removed by activated alumina.

3.4.3.3 Iron Oxide Coated Sand

Iron oxide coated sand has been successfully employed in fixed beds to treat metal bearing wastewater (Edward and Benjamin, 1989). Iron oxide-coated sand showed promise as a medium for use in small systems or home treatment units in some developing areas of the world for removing As(III) and As(V). Iron oxide coated sand is prepared by washing and drying river sand and then mixing it with ferric nitrate solution. Water is passed through the column with sufficient contact time and arsenic is adsorbed on iron oxide coated sand. The medium is regenerated by sodium hydroxide solution. Iron oxide coated sand is a low cost and simple process for use in small systems or home treatment units in developing areas of the world .

3.4.3.4 Other Adsorptive Processes

Bone char was used by Bellack (1971) as a fixed bed adsorber to remove arsenic. After exhaustion, the char could not be regenerated and had to be disposed of. The bone char probably contained ferric oxide, which would be responsible for the adsorptive removal. The passage of a surface water underground, as practiced in Europe in bank filtration and groundwater recharge for water purification, can be an effective process for arsenic removal, even at low concentration. Experiences with such systems are available from the Rhine river and from dune infiltration in the Netherlands (Jekel, 1994).

3.4.4 Ion Exchange

Ion exchange is usually used to demineralize, to soften and to de-nitrate water. During treatment ion exchange involves the reversible exchange of ions between a solution and a solid phase that are in direct contact. The solid phase can be natural zeolite or a synthetic resin consisting of a cross linked polymeric network with charged ionic species that retain them by electrostatic forces . Resins exhibit affinity to all ionic species of opposite charge, depending upon the specific ionic charge, the hydrated ionic radius, the concentration in solution, the degree of resin cross-linking and the nature of the functional group on the resin (e.g., sulphonic, phosphonic or carbonic acid groups). In fixed bed type units, this process continues until the solution being treated exhausts the resin exchange capacity. At that stage, the exhausted resin must be regenerated by an acid/base or other chemical replacing the ions and converting the resin back to its original composition and yielding up to a 500 times concentrated regenerant brine.

For arsenic removal, an ion- exchange resin, usually loaded with chloride ions at the "exchange sites", is placed in vessels (Kartinen and Martin., 1995). The arsenic containing water is passed through the vessels and the arsenic exchanges for the chloride ions.

Arsenic exchange (R= Resin):

$$2R\text{-}Cl \;+\; HAsO_4^{2-} \;=\; R_2\,AsO_4 \;+\; Cl^- \tag{3-3}$$

Regeneration:

$$R_2\,AsO_4 \;+\; 2Na^+ + 2Cl^- \;=\; 2R\text{-}Cl \;+\; HAsO_4^{2} \;+\; 2Na^+ \tag{3-4}$$

As ion exchanged is effective only in removing ions from the water, only As(V) which is present in ionic form in the neutral pH range (the pH range of most natural water) can be exchanged in resins. So the efficiency of the ion exchang process can be improved by pre-oxidation of As(III) to As(V). This, however, has the drawback that the excess of oxidant has to be removed before the ion exchange in order to avoid the damage of the resin by it (Dahi, 1997).

A special ion exchanger was described by Yoshida and Ueno (1978) where a resin with chelating groups was saturated ferric ions and applied for As(III) and As(V) removal. Both redox forms were effectively removed, but with a different optimum pH; pH 3-6 for As(V) and pH 8-9 for AS(III). The resin capacity was about 0.5 mmol/g for both As(V) and As(III). Applications in pilot and full-scale plants and modes of regeneration were not reported. Elson et al. (1980) studied As(V) removal by chitosan and chitin anion exchanges derived from modified natural glucosamines. The capacity of this media was about 0.13 mmol/kg, well below that of the synthetic resin. Removal of arsenic by ion exchange is not practical for large scale because the cost is too high and its operation is rather complex. This process may be used for small scale special application.

3.4.5 Membrane Techniques

Demineralization of water can be accomplished using micro-porous membrane. There are two basic modes of operation in use. One system uses pressure to drive water through the membrane against the force of osmotic pressure and is called reverse osmosis, even though the pressure applied is several orders of magnitude in excess of the natural osmotic pressure. The other process, called electrodialysis, uses electrical forces to drive ions through ion-selective method.

Reverse osmosis or electrodialysis can be effective process for arsenic removal, but may be applied only if partial or total desalting is necessary in addition to arsenic separation (Jekel, 1994). Clifford (1986) pointed out that in reverse osmosis, only As(V) is effectively removed (98-99%; initial concentration up to 2 ppm), while As(III) is only partially separated (46-75%) due to neutral form of As(III). It is a precondition that the water does not contain suspended solids and that arsenic is in its pentavalent state (Dahi, 1997). Most membranes, however, cannot withstand oxidizing agents. Moreover, these methods are already of no interest in developing countries, because of their nature as high technology and high cost (Dahi, 1997).

3.4.6 Microbial Process

Microbial removal of arsenic is based on two important metal-microbe interactions: (i) microbial oxidation of As(III) to As(V) to facilitate its removal by conventional arsenic removal processes and (ii) bioaccumulation of arsenic in bacterial biomass from the surrounding water environment. There are a number of microorganisms capable of oxidizing arsenite at neutral pH. The common iron bacteria which oxidizes ferrous iron to ferric iron can oxidize as well as absorb arsenic. Removal of trace metal from water through accumulation in algae is well recognized. Several form of algae are known to assimilate arsenic from water in a biological process. Arsenic can conventionally be oxidized from As(III) to As(V), adsorbed or assimilated through microbial growth in a simple reactor in nutritionally balanced condition at appropriate temperature and pH and subsequently removed by precipitation/filtration. Microbial growth on fixed media or suspended growth should be equally effective for arsenic removal.

3.5 COMPARATIVE MERITS AND DEMERITS OF ARSENIC REMOVAL TECHNOLOGIES

Table 3.2 summarizes the relative advantages and disadvantages of different arsenic removal technologies. From the overview of different technologies presented above it appears that ion exchange and membrane techniques may prove to be too costly for large scale implementation in Bangladesh. Apart from cost, both ion exchange and membrane techniques would require higher levels of technical expertise on the part of the user for operation and maintenance. Presence of high concentrations of iron in the groundwater, which precipitates as ferric hydroxide solids after extraction, would definitely interfere with the efficiency of membranes. However, significant advances are being made in ion exchange and membrane technologies and these advances in these should be closely monitored by the scientific community. Microbial processes for removal of arsenic from drinking water is still at a development stage and does not appear to be a suitable technology for implementation at this stage.

Table 3.2 Overview of Dearsinazation Methods and their Advantages and Disadvantages

Method	Advantages	Disadvantages
Coagulation, Adsorption, and Co-precipitation	No monitoring of break through is required. Relatively low cost. Uses simple, easily available chemicals. Low capital cost	Short and long term problems with sludge disposal. Require regular supply of chemicals. Operation requires training and discipline. Efficient pre-oxidation of arsenite to arsenate is a must.
Alum coagulation	*Durable powdered chemicals normally available.*	
Iron coagulation	*More efficient than alum on weight basis.*	
Lime softening	*Most common chemicals. Less efficient than alum and iron coagulation.*	*Readjustment of pH is required.*
Naturally Occurring Iron	*May provide simple a cost-effective solution for iron rich areas.*	*Effectiveness less than iron and aluminum precipitates formed upon addition of coagulant*
Sorption Techniques	No daily sludge problem	Requires monitoring of break through. Requires periodical regeneration, backwashing or medium shift. Clogging of filter bed with iron precipitates is a particular concern.
Activated Alumina	*Relatively well known and commercially available.*	*Yet to be standerdised, toxic solid waste, high cost medium. Clogging problem.*
Iron oxide coated sand	*Expected to be cheap. No regeneration is required.*	*Clogging problem.*
Other Sorbents	*Plenty of possibilities and combinations*	*Not yet properly studied.*
Ion Exchange Resin	Well defined medium and hence high capacity.	Regeneration creates a sludge problem. High cost. High tech operation and maintenance.
Membrane Techniques	Well defined performance High removal efficiency No solid waste Low space requirement Capable of removal of other contaminants.	High running cost. High investment cost. High tech operation and maintenance toxic waste water Readjustment of water quality is required.
Reverse Osmosis		*Membrane does not withstand oxidizing agents.*
Electrodialysis		*Membrane does not withstand oxidizing agents.*
Microbial Processes	Should be less costly.	Not yet full established. *Require extensive research.*
Microbial oxidation		
Microbial Removal		

Arsenic removal by coagulation-adsorption-coprecipitation and by sorption appear to be the most promising techniques for use in Bangladesh. However, recent experiences (Ahmed et al., 1998; Ahmed and Jalil, 1999) with adsorptive filtration devices designed for arsenic removal suggest that high iron concentration of groundwater in Bangladesh is a particular concern for such systems. Dissolved iron present in groundwater precipitates upon extraction and rapidly clogs filter bed resulting in quick failure of these systems. A pre-treatment step designed for removal of excess iron is likely to improve the efficiency of adsorptive filtration systems. Co-precipitation based systems can be developed with simple and easily available chemicals and may be cost-effective for use in Bangladesh. It requires regular dosing of chemicals and careful operation. Safe disposal of sludge is a concern for such systems. Appropriate doses of alum or ferric salt for arsenic removal need to be determined for typical arsenic levels and composition of groundwater in Bangladesh. In iron rich areas of the country, naturally occurring iron in groundwater can be effectively utilized for removal of arsenic. Although effectiveness of natural iron precipitates in removing arsenic appears to be less than that of ferric salts, the process involving naturally occurring iron flocs does not involve cost of chemicals. Naturally occurring iron is likely to improve efficiency of all coagulation based removal systems.

Chapter 4

REMOVAL OF ARSENITE AND ARSENATE BY FERRIC CHLORIDE

4.1 INTRODUCTION

Coagulation is a promising technique to remove inorganic contaminants (e.g., heavy metals) from water when the constituent metal of the coagulant precipitates as an amorphous metal hydroxide with which the inorganic contaminants become associated (e.g., by adsorption) and are removed by sedimentation. By addition of a coagulant (such as ferric chloride or alum), soluble arsenic can be removed through adsorption (association of the dissolved contaminant with the surface of the precipitate), occlusion (entrapment of adsorbed contaminants in the interior of the growing particle), and solid-solution formation (incorporation of the contaminant into the bulk phase, rather than only onto the surface of the precipitate) (Benefield & Morgan, 1990). The consistent behavior of arsenic in adsorption [using pre-formed Hydrous Ferric Oxide (HFO) as the adsorbent] and coagulation [using ferric chloride as coagulant] studies indicates that adsorption is a dominant mechanism for arsenic removal by coagulants (Hering et al., 1996) when $FeCl_3$ is added to water. Arsenic is primarily removed by adsorption onto coagulated flocs of amorphous ferric hydroxide which is formed upon addition of $FeCl_3$ solution to water.

Many studies have been conducted to determine the efficiency of arsenic removal by coagulants. Most work has focused on removal of arsenate [As(V)], the thermodynamically stable form of inorganic arsenic in oxic waters. Arsenite [As(III)] removal during coagulation with alum, ferric chloride, and ferric sulfate has been shown to be less efficient than As(V) removal under comparable conditions (Shen, 1973; Gulledge and O'Conner, 1973; Sorg & Logsdon, 1978; Leckie et al., 1980; Wilkie & Hering, 1996). For As(V), better removal is achieved during coagulation with Fe(III) than aluminum salts on a weight basis (i.e. mg/L as ferric chloride or alum) (Shen, 1973; Gulledge and O'Conner, 1973; Sorg & Logsdon, 1978). Removal efficiency is affected by initial concentration of arsenic, pH, coagulant dosages, oxidation state of arsenic, sorbate/sorbent ratio and the concentration of co-occurring solutes in the solution.

In general higher removal efficiency can be achieved with increased coagulant dosages (Cheng et al., 1994; Edwards, 1994; Gulledge and O'Conner, 1973) and oxidative transformation, that is converting As(III) to As(V) (Frank & Clifford, 1986). Hering et al. (1996) reported almost complete removal of As(V) at initial concentrations of up to 0.10 mg/L with $FeCl_3$ dose of 4.9 mg/L; however, removal of As(III) present at the same concentrations were significantly lower. Shen (1973) showed that addition of 15 mg/L of chlorine followed by coagulation with 30 mg/L of $FeCl_3$ reduce arsenic (0.8 mg/L) concentration to trace amounts in the treated water. In pilot scale studies conducted using raw water from contaminated wells containing 0.8 to 0.9 mg/L arsenic, addition of about 20 mg/L of chlorine during aeration process followed by coagulation with $FeCl_3$ (about 60 mg/L), settling and filtration resulted in an effluent arsenic concentration below detection limit (Shen, 1973).

This chapter presents results of arsenic (both arsenate and arsenite) removal from groundwater by coagulation with ferric chloride. The effects of initial arsenic concentration, coagulant dose, and pre-oxidation of arsenite (with bleaching powder) on arsenic removal have been evaluated. In addition, effect of adsorbate/adsorbent ratio and adsorption density on arsenic removal have been evaluated. Based on these results, ferric chloride doses required for achieving WHO and Bangladesh standard for arsenic have been determined for different initial concentrations of arsenic.

4.2 MATERIALS AND METHODS

Efficiency of $FeCl_3$ in removing As(V) and As(III) from groundwater was evaluated in a series of jar tests. All jar tests were conducted in 1 L glass beakers using arsenic-free groundwater spiked with As(V) and As(III) standard solutions. The arsenic-free groundwater was collected from the groundwater supply at Bangladesh University of

Engineering and Technology (BUET), Dhaka. Groundwater is extracted using a number of deep tubewells at the BUET premises and is supplied directly to different academic and administrative buildings through a distribution system. Groundwater samples collected from a tap at the Environmental Engineering Laboratory of the Department of Civil Engineering, BUET were found to be free from arsenic. This arsenic free tap water was used in all jar tests. Groundwater collected from the tap was analyzed for detailed characterization a number of times during the course of the study. As(V) stock solution was prepared by dissolving its sodium salt $Na_2HAsO_4.7H_2O$ in distilled water, while As(III) stock solution was prepared by dissolving arsenic trioxide (As_2O_3) in distilled water containing sodium hydroxide (NaOH). Required quantity of As(V) or As(III) stock was added to the beakers to achieve the desired initial arsenic concentrations. Ferric chloride stock solution (prepared by dissolving $FeCl_3.6H_2O$ to distilled water) was then added to the beakers to achieve iron concentration ranging from 1 to 25 mg/L. No attempt was made to adjust pH of the samples. The beakers were then subjected to 1 minute of rapid mixing, 15 minutes of slow mixing, and the flocs were then allowed to settle for 30 minutes. Clear supernatant samples were then collected using a pipette from about 2 cm below the liquid surface. The supernatant samples were analysed for arsenic and iron concentrations. In all cases 200 ml samples were collected for arsenic analysis; 10 to 50 ml samples were collected for iron analysis. In the jar tests, initial pH of groundwater and final pH after coagulation were recorded.

In all cases, removal of arsenic was calculated by subtracting arsenic concentration in the clear supernatant from the initial concentration. Concentration of iron present as ferric hydroxide flocs was calculated by subtracting the residual iron present in the supernatant solution from the iron added to water as ferric chloride.

All chemicals, except bleaching powder, used in this study were of reagent grade. Commercial bleaching powder available in the market was used in this study. Arsenic concentrations in this study were determined using Silver Diethyldithiocarbamate Method (Standard Methods, 1985). In all cases 200 ml samples were collected for analysis of arsenic and volume (200 ml) of the samples were reduced to about 35 - 40 ml in an water bath before analysis. Iron concentrations were determined by colorimetric method (potassium thiocynate method). Detailed characterization of groundwater used in this was carried out by analyzing it for pH, conductivity, alkalinity, hardness, chloride, phosphate, nitrate, sulphate, iron, manganese, calcium, magnesium, sodium and potassium.

4.3 RESULTS AND DISCUSSION

Composition of groundwater used in this study is reported in Table 4.1. Arsenic concentration of the water was below detection limit (i.e., less than 0.001 mg/L). Iron concentration of the groundwater was found to be very low (0.10 mg/L), which is typical of groundwater in this region of Dhaka. Ferric chloride doses used in this study resulted in iron concentration ranging from about 1 to 25 mg/L, which means that naturally occurring iron (0.10 mg/L) had negligible effect on the final iron concentration after addition of ferric chloride.

Figures 4.1 and 4.2 show effect of coagulant dose and initial arsenic concentration of removal efficiency of As(V) and As(III). Fig. 4.1(a) shows removal of As(V) as a function of ferric chloride dose and Fig. 4.1(b) shows the removal as a function of Fe(III) (added as ferric chloride) concentration (from the same set of experiments) for three different initial arsenic concentrations (0.10, 0.25, and 0.50 mg/l). Figure 4.2 shows a comparison of the removal efficiency of As(III) and As(V), both present at an initial concentration of 0.25 mg/L. It should be noted that in the jar tests, initial pH of the groundwater varied from 6,6-6.9 and final pH after coagulation varied from 6.3 to 6.7.

Figures 4.3 through 4.5 show comparison of As(V) and As(III) removal and effect of pre-chlorination on As(III) removal. Figures 4.6 through 4.10 show effect of sorbat/sorbent ratio (expressed as μg/L As/mg/L Fe) on arsenic removal efficiency. Figures 4.11 and 4.12 show residual arsenic concentrations as a function of iron dose for different initial arsenic concentration, from experiments with As(V) and pre-oxidized As(III). Figures 4.13 and 4.14 shows requirement ferric chloride doses for removing As(V) or pre-oxidized As(III) present at different initial concentrations. The following sections provide detailed discussions on the results obtained from the experimental study.

Table 4.1 Composition of Groundwater Used in this Study

Sl. No.	Water Quality Parameter	Unit	Concentration Present
1	pH	--	6.6 - 6.9
2	Colour	Pt.Co.	5.0
3	Turbidity	NTU	1.5
4	Total Dissolved Solids, TDS	mg/L	310.0
5	Total Alkalinity as $CaCO_3$	mg/L	220.0
6	Total Hardness as $CaCO_3$	mg/L	330.0
7	Chloride, Cl^-	mg/L	290.0
8	Iron, Fe	mg/L	0.10
9	Manganese, Mn	mg/L	Trace
10	Arsenic, As	mg/L	< 0.001
11	Calcium, Ca	mg/L	93.1
12	Magnesium, Mn	mg/L	23.7
13	Nitrate, NO_3	mg/L	1.2
14	Sulphate, SO_4	mg/L	43.0
15	Phosphate, PO_4	mg/L	Trace
16	Silica, SiO_2	mg/L	28.9

4.3.1 Effects of Coagulant Dose and Initial Arsenic Concentration

Figure 4.1(a) and 4.1(b) shows removal of As(V) as a function of ferric chloride dose and iron dose, respectively, for three different initial arsenic concentrations - 0.10, 0.25, and 0.50 mg/L These concentrations are typical of arsenic concentrations reported for groundwater in Bangladesh. Figures 4.1(a) and (b) show that removal of As(V) increases with increasing coagulant (or iron) dose. At lower coagulant (or iron) doses, removal efficiency appears to decrease with increasing As(V) concentration. However, for higher coagulant (or iron) doses, removal efficiencies appear to be independent of initial arsenic concentration. At coagulant (or iron) dose beyond 25 mg/L of ferric chloride (or 5.165 mg/L of iron), removal efficiencies exceeding about 95 percent were achieved for all three initial concentrations of As(V). Similar effect can also be observed for pre-oxidized As(III) as shown in

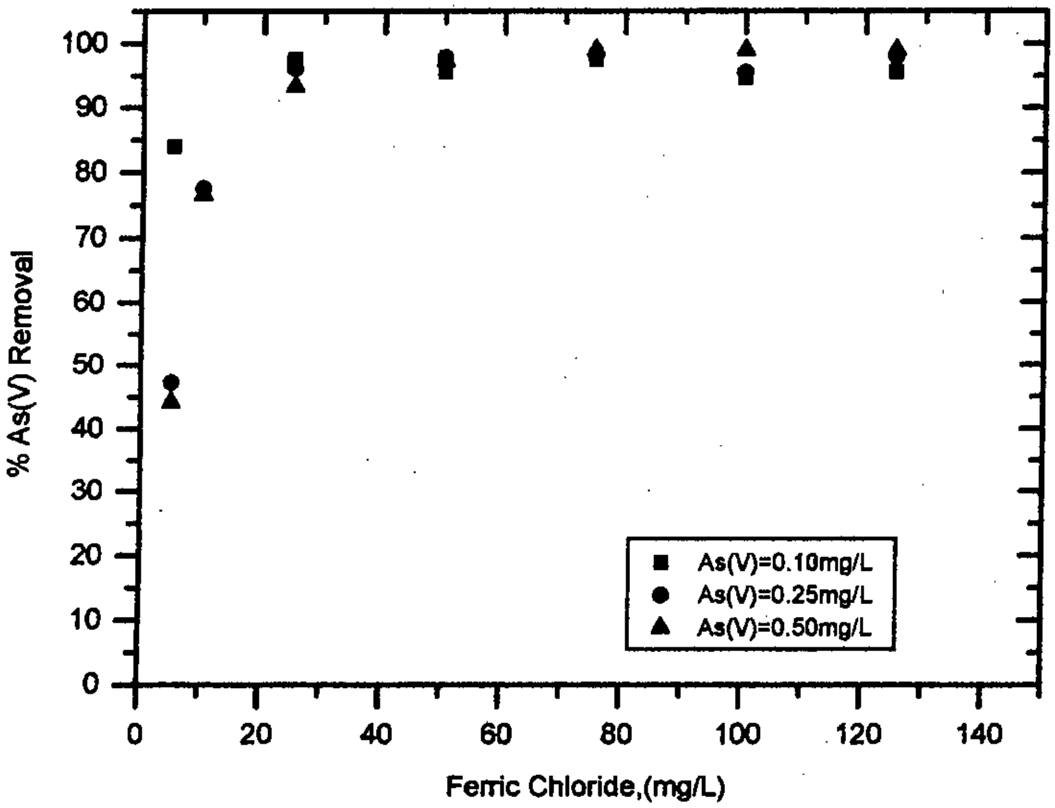

Figure 4.1(a) Removal of As(V) as a function of Ferric Chloride Dose for three different initial As(V) concentrations.

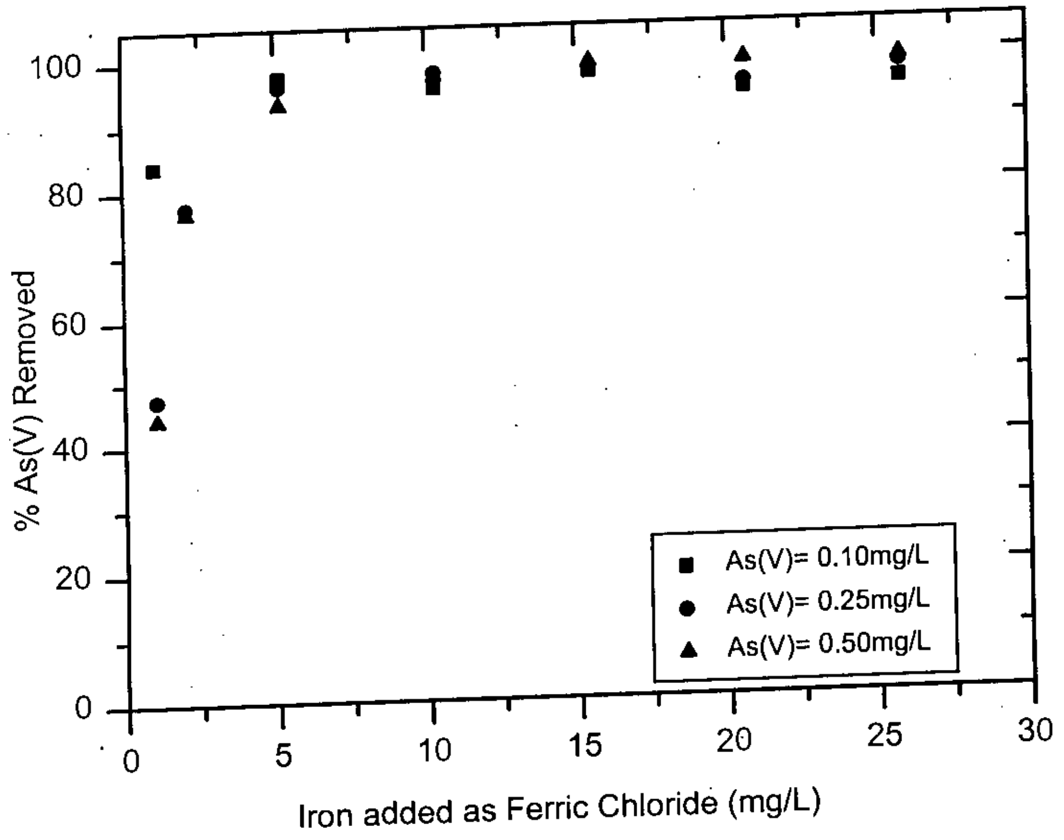

Figure 4.1(b) Removal of As(V) as a function of iron concentration (added as $FeCl_3$) for three different initial As(V) concentrations.

Figures 4.3 through 4.5. It appears that for higher coagulant (or iron) dose, removal is independent of initial concentration of As(V) [or pre-oxidized As(III)]. This result can be explained by the Langmuir expression which indicates that as long as the surface sites are not saturated by adsorbed As (or any other adsorbate), the percent of arsenic (or adsorbate) removal for a given coagulant dosage should be independent of the initial As (or adsorbate) concentration (Hering et al., 1996). Result from this study is also consistent with the observations of As(V) removal from source water by both ferric chloride and alum in modified jar tests (Cheng et al., 1994) and with previous studies of As(V) removal from synthetic waters by ferric chloride (Hering et al., 1996). At lower coagulant (or iron) dose, arsenic removal appears to be limited by the availability of adsorption sites.

Figure 4.2 shows removal of As(III) and As(V) both present at an initial concentration of 0.25 mg/L as a function of iron (added as ferric chloride) dose. This figure shows that although removal of As(III) increases with increasing coagulant (i.e., iron) dose, removal efficiency of As(III) is far less than that of As(V). Lower removal efficiency of As(III) compared to As(V) was observed in a number of other studies (e.g., Shen, 1973; Jekel, 1986; Edwards, 1994; Hering et al., 1996, 1997). Figure 4.2 shows that even with a iron dose as high as 25.83 mg/L (i.e., ferric chloride dose of 125 mg/L), removal efficiency approaching only 80% could be achieved. For the same initial concentration (i.e., 0.25 mg/L), similar removal efficiency (i.e., close to 80%) of As(V) could be achieved with iron dose as low as 2.065 mg/L (i.e., ferric chloride dose of 10.0 mg/L). In Bangladesh, both As(III) and As(V) have been detected in groundwater (Smedely et al., 1998; Safiullah et al., 1998) and Safiullah et al. (1998) reported that 12 to 50 percent of total arsenic in groundwater of Faridpur district exists as As(III). Results from this study suggests that higher concentration of As(III) would interfere with the efficiency of arsenic removal by ferric chloride. However, as discussed in the following section, pre-oxidation of As(III) can significantly improve removal efficiency of As(III).

4.3.2 Effects of Pre-oxidation on Removal Efficiency of As(III)

In this study, pre-oxidation of As(III) to As(V) was performed with bleaching powder. Bleaching powder [Ca(OCl)Cl] is a common disinfectant and is widely used in

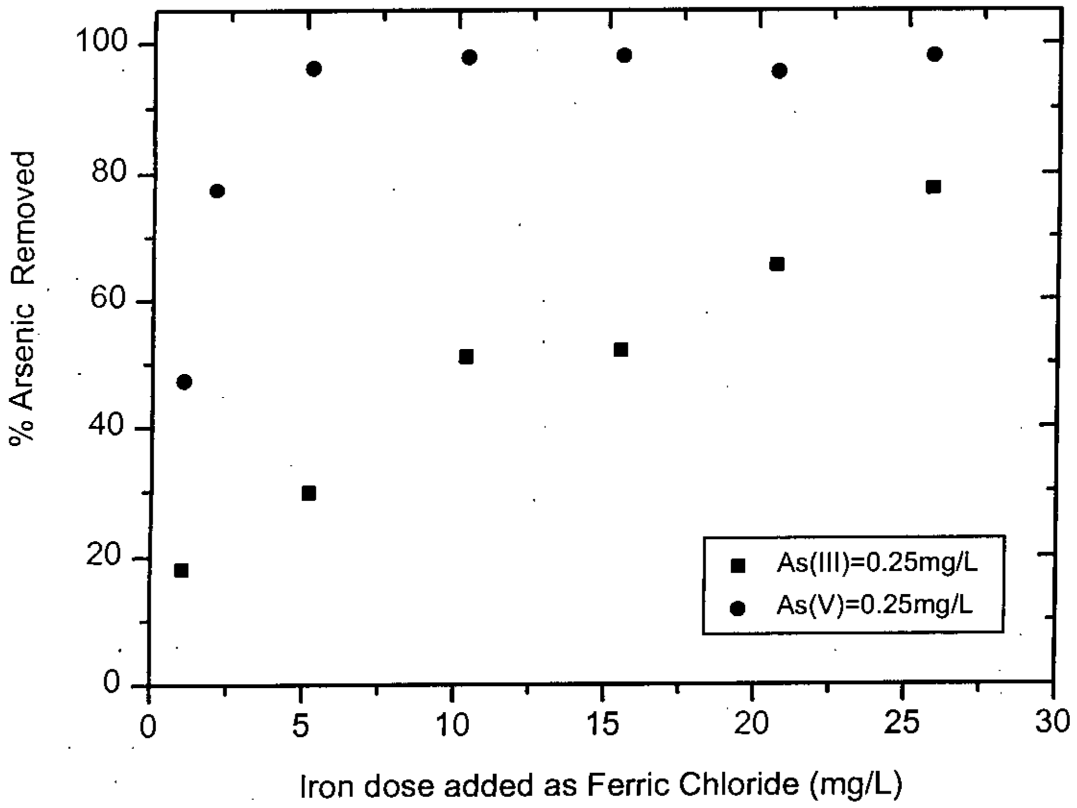

Figure 4.2 Comparison of removal of As(V) and As(III) as a function of iron dose (added as $FeCl_3$) for an initial arsenic concentration of 0.25 mg/L

Bangladesh. Chlorine in bleaching powder can oxidize As(III) to As(V) according to the following reactions:

$$H_2AsO_3 + HOCl = HAsO_4^{2-} + Cl^- + 3H^+ \qquad (4\text{-}1)$$

Commercial bleaching powder available in the market with chlorine content varying from about 15% to 35% (on a weight basis) was used in this study. From stoichiometric consideration (Eq. 4-1), about 0.47 mg/L of chlorine is required for oxidation of 1mg/L of arsenic. In this study, jar tests were conducted with chlorine dose 3 to 4 time that calculated from stoichiometric consideration. This was done partly due to possible presence of unknown reducing constituents and partly due to the very unstable nature of commercial bleaching powder. It should be noted that during the course of this study it was found that chlorine content of commercial bleaching powder available in the market vary from batch to batch and also vary over time for the same batch. Residual chlorine concentrations were measured in limited number of studies and chlorine concentrations in the treated groundwater samples were found to vary from 0.04 to 0.06 mg/L

Figures 4.3 and 4.4 shows effect of pre-oxidation (with bleaching powder) on the removal efficiency of As(III). Figure 4.3 shows that removal efficiency of As(III) is significantly less than that of As(V), both present at an initial concentration of 0.25 mg/L. However, pre-oxidation with bleaching powder significantly improved removal efficiency of As(III). From a comparison of removal of As(V) and pre-oxidized As(III) shown in Figs. 4.3 and 4.4, it appears that removal efficiencies are almost identical for both. This probably suggest that complete oxidation of As(III) to As(V) by commercial bleaching powder was achieved within the time frame of the experiments, i.e., about 45 minutes. Figure 4.5 shows removal of pre-oxidized As(III) as a function of iron (added as ferric chloride) dose. Very efficient removal of pre-oxidized As(III) even at concentrations as high as 2.0 mg/L suggest that commercial bleaching power can effectively oxidize As(III) to As(V). Results from this study, therefore, suggest that commercial bleaching powder can be effectively used for pre-oxidation of As(III) to As(V) in order to improve removal efficiency of arsenic by

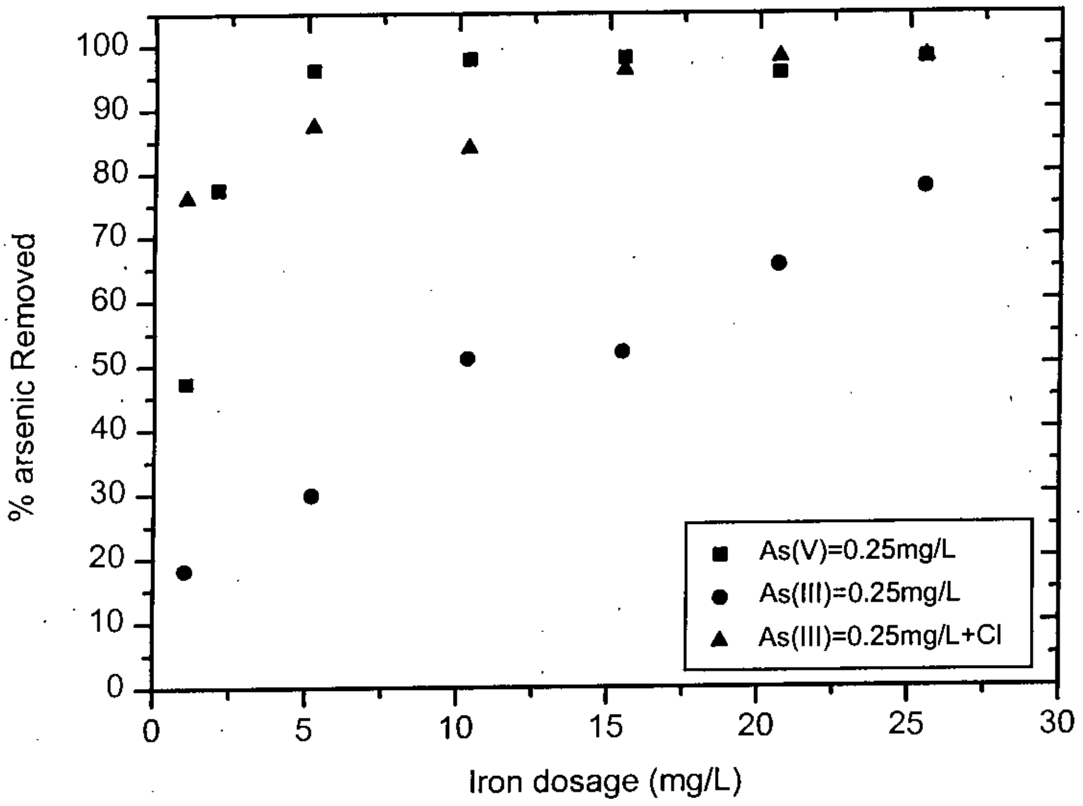

Figure 4.3 Comparison of removal efficiencies of As(V), As(III) and pre-oxidized As(III) as a function of iron dose for an initial arsenic concentration of 0.25 mg/L

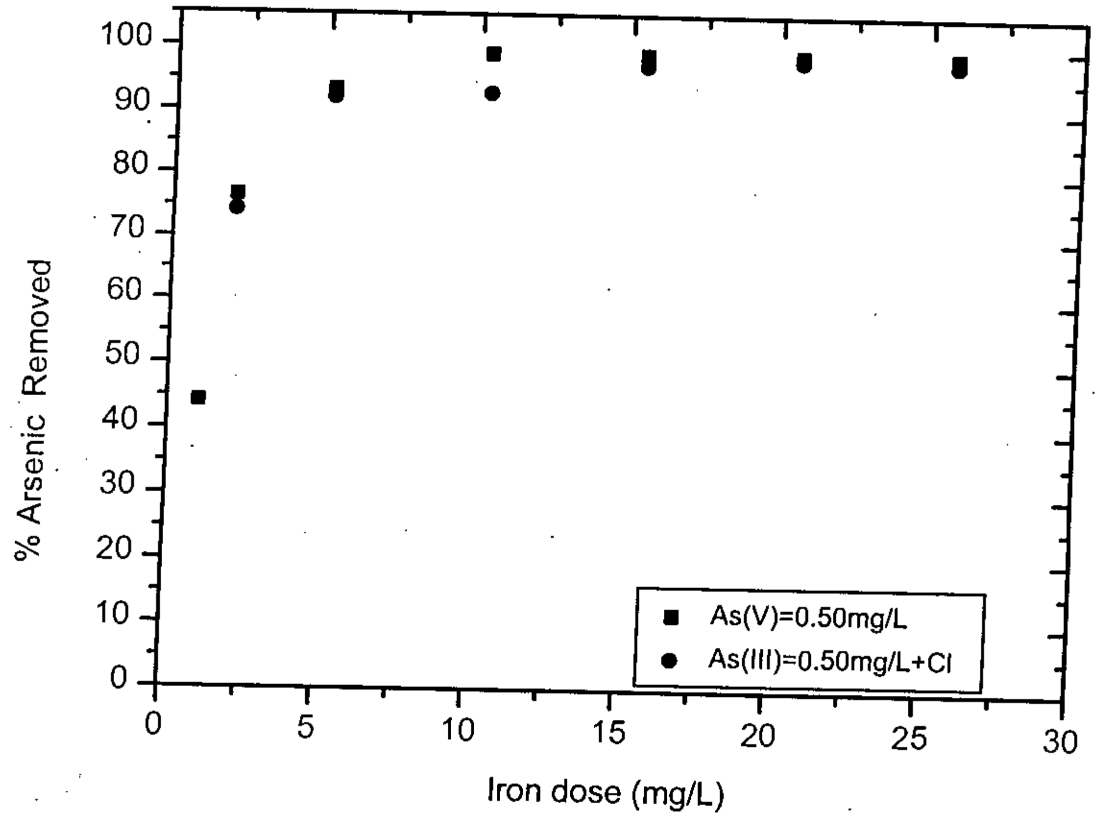

Figure 4.4 Comparison of removal efficiencies of As(V) and pre-oxidized As(III) as a function of iron dose for an initial arsenic concentration of 0.50 mg/L

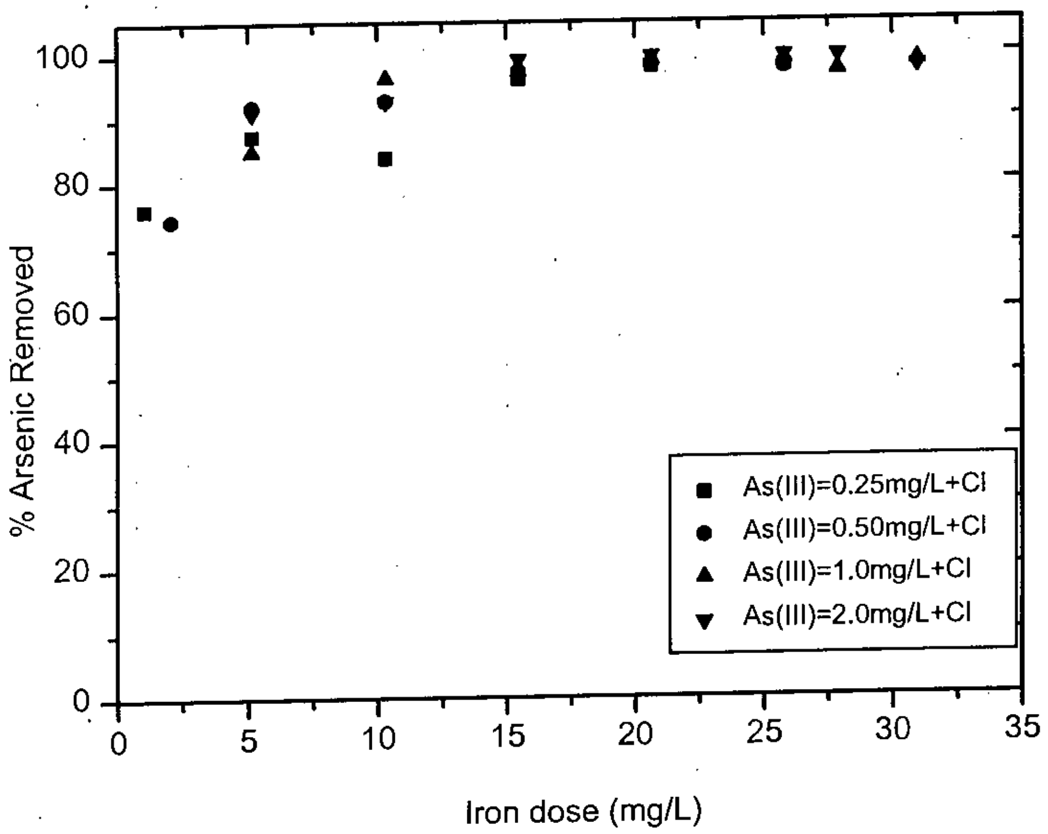

Figure 4.5 Removal of pre-oxidized As(III) as a function of iron dose for four different initial As(III) concentration.

ferric chloride. However, poor quality and unstable nature of bleaching powder is a major concern in this regard.

4.3.3 Effects of Adsorption Density

Figure 4.6 shows removal efficiency of As(V) as a function of sorbate/sorbent ratio (expressed as μg As/mg Fe); Fig. 4.7 shows the same for As(III) removal. From Figure 4.6 it appears that for a sorbate/sorbent ratio of about 50 or less, removal efficiencies exceeding 95 percent can be achieved, irrespective of the initial As(V) concentration (for a initial arsenic concentration of up to 0.50 mg/L). This result in effect gives the adsorption capacity of ferric hydroxide flocs (formed upon coagulation with ferric chloride) at the optimum sorbate sorbent ratio. In other words, this result suggest that at the optimum sorbate/sorbent ratio (which is 50 or less), 1 mg/L of iron (in the form of ferric hydroxide flocs) can effectively remove about 50 μg/L of dissolved As(V). Figure 4.7 which represents percent removal of As(III) as a function of sorbate/sorbent ratio shows no such trend and much poorer As(III) removal capacity of ferric hydroxide flocs.

Figure 4.8 shows adsorption density (expressed as μg As/mg Fe) as a function of iron (added as ferric chloride) dose for three different As(V) concentrations. Figure 4.9 shows the same for four different As(III) concentrations (pre-oxidized with bleaching powder). From Figs 4.8 and 4.9 it is clear that higher adsorption density is achieved with lower iron concentration (i.e., lower adsorption sites) and higher arsenic concentration. For a fixed arsenic concentration, as iron concentration increases adsorption density decreases. With increasing iron concentration, adsorption density is decreased because of the increasing number of adsorbent site. Or in other words, for a fixed iron concentration, when arsenic concentration is increased, adsorption density is also increases. The maximum adsorption density (about 353 μg As/mg Fe) was achieved with a As(III) (pre-oxidized) concentration of 2.0 mg/L and iron (added as ferric chloride) concentration of 5.165 mg/L (Fig. 4.9). However, as discussed earlier, at optimum sorbate/sorbent ratios (i.e., 50 or less), maximum adsorption density achieved is much less, about 50 μg As/mg Fe. Figure 4.10 shows comparison of adsorption densities achieved for As(V) and pre-oxidezed As(III) and it can be seen that similar adsorption densities are achieved for both under similar conditions.

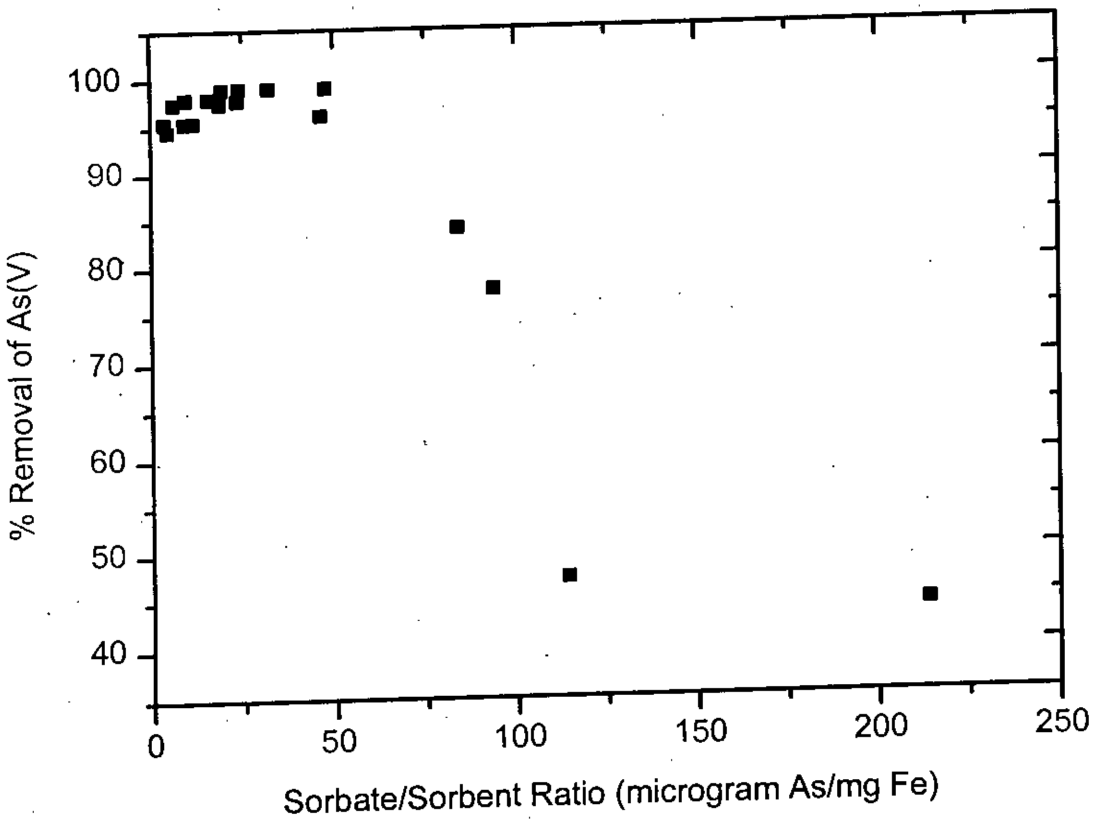

Figure 4.6 Removal of As(V) as a function of Sorbate/Sorbent Ratio

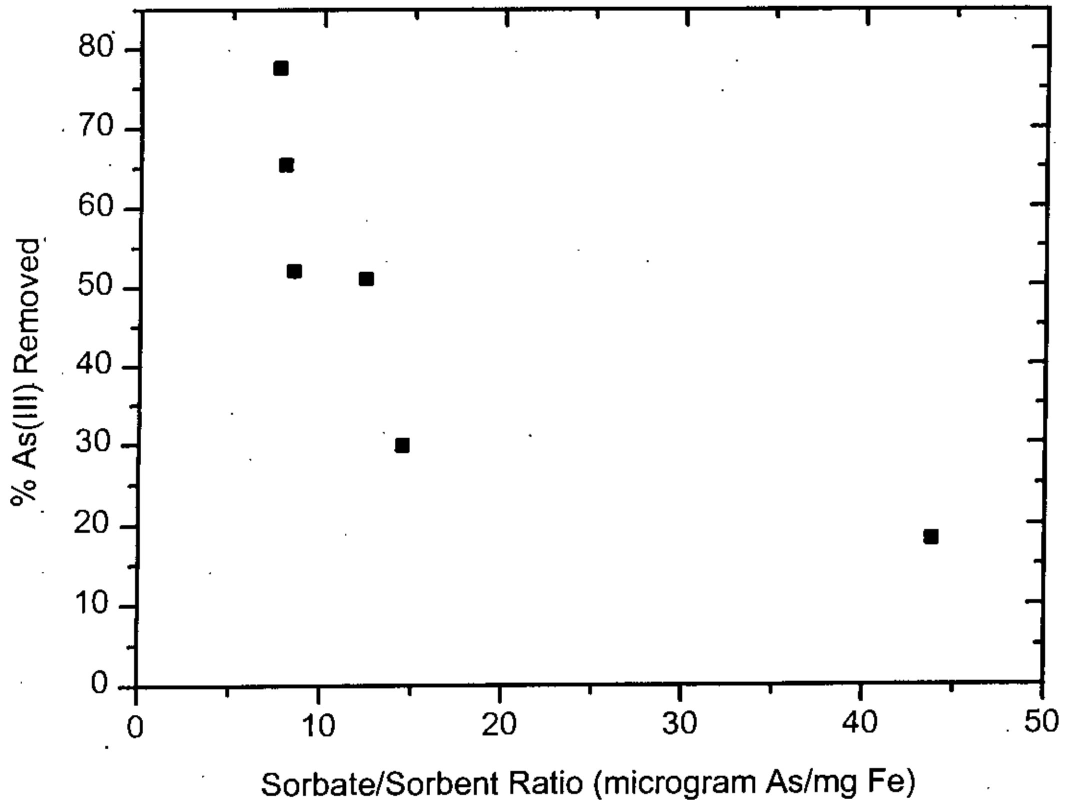

Figure 7. Removal of As(III) as a function of Sorbate/Sorbent ratio.

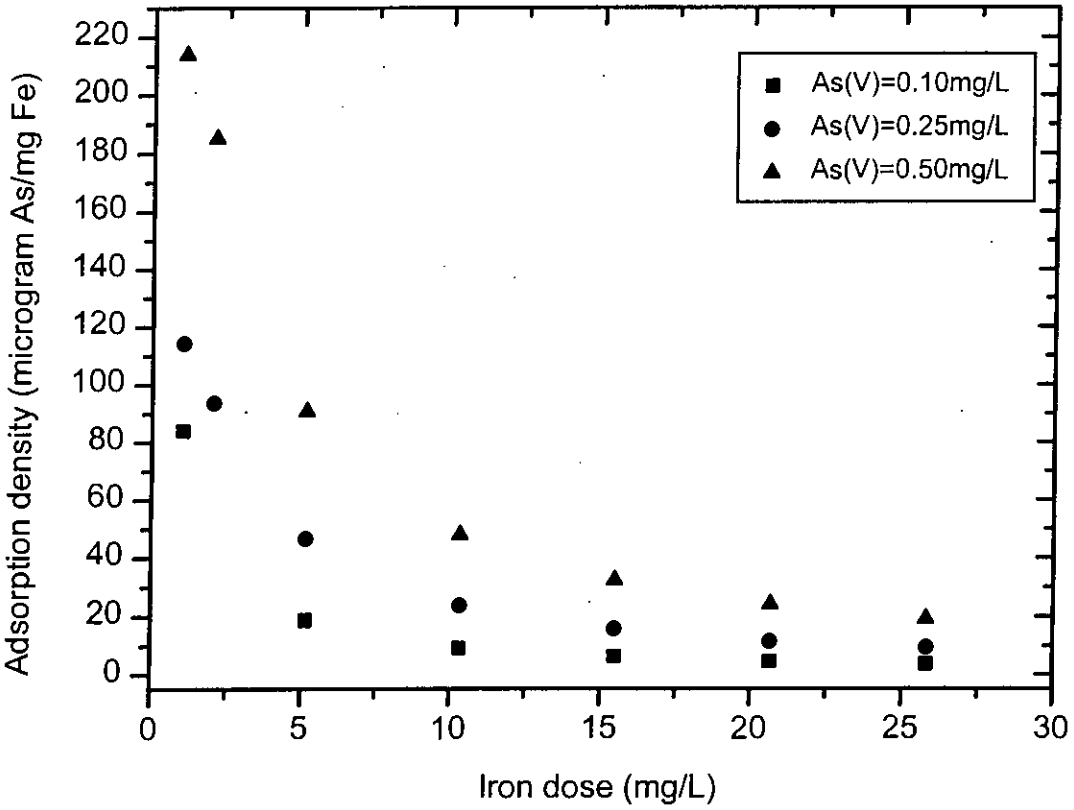

Figure 4.8 Calculated adsorption density as a function of iron dose for three different initial As(V) concentration.

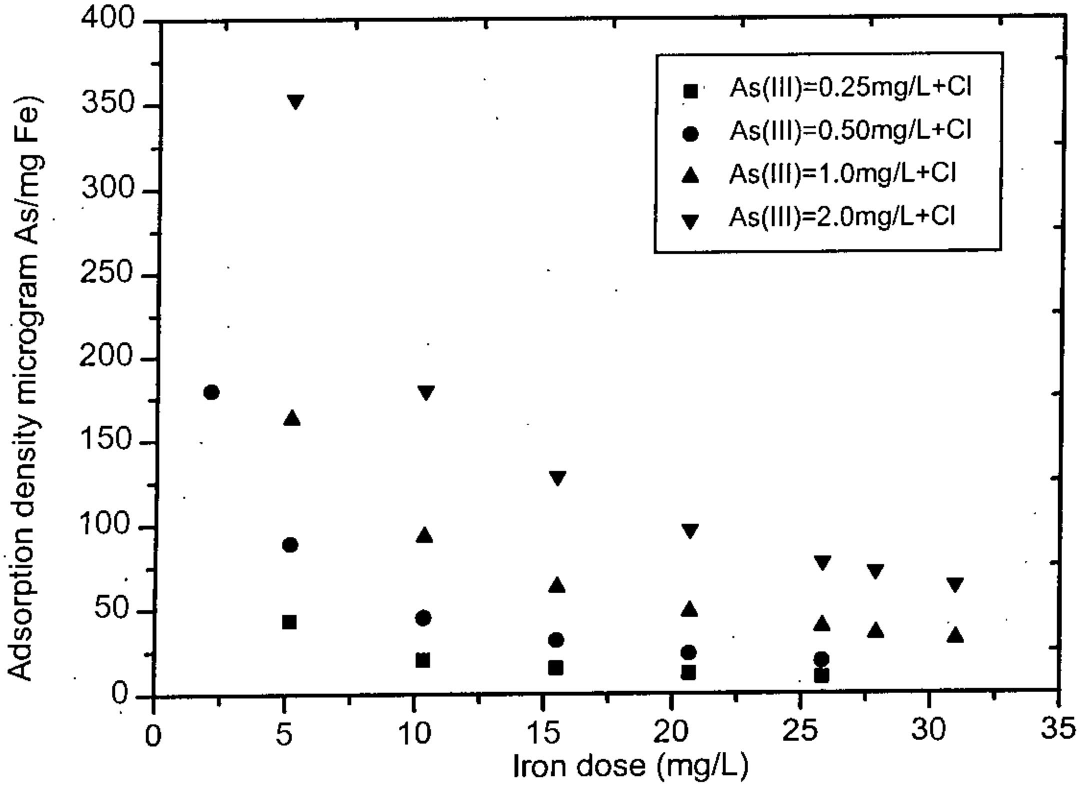

Figure 4.9 Calculated adsorption density as a function of iron dose for four different initial As(III) concentration (pre-oxidized).

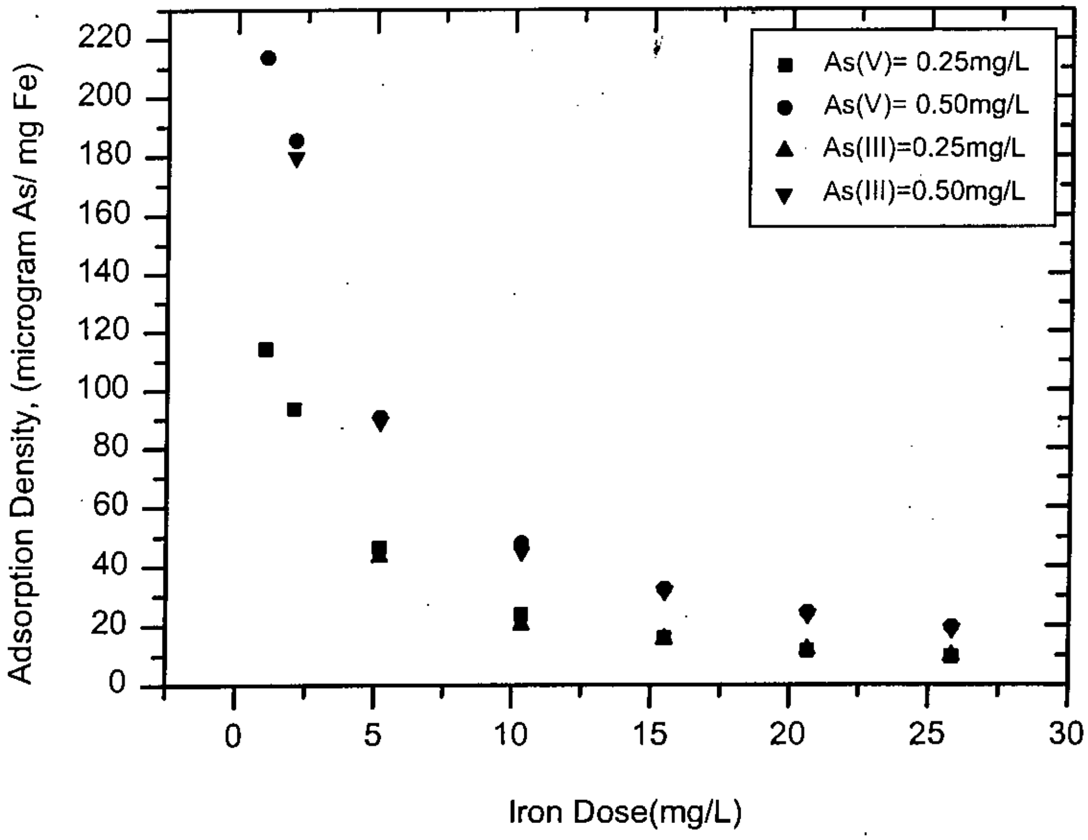

Figure 4.10 Comparison of adsorption densities of As(V) and pre-oxidized As(III).

4.3.4 Requirement of Ferric Chloride

From the experimental data and discussions presented in Sections 4.3.1 and 4.3.2, it is clear that ferric chloride removes As(V) much more efficiently than As(III). For example, about 5 mg/L of iron (i.e., about 25 mg/L of ferric chloride) can bring down As(V) concentration to less than 10 μg/L from an initial concentration of 0.25 mg/L; whereas in case of As(III) (present at the same initial concentration of 0.25 mg/L) iron dose as high as about 25 mg/L (i.e., ferric chloride dose of 125 mg/L) results in a residual arsenic concentration of about 55 μg/L, higher than the standard (50 μg/L) set by the Bangladesh EQS. However, experimental data presented above also suggest that pre-oxidation with commercially available bleaching powder can dramatically improve removal efficiency of As(III). In fact, results (see Figs. 4.3, 4.4) from this study suggests that removal efficiency (by ferric chloride) of As(V) and pre-oxidized As(III) are almost identical.

Since removal efficiency of As(III) by ferric chloride is considerably low and significant fraction of arsenic in the groundwater of Bangladesh can exist as As(III), it appears that arsenic removal technology based on ferric chloride coagulation must involve a pre-oxidation step for pre-oxidation of As(III) to As(V). Figure 4.11 shows residual As(V) concentration as a function of ferric chloride dose; while Fig. 4.12 shows residual concentration of pre-oxidized As(III) as a function of ferric chloride dose. Figure 4.11 shows that in case of As(V) present at an initial concentration of 0.1 mg/L, a ferric chloride dose as low as 5 mg/L (i.e., 1.03 mg/L of iron) can bring down the arsenic concentration below the Bangladesh standard of 50 μg/L, while a dose of about 25 mg/L (i.e., 5.17 mg/L of iron) is required to satisfy the WHO guideline value of 10 μg/L. Higher doses are required for higher initial concentration of As(V). For example, for an initial As(V) concentration of 0.5 mg/L, a ferric chloride dose of 25 mg/L is required to satisfy the Bangladesh standard and a dose of about 75 mg/L (i.e., 15.5 mg/L iron) is required to satisfy the WHO guideline value. Similar results were also obtained for pre-oxidized As(III) as can be seen from Fig. 4.12. Figure 4.12 shows residual arsenic concentration for arsenic present at much higher initial concentration, up to 2.0 mg/L.

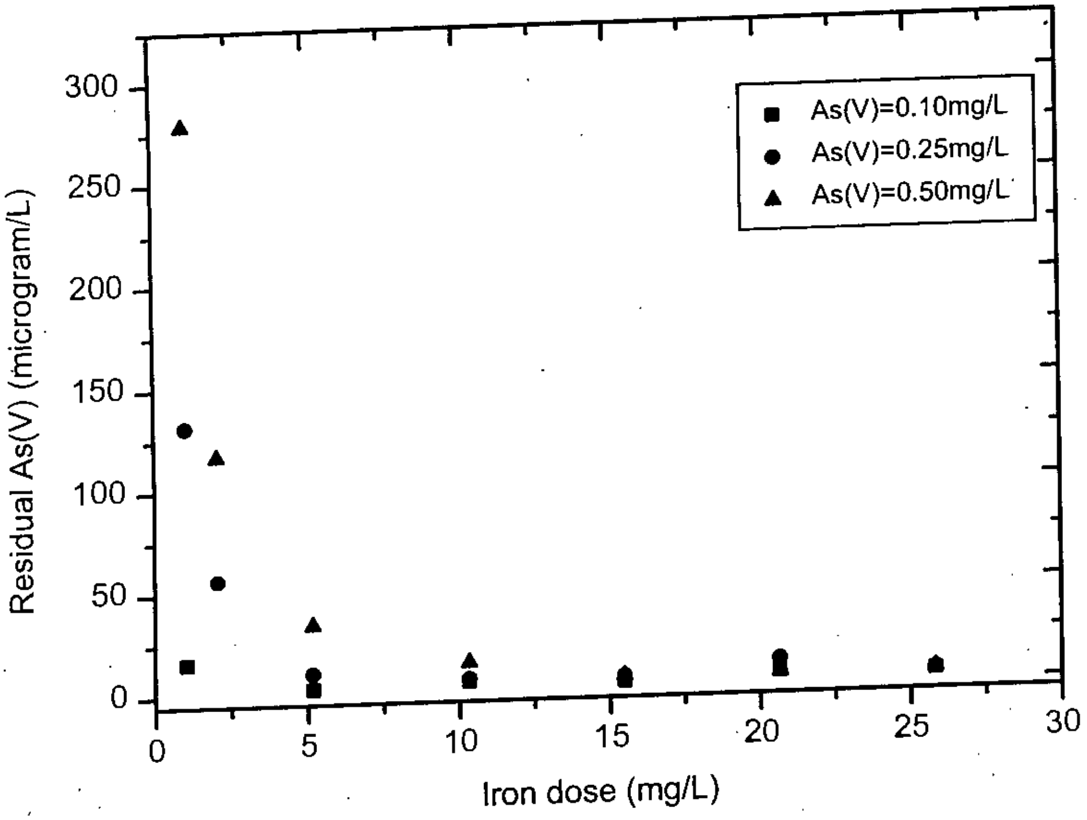

Figure 4.11 Residual arsenic concentration as a function of iron dose for three different initial As(V) concentration.

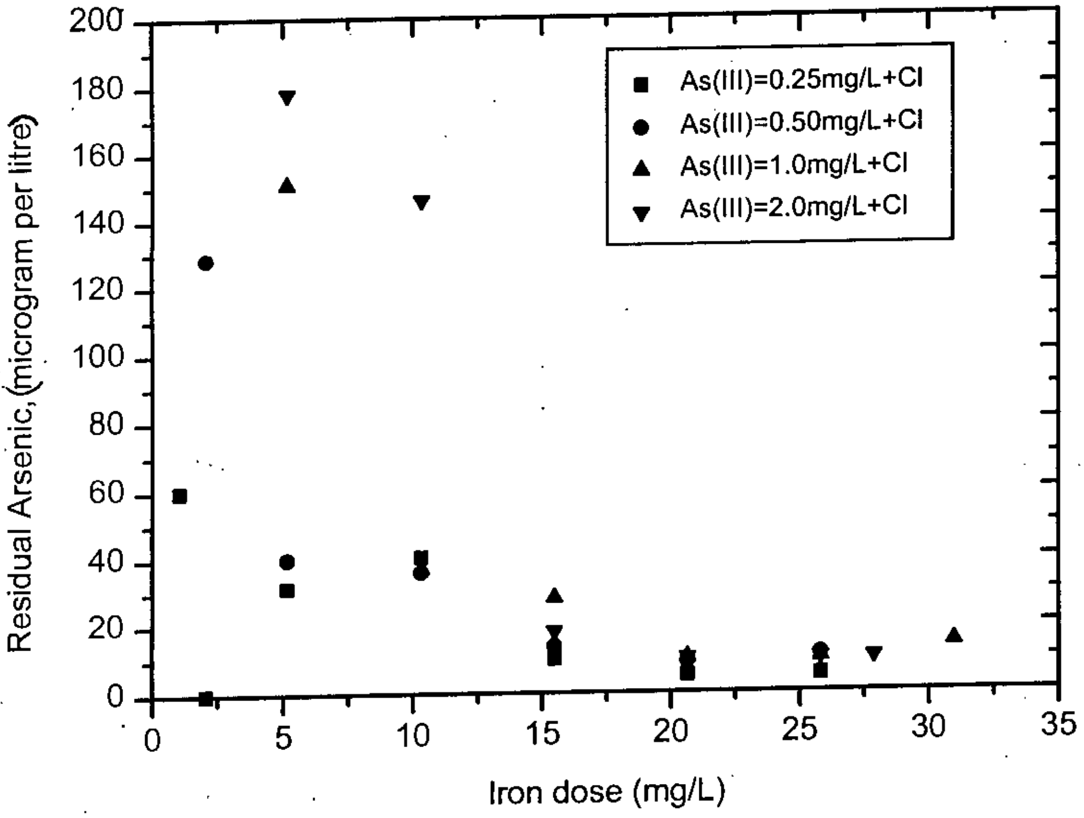

Figure 4.12 Residual arsenic concentration as a function of iron dose for different initial As(III) concentration (pre-oxidized).

Based on the results obtained from Figures 4.11 and 4.12, ferric chloride dose required for achieving a particular removal goal can be calculated for arsenic present at different initial concentrations. Figure 4.13 shows requirement of ferric chloride to satisfy the Bangladesh standard of 50 μg/L (or 0.05 mg/L) for arsenic present at different initial concentrations (up to 2.0 mg/L); whereas Fig. 4.14 shows requirement of ferric chloride to satisfy the WHO guideline value of 10 μg/L (or 0.01 mg/L). It should be noted that these requirements assume pre-oxidation of As(III), if present. From a comparison of Fig. 4.13 and 4.14, it is apparent that ferric chloride requirement for satisfying the WHO standard is significantly higher that required for satisfying the Bangladesh standard. For example, for an initial arsenic concentration of 0.25 mg/L, a dose of about 25 mg/L of ferric chloride is required to satisfy the Bangladesh standard, whereas about 75 mg/L or a dose three times as much is required to satisfy the WHO standard. This will have direct implications on cost of removal and the volume of sludge to be handled.

4. 4 CONCLUSIONS

In this study efficiency of ferric chloride in removing As(III) and As(V) was investigated for typical concentrations of arsenic present in groundwater of Bangladesh. Effect of pre-oxidation with bleaching powder on As(III) removal was evaluated in this study. Results of laboratory experiments were then used to determine the dose of ferric chloride required to remove arsenic present in groundwater at different initial concentrations. Natural groundwater spiked with arsenic was used in all experiments in order to simulate field condition as closely as possible. No effort was made to adjust pH of groundwater.

Removal of both As(V) and As(III) was found to increase with increasing coagulant dose. At lower coagulant (or iron) doses, removal efficiency decreased with increasing arsenic [both As(III) and As(V)] concentration. At lower coagulant (or iron) dose, arsenic removal appears to be limited by the availability of adsorption sites. For higher coagulant (or iron) doses, removal efficiencies of As(V) appear to be independent of initial arsenic concentration. Similar results were also observed for

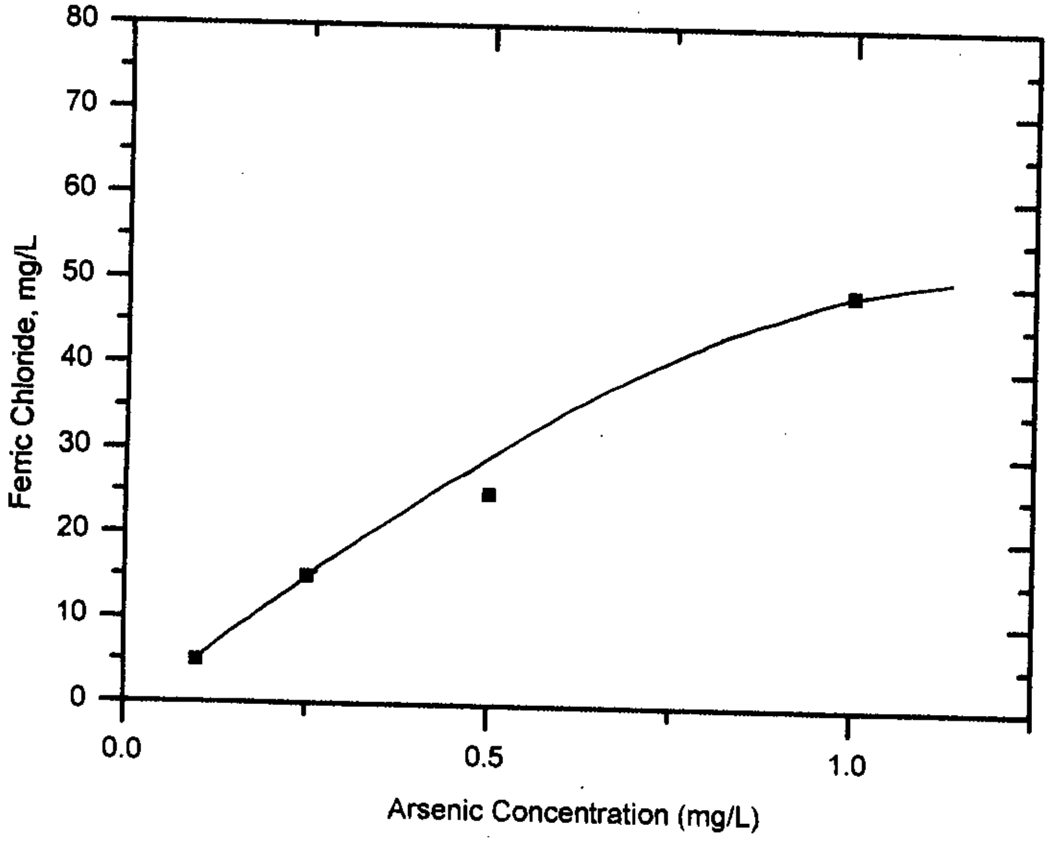

Figure 4.13 Requirement of Ferric Chloride to attain residual arsenic conc. below 0.05 mg/L for different initial arsenic concentration.

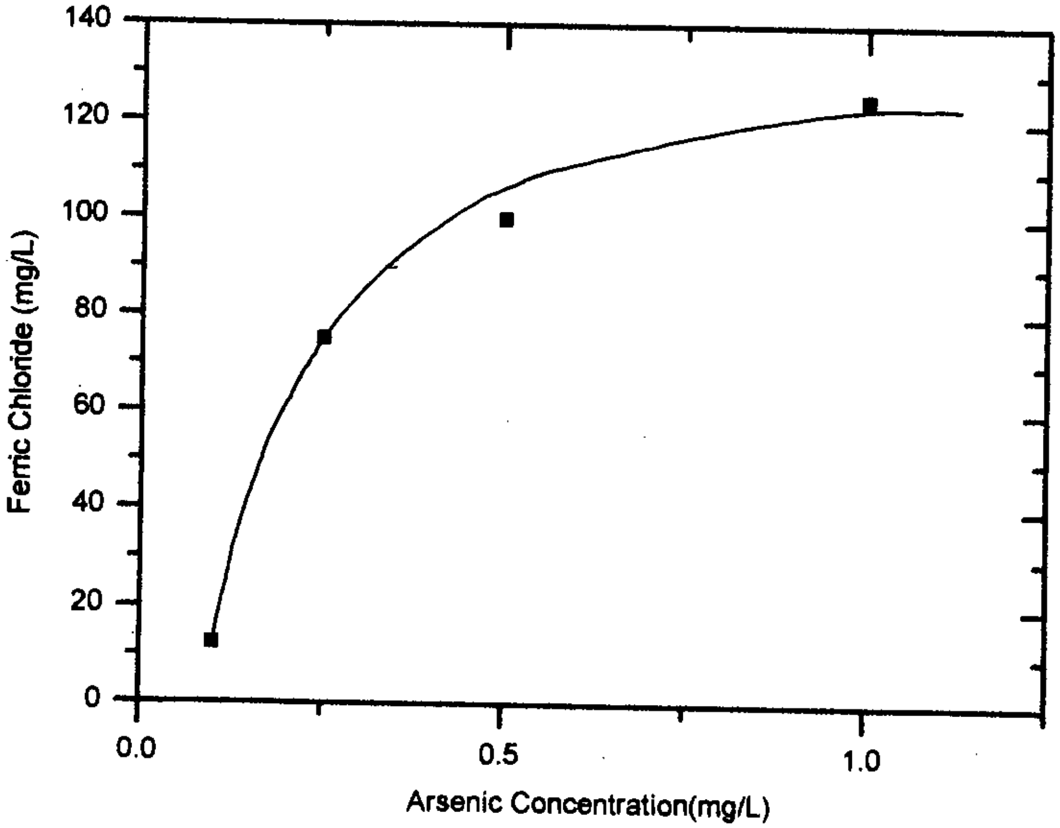

Figure 4.14 Requirement of Ferric Chloride to attain arsenic concentration below 0.01 mg/L for different initial arsenic concentration.

pre-oxidized As(III). This result is consistent with the proposition that as long as the surface sites are not saturated by adsorbed As, arsenic removal for a given coagulant dosage should be independent of the initial As concentration (Hering et al., 1996).

Results from this study suggest that removal efficiency of As(III) is significantly lower than that of As(V). For example, about 5 mg/L of iron (i.e., about 25 mg/L of ferric chloride) can bring down As(V) concentration to less than 10 μg/L from an initial concentration of 0.25 mg/L; whereas in case of As(III) (present at the same initial concentration of 0.25 mg/L) iron dose as high as about 25 mg/L (i.e., ferric chloride dose of 125 mg/L) resulted in a residual arsenic concentration of about 55 μg/L, higher than the standard (50 μg/L) set by the Bangladesh EQS. Since significant fraction of arsenic in the groundwater of Bangladesh can exist as As(III), it appears that arsenic removal technology based on ferric chloride coagulation must involve a pre-oxidation step for converting As(III) to As(V).

Results from this study suggest that bleaching powder which is widely available in Bangladesh can be effectively used for pre-oxidation of As(III) to As(V). It was found that removal efficiency of As(III) pre-oxidized with bleaching powder was almost identical to that of As(V), for identical coagulation times (about 45 minutes). While bleaching powder was successful in enhancing the removal efficiency of As(III), unstable nature and variable quality of commercial bleaching powder available in the market interfered with the determination of its required dose for pre-oxidation. From stoichiometric consideration (Eq. 4-1), about 0.47 mg/L of chlorine is required for oxidation of 1mg/L of arsenic. In this study, good removal of As(III) was achieved in jar tests using a chlorine dose 3 to 4 time that calculated from stoichiometric consideration. Residual chloride concentrations were also found to be relatively low, about 0.04 to 0.06 mg/L. Role of the oxidizing agent is vital in the removal of arsenic from water and the unstable nature of bleaching powder is a cause of concern in using bleaching powder as an oxidant for arsenic removal.

Results from this study enabled determination of particular sorbate/sorbent ratio beyond which removal efficiency drops beyond acceptable level. Results obtained suggest that for a sorbate/sorbent ratio (expressed as μg As/mg Fe) of about 50 or less, removal efficiencies [for As(V) and pre-oxidized As(III)] exceeding 95 percent can be achieved, irrespective of the initial As(V) concentration (for a maximum initial concentration of 0.50 mg/L). This can serve as a guideline value or thumb rule in determining required dose of ferric chloride for arsenic removal.

It was found that for a fixed arsenic concentration, as iron concentration increases adsorption density decreases. With increasing iron concentration, adsorption density is decreased because of the increasing number of adsorbent site. A maximum adsorption density of about 353 μg As/mg Fe was achieved with a As(III) (pre-oxidized) concentration of 2.0 mg/L and iron (added as ferric chloride) concentration of 5.165 mg/L (Fig. 4.9). However, as discussed earlier, at optimum sorbate/sorbent ratios (i.e., 50 or less), maximum adsorption density achieved is much less, about 50 μg As/mg Fe.

Based on the results of the experimental study, ferric chloride dose required for achieving a arsenic particular removal goal was determined for arsenic present at different initial concentrations and these are presented in graphical forms in Figures 4.13 and 4.14. These requirements assume pre-oxidation of As(III) to As(V). It was found that ferric chloride requirement for satisfying the WHO standard (10 μg/L) was significantly higher than that required for satisfying the Bangladesh standard of 50 μg/L. For example, for an initial arsenic concentration of 0.25 mg/L, a dose of about 25 mg/L of ferric chloride is required to satisfy the Bangladesh standard, whereas about 75 mg/L or a dose three times a much is required to satisfy the WHO standard. Thus the cost of arsenic removal by ferric chloride would depend on the water quality standard it is designed for. This is important in view of the fact that a number of countries have already reduced the safe limit of arsenic in drinking water and Bangladesh will also have to deal with this issue in the near future. Results from this study suggest that while ferric chloride can reduce arsenic concentrations (present at initial concentrations typical of those found in Bangladesh) below the current WHO standard of 10 μg/L, a much higher dose of the coagulant is needed to achieve that goal. This will in turn significantly increase the cost of removal and will also add to the sludge problem.

Chapter 5

EFFECT OF SOURCE WATER COMPOSITION ON ARSENIC REMOVAL

5.1 INTRODUCTION

Coagulation with hydrolyzing metal salts (e.g., alum and ferric chloride) is the most commonly used technique for removal of arsenic from water. In this process, arsenic is removed primarily by adsorption onto coagulated flocs of amorphous aluminum and iron hydroxides. Adsorption of ionic solutes onto hydrous oxide surfaces can vary significantly with pH and the presence of other competing ions in water. As a result, removal of arsenic from groundwater by ferric chloride (as well as alum) is likely to be influenced by pH and the composition of groundwater.

Effect of pH on arsenic removal was investigated in a number of studies (e.g., Sorg and Logsdon, 1978; Edwards, 1994; Katrinen and Martin, 1995; Hering et al., 1996). Decreased As(V) removal of arsenic was observed above pH 8 for ferric chloride and above 7 for alum (Sorg and Logsdon, 1978; Edwards, 1994). These decreases were probably related to the pH dependence of both adsorption and the solubility of amorphous iron (III) and aluminum hydroxides. Katrinen and Martin (1995) found efficient removal of As(V) with ferric sulfate between pH 6 and 8.5. Hering et al. (1996) found that below the neutral range, pH has a minimum effect on As(V) removal, whereas above pH 7, As(V) adsorption was slightly depressed.

Hering et al. (1996) however did not find any definite trend of pH dependence for As(III) removal. In coagulation experiments with ferric chloride, adsorption of As(III) was found to be minimum in the neutral pH range and increasing at both acidic and alkaline pH conditions (Hering et al., 1996).

arsenic and silica are scarce. In Bangladesh, groundwater usually contains relatively high concentration of silica. Silica concentration in the groundwater samples used in this study was about 30 mg/L, which is typical of silica concentration in groundwater of Bangladesh. Chloride, at concentrations typical for groundwater in Bangladesh (except for the saline coastal zone), is not likely to influence adsorption of arsenic onto ferric hydroxide flocs. Bi-carbonate is also not likely influence adsorption or removal of arsenic by ferric chloride.

In the presence of natural organic substances (i.e., fulvic acid), competitive effects resulting in decreased adsorption of As(V) on alumina have been observed, though the extent of competition varied markedly with pH, solid-solution ratio, and fulvic acid concentration (Xu et al., 1988, 1991). In coagulation tests with groundwater containing different concentrations of total organic carbon (TOC), As(V) was less efficiently removed by both ferric chloride and alum from the organic-rich groundwater and the effect was most pronounced at lower coagulant doses (Chang et al., 1994). Data on the presence of organic matter in the groundwater of Bangladesh are not available. In general, organic matter concentration in groundwater is usually low and thus it is not likely to play a significant role (resulting from competitive effects) in the removal of arsenic from groundwater by ferric chloride.

Hering et al. (1996) reported slight decrease in As(V) removal in the presence of phosphate at relatively low concentration (0.8 μM or about 0.076 mg/L). McNeill and Edwards (1997) also reported a slight decrease in As(V) removal in the presence of 32 μg/L of phosphate. Thanabalasingam and Pickering (1986) reported that about 60% of the adsorbed As(V) and 70% of the adsorbed As(III) were displaced by $H_2PO_4^-$ in a solution of 10^{-6} M phosphate. Phosphate has strong affinity for hydrous oxides of iron, manganese and aluminum and the adsorption characteristics of phosphate is very close to that of arsenate. Retention of arsenate and arsenite is therefore subjected to competition from phosphate (Hingston et al., 1971; Livesey and Huang, 1981; Pierce and Moore, 1982). Relatively high concentrations of phosphate, reaching as high as 5.8 mg/L, have been found in many regions of Bangladesh (Ahmed et al., 1997) and such high concentrations of phosphate can potentially influence removal of arsenic from groundwater by ferric chloride. In addition, a recent study by the British Geological Survey has found a somewhat positive correlation between the presence of arsenic and phosphate in some regions of Bangladesh. Thus, a better understanding of the influence of phosphate on arsenic removal is needed for evaluating the effectiveness of ferric chloride in removing arsenic from groundwater.

In addition to its influence on arsenic removal (by ferric chloride), phosphate can play an important role in the release of arsenic in the subsurface. Arsenic derived from weathering of arsenic-rich base metal sulfides are often found to be associated with iron oxyhydroxides in downstream sediments. Arsenic has high affinity for hydrous iron oxyhydroxides ($\equiv FeOH^0$) and become associated with them as a result of adsorption (Eqs. 5.1, 5.2).

$$\equiv FeOH^0 + AsO_4^{3-} + 3\,H^+ \quad = \quad \equiv FeH_2AsO_4 + H_2O \qquad (5.1)$$

$$\equiv FeOH^0 + AsO_4^{3-} + 2\,H^+ \quad = \quad \equiv FeHAsO_4^- + H_2O \qquad (5.2)$$

Sediments in the Ganges delta region are known to have iron oxyhydroxide coatings on the mineral grains and at many places these coatings have been found to be rich in arsenic (Khan, 1998; Rahman and Rahman, 1998). In Bangladesh, arsenic-rich iron oxyhydroxides appear to be the major source of arsenic from which arsenic is released as a result of dissolution and desorption (Ali and Ahmed, 1999). Desorption of arsenic form iron oxyhydroxides can be promoted in the presence of a competing anion such as phosphate. Possible reactions for desorption of arsenic in the presence of phosphate are shown below.

$$\equiv FeH_2AsO_4 + PO_4^{3-} \quad = \quad \equiv FeH_2PO_4 + AsO_4^{3-} \qquad (5.3)$$

$$\equiv FeHAsO_4^- + PO_4^{3-} \quad = \quad \equiv FeHPO_4^- + AsO_4^{3-} \qquad (5.4)$$

In soil environment, phosphate is mainly adsorbed by both soil colloidal iron and aluminum oxides, whereas arsenic is adsorbed primarily by soil colloidal iron oxide

(Gile, 1936). Arsenic and phosphate in soil exhibit similar behavior, but the amount of phosphate sorbed is greater than that of arsenic (Dean and Rubins, 1947). Under similar conditions, a larger quantity of phosphate is sorbed onto soil, presumably due to the different ionic radii of the anions in question. The radius of phosphate ion is smaller, and in a given soil surface a larger number of phosphate ions can be sorbed. Phosphate can substantially suppress arsenic adsorption by soils and the extent of suppression varies from soil to soil (Livesey and Huang, 1981). Clement and Faust (1981) showed that during water-sediment interactions, the concentration of phosphate present in the system is a significant factor in the release of arsenic from the sediments. In a laboratory leaching experiment with contaminated sediments under aerobic conditions and the in presence of phosphate (3×10^{-3} M), arsenic was substantially released to the overlying water. Enhanced phosphate concentration in the groundwater may result from the application of phosphate fertilizer. A better understanding of arsenic-phosphate adsorption behavior onto amorphous ferric hydroxides could provide insight into the possible role of phosphate on the release of arsenic from arsenic-rich iron oxyhydroxides in the subsurface.

This chapter presents experimental results of the effects of pH on removal of As(V) during coagulation with ferric chloride. Experimental results on effect of phosphate on removal of As(V) by ferric chloride are also presented in this chapter. Possible implications of the presence of high concentration of phosphate in the groundwater environment have been discussed in details.

5.2 MATERIALS AND METHODS

The effect of pH on arsenic [As(V)] removal was evaluated in experiments (that is in jar tests) similar to those described in Chapter 4. All jar tests were conducted in 1 L glass beakers using arsenic-free groundwater (characteristics summarized in Chapter 4) spiked with As(V) standard solutions. As(V) stock solution was prepared by dissolving its sodium salt $Na_2HAsO_4.7H_2O$ in distilled water. Required quantities of As(V) stock solutions were added to the beakers to achieve the desired initial arsenic concentrations.

Ferric chloride stock solution (prepared by dissolving $FeCl_3.6H_2O$ to distilled water) was then added to the beakers to achieve the desired iron concentrations. pH adjustments were made with sodium hydroxide (NaOH) or hydrochloric acid (HCl) solutions. The beakers were then subjected to 1 minute of rapid mixing, 15 minutes of slow mixing, and the flocs were then allowed to settle for 30 minutes. In each beaker, pH of the supernatant was measured with a pH meter. Clear supernatant samples were then collected using a pipette from about 2 cm below the liquid surface. The supernatant samples were analysed for arsenic and iron concentrations. In all cases 200 ml samples were collected for arsenic analysis; 10 to 50 ml samples were collected for iron analysis.

Effect of phosphate (PO_4) on arsenic [As(V)] removal also evaluated in similar experiments where the beakers were spiked with standard solution of potassium dihydrogen phosphate (KH_2PO_4) to attain desired phosphate concentration. Residual phosphate concentration in the supernatant after coagulation was also determined for a limited number of experiments.

In all cases, removal of arsenic was calculated by subtracting arsenic concentration in the clear supernatant from the initial concentration. Concentration of iron present as ferric hydroxide flocs was calculated by subtracting the residual iron present in the supernatant solution from the iron added to water as ferric chloride.

All chemicals used in the laboratory work were of reagent grade. Arsenic concentrations in this study were determined using Silver Diethyldithiocarbamate Method (Standard Methods, 1985). In all cases 200 ml samples were collected for analysis of arsenic and volume (200 ml) of the samples were reduced to about 35 - 40 ml in an water bath before analysis. Detection limit of arsenic for the Silver Diethyldithiocarbamate Method is about 1 μg. With a detection limit of 1 μg and an initial sample volume of 200 ml, the lowest detectable concentration was therefore about 5 μg/l or 0.005 mg/l. Iron concentrations were determined by colorimetric method (potassium thiocynate method).

5.3 RESULTS AND DISCUSSION

Table 5.1 shows composition of groundwater used in this. Arsenic concentration of the water was below detection limit (i.e., less than 0.001 mg/L). Iron concentration of the groundwater was found to be very low (0.10 mg/L), which is typical of groundwater in this region of Dhaka. Ferric chloride doses used in this study resulted in iron concentration ranging from about 1 to 25 mg/L, which means that naturally occurring iron (0.10 mg/L) had negligible effect on the final iron concentration after addition of ferric chloride.

From Table 5.1 it can be seen that ions that can compete with arsenic for adsorption onto ferric hydroxide flocs and influence removal of arsenic include pH (i.e., H^+/OH^- ions), sulphate (SO_4^{2-}), Phosphate (PO_4^{3-}), silica (SiO_2) and calcium (Ca^{2+}). Available data suggest that bi-carbonate (HCO_3^-), chloride (Cl^-), nitrate (NO_3^-), and magnesium (Mg^{2+}) are not likely to have any significant effect on arsenic adsorption or removal. As discussed earlier, calcium has been found to enhance arsenic adsorption at relatively high concentrations, while sulphate has been found to suppress arsenic adsorption when present at relatively high concentrations. However, at concentrations typically encountered in Bangladesh groundwater, these ions are not likely to have any significant influence on arsenic removal. Silica can potentially influence arsenic removal by competing with arsenic for adsorption sites. However data on effects of silica on arsenic removal is scarce. Silica has been found to be present at relatively high concentrations in groundwater all over Bangladesh and in this study all experiments were conducted with natural groundwater containing about 30 mg/L of silica. Phosphate concentration has been found to vary significantly in groundwater of Bangladesh and limited data on competitive sorption of arsenic and phosphate suggest that it can have a significant effect on arsenic removal. The pH of groundwater, varies over a limited range, it is important to investigate the sensitivity of pH on arsenic removal. The following sections describe effects of pH and phosphate on arsenic removal by ferric chloride.

Table 5.1 Composition of Natural Groundwater Used in this Study

Sl. No.	**Water Quality Parameter**	**Unit**	**Concentration Present**
1	pH	--	6.6 - 6.9
2	Colour	Pt.Co.	5.0
3	Turbidity	NTU	1.5
4	Total Dissolved Solids, TDS	mg/L	310.0
5	Total Alkalinity as $CaCO_3$	mg/L	220.0
6	Total Hardness as $CaCO_3$	mg/L	330.0
7	Chloride, Cl^-	mg/L	290.0
8	Iron, Fe	mg/L	0.10
9	Manganese, Mn	mg/L	Trace
10	Arsenic, As	mg/L	< 0.001
11	Calcium, Ca	mg/L	93.1
12	Magnesium, Mn	mg/L	23.7
13	Nitrate, NO_3	mg/L	1.2
14	Sulphate, SO_4	mg/L	43.0
15	Phosphate, PO_4	mg/L	Trace
16	Silica, SiO_2	mg/L	28.9

5.3.1 Effects of pH

Figures 5.1 and 5.2 show the influence of pH on the removal of As(V). Figure 5.1 shows removal of As(V) at an initial concentration of 0.25 mg/L with 5.165 mg/L of iron (25 mg/L $FeCl_3$). From this figure removal of arsenic appears to be maximum in the neutral pH range (close to 95 percent at pH 7.1) and slightly depressed both at higher and lower pH values. Figure 5.2 shows removal of As(V) at an initial concentration of 0.25 mg/L with 20.66 mg/L iron (100 mg/L of $FeCl_3$). This figure shows no significant influence of pH on arsenic removal, except for a fall in removal efficiency beyond pH 9.

This result is consistent with those reported in the literature (e.g., Sorg and Logsdon, 1978; Edwards, 1994; Hering et al., 1996). Sorg and Logsdon (1978) observed decreased removal of As(V) above pH 8. Hering et al. (1997) reported significant reduction in

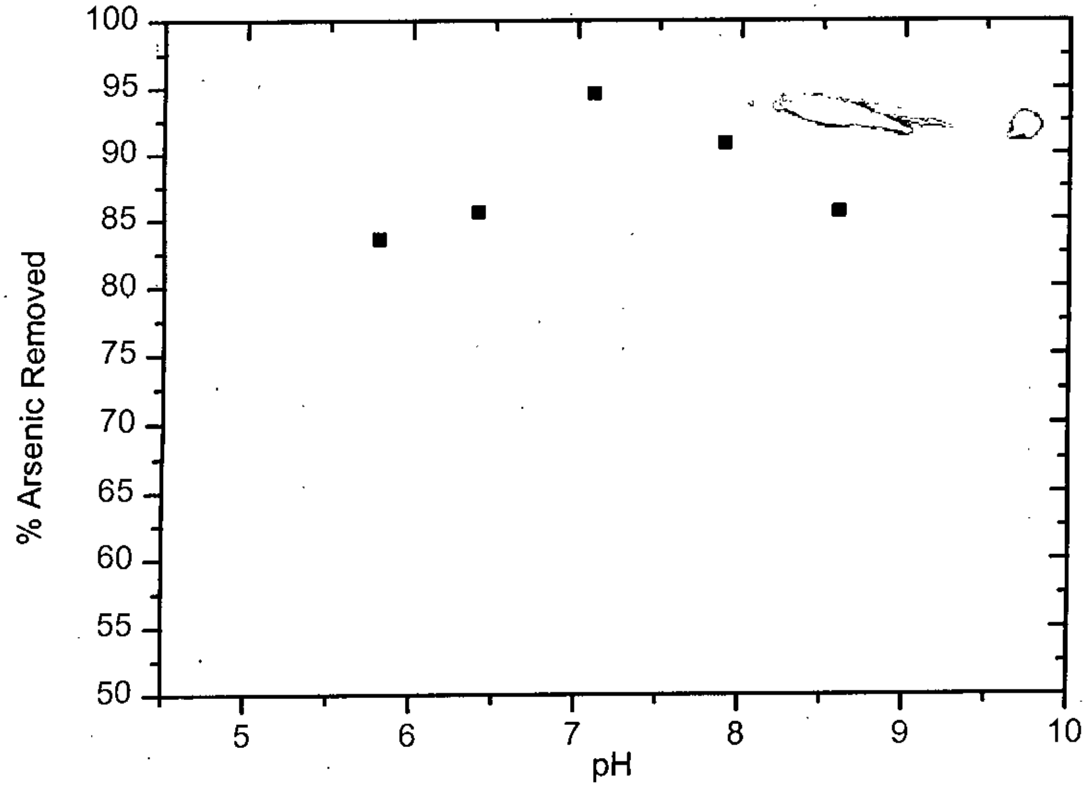

Figure 5.1 Effect of pH on removal of As(V) at an initial concentration of 0.25 mg/L during coagulation with 25 mg/L of Ferric Chloride.

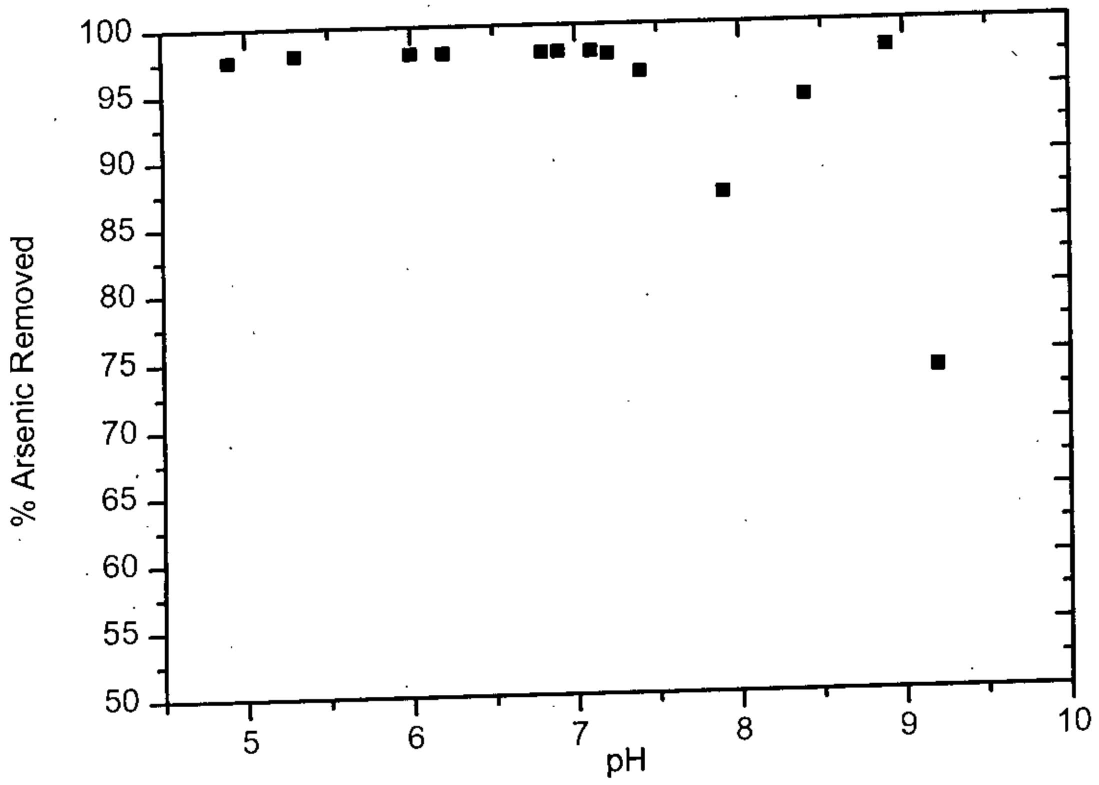

Figure 5.2 Effect of pH on removal of As(V) at an initial concentration of 0.25 mg/L during coagulation with 100 mg/L of Ferric Chloride.

removal efficiency of As(V) by ferric chloride at pH values above 9. It should be noted that the reduction of adsorption (removal) of As(V) at higher pH values shown in Figure 5.2 is not as pronounced as those observed by Hering et al. (1997). One reason for this could be the very high concentration of (adsorbent) iron (20.66 mg/L or equivalent to 100 mg/L $FeCl_3$) used in this experiment. Reduction in adsorption (removal) at higher pH is likely to be more pronounced at relatively lower adsorbent (ferric chloride) concentration. Edward (1994) experienced that at all dosages exceeding 20 mg/L as $FeCl_3$, greater than 90 percent removal of As(V) was always achieved at pH less than 8.0. As discussed earlier, reduction in arsenic removal at higher pH values is probably related to the pH dependence of adsorption (which goes down with increasing pH, as is the case for most anions) as well the solubility of amorphous iron (III), which is minimum at around pH 8 and goes up above and below this pH value. Greater solubility of amorphous iron (III) would result in a reduction of available oxide surface for adsorption.

Effect of pH on As(III) removal was not investigated in this study. Hering et al. (1996) did not find any definite trend of pH dependence for arsenite [As(III)] adsorption. In coagulation experiments with ferric chloride, adsorption of As(III) was found to be minimum in the neutral pH range and increasing at both acidic and alkaline pH conditions. These effects [for As(III)] were consistent with the formation of smaller ferric hydroxide precipitates at the extreme pH values because smaller precipitates would provide a higher effective surface area for arsenic adsorption. The size of ferric hydroxide precipitates were found to vary with pH, as demonstrated by the absence of visible flocs at the extreme pH values (Hering et al., 1996).

Somewhat opposite trend was observed by Hering et al. (1996) for adsorption of arsenite [As(III)] onto pre-formed hydrous ferric oxide (HFO). Pierce and Moore (1980, 1982) also found the same trend for arsenite [As(III)] adsorption on hydrous ferric oxide (HFO); decreased adsorption was observed below pH 6 and above pH 8. The different pH trends observed in the coagulation and adsorption (onto HFO) experiments probably suggest that arsenic removal during coagulation is influenced by factors that do not significantly affect adsorption onto pre-formed HFO.

In Bangladesh, pH of groundwater usually falls between 6 and 8. Reported arsenic speciation data for groundwater in Bangladesh, though limited, suggest that arsenic is present both as arsenite [As(III)] and arsenate [As(V)]. Results from this study suggest that pH is not likely to play a major role in determining the removal efficiency of As(V) from groundwater by ferric chloride. On the other hand, a lower removal efficiency may be achieved if arsenic is primarily present as As(III).

As can be seen from the results presented in Chapter 4, significantly lower removal efficiency of As(III) in the neutral pH range, compared to As(V), is the primary concern in arsenic removal by ferric chloride. Thus if arsenic concentration is high and if a significant fraction of arsenic in groundwater is present as As(III), removal efficiency may be enhanced either by using an oxidizing agent (e.g., bleaching powder or potassium permanganate) for pre-oxidation of As(III) to As(V), or by increasing the dose of ferric chloride. Since it is not always easy to measure the arsenite/arsenate ratio in a groundwater sample, it is better to be conservative in determining ferric chloride dose for arsenic removal.

Care should however be taken in determining ferric chloride dose for treating water with high pH values. On the other hand, it should be noted that addition of ferric chloride to water may result in a drop of pH of the water, especially for groundwater with low alkalinity (i.e., low buffer capacity). Greater solubility of amorphous iron (III) at lower pH values may result in lower removal efficiency.

5.3.2 Effect of Phosphate

Figures 5.3 and 5.4 show the influence of phosphate on removal of As(V) by ferric chloride. Figure 5.3 shows effect of phosphate on removal of As(V) with an initial concentration of 0.10 mg/L in the presence of 2.066 mg/L of iron (10 mg/L $FeCl_3$). Figure 5.4 shows removal of As(V) with an initial concentration of 0.25 mg/L.

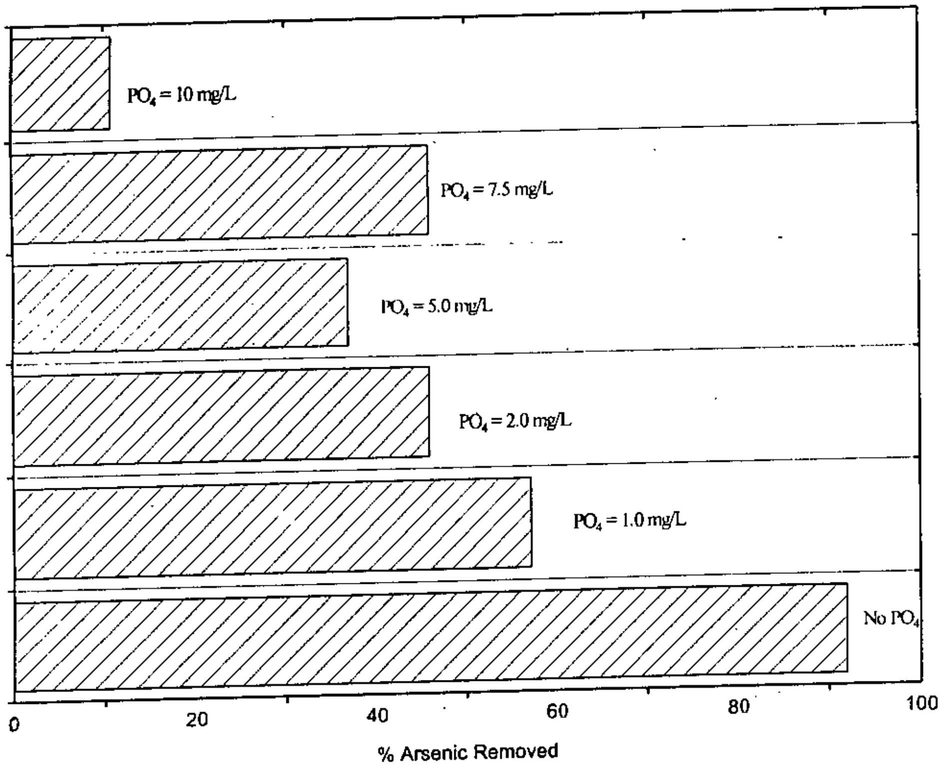

Figure 5.3 Effect of Phosphate (PO_4) on removal of As(V) at an initial concentration of 0.10 mg/L during coagulation with 10 mg/L of Ferric Chloride.

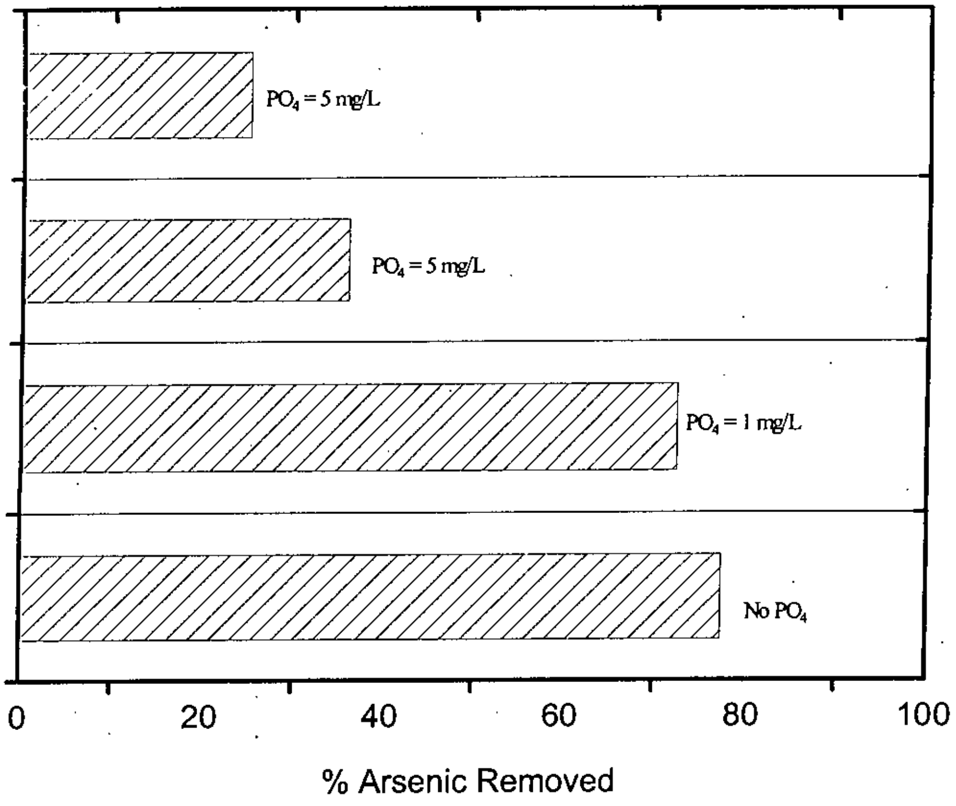

Figure 5.4 Effect of Phosphate (PO_4) on removal of As(V) at an initial concentration of 0.25 mg/L during coagulation with 10 mg/L of Ferric Chloride.

Figures 5.3 and 5.4 shows a steady decrease in As(V) removal with increasing phosphate concentration. Fig. 5.3 shows that phosphate can have a dramatic effect on removal of As(V) by ferric chloride. Figure 5.3 shows that phosphate (PO_4) present at 2.0 mg/L can reduce removal from more than 90 percent (in the absence of phosphate) to about 46 percent; while at concentration of 5.0 mg/L PO_4, removal comes down to about 37 mg/L. This means that while a ferric chloride dose of 10 mg/L (or 2.066 mg/L iron) is sufficient to treat (i.e., to bring arsenic concentration below 0.05 mg/L) a water sample with an initial As(V) concentration of 0.1 mg/L, in the presence of phosphate exceeding 2 mg/L the ferric chloride dose needed for treatment would be much higher. Figure 5.4 also shows the dramatic effect of phosphate on the removal of As(V) by ferric chloride; removal efficiency of As(V) came down from more that 75 percent to about 30 in the presence of 5.0 mg/L of phosphate.

The effect of phosphate on As(V) removal observed in this study are much more dramatic than those observed by Hering et al. (1996) and McNeill and Edwards (1997). The primary reason for this is the fact that both Hering et al. (1996) and McNeill and Edwards (1997) used very low concentrations of phosphate (0.076 mg/L and 0.032 mg/L, respectively); while phosphate concentration used in this study ranged from 1.0 to 10.0 mg/L. Relatively high concentrations of phosphate, reaching as high as 5.8 mg/L, have been found in some places of Bangladesh (Ahmed et al., 1997) and that was the main reason behind using higher concentration of phosphate in this study.

Results from this study suggest that in determining ferric chloride doses for arsenic removal, due consideration should be given to the phosphate concentration of the actual raw groundwater. Ferric chloride doses determined from laboratory batch studies with synthetic water (without the presence of phosphate) can significantly underestimate the actual dose requirement.

In Bangladesh, arsenic-rich iron oxyhydroxides appear to be the major source of arsenic from which arsenic is released as a result of desorption in the presence of a competing anion. Results from this study suggest that phosphate can play an important role in the release of arsenic in the groundwater environment in Bangladesh.

5.4 CONCLUSIONS

From experimental results obtained in this study, removal of arsenic appears to be maximum in the neutral pH range (close to 95 percent at pH 7.1) and slightly depressed both at higher pH values, exceeding 8. Reduction of adsorption at higher pH values is likely to be more pronounced at higher sorbate/sorbent ratios (i.e., at lower ferric chloride doses). This result is consistent with those reported in the literature (e.g., Sorg and Logsdon, 1978; Edwards, 1994; Hering et al., 1996). Reduction of arsenic removal at higher pH values appears to be related to the pH dependence of adsorption and the solubility of ferric hydroxide flocs, which is minimum at around pH 8 and goes up above and below this pH value. Greater solubility of amorphous iron (III) would result in a reduction of available oxide surface for adsorption.

In Bangladesh, pH of groundwater usually falls between 6 and 8. Results from this study suggest that pH is not likely to play a major role in determining the removal efficiency of As(V) from groundwater by ferric chloride. On the other hand, a lower removal efficiency may be achieved if arsenic is primarily present as As(III). Although pH has a more pronounced effect on As(III) removal, this may not be an important consideration for arsenic removal by ferric chloride in Bangladesh. As discussed in Chapter 4, for successful arsenic removal by ferric chloride, pre-oxidation of As(III) to As(V) appears to be a prerequisite. Hence effect of pH on As(III) removal in probably not an important consideration in the Bangladesh context. Thus, unless pH is very high (exceeding 8), this parameter is unlikely have any major influence on removal of arsenic by ferric chloride. It should be remembered that addition of ferric chloride to groundwater may result in a drop of pH of the water, especially for groundwater with low alkalinity (i.e., low buffer capacity). Greater solubility of amorphous iron (III) at lower pH values may result in lower removal efficiency of arsenic in such cases.

Experimental results obtained in this study showed dramatic effect of phosphate on arsenic removal by ferric chloride. Arsenic removal was found to decrease significantly with increasing concentration of phosphate, which competed with arsenic for adsorption sites on ferric hydroxide flocs. Phosphate concentrations in groundwater of Bangladesh have been reported to be high in many places and, unlike many previous studies, this study used much higher concentrations of phosphate concentration in coagulation experiments in order to simulate the field conditions in Bangladesh.

In the presence of 2 mg/L of phosphate, removal of arsenic present at an initial concentration of 0.10 mg/L and treated with 10 mg/L of ferric chloride came down from 92 percent (in the absence of phosphate) to about 46 percent. This means that in the presence of phosphate much higher doses would be required in order to treat water with ferric chloride. Relatively high concentrations of phosphate, reaching as high as 5.8 mg/L, have been found in some places of Bangladesh (Ahmed et al., 1997) and results from this study suggest that in determining ferric chloride doses for arsenic removal, due consideration should be given to the phosphate concentration of the groundwater. Ferric chloride doses determined from laboratory batch studies with synthetic water (without the presence of phosphate) can significantly underestimate the actual dose requirement.

Effect of phosphate on arsenic removal by ferric chloride also suggest that phosphate ions can play an important role in the release of arsenic in the groundwater environment in Bangladesh. In Bangladesh, arsenic-rich iron oxyhydroxides appear to be the major source of arsenic from which arsenic is released as a result of dissolution and desorption (Ali and Ahmed, 1999). Desorption of arsenic form iron oxyhydroxides can be promoted in the presence of a competing anion and results from this study suggests that phosphate can play a major role in the release of arsenic from iron oxyhydroxides through desorption. The primary source of phosphate in the groundwater of Bangladesh is the phosphate fertilizer which is abundantly used in agriculture. More study is needed to understand the role of phosphate in the mobilization of arsenic in the groundwater environment.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 GENERAL

The present study focussed on removal of arsenic from groundwater by coagulation with ferric chloride. In order to simulate the field conditions in Bangladesh as closely as possible, natural groundwater was used in all laboratory experiments in this study. Arsenic concentrations used in this study were typical of those reported for groundwater of Bangladesh. The primary objectives of this study were (i) to evaluate the removal efficiency of ferric chloride in removing As(III) and As(V) from groundwater; (ii) to evaluate effect of pre-oxidation (by bleaching powder) on removal of As(III) by ferric chloride; (iii) to evaluate the need for pre-oxidation in arsenic removal by ferric chloride in Bangladesh; (iv) to determine the doses of ferric chloride (and oxidizing agent) for removal of arsenic present at different initial concentrations; (v) to evaluate the effect of source water composition, especially effect of pH and phosphate, on arsenic removal by ferric chloride.

6.2 CONCLUSIONS

Major results obtained from this study are summarized below:

(1) Removal of both As(V) and As(III) was found to increase with increasing coagulant (ferric chloride) dose. At lower coagulant (or iron) doses, removal efficiency decreased with increasing arsenic [both As(III) and As(V)] concentration and arsenic removal appears to be limited by the availability of adsorption sites. For higher coagulant (ferric chloride) doses, removal efficiencies of As(V) appear to be

independent of initial arsenic concentration. Similar results were also observed for pre- oxidized As(III). Pre-oxidation with bleaching powder significantly improved removal of As(III). It was found that removal efficiency of As(III) pre-oxidized with bleaching powder was almost identical to that of As(V), for identical coagulation times (about 45 minutes).

(2) There appears to be a particular sorbate/sorbent ratio beyond which removal efficiency of As(V) [also pre-oxidized As(III)] drops beyond acceptable level. For a sorbate/sorbent ratio (expressed as μg As/mg Fe) of about 50 or less, removal efficiencies exceeding 95 percent could be achieved, irrespective of the initial arsenic concentration (for a maximum initial concentration of 0.50 mg/L). This can serve as a guideline value or thumb rule in determining required dose of ferric chloride for arsenic removal.

(3) As ferric chloride dose (i.e., iron dose) increases adsorption density (expressed as μg/L As per mg/L Fe) decreases. With increasing iron concentration, adsorption density is decreased because of the increasing number of available adsorbent sites.

(4) Bleaching powder which is widely available in Bangladesh can be effectively used for pre-oxidation of As(III) to As(V). While bleaching powder was successful in enhancing the removal efficiency of As(III), unstable nature and variable quality of commercial bleaching powder available in the market interfered with the determination of its required dose for pre-oxidation. From stoichiometric consideration, about 0.47 mg/L of chlorine is required for oxidation of 1mg/L of arsenic. In this study, good removal of As(III) was achieved in jar tests using a chlorine dose 3 to 4 time that calculated from stoichiometric consideration. Residual chloride concentrations were also found to be relatively low, about 0.04 to 0.06 mg/L.

(5) Role of the oxidizing agent is vital in the removal of arsenic from groundwater and the unstable nature of bleaching powder is a cause of concern in using bleaching powder as an oxidant for arsenic removal.

(6) Ferric chloride dose required for achieving a particular removal goal was determined for arsenic present at different initial concentrations (Figures 4.13 and 4.14). These requirements assume pre-oxidation of As(III) to As(V). It was found that ferric chloride requirement for satisfying the WHO standard (10 µg/L) was significantly higher than that required for satisfying the Bangladesh standard of 50 µg/L. For example, for an initial arsenic concentration of 0.25 mg/L, a dose of about 25 mg/L of ferric chloride is required to satisfy the Bangladesh standard, whereas about 75 mg/L or a dose three times a much is required to satisfy the WHO standard. This will in turn significantly increase the cost of removal and will also add to the sludge problem.

(7) In Bangladesh, arsenic removal by adsorption and co-precipitation onto coagulated flocs of ferric hydroxide could be a very effective technique, particularly in view of the presence of elevated levels of iron in many regions of the country. Available data, however, show relatively lower effectiveness of naturally occurring iron flocs in removing arsenic compared to ferric chloride.

(8) Removal of As(V) appears to be maximum in the neutral pH range and slightly depressed at higher pH values, exceeding 8. Reduction of adsorption at higher pH values is likely to be more pronounced at higher sorbate/sorbent ratios (i.e., at lower ferric chloride doses).

(9) Since pH of groundwater usually falls between 6 and 8 in Bangladesh, pH is not likely to play a major role in determining the removal of arsenic from groundwater by ferric chloride. Although pH has a more pronounced effect on As(III) removal, this

may not be an important consideration for arsenic removal by ferric chloride involving pre-oxidation.

(10) Phosphate appears to have a dramatic effect on arsenic removal from ground water. Arsenic removal was found to decrease significantly with increasing concentration of phosphate, which competed with arsenic for adsorption sites on ferric hydroxide flocs. Removal of arsenic present at an initial concentration of 0.10 mg/L (and treated with 10 mg/L of ferric chloride) came down from 92 percent (in the absence of phosphate) to about 46 percent in the presence of 2 mg/L of phosphate. This means that in the presence of phosphate much higher doses would be required in order to treat water with ferric chloride. Relatively high concentrations of phosphate, reaching as high as 5.8 mg/L, have been found in some places of Bangladesh (Ahmed et al., 1997) and it appears that ferric chloride doses determined from laboratory batch studies (without the presence of phosphate) can significantly underestimate the actual dose requirement.

(11) Effect of phosphate on arsenic removal by ferric chloride also suggest that phosphate ions can play an important role in the release of arsenic in the groundwater environment in Bangladesh. Desorption of arsenic form iron oxyhydroxides can be promoted in the presence of a competing anion and it that phosphate can play a major role in the release of arsenic from iron oxyhydroxides through desorption. The primary source of phosphate in the groundwater of Bangladesh is the phosphate fertilizer which is abundantly used in agriculture.

6.3 RECOMMENDATIONS

Ferric chloride has been found to be very effective in removing As(V) from groundwater in laboratory batch experiments. It was also found to be effective in removing As(III) in the presence of an oxidizing agent. The doses of ferric chloride needed to achieve a particular removal goal (e.g., WHO standard of 10 μg/L or Bangladesh standard of 50 μg/L) have also been determined in this study. However, these requirements were determined based on experimental results that were performed in laboratory under controlled conditions. Effectiveness of ferric chloride in removing arsenic should be evaluated at the field (or household level); the doses determined in this study could serve as guideline values in the field trials.

This study was conducted under the laboratory condition where mixing time and mixing velocity maintained carefully. To adsorbed arsenic onto iron flocs, the effects of mixing time and velocity of mixing must be evaluated for the field condition.

Role of an oxidizing agent is vital in the removal of arsenic by ferric chloride, since a significant fraction of arsenic in groundwater of Bangladesh may exist as As(III), whose removal efficiency is significantly lower compared to that of As(V). While bleaching powder was found to be very effective in enhancing the removal of As(III), it was found during the course of this study that the quality of bleaching powder available in the local market varies considerable and that chlorine content of bleaching powder decreases significantly during storage. As a result there is a risk of using this chemical in arsenic removal. Alternative oxidizing agents such as potassium permanganate could be used in place of bleaching powder. Effectiveness and required dose of potassium permanganate for arsenic removal should be determined.

In Bangladesh effectiveness of arsenic removal by ferric hydroxide flocs (which for upon addition of ferric chloride) is of particular interest because high concentrations of naturally occurring iron are present in many arsenic affected areas and these iron form ferric hydroxide flocs upon extraction (in contact with air) quickly, especially if alkalinity of water is high. These naturally occurring iron flocs could play a major role in removing arsenic from groundwater in areas with high iron concentrations. Limited available data, however, show relatively lower effectiveness of naturally occurring iron flocs in removing arsenic compared to ferric chloride. More study is needed to determine the effectiveness of naturally occurring iron flocs in removing arsenic from water.

Phosphate was found to have a significant effect on arsenic removal from water and more study is needed to evaluate its impact on arsenic removal by ferric chloride. Appropriate doses of ferric chloride for removal of arsenic in the presence of phosphate should be determined. Besides phosphate, effect of silica also needs to be studied in order to determine the extent of its effect on arsenic removal.

Apart from its influence in the removal of arsenic from groundwater, phosphate can play an important role in the mobilization of arsenic in the subsurface. The principal source of phosphate in groundwater of Bangladesh is the phosphate fertilizer used in agriculture and the phosphate can promote desorption of arsenic from iron oxyhydroxide in the subsurface environment. More study is needed to understand the geochemistry of arsenic release in the subsurface and the role of phosphate, if any, in the mobilization process.

REFERENCES

Abernethy, C.O., & Ohanian, E.V. 1993 Health effects of Inorganic Arsenic in Drinking Water. Proc. AWWA WQTC, Miami, Florida, Nov7-11.1993.

Ahmed, F., Hossain, M.D., Badruzzaman, A.B.M., Jalil, M.A., and Ali, M.A. (1997), A Study on Concentration of Arsenic in Groundwater of North-Eastern Zone of Bangladesh, report submitted to Department of Agriculture, Govt. of People's Republic of Bangladesh.

Ahmed, M. F., Ali, M. A., and Hossain, M. D. (1998), "Groundwater Treatment for Arsenic-Iron Removal", paper presented at the International Conference on *Arsenic Pollution of Groundwater in Bangladesh: Causes, Effects and Remedies* organised by Dhaka Community Hospital and the School of Environmental Studies, Jadavpur University, Calcutta, India during 8-12 February, 1998, LGED auditorium, Dhaka, Bangladesh.

Aitchinson, L. (1960). A History of Metals. McDonald & Evans, London.

Alloway, B.J.1990 Heavy metals in soil, Jhon Willey and Sons Inc.

Anonymous (1978) Effects of Arsenic in the Canadian Environment. National Research Council of Canada, Associate Committee on Scientific Criteria for Environmental Quality and Subcommittee on Heavy Metals and other Compounds, Ottawa, 349 pp.

APHA, AWWA and WEF, 1995, Standard methods for the examination of water and wastewater, Washington DC, 19th ed.

AWWA (1985), Standard Methods for Analysis of Water and Wastewater, American Water Works Association.

Bates, M.N.; Smith, A.H.;& Hopenhayn Rich, C. Arsenic Ingestion and Internal Cancers: A Review. Amer. Jour. Epidemiol., March 1, 1992.

Backer, D.E., and Chesnin, L. (1975). Chemical monitoring of soils for environment quality and animal and human health. Adv. Agron, 27, 305-374.

Bagachi, K. N. (1969). Poisons and Poisoning –Their History and Romance and Their Detection in Crimes. University of Calcutta press, Bengal.

Bellack E., 1971, Arsenic removal from potable water, J. American Water Works Association, vol. 63, p. 454-458.

Bhumbla, D.K. and Keefer, R.F. 1994 Arsenic Mobilization and Bioavailability in Soils. Arsenic in the Environment, partI: Cycling and Characterization. Editor J.O. Nriagu. Willey Interscience, Newyork,1994.

Bowen, H. J. M. (1979). Elemental Chemistry of the Elements. academic Press. London and New York, pp. 60-61.

Borgono, J.M. et al., Arsenic in the drinking water of the city of Antofagasta: epidemiological and clinical study before and after the installation of a treatment plant. Envir. Health Perspectives, vol 19 pp. 103 (1977).

Borho M., and Wilderer P., 1971, Optimised removal of arsenate(III) by adaptation of oxidation and precipitation processes to the filtration step, J. Water Sci. Tech., vol. 34, no. 9, p.25-31.

Boyle, R.W. and Jonasson, I.R. 1973 The geochemistry of arsenic and its use as an indicator elematn in geochemical prospecting. J. Geochem. Explor. 2: 251-296.

Braman, R.S. and Jhonson 1975 Arsenic in the environment . in E.A. Woolsen, ed., Arsenical pesticides. American Chemical Society, Washington, D.C. ACS Symposium series 7,pp. 108-123.

Carapella, S.C. 1978 Arsenic and Arsenic alloys. In M. Grayson and D. Ecroth (Eds.), Krik-Othemer Encyclopedia of chemical Technology, 3rd edition, Willey, NewYork. Vol. 3, pp.243-250.

Chen H.W. and Edward M.., 1996, Predicting particulate arsenic occurrence in natural waters, presented at the 1996 Rocky Mountain Regional ACS Conference, June.

Cheng C.R., Liang S., Wang H-C and Beuhler M.D., 1994, Enhanced coagulation for arsenic removal, J. American Water Works Association, vol. 86, no. 9, p.79-90.

Cherry, J.A. et al.,1979 Arsenic species as an indicator of redox conditions in ground water, J. Hydrology Vol. 23, page 379-392.

Cliifford D., 1986, Removing dissolved inorganic contaminants from water, j. Environ. Sci. Technol., vol. 20, p. 1072-1080.

Clifford, D. A. & Zhang, Z. Arsenic Chemistry and Speciation. Proc. AWWA WQTC, Miami, Fla., Nov. 7-11, 1993.

Coghlan, H. H. (1975). In T.K. Penniman and B.M. Blackwood (Eds.), Notes on the prehistoric Metallurgy of Cooper and Bronze in the Old World. Oxford University Press. Oxford.

Crecelius, E.A. et al., 1974 Conmination of soils near a copper smelter by arsenic, antimony and lead. J. Water, air and soil Pollut. vol. 3, pp.337-342.

Cullen, W.R. and Reimer, K.J. 1989 Arsenic Speciation in the environment. Chem. Rev vol.89 pp 713-764.

Dahi, Eli and Liang, Qin (1998), "Arsenic Removal in Handpump Connected Iron Removal Plants in Noakhali, Bangladesh", paper presented at the International Conference on *Arsenic Pollution of Groundwater in Bangladesh: Causes, Effects and Remedies* organised by Dhaka Community Hospital and the School of Environmental Studies, Jadavpur University, Calcutta, India during 8-12 February, 1998, LGED auditorium, Dhaka, Bangladesh.

Davenport, J. R., Peryea, F. J. 1991 Phosphate Fertilizers Influence Leaching of Lead and Arsenic in a Soil Contaminated With Lead Arsenate, Water Air, And Soil Pollution, 57-58: 101(1991).

Dabeka, R.W. et al., 1993. Survey of arsenic in total diet food composites and estimation of the dietary intake of arsenic by Canadian adults and children , j. AOAC, vol.76,no.1 pp.14.

Dahi E, 1997 Arsenic and Dearsenization of Water , paper presented in the ITN-B course on Water Supply & Waste management, during 9th –12th Aug. 1997, ITN Center, BUET, Dhaka.

Devilliers, A.J. and Beker,P.M. 1969 An investigation of the health status of inhabitants of Yellowknife, N.W.T. environ. Health Dir., Health and Welfare canada. 119pp

Derry, T. K. and Williams, T. I. (1961). A Short History of Technology. Oxford University Press, New York and Oxford.

Dove P.M. & Rimstid, J.D. 1985 The Solubility and Stability of Scoroite, $FeAsO_4.2H_2O$. Amer. Mineralogist, no70 pp838 (1985).

Dutta A. and Chaudhury M.,1991, Removal of arsenic from ground waters by lime softening with powdered coal additive, j. Water SRT-AQUA, vol. 40, p. 13-17.

Dzombak, D. A. and Morel, F. M. M. (1990) *Surface Complexation Modeling: Hydrous Ferric Oxode,* Wiley-Interscience, New York.

Edwards M, and Benjamin, M.N. 1989, Adsorption filtration using coated sand: A new approach for treatment of metal bearing wastes. J. Water Pollution control Fed. Vol. 61 pp 1523-1533.

Edwards M., 1994, Chemistry of arsenic removal during coagulation and Fe-Mn oxidation, American Water Works Association, vol. 86, no. 9, p.64-78.

Edelstein, D.L. 1985 In Mineral facts and problems; U.S. department of the interior: Washington DC, 1985; bulletin 675, p 1.

Elson, C.M., et al., 1980, Removal of Arsenic from Contaminated drinking water by a chitosan/chitin mixture. J. water Resource. Vol 14,pp 11307-1311.

Ferguson J.F. and Gavis J., 1972, A review of arsenic cycle in natural waters, J. Water Research, vol. 6, p. 1259-1274.

Forbes, R.J. 1964 Studies in ancient Tecnology. E.J. Brill, Leiden, The Netherlands.

Frederick W and coleagues, 1994 Health implications of arsenic in drinking water. Journal AWWa, Sept. 1994.

Frank P. and Clifford D., 1986, As(3) oxidation and removal from drinking water, USEPA proj. Summary 600/S2-86/O21.

Gibb , P. , 1995 Death and Devils water Journal New Scientist Sept. 1995.

Gimlette, J. D., and Desmond, J. (1981). Malay Poisons and Charm Cures. Oxford University Press, London

Gupta, S.K. and K.Y. Chen , 1978 arsenic removal by adsorption, Water pollution Control federation Journal ,1987 pp 493-506.

Gulledge J.H. and O'Conor J.T., 1973, Removal of As(V) from water from by adsorption on aluminium and ferric hydroxide, J. American Water Works Association, vol. 65, no. 8, p.548.

Gupta S.K. and Chen K.Y., 1978, Arsenic removal by adsorption, J. WPCF, vol. 50, p. 133-154.

Gur Prashad, 1994, Removal of arsenic(V) from aqueous systems by adsorption onto some geological materials, Wiley series in advances in Env. Science., vol. 26, part I, p. 133-154.

GOB (1997), Gazette Publication, Government of the Peoples' Republic of Bangladesh, Ministry of Environment and Forestry, August 28, 1997.

Hering J.G., Chen P-Y, Wilkie J.A., Elimelech M. and Liang S., 1996, Arsenic removal by ferric chloride, J. American Water Works Association, vol. 88, no. 4, p.155-`167.

Herring J.G., Chen P, Wilkie J.A., Elimelech M., 1997, Arsenic removal by drinking water during coagulation, J. Env. Eng. ASCE, vol.123, no.8, p.800-807.

Hindmarsh, J.T. and Coleagues, 1977 Electromyographic abnormalities in chrinic environmental arsecalism. Submitted J. Anal. Toxicol, 1977.

Hossain, M.D. and Huda, M. K. (1997), "Study of Iron Content in Groundwater of Bangladesh", submitted to Journal of Civil Engineering, Institution of Engineers, Bangladesh.

Hossain, M. D. and Ali, M. A. (1997), "Arsenic Removal from Groundwater by Co-precipitation with Iron", paper presented at the workshop on *Arsenic Pollution and Dearsination of Water*, Organised by ITN, Bangladesh, July, 1997

Horowitz, A.J. 1984 A primer of trace metal sediment Chemistry. U.S. Geological Survey open file report 84-709 pp

Huang, C.P. and Vane, I.M., 1989 Enhancing As^{3+} removal by a Fe^{3+} treated Activated Carbon .J. Water Pollution Control Fed. Vol. 61 pp 1596-1603.

Hunter, D. (1978). The Diseases of Occupations. Hodder & Stoughton, London.

Jackson, R and Grainge, Med. J.W. 1975 Arsenic and Cancer. Canadian Association. J. 113(5)pp 396-401

Jekel M.R. 1994 Removal of Arsenic in Drinking Water Treatment. Arsenic in the Environment, partI: Cycling and Characterization. Editor J.O. Nriagu. Willey Interscience, Newyork,1994.

Jhonson D.L. 1972, Arsenate and arsenite, Doctoral dissertation, University of Rhode, Island.

Jones, D. 1982 The singular case of Nepoleon's wallpaper. New Science. Oct., pp. 101-104.

Kartinen E.O. and Martin C.J., 1995, An overview of arsenic removal processes, J. Desalination, vol.103, p.79-88.

Kim R. Fox 1989 Field experience with point of treatment systems for arsenic removal. Joun. AWWA, February.

Kobayashi, A. and Ohbe, Y. 1971 Protein losing enteropathy associated with arsenic poisoning. Am. J: dis. Child. 121(6) : 515-517.

Korte, N.(1991) Naturally Occurring Arsenic in Groundwaters of the Midwestern United States, Envir. Geol. Water Sci., vol.18 no.2 pp.137 (1991).

Lauf G.F. and Waer M.A., 1993, Arsenic removal using potassium permenganat, AWWA WQTC, Miami, Florida.

Leonard, A. 1991 Arsenic. In E. Merian (ed.) Metals and their compounds in the environment. VCH Veragsgesellschaft, Weinheim, Germany.

Lender,J.J. and et al., 1975 Angeosarcoma of the lever associated with flower's solution. Gastroenterology Vol 68 no. 6 pp. 1582-1586.

Livesey, N. T., and Huang, P. M. (1980). Adsorption of arsenate by soils and its relation to selected chemical properties and anions. In soils and. Fertillizers in Taiwan, Department of Soil Science, University of Aberdeen, Scotland, UK, 1980, pp. 13-23

Luh, M. D., Baker, R. A. and Henley, D.E. 1973 Arsenic analysis and toxicity a review. Sci. Total Environ. 2(1): pp1-12

Masscheleyn, P.H. et al., (1991) Effect of Redox Potential and pH on as Speciation and Solubility in a contaminated Soil. Envir. Sci. & Technol., Vol 25 no.8 pp.1414 (1991).

Mackenzie, F. T., Langrzy, R. J., and Paterson, V. (1979). Global trace metal cycles and predictions. J. Int. Assoc, Math, Geol. vol 11,b pp. 99-142

Mandal B. K., Samanta G., Choudhury T.R., Dhar R.K., Biswas B.K., Chanda C.H., Mukharjee K.C., Chakraborty D., (1998) –Ground Water Arsenic Calamity in Eight Districts of West Bengal, India, presented at International Conference on Arsenic Pollution of Ground Water in Bangladesh: Causes, Effect and Remedies, Dhaka, 8-12 February, 1998.

Majumder D.N., Santra A., De B.K., Gupta J.D., Ghosh A., Pal A., Roy B., Pal S., Saha J., (1998) Clinical Manifestations of Chronic Arsenic Toxicity: It's Natural History and Therapy: Experience of Study In West Bengal, India, presented at International Conference on Arsenic Pollution of Ground Water in Bangladesh: Causes, Effect and Remedies, Dhaka, 8-12 February, 1998.

Meyer, E.V.(1975). A History of Chemistry –from Earliest Times to Present Day. Arno Press, New York.

McBride B.C and Wolfe R.S., 1971, Biochemistry, vol. 10, p.4312

Mcneill L.S. and Edward M., 1997, Predicting Arsenic removal during metal hydroxide precipitation, J. American water Works Association, vol.89, no.1, p. 75-86.

Morris, J. S. and Colleague Arsenic and non cirrhotic portal 1974. Hypertension. Gastroenterology 66(1): pp86-94.

National Research Council Effects of arsenic in the Canadian environment, Canada. NRCC-15391.

Nriagu, J. O., and Azcue, J. M. (1990). Environmental sources of arsenic in food. Adv. Environ. Sci. Technol. vol 23, pp. 103-127.

Nriagu, J. O. (1994) *Arsenic in the Environment: Part I*, John Wiley & Sons, London

Nikolaidis, N.P. &Lackovic, J. 1998, Arsenic Remediation Technology-ASRT. Presented at International Conference on Arsenic Pollution of Ground Water in Bangladesh: Causes, Effect and Remedies, Dhaka, Feb 8-12, 1998.

Oscarson D.W. et al, 1983, Kinetics of Oxidation of arsenite by various manganese di oxide, Soil Sci. Soc. American Journal, Vol. 47, p.644.

Onishi, H. and Sandell, Geochim. E.B.1955 Geochemistry of arsenifc. Cosmochim Acta 7: pp 1-33.

Papassiopi N. et al, 1996, Removal and fixation of arsenic in the form of ferric arsenates. Three parallel experimental studies, J. Hydromettallurgy, vol. 41, p. 243-253.

Parr, J. G., (1958). Man. Metals and Modern Magic. American Society for Metals, Metals Park, OH.

Pierce M.L. and Moore C. B., 1982, Adsorption of As(III) and As(V) on amorphous iron hydroxide, J. Water Research, Vol. 16, p. 1247.

Peng F.F., Di P., 1994, Removal of arsenic from aqueous solution by adsorbing colliod floatation, J. Ind. eng. Chem. Res., vol.33, p. 922-928.

Pontius F. W., Brown K.G. and Chen C. J., 1994, Health implication of arsenic in drinking water, J. American Water Works association, vol. 86, no. 9, p.52-62.

Peterson, P. J., Benson, L. M. and Zieve, R. (1981). Metalloids, Sec. 3- Arsenic. In N. W. Lepp (Ed.), Effect of Heavy Metal Pollution on Plants. Applied Science Publ, London, 1981, Vol. I, pp. 299-322.

Ragini, R.C. Ralston, H.R. and Roberts, N. 1977 Environmental trace Metals Contamination in Kellogg, Idahoo, near a lead smelting complex. Environ. Sci. Technol. vol.11. pp. 773-781.

Richardson, F. (1974). Napoleon Death: An Inquest. W. Kimber, London.

Roseheart, R.G. and Lee, J.Y. 1973 The effect of arsenic on the growth of white spurce seedlings. J. Water, Air and Soil Pollut. Vol.2. pp. 439-443.

Sandberg, G.R., and Allen, I.K. 1975 A proposed arsenic cycle in an agronomic ecosystem. In E.A. Woolson (Ed.) Arsenical pesiticides. american Chemical soviety, washington DC, pp. 124-147.

Singer, C., Holmyard, E.J., Hall, A. R., and williams. T. I. (1957). A History of Technology. Oxford University Press (Clarendon), Oxford.

Shen Y.S., 1973, Study of arsenic removal from drinking water, J. American Water Works Association, vol. 65, no. 8, p. 543-548.

Sorg T.J. and Logsdon G.S., 1978, Treatment technology to meet the interim primary drinking water regulations for inorganics: part 2, j. American Water Works Association, vol. 70, p.379-39

Sueart, R. D. et al. (1995), Drinking water without arsenic. Drinking water without Arsenic- A review of treatment technologies. pp. 37, Environmental systems reviews, ISSN 0125-5088.

Stumm W. and Morgan J.J., 1981, Aquatic chemistry, an introduction emphasizing chemical equilibria in natural waters, 2e, NY, Jhon Willey and sons, inc.

Stow. S.H. 1969 The occurrence of arsenic and color causing components in Florida land pebble phosphate rock. Economic Geology, v. 64. Pp. 667-671.

Southwick, J.W. et al., 1983 An Epidemiological study of arsenic in drinking water in Millard county, Utah. Arsenic: Industrial, Biomedical, Environmental perspectives, New York, 1993.

Takamatsu, T.; Kashima, M.; & Koyama, M.(1985) The Role of Mn(II) – Rich Hydrous Manganese Oxide in the Accumulation of As in Lake Sediments. Water Res. Vol 19 pp. 1020

Tamaki, S. & Frankeberger, W.T. 1992 Environmental Biochemistry of Arsenic. rev. Environ Contam. Toxicol., 124:79 (1992).

Thompson, D. V. (1956). The Materials and Techniques of Medieval Painting. Dover, New York.

Tourtelot, H.A. 1964 Minor element composition and organic carbon content of marine and nonmarine shales of late cretaceous age in the Western interior of the United States. Geochimica at Cosmochimica Acta. V.28 pp. 1579-1604.

Tseng, W.P. 1977 Effects and dose response Relationships of skin cancer and blackfoot disease with arsenic. Envir. Health Perspectives. Vol 19 pp.109.

Tseng W.P. et al., 1968, prevalence of Skin cancer in an endemic area of chronic arsenism in Taiwan, j. National Cancer Inst., vol. 40, p. 453-463.

Valee, B.L., Ulmer, D.D. & Wacker , W.E.C. Arsenic Toxicology and Biochemistry. AMA Arch. Indus. Health, vol. 21 pp 56. 1960.

Vinogradov, A. P. (1959). The Geochemistry of Rare and Dispersed Chemical Elements in Soils, 2nd ed, New York, pp. 65-70.

Waychunas, G.H. et al., Surface Chemistry of Ferrihydrite: Part I, EXAFS Studies of GeoChemistry of Coprecipitation and Adsorbed Arsenate. Geochim. et Cosmochim. Acta., Vol 57 pp2251(1993).

Wedphol K.H. (ed), 1969, handbook of Geochemistry, Springer-verlag, Berlin, vol.2, chapter 33.

Welch, H.H., Lia, M.S. & Hughes. J.L. As in groundwater of the Western United States. Groundwater, vo.26 no.3 pp.323 (1988).

Winship, K.A. Toxicology of Inorganic Arsenic Salts. Adv. Drug React. Act. Poison Rev., vol3 pp 129 (1984).

Wolfgang D. and Jekel M., 1992, Determination of As(III) and total inorganic arsenic by online pretreatment in hydride generation atomic adsorption spectrometry, Fresenius J. Anal Chem., vol. 343, p. 352-356.

Xu, H., Allard B., & Grimvell 1991A Effects of Acidification and Natural Organic Materials on the Mobility of Arsenic in the Environment. Water, Air and Soil Pollution, Vol 57-58 pp 269.

Yeh, S. 1973 Skin cancer in chronic arsenicism. Human pathol.
4(4) : 469-485

Yoshida I. and Ueno K., 1978, Selective separation of arsenic(III) with ferric complex of chelating ion exchange resin, J. Sci. Technol. Sept., vol. 13, p. 173-184.

Zaldivar, R.1977 Ecological investigations or arsenic dietary intake and endemic intake chronic poisoning in man: Dose-response curve. Zbl.Bakt. Hyg., i. Abt. Orig. B164. 481-484.

Appendix

Table-1 **% Removal of As(V) as a function of $FeCl_3$ for different initial concentrations of arsenic.**

Sl.No	$FeCl_3$, mg/L	% Removal		
		As(V)=0.10mg/L	As(V)=0.25mg/L	As(V)=0.50mg/L
1	5	84.0	47.3	44.2
2	10	-	77.5	76.6
3	25	>97.5	96.1	93.3, 93.7
4	50	95.5	97.8	>99.0, 97.3
5	75	97.5	>98.0	>99.0
6	100	94.6	95.5	>99.0, >99.0
7	125	95.5	>98.0, 92.8	98.9, >99.0

Table 2 **% Removal of As(V) as function of iron for different initial concentrations of arsenic.**

Sl.No	Iron mg/L	% Removal		
		As(V)=0.10mg/L	As(V)=0.25mg/L	As(V)=0.50mg/L
1	1.033	84.0	47.3	44.2
2	2.066	-	77.5	76.6
3	5.165	>97.5	96.1	93.3, 93.7
4	10.33	95.5	97.8	>99.0, 97.3
5	15.495	97.5	>98.0	>99.0
6	20.660	94.6	95.5	>99.0, >99.0
7	25.825	95.5	>98.0, 92.8	98.9, >99.0

Table 3.1. **Comparison of As(III) & AS(V) Removal & Effect of Cl_2 for an initial concentration of 0.25 mg/L of arsenic.**

As(III) = As(V) = 0.25 mg/L

Sl.No	Iron mg/L	% Removal		
		As(V)	As(III)	As(III) + Cl_2
1	1.033	47.3	18.1	76.0
2	2.066	77.5	-	-
3	5.165	96.1	29.8	87.4
4	10.330	97.8	51.0	83.8
5	15.495	>98.0	52.0	96.0
6	20.660	95.5	65.4	>98.0
7	25.825	>98.0, 92.8	77.6	>98.0

Table 3.2 **Comparison of Removal of arsenite and arsenite for an initial concentration of 0.50 mg/L.**
As(III)= As(V) = 0.50 mg/L

Sl.No	Iron mg/L	% Removal	
		As(V)	As(III)+ Cl_2
1	1.033	44.2	-
2	2.066	76.6	74.3
3	5.165	93.3, 93.7	92.0
4	10.330	>99.0, 97.3	92.8
5	15.495	>99.0	97.3
6	20.660	>99.0,>99.0	98.2
7	25.825	98.9, >99	97.8

Table 4 **Effect Of Cl_2 on the removal of As(III) for different initial concentration.**

Sl.No	Iron mg/L	% Removal	
		As(III)=1.0 mg/L+ Cl_2	As(III)= 2.0mg/L+ Cl_2
1	1.033	-	-
2	2.066	-	-
3	5.165	84.9	91.1
4	10.330	96.3	92.69
5	15.495	97.2	99.1
6	20.660	>99.0	>99.5
7	25.825	>99.0	>99.5
8	27.891	97.2	>99.5
9	30.99	98.6	97.8

Table 5.1 **Effect of pH on the removal of arsenic from groundwater by ferric chloride.**

As(V) = 0.25 mg/L
Iron = 5.165 mg/L

Sl.No.	pH	% Removal
1	5.8	83.6
2	6.4	85.6
3	7.1	94.6
4	7.9	90.8
5	8.6	85.6

Table 5.2 **Effect of pH on the removal of arsenic from groundwater by ferric chloride.**

As(V) = 0.25 mg/L
Iron = 20.66 mg/L

Sl.	pH	% Removal
1	4.9	97.6
2	5.3	>98.0
3	6.0	>98.0
4	6.2	>98.0
5	6.8	>98.0
6	6.9	>98.0
7	7.1	>98.0
8	7.2	97.8
9	7.4	96.4
10	7.9	87.2
11	8.4	94.4
12	8.9	>98.0
13	9.2	73.9

Table 6.1 **Effect of Phosphate on the removal of arsenic from groundwater by ferric chloride.**

As(V) = 0.1 mg/L
Iron = 2.066 mg/L

Sl. No	PO_4 (mg/L)	% removal
1	0.0	60.00
2	1.0	57.25
3	2.0	46.00
4	5.0	37.00
5	7.5	46.00
6	10.0	10.90

Table 6.2 **Effect Of PO_4 on the removal of arsenic from groundwater by ferric chloride.**

As(V) = 0.25 mg/L
Iron= 2.066mg/L

Sl. No.	PO_4, mg/L	% Removal
1	0.0	77.5
2	1.0	72.6
3	5.0	36.0
4	25.0	25.0

Table 7 **Residual As(V) concentration for different initial concentration of arsenic**

Sl. No	Iron mg/L	Residual As(V) in µg/L		
		As(V)=0.10 mg/L	As(V)=0.25mg/L	As(V)=0.50mg/L
1	1.033	16.0	131.80	279.0
2	2.066	-	56.30	117.0
3	5.165	<2.5	9.75	33.5, 31.5
4	10.330	4.5	5.50	< 5.0, 13.5
5	15.495	<2.5	<5.00	< 5.0
6	20.66	5.4	11.30	< 5.0, < 5.0
7	25.825	4.5	<5.00	5.5, < 5.0

Table 8 **Residual Concentration of As(III) (Removal with Cl_2) for different initial arsenic concentration**

Sl.No	Iron mg/L	Residual As(III) in µg/L			
		As(III)= 0.25 mg/L +Cl_2	As(III) = 0.50 mg/L +Cl_2	As(III) = 1.0 mg/L +Cl_2	As(III)= 2.0 mg/L +Cl_2
1	1.033	60.0	-	-	-
2	2.066	-	128.5	-	-
3	5.165	31.5	40.0	151.0	178.0
4	10.330	40.5	36.0	37.0	146.2
5	15.495	10.0	13.5	28.0	18.0
6	20.660	5.0	9.0	<10.0	<10.0
7	25.825	5.0	11.0	<10.0	<10.0
8	27.891	-		-	<10.0
9	30.990	-		14.0	-

Table 9 Requirement of iron(III) (added as $FeCl_3$) to achieve the Bangladesh standard of 0.50µg/L and the current WHO standard of 10µg/L.

Initial As Conc.	Required Fe(III) , mg/L (Calculated)		Required Fe(III) , mg/L(Graph)	
	Residual con.< 50µg/L	Residual con.< 10µg/L	Residual con.< 50µg/L	Residual con.< 10µg/L
As(V) = 0.10 mg/L	1.0	5.0	1.0	2.5
As(V) = 0.25 mg/L	5.0	15.0	3.0	12.5
As(III) = 0.25mg/L	5.0	15.0	3.0	12.0
As(V) = 0.50 mg/L	5.0	15.0	5.0	15.0
As(III) = 0.50 mg/L	5.0	20.0	5.0	20.0
As(III) = 1.0mg/L	10.0	25.0	9.75	25.0
As(III) = 2.0 mg/L	10.0	25.0	12.50	25.0

Table 10.1 **Adsorption Density (As in mg/L/ Fe in mg/L) for different initial concentration of As(V).**

Fe(III), mg/L	Adsorption density (As mg/Fe mg)		
	As(V)=0.1 mg/L	As(V)=0.25 mg/L	As(V)=0.50 mg/L
1.033	84* 10^{-3}	114.23* 10^{-3}	213.94* 10^{-3}
2.066		93.79* 10^{-3}	185.38* 10^{-3}
5.165	18.9* 10^{-3}	46.55* 10^{-3}	90.71* 10^{-3}
10.33	9.3* 10^{-3}	23.72* 10^{-3}	47.92* 10^{-3}
15.495	6.29* 10^{-3}	15.82* 10^{-3}	32.27* 10^{-3}
20.66	4.58* 10^{-3}	11.56* 10^{-3}	24.20* 10^{-3}
25.825	3.74* 10^{-3}	9.49* 10^{-3}	19.36* 10^{-3}

Table 10.2 **Adsorption Density (As in mg/L/ Fe in mg/L) for different initial concentration of As(III).**

Fe(III), mg/L	Adsorption Density (As in mg/ Fe in mg)			
	As(III)=0.25 mg/L + Cl_2	As(III)=0.5 mg/L+ Cl_2	As(III)=1.0 mg/L+ Cl_2	As(III)=2.0 mg/L+ Cl_2
1.033	-	-	-	-
2.066	-	179.81* 10^{-3}	-	-
5.165	43.31* 10^{-3}	89.06* 10^{-3}	162.83* 10^{-3}	352.76* 10^{-3}
10.33	20.28* 10^{-3}	44.92* 10^{-3}	93.23* 10^{-3}	179.46* 10^{-3}
15.495	15.49* 10^{-3}	31.41* 10^{-3}	62.73* 10^{-3}	127.91* 10^{-3}
20.66	11.98* 10^{-3}	23.77* 10^{-3}	47.92* 10^{-3}	96.32* 10^{-3}
25.825	9.68* 10^{-3}	18.94* 10^{-3}	38.69* 10^{-3}	77.06* 10^{-3}
27.891	-	-	34.85* 10^{-3}	71.35* 10^{-3}
30.99	-	-	31.82* 10^{-3}	63.12* 10^{-3}

Table 11 **Residual Iron Concentration after Coagulation for different initial arsenic concentration coagulated with different dose of ferric chloride**

Iron, mg/L	Residual Fe(III),mg/L		
	As(V)=0.1 mg/L	As(V)=0.25 mg/L	As(V)=0.50 mg/L
1.033	0.5	0.70	0.090
2.066	1.0	0.95	0.25
5.165	1.0	1.15	0.300
10.33	1.0	1.20	0.75
15.495	0.5	1.00	1.20
20.66	0.5	1.00	0.50
25.825	1.0	1.00	0.50

Table 12 **Residual Iron Concentration after Coagulation for pre-oxidized arsenic coagulated with different iron doses.**

Iron, mg/L	Residual Fe(III), mg/L			
	As(III)=0.25 mg/L + Cl_2	As(III)=0.5 mg/L+ Cl_2	As(III)=1.0 mg/L+ Cl_2	As(III)=2.0 mg/L+ Cl_2
1.033	0.9	-	-	-
2.066	0.6	0.75	-	-
5.165	-	1.00	0.90	0.25
10.33	2.5	0.90	1.25	0.50
15.495	1.0	1.00	1.00	0.50
20.66	1.0	0.75	0.90	0.75
25.825	0.5	1.00	1.20	0.90
27.891	-	-	0.50	0.60
30.99	-	-	0.50	0.50

Table 12 **Residual chlorine after coagulation and pre-oxidized by bleaching p[owder for 0.25mg/L As(III)**

Iron mg/L	Residual Chlorine, mg/L
1.033	0.06
2.066	0.06
5.165	0.06
10.330	0.04
15.495	0.05
20.660	0.06
25.825	0.05

Table 13 **% Removal of As(V) for different sorbate/sorbent (As in µg/ Fe in mg)**

Sl.	As in µg/ Fe in mg	% As(V) Removed
1	3.74	95.50
2	4.58	94.60
3	6.29	97.50
4	9.49	98.00
5	11.56	95.50
6	15.82	98.00
7	18.90	97.50
8	19.36	98.90
9	23.72	97.80
10	24.20	99.00
11	32.27	99.00
12	46.55	96.10
13	47.92	97.30
14	84.00	84.00
15	93.79	77.50
16	114.23	47.30
17	213.94	44.20

Table 14 % As(III) removed for different sorbate/sorbent ratio (As in μg/ Fe in mg)

Sl No.	As in μg/ Fe in mg	% As(III) removed
1	43.80	18.1
2	14.43	29.8
3	12.34	51.0
4	8.39	52.0
5	7.92	65.4
6	7.57	77.6