

Assessing the Effectiveness of Iron-Coated Bottom Ash in Removing Arsenic, Manganese, and Iron from Groundwater

by
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MASTER OF SCIENCE IN CIVIL ENGINEERING (ENVIRONMENTAL)



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of Engineering and Technology, Dhaka, in partial fulfilment of the requirements for
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It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

28th July, 2009

MAHBUBA
04-08-2009
Most. Mahbuba Iasmin

Dedicated

to

My father,
Late Mohammad Abdul Karim Sarker

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ABBREVIATIONS

A-BC, B-BC, C-BC, D-BC = Samples from Batch-A, B, C, D respectively Before Chlorination

AC = After Chlorination

BAAG = Berkeley Arsenic Alleviation Group

B-AC, C-AC, D-AC = Samples from Batch-B, C, D respectively After Chlorination

BC = Before Chlorination

BGS = British Geological Survey

BUET = Bangladesh University of Engineering and Technology

DO = Dissolved Oxygen, mg/L

DPHE = Department of Public Health Engineering

EC = Electrical Conductivity, $\mu\text{S}/\text{cm}$

FLAAS = Flame Analysis Atomic Absorption Spectrophotometer

GFAAS = Graphite Furnace Atomic Absorption Spectrophotometer

GoB = Government of Bangladesh

ICBA = Iron Coated Bottom Ash

NGO = Non-Government Organization

T = Temperature, $^{\circ}\text{C}$

TCLP = Toxicity Characteristic Leaching Procedure

US EPA = United States Environmental Protection Agency

ZHE = Zero Headspace Extractor

ABSTRACT

Arsenic removal using iron-coated bottom ash (ICBA) is a novel process of removing arsenic from groundwater invented by researchers at Lawrence Berkeley International Laboratory, USA. Adsorption/co-precipitation method has been employed in this new technology. The present study involves development of a community-based treatment unit and investigations relating its performance using iron coated bottom ash (ICBA) in reducing the elevated levels of arsenic, and other contaminants such as iron and manganese from groundwater of Bangladesh. In this research, the samples have been collected for batch analyses from Besgao village, Sreenagar, Munshiganj, an arsenic affected area which has been the subject of several arsenic related investigations for the last five years.

From the investigations performed in the laboratory scale, an ICBA dosage of 4 g/L and coagulant dosage of 0.25 g/L have been found to be optimum for good arsenic removal and therefore selected for subsequent batch experiments. ICBA seems to work better for pH levels 5.71~8.78 for synthetic groundwater samples. The higher the initial pH, the higher is the arsenic removal. Interference of phosphate content with arsenic removal has been observed to increase with the increase in phosphate concentration. Further investigations are necessary to better understand the mechanism of phosphate with arsenic adsorption using ICBA.

Results from the investigations performed with the community based treatment unit show that the performance of the unit varies with the flow rate. A flow rate of 100 Liters per hour provides the best performance. The lower the initial arsenic concentration, the better is the performance of the prototype in reducing arsenic concentration in the treated water below the Bangladesh drinking water standard. Performance of the unit in removing inevitable bacteriological contamination is enhanced when there is low level of contamination. For higher TC/FC, it takes around eight days to attain the required bacteriological quality of water. Presence of Iron-Related Bacteria (IRB) seems to change the performance of ICBA in removing As, Fe and Mn by attacking the adsorptive bonds between the contaminants and the ICBA. The number of IRB population has been observed to be as high as 1,40,000

cfu/ml in the raw groundwater. This number can be reduced to 9000 cfu/ml after treatment with ICBA and chlorination dose of 1.55 mg/L, but cannot be completely removed within a reasonable time. It is important to mention that the number of TC/FC present in the same water is also very high. In that case, presence of high IRB may have some contribution in giving false notion of presence of such high TC/FC.

Arsenic sludge from iron coated bottom ash does not allow arsenic to leach out under low pH environment. However, very high pH conditions (≈ 11) can cause leaching of arsenic from the sludge. Both arsenic and cadmium contents in raw wastes and leachates are within the guideline practiced for surface disposal according to US EPA (1995).

For groundwater having low initial arsenic concentration (around 200 $\mu\text{g/L}$), low initial manganese content (≤ 0.125 mg/L), and low bacteriological contamination, a hundred liter per hour prototype can be successfully implemented in treating the groundwater to achieve the Bangladesh drinking water standard. However, aesthetic quality of the treated water is not possible to obtain for high level of iron content (> 6 mg/L) without incorporation of a filtration unit.

However, acceptability of this prototype system to the community could not be ascertained as the prototype has not been installed in the field for use of the community.

CHAPTER – I

INTRODUCTION



1.1 GENERAL

The arsenic pollution of groundwater has become a major disaster for the developing country, Bangladesh. This has been an unforeseen consequence of a large-scale program to replace contaminated surface water sources by 'safe' groundwater. Over a period of about 20-25 years about four million wells have been installed to utilize the groundwater from deeper aquifer layers, typically less than 200m deep (UNICEF, 1999). Exploitation of groundwater from these wells has resulted in mobilizing the arsenic from the aquifer layers lying below the river basin and led to mass poisoning in the region, which is defined by the generic term arsenicosis (Rahman et al., 2001). Many technologies have been developed so far for mitigation of this problem. However the biggest challenges lie ahead in applying them in poor, rural settings, and enabling those communities to choose them as safe sources of water for drinking and cooking.

1.2 BACKGROUND AND RESEARCH SIGNIFICANCE

In the context of prevalence of high concentrations of arsenic in tubewell water, a wide range of technologies has been tried for the removal of arsenic from drinking water. The most common technologies utilized the conventional processes of oxidation, co-precipitation and adsorption onto coagulated flocs, adsorption onto sorptive media, ion exchange and membrane techniques for arsenic removal. A removal system based on sorptive filtration using iron-coated sand filter was developed and shown to be effective as a household unit in removing arsenic to

below 20 ppb (Ali et al., 2001). The fact that this technology could not be proven to be viable due to the difficulties in mass production of iron-coated sand it could not be established in community-based settings. However, Bottom Ash, a widely available material from coal-fired power plants has higher surface area to volume ratio than sand and will be used here as the media in removing arsenic from drinking water of Bangladesh. Iron-coated bottom ash, because of its wide availability and low-cost, has a great potential in inexpensively removing arsenic from arsenic-laden groundwater. This method coats ash with rust, which binds to arsenic. The arsenic can then be removed from the water through settling and/or filtration.

A number of experiments using iron-coated bottom ash were conducted in Bangladesh to determine the effectiveness of various treatment protocols in small-scale (Mathieu et al., 2008). It was found that (1) Iron-coated Bottom Ash removes more than half of the arsenic from water within five minutes of treatment, (2) Iron-coated Bottom Ash, that has settled at the bottom of a treatment vessel, continues to remove arsenic for 2-3 days, (3) Iron-coated Bottom Ash's arsenic removal efficiency can be improved through sequential partial dosing (adding a given amount Iron-coated Bottom Ash in fractions versus all at once), and (4) allowing water to first stand for two to three days followed by treatment with Iron-coated Bottom Ash produced ten times lower than treating water directly out of the well. It was proposed that the most attractive option of using Iron-coated Bottom Ash would be in community-scale water treatment centers, installed as public-private partnerships, in Bangladeshi villages.

The investigation continues, therefore, to understand the performance of a community scale water treatment unit using iron coated bottom ash in removing arsenic and other contaminants, such as iron, and manganese, etc.

1.3 OBJECTIVES OF THE PRESENT STUDY

The objectives of the present study are as follows:

1. Development of an arsenic removal unit for use in a community.

2. Assessment of the performance of Iron-Coated Bottom Ash in treating arsenic laden water in the laboratory.
3. Assessment of the community-scale water treatment unit using iron-coated bottom ash in removing As, Mn and Fe from groundwater.

1.4 METHODOLOGY OF THE STUDY

For the purpose of carrying out the investigation, independent studies have been performed to determine and select the required doses of ICBA and coagulant in the laboratory for the purpose of its use in community based treatment unit. Then, the arsenic removal capacity of iron coated bottom ash with the selected dose of ICBA and coagulant have been studied in the laboratory. Selection of ICBA and coagulant mixing times has also been performed in the laboratory for their use in community-based treatment unit. Then, the performance of ICBA under several environmental conditions such as pH, presence of other competing ions, such as, phosphate, etc have been studied in the laboratory. Then, a community scale water treatment unit capable of removing arsenic, iron, and manganese has been investigated. This research work has also included measurement of different environmental and chemical parameters such as Phosphate, Silica, pH, DO, electrical conductivity, alkalinity, etc. The unit has also been investigated in order to achieve the final bacteriological quality of the treated water. Finally, the sludge produced in the treatment unit has been examined for arsenic leaching and presence of heavy metals.

1.5 ORGANIZATION OF THE THESIS

The study has been organized so as to best describe and discuss the problem and the resulting findings. Chapter 1 introduces the problem and presents an overall idea of the present study. Chapter 2 introduces the arsenic related problems and reviews the available literature that is required to understand the background theories of arsenic removal technologies. Chapter 3 describes the results from the experiments on the selection of the required doses of iron coated bottom ash and coagulant for its use in community scale treatment systems. It also describes the arsenic removal capacity with the selected doses of ICBA and coagulant, selection of ICBA and coagulant mixing times for their use in large scale. This chapter also presents the arsenic

removal using ICBA under several environmental conditions such as pH, presence of competing ions such as phosphate, etc. Chapter 4 presents the development of a community-based treatment unit in context to Bangladesh, its modifications and the results of the comprehensive study performed with this treatment unit in understanding its efficiency in removing As, Mn and Fe from groundwater using iron-coated bottom ash. Chapter 5 illustrates the results of the arsenic leaching and presence of heavy metals in the sludge produced in the treatment unit. This chapter also presents the important points to be noted while maintaining the arsenic removal unit. Chapter 6, the concluding chapter, summarizes the entire work and makes some recommendations for future research.

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 the other elements such as oxygen, sulfur and iron. Arsenic may be found in organic form when it is combined with carbon and hydrogen. Sometimes arsenic occurs naturally in the soil, from where it leaches into groundwater. Sometimes it may be found in effluents of different industries.

Arsenic occurs in many forms, but is most toxic as an ion because it reacts with sulfur-containing groups on certain enzymes. Exposure to non-lethal levels of arsenic over a long period of time may result in chronic poisoning and carcinogenic effects. For this reason, arsenic remains a work safety issue in industries where it is still used, such as in the manufacture of weed killers and insecticides, the preservation of wood, and in the extraction of lead and copper ores. The symptoms of acute arsenic poisoning occur in two forms. In the paralytic form, a severe paralysis develops within 1-2 hours, often accompanied by signs of delirium. In the gastrointestinal form, symptoms such as nausea, headache, intense pain, vomiting and diarrhea are dominant. It may be introduced into water through the dissolution of minerals and ores. Arsenic is naturally found at concentration levels of about 0.4 to 30 ng/m³ in the atmospheric air, about 0.4 to 120 µg/kg in food and at concentrations from undetectable level to a few µg/L in natural water. Thus, humans all over the world are exposed to small amounts of arsenic, mostly through food, water and air. Groundwater contamination by this toxic element has been reported from several

countries viz. Argentina, Mongolia, China, Taiwan, Thailand, Mexico, Chile, Hungary, Greece, Ghana and some parts of USA, but the extent of groundwater arsenic contamination in Bangladesh is by far the most severe arsenic contamination, both in terms of area and population exposed.

This chapter enfold historical reviews, occurrence, health concerns, and drinking water standards relating to arsenic. Also it briefly summarizes the status of arsenic contamination in groundwater of Bangladesh. This chapter then describes the conventional arsenic removal technologies in practice, along with their inherent limitations and the use of different adsorbents for arsenic removal. It also reviews the potential use of iron-coated bottom ash for removal of arsenic. Finally a comparison among different adsorbents used for arsenic removal is presented for better evaluation of the present research work.

2.2 HISTORICAL REVIEW

The word *arsenic* is borrowed from the Persian word *Zarnikh* meaning "yellow orpiment". *Zarnikh* was borrowed by Greek as *arsenikon*, which means masculine or potent. Arsenic has been known and used in Persia and elsewhere since ancient times (Bentley and Chasteen, 2002). As the symptoms of arsenic poisoning were somewhat ill-defined, it was frequently used for murder until the advent of the Marsh test, a sensitive chemical test for its presence. (Another less sensitive but more general test is the Reinsch test.) Due to its use by the ruling class to murder one another and its potency and discreetness, arsenic has been called the *Poison of Kings* and the *King of Poisons*.

During the Bronze Age, arsenic was often included in bronze, which made the alloy harder (so-called "arsenical bronze"). Arsenic was first isolated by Geber (721-815), an Arabian alchemist (George Sarton). Albertus Magnus (Albert the Great, 1193-1280) is believed to have been the first European to isolate the element in 1250 (Emsley, 2001) In 1649, Johann Schröder published two ways of preparing arsenic.

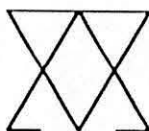


Figure 2.1 Alchemical symbol for arsenic.

(Source: <http://en.wikipedia.org/wiki/Arsenic>)

Cadet's fuming liquid, the first organometallic compound, was synthesized in 1760 by Louis Claude Cadet de Gassicourt by the reaction of potassium acetate with arsenic trioxide (Seyferth, 2001).

In the Victorian era, "arsenic" (colourless, crystalline, soluble "white arsenic") was mixed with vinegar and chalk and eaten by women to improve the complexion of their faces, making their skin paler to show they did not work in the fields. Arsenic was also rubbed into the faces and arms of women to "improve their complexion". The accidental use of arsenic in the adulteration of foodstuffs led to the Bradford sweet poisoning in 1858, which resulted in approximately 20 deaths and 200 people taken ill with arsenic poisoning (Turner, 1999).

The first reported case of arsenic-contaminated groundwater (greater than 50 ppb As) from the Bengal Basin was recorded in 1978 in West Bengal (Acharrya et al., 2000) and the first cases of arsenic poisoning there were diagnosed in 1983. These early cases of arsenic-induced skin lesions were identified by K.C. Saha then at the Department of Dermatology, School of Tropical Medicine in Calcutta, India (Saha, 1997; Smith et al., 2000). The issue of arsenic contamination in West Bengal achieved international recognition in 1995 when the School of Environmental Studies (SOES) at Jadavpur University, Calcutta hosted an international conference on the subject (BGS, 2001).

2.3 OCCURRENCE OF ARSENIC

Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms. It is the 20th most abundant element in the earth's crust and the 12th most abundant element in the biosphere, where it is said to be an essential element at least for some animal species, but not for human. It is the king of poisons and has plagued human beings since the days of antiquity. It is mobilized in the

environment through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities. Figure 2.2 shows a simplified, comprehensive cycle of transfer of arsenic (after Bhumbra and Keefer, 1994). Most environmental arsenic problems are the result of mobilization under natural conditions, but man has had an important impact through mining activity, combustion of fossil fuels and through the use of arsenic in pesticides, herbicides, crop desiccants and as an additive to animal feed. Although the use of arsenical products such as weed-killers and wood preservatives has decreased in the last few years, their impact on the environment at least locally, is likely to remain for some years.

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 (Vinogradov, 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, adsorption-desorption and organic and biochemical methylation. All of these reactions control the mobilization and bio-accumulation of arsenic in the environment (Bhumbra and Keefer, 1994).

2.4 SOURCES OF ARSENIC

2.4.1 Natural Sources of Arsenic

Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites (BGS, 2001). A list of some of the most common arsenic minerals is given in Table 2.1. Most are ore minerals and their alteration products. The greatest concentration of these minerals therefore occur in mineralized areas and are commonly found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. The most

widespread arsenic ore mineral is arsenopyrite, FeAsS . It is generally assumed that arsenopyrite, together with the other dominant As-sulphide minerals realgar and orpiment, are only formed under high temperature conditions in the earth's crust, although there is recently some debate about whether arsenopyrite can form at low temperatures as an authigenic mineral (BGS, 2001).

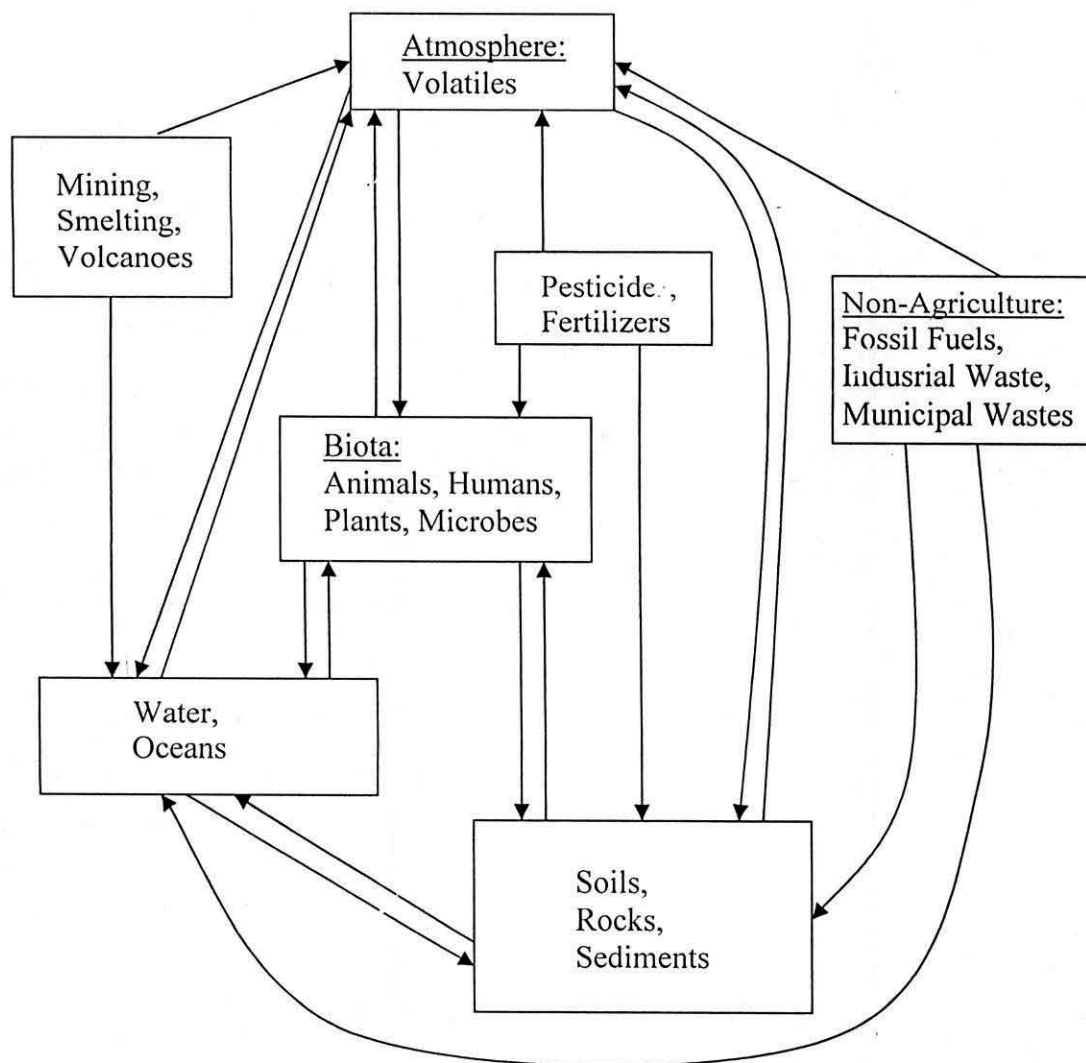


Figure 2.2 A simplified comprehensive cycle of transfer of arsenic (after Bhumbra and Keefer, 1994)

Table 2.1 Major Arsenic minerals occurring in nature

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal Veins
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays or limestones, also hot-spring deposits
Orpiment	As ₂ S ₃	Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
Arsenopyrite	FeAsS	The most abundant arsenic mineral, dominantly mineral veins
Tennantite	(Cu,Fe) ₁₂ As ₄ S ₁₃	Hydrothermal veins
Enargite	Cu ₃ AsS ₄	Hydrothermal veins
Arsenolite	As ₂ O ₃	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals
Claudetite	As ₂ O ₃	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals
Scorodite	FeAsO ₄ .2H ₂ O	Secondary mineral
Annabergite	(Ni,Co) ₃ (AsO ₄) ₂ .8H ₂ O	Secondary mineral
Hoernesite	Mg ₃ (AsO ₄) ₂ .8H ₂ O	Secondary mineral, smelter wastes
Haematolite	(Mn,Mg) ₄ Al(AsO ₄)(OH) ₈	
Conichalcite	CaCu(AsO ₄)(OH)	Secondary mineral
Pharmacosiderite	Fe ₃ (AsO ₄) ₂ (OH) ₃ .5H ₂ O	Oxidation product of arsenopyrite and other As minerals

Arsenic concentrations are generally low in most igneous rocks (BGS, 2001). Ure and Berrow (1982) quoted an average value of 1.5 mg kg⁻¹ for all rock types (undistinguished). The concentrations of arsenic in natural reservoir with respect to

soils have been shown in Table 2.2. 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. Baseline concentrations of arsenic in soils are in the order of $5\text{--}10\text{ mg kg}^{-1}$ (BGS, 2001). The concentration of arsenic in the atmosphere are usually low, but are increased by inputs from smelting and other industrial operations, fossil-fuel combustion and volcanic activity. Total arsenic deposition rates in the atmosphere have been calculated in the range $< 1\text{--}1000\text{ }\mu\text{g m}^{-2}\text{ a}^{-1}$ depending on the relative proportions of wet and dry deposition and proximity to contamination sources (Schroeder et al., 1987).

Table 2.2 Ratios of arsenic concentrations in natural reservoir with respect to soil (Mackenzie et al. 1979)

Reservoirs	Ratios with respect to soil
Rocks and minerals	25,000
Oceans	4
Soils	1
Biota (Plant, animals, microbes)	0.0005
Atmosphere	0.000001

2.4.2 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 survey are shown in Table 2.3.

Table 2.3 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, dusts from the burning fuels, and disposal of industrial and animal wastes (Sandberg and Alien, 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 (Crecelious et al., 1974; Ragaini et al., 1977). Arsenic is also commonly associated with phosphate minerals, in an average concentration of 7.7 ppb (Alloway, 1990).

2.5 CHEMISTRY OF ARSENIC

2.5.1 Properties of Arsenic

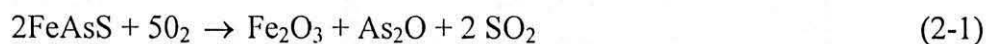
Arsenic is a chemical element in the nitrogen family (group VA of the periodic table), existing in both grey and yellow crystalline forms. Although some forms of arsenic are metal-like, it is best classified as metalloid and non-metal. It can be manufactured in three allotropic forms, the yellow (α) form, the black (β) form and the steel grey (γ) form. These have different physical properties. The cubic α - form is made by condensing the vapor at very low temperatures; it is metastable and is soluble in CS_2 and consists of tetrahedral As_4 units. The black β - polymorph is iso-structural with black phosphorous (II), also metastable. Both of these modifications revert to the stable γ form, grey or metallic, rhombohedral arsenic, on heating or exposure to light. Grey or metallic arsenic, which is more stable and more common than the softer yellow form, is very brittle, tarnishes in air and sublimates when heated at 610°C , i.e., it passes directly into vapor form without melting and reverts to the crystalline solid without liquefying upon cooling the vapor (Encyclopaedia Britannica, 1994). Apart from the elementary arsenic, where the oxidation state by definition is 0, arsenic is stable in its states +5, +3 and -3. Some important properties of arsenic are listed in Table 2.4.

Table 2.4: Properties of arsenic (Encyclopedia Britannica, 1994)

Parameter	Value
Atomic number	33
Atomic weight	74.92158
Melting point (grey form)	814°C at 36 atm
Boiling point	616°C (sublimes)
Density (grey form)	5.73 g/cm ³ at 14°C
Density (yellow form)	2.03 g/cm ³ at 18°C
Specific gravity (α , β , γ)	2.026, 4.700, 5.727
Latent heat of fusion	27,740 J/(mol-K)
Latent heat of sublimation	31,974 J/(mol-K)
Oxidation number	-3, 0, +3, +5
Electronic configuration	Is ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ² 4p ³ (2-8-18-5)
Electrical resistivity	33.3 μ ohm cm (273 K)
Crystal system (grey form)	Hexagonal (rhombohedral)
Lattice constant at 26°C	a = 0.376 nm, c = 1.0548 nm
Covalent radius	121 pm
Ionic radius (As ⁺³)	69 pm
Metallic radius	139 pm
Hardness (Mohs' scale)	3.5

2.5.2 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 oxides, the principal forms of which are arsenious oxide (As₂O₃) and arsenic pentoxide (As₂O₅). Arsenious oxide, commonly known as white oxide, is the material most widely used for the synthesis of arsenic compounds. It is produced as a byproduct of the nonferrous metal industry, primarily from the smelting of copper ores. Naturally occurring metal arsenide's realgar and orpiment also convert to the trivalent oxide when roasted in air. The formation of the trioxide by the roasting of a sulfide ore is illustrated in Eq. (2-1).



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



The trioxide is moderately soluble in water, but dissolves easily in aqueous alkali to

produce a solution of arsenic, AsO_4^{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. 3) gives the pentoxide.



Hypochlorous, hydrochloric 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 (e.g. zinc) of arsenic compounds in acidic solutions. Other hydrides of arsenic are diarsine (As_2H_4), diarsine hydride (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, $\text{H}_3\text{AsO}_4 \cdot 0.5\text{H}_2\text{O}$, by the evaporation of a cold aqueous solution. Arsenic trioxide is the anhydride of arsenious acid. The solubility of arsenic trioxide in water at 25°C is 21.6 g/L. The rate of dissolution of trioxide in water is painstakingly slow, sometimes requiring up to 50h of continuous agitation. 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 ($\text{H}_2\text{AsO}_4^{2-}$) are known. Diarsenic disulfide (As_2S_2), but more properly written as As_4S_4 , exists in nature as mineral realgar. As_2S_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), found in nature in orpiment, has been described as yellow arsenic sulfide. Diarsenic pentasulfide (As_2S_5), has been described as 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 have been reported. They are As_2P and AsP . Diarsenic phosphide is black and

lustrous and turns 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 $[(\text{CH}_3)_2\text{As}-\text{As}(\text{CH}_3)_2]$, 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 dysentery, caused by microorganism. Some of the most important compounds and species of arsenic are shown in Table 2.4.

2.5.3 Acid-Base Reaction

Apart from the elementary arsenic with oxidation state 0, arsenic is stable in the oxidation states of +5, +3, and -3 (see Table 2.4), but generally found in water only in the trivalent and pentavalent states. The oxides of both As (III) and As (V) are soluble in water. The dissolution implies direct reaction with water, hydration, where the oxides behave like non-metals and exhibit acidic character. As (III) forms arsenious, also called arsonic acid and As (V) forms the arsenic acid, also called arsinic acid. The two acids dissociate to form respectively arsenite and arsenate ions as shown in the following reactions.

Arsenious Acid Dissociation:



Arsenic Acid Dissociation:



Table 2.4: 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 Oxidation state: -3	As^{3-}	Minor importance [Most toxic As species]
Elemental Arsenic Oxidation state: 0	As	Minor importance [Least toxic As species]
Trivalent Arsenic Oxidation state: +3	As(III)	Dominant under anaerobic condition [10 times more toxic than As(V)]
Arsenite, Inorganic	H_3AsO_3	pH = 0-9
	$\text{H}_2\text{AsO}_3^{1-}$	pH = 10-12
	HAsO_3^{2-}	pH = 13
	AsO_3^{3-}	pH = 14
Methylated As(III)		
MMAs(III)	$\text{CH}_3\text{As(III)O}_2^{2-}$	Minor importance
DMA(III)	$(\text{CH}_3)_2\text{As(III)O}^{1-}$	[Less toxic than inorganic As(III)]
TMA(III)	$(\text{CH}_3)_3\text{As(III)}$	
Organo-As(III)		
Pentavalent Arsenic Oxidation state: +5		Dominant under aerobic condition [10 times less toxic than As(III)]
Arsenate, Inorganic	H_3AsO_4	pH = 0-2
	$\text{H}_2\text{AsO}_4^{1-}$	pH = 3-6
	HAsO_4^{2-}	pH = 7-11
	AsO_4^{3-}	pH = 12-14 Important
Methylated As(V)		
MMAs(V)	$\text{CH}_3\text{As(V)O}_3^{2-}$	Minor importance
DMA(V)	$(\text{CH}_3)_2\text{As(V)O}_2^{1-}$	[Less toxic than inorganic As(V)]
TMA(V)	$(\text{CH}_3)_3\text{As(V)O}$	
Organo As(V)		

Figure 2.3 shows the predominance diagram of arsenic species as a function of pH. From Figure 2.3 it is seen that arsenic acid is stronger than arsenious acid. Within the range of natural waters (particularly groundwater) where pH is usually between 6 and 9, the trivalent inorganic arsenic is found as non-dissociated arsenious acid (H_3AsO_3); while the pentavalent arsenic is primarily found as the ionized dihydrogen arsenate (H_2AsO_4); and mono-hydrogen arsenate (HAsO_4^{2-}). The

relatively more mobile mono-methylated and di-methylated forms are observed in ocean and lake waters, but seldom in groundwater.

As most treatment processes are more capable to remove ions, the trivalent arsenic is more difficult to remove from the water than the pentavalent (Kartinen and Martin, 1995). Probably this ionization of arsenic (V) is also important for the fate of arsenic in the human body. The reduced toxicity of the arsenic (V) may be, to a large extent, due to ionization, which enables easier control of its intracellular transportation (Dahi, 1997).

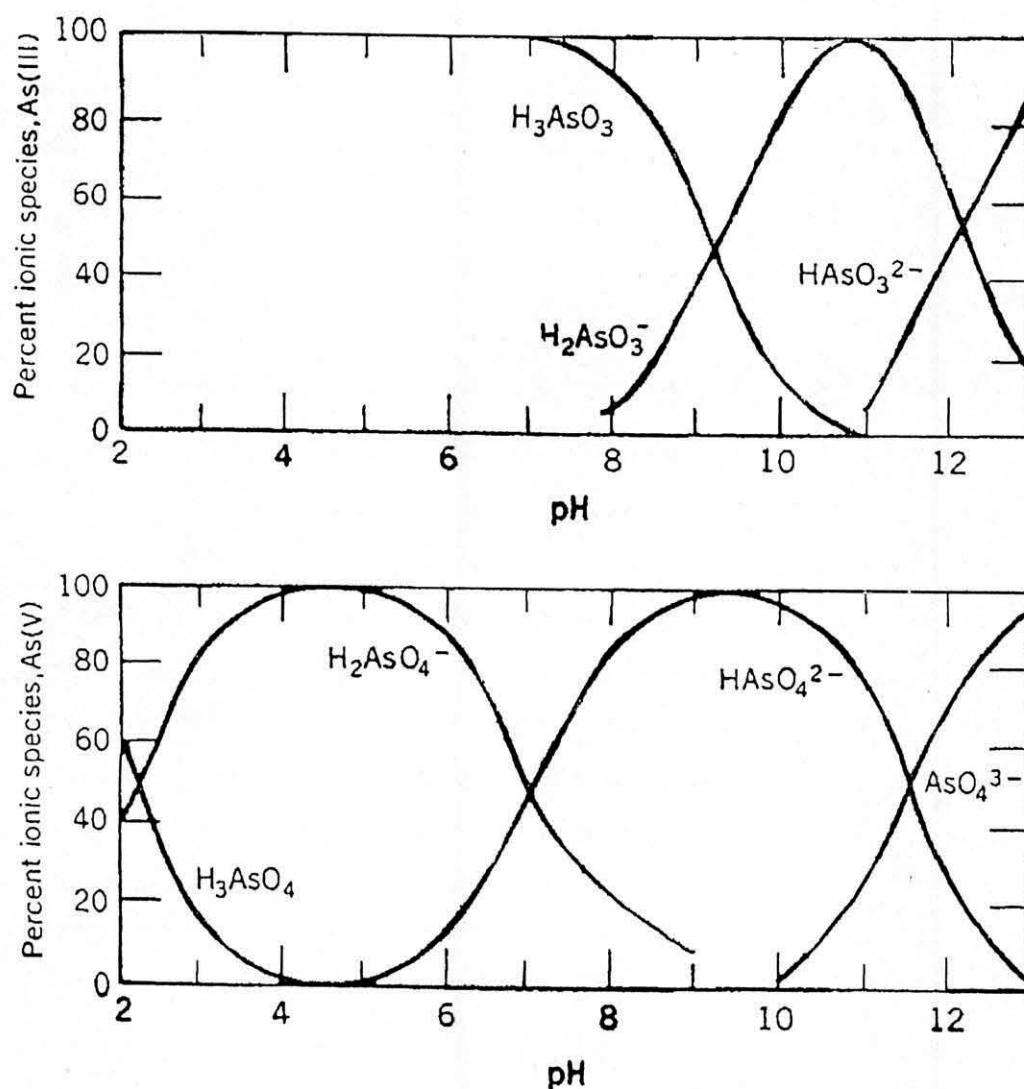


Figure 2.3 Predominance diagram of As(III) and As(V) as a function of pH (Montgomery, 1985)

2.5.4 Red-ox Reaction

Arsenic is a redox sensitive element. Arsenate [As(V)] and Arsenite [As(III)] are common oxidation states of arsenic in water. The mobility of arsenic is controlled, in large part, by the oxidation-reduction (redox) transformations. The valence in which arsenic exists is related to both pH and the redox potentials, E_h . The hypothetical electron activity at equilibrium, pE , is used interchangeably with E_h . These parameters are related by $pE = (F/2.3 RT) E_h$, where T is the absolute temperature and F & R are the Faraday and Gas constants respectively. Thus at 25°C, $2.3RT/F = 0.059$ V and $pE = E_h/0.059$. The equation linking arsenic speciation to pH and pE are readily available, but E_h versus pH diagrams (Figure 2.4), are the most concise way of presenting this information.

The diagram represents equilibrium conditions of arsenic under various redox potentials. Well-aerated surface waters would tend to induce high E_h values, therefore, any arsenic present should be in the arsenate [As (V)] form. Mildly reducing conditions, such can be found in groundwater, should produce arsenite [As (III)]. By determining the pH and E_h of water, it is possible to determine which species of arsenic will be prevalent and, through this, the solubility and dissolution/desorption of arsenic from rocks.

There are two main "triggers" that can cause arsenic to leach out of the rocks and sediments into groundwater: strongly reducing conditions or very high pH water. There are also a variety of human inputs and influences, although those are only found to be significant on a regional scale. (Smedley, 2002)

2.5.5 Oxidation Reaction

As stated earlier, arsenate is dominant in oxygenated water, while arsenite is dominant in non-oxygenated water. Although thermodynamics can provide an accurate prediction of prediction of possible changes in a given non-equilibrium conditions, they give no insight to the rate at which those changes will occur. While As(III) and As(V) acid-base reactions can be assumed to occur instantaneously, 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 or months depending on the specific conditions. The reduction of As(V) to As(III) is similarly kinetically constrained. This is the reason why arsenic (V) can be found in some anoxic waters (Dahi, 1997). This process is however also known to be facilitated through catalysis and bacterial mediation.

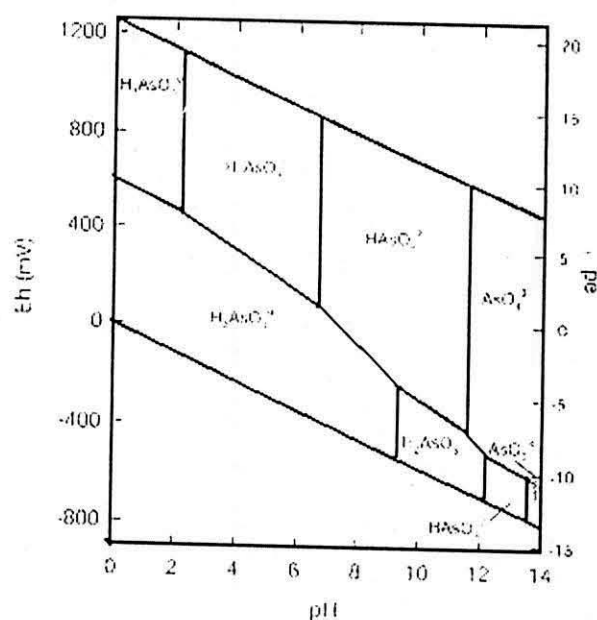


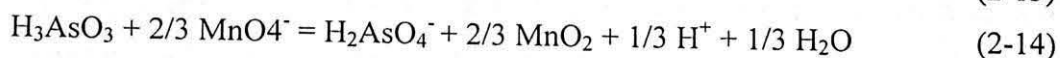
Figure 2.4 An Eh-pH diagram of aqueous, aerobic As-solution at 25°C and 1 bar of pressure (Smedley, 2002)

In strongly acidic or alkaline solutions, the presence of copper salts, carbon, certain catalysts and higher temperatures can increase the arsenic oxidation rate (Ferguson and Gavis, 1972). Catalytic oxidation can be achieved by powered active carbon and dissolved oxygen in stirred reactions. The rate of oxidation can be described by the first-order equation.

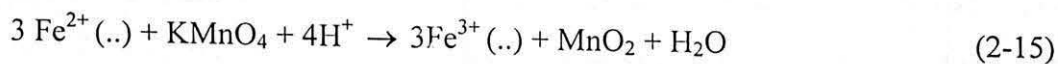
The effective removal of arsenic from water requires the complete oxidation of As(III), especially if the drinking water standard is low. There are various means of oxidation available, but in drinking water treatment there are important considerations such as the limited list of safe chemicals, the residuals of oxidants, oxidation by products and the oxidation of other inorganic and organic compounds.

In the oxidation processes with dosing of chemicals, effective oxidants are free chlorine, hypochlorite, ozone, permanganate, and hydrogen peroxide/ 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. Chlorine is widely used for oxidation purpose, but may lead to chlorinated by-products, namely trihalomethanes (THMs), from 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 are potassium permanganate and Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$). Permanganate oxidizes As(III), Ferrous and manganese ions specifically and quickly. Chlorine and permanganate are able to oxidize As(III) to As(V) within a very short time, e.g., half an hour or even few minutes (Dahi, 1997).

Arsenious acid oxidations by most common oxidants are shown in the following reactions (Dahi, 1997):



Possible reaction with ferrous ion and permanganate is given bellow:



2.5.6 Adsorption – Desorption

Adsorption-desorption reactions are very important in determining the mobility of arsenic in nature as well as its removal in many treatment systems. Attachment of arsenic to an iron-oxide surface is an example of an adsorption reaction. The reverse of this reaction, arsenic becoming detached from such a surface is an example of desorption. Both arsenate and arsenite adsorb to surfaces of a wide range of solids including iron, aluminum and manganese oxides (e.g., iron oxyhydroxides), and clay minerals.

The strong adsorption characteristics of arsenic has been utilized in its removal from water by coagulation using alum, lime or ferric salts, where arsenic is removed primarily by adsorption onto solid flocs (e.g., aluminum hydroxide or ferric hydroxide) and subsequent precipitation. Arsenate is much more strongly adsorbed and removed than arsenite. Ferric salts have been found to be more effective in removing arsenic than alum on a weight basis and effective over a wider pH range. The strong adsorption of arsenic onto hydrous iron, aluminum and other solids has also been utilized in removing arsenic using a wide range of solid sorption media. These include activated alumina, iron coated sand, granular ferric hydroxide, and a wide range of other materials. Besides arsenic, a number of other ions present in natural water (e.g., phosphate, silicate, sulfate) also have strong affinity for solid surfaces and presence of high concentrations of these ions can reduce removal efficiency of arsenic in adsorption-based treatment systems.

Adsorption-desorption of arsenic onto iron-oxide surfaces are important controlling reactions in the subsurface because iron-oxides are widespread in the hydro-geologic environment as coatings on other solids, and because arsenate adsorbs strongly to iron oxide surfaces in acidic and near-neutral pH conditions. Desorption of arsenate is favored at higher (i.e., alkaline) pH values. The pH dependence of arsenate adsorption-desorption appears to be related to the change in net charge on iron-oxide surface with pH. The net charge on iron oxide surface changes from positive to negative as pH increases above the "zero-point-of-charge" (pH at which net surface charge is zero). The "zero-point-of-charge" is about 7.7 for goethite (crystalline iron oxide) and about 8.0 for ferrihydrite (amorphous iron oxide). Thus as pH increases above about 8, the net negative surface charge on iron oxides can repel the negatively charged ions such as arsenate. Compared to arsenate, arsenite is less strongly adsorbed by iron-oxides. Arsenate and arsenite adsorption-desorption reactions onto other common surfaces are less well characterized.

In Bangladesh, arsenic-rich iron oxyhydroxides present in aquifer materials appear to be the primary source of arsenic in groundwater. In the subsurface environment, adsorption-desorption of arsenic onto iron oxyhydroxides is an important mechanism

controlling its mobility. As noted earlier, presence of ligands, which may compete with arsenic for adsorption sites on iron oxyhydroxides, e.g., phosphate, silicate and sulfate can also influence the mobility of arsenic in the subsurface, if present in large enough concentrations. Besides oxyanions of molybdenum, selenium and vanadium can also compete with arsenic for adsorption sites.

As a result of pH dependence of arsenic adsorption, changes in groundwater pH can promote adsorption or desorption of arsenic. Similarly, redox reactions can control aqueous arsenic concentration by their effect on arsenic speciation and hence on adsorption-desorption reactions. For example, reduction of arsenate to arsenite can promote arsenic mobility because arsenite is less strongly adsorbed than arsenate. It should be noted that in nature, bacteria often mediate oxidation reduction reactions. Finally, structural changes in solid phases at the atomic level can also affect arsenic adsorption-desorption (USGS, 1999). For example, conversion of amorphous ferrihydrite to crystalline goethite may occur gradually over time (Dzombak and Morel, 1990) and this can be accompanied by a decrease in adsorption site density.

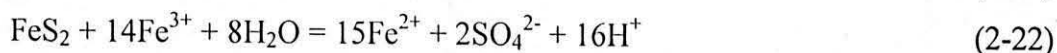
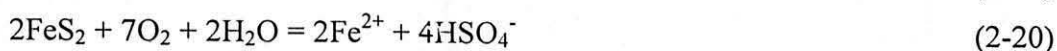
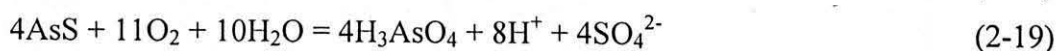
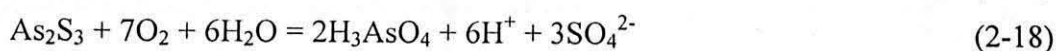
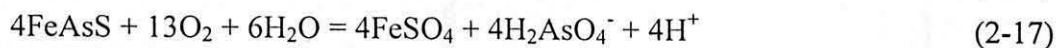
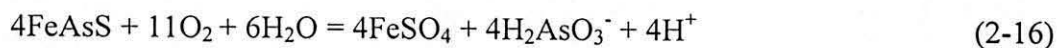
This reduction in site density may result in desorption of adsorbed arsenic. Structural changes in other solid phases may also affect arsenic mobility (USGS, 1999).

2.5.7 Precipitation and Dissolution

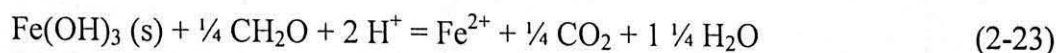
Precipitation-dissolution reactions are important mechanisms controlling mobility of arsenic in the subsurface. Arsenic contained within solid phases, either as a primary structural component of arsenic bearing minerals (e.g., arsenopyrite) or an impurity in any of a variety of solid phases (e.g., pyrite), is released to groundwater when these solid phases dissolve. Similarly, arsenic is removed from groundwater when solid phases containing arsenic precipitate from aqueous phase. As an example, because arsenic often co-precipitates with iron-oxide, iron-oxides may act as an arsenic source (case of dissolution) or a sink (case of precipitation) for groundwater (USGS, 1999). Besides, solid phase dissolution will contribute not only arsenic contained within that phase, but also any arsenic adsorbed to the solid-phase surface. In Bangladesh, reductive dissolution iron oxyhydroxides and consequent release of

adsorbed arsenic could be an important mechanism of arsenic mobilization in the subsurface.

Oxidative dissolution reactions (Bhumbla and Keefer, 1994) of arsenopyrite (FeAsS) (Eq. 2-16 & 17), Orpiment (As_2S_3), (Eq. 2-18) and Reagler (AsS) (Eq. 2-19) are shown below. Oxidative dissolution of pyrite (FeS_2) is shown in Eq. 2-20, 21 & 22 (Chowdhury et al., 1998).



The interplay of redox reactions and solid phase precipitation and dissolution may be particularly important with regard to aqueous arsenic and solid-phase iron oxides and sulfide minerals (USGS, 1999). High concentrations of arsenic often are associated with iron oxides and sulfide minerals. Iron-oxides frequently dissolve under reducing conditions (e.g., in the presence of organic matter, as shown in Eq. 2-23), but often precipitate under oxidizing conditions. Sulfide minerals generally are unstable under oxidizing conditions, but may precipitate under reducing conditions (e.g., precipitation of As_2S_3 , as shown in Eq. 2-24). Thus, as a result of redox sensitive nature of iron-oxides and sulfide minerals, transfer of large amounts of arsenic between these solid phases and neighboring water may result from redox-facilitated precipitation and dissolution reactions (USGS, 1999).



According to ECR 1997, drinking water standard for arsenic in Bangladesh is 50 µg/L (or 0.05 mg/L). The WHO guideline value for arsenic in drinking water is 10 µg/L (or 0.01 mg/L). The USEPA has also introduced a revised maximum contaminant level (MCL) to 10 µg/L for public water supplies in the USA (BGS, 2001). The Japanese limit for drinking water is also 10 µg/L.

In a population drinking arsenic contaminated water, a great variety of specific as well as non-specific symptoms may be observed. Table 2.5 lists some of the effects of arsenic reported to be due to exposure through drinking water.

Table 2.5 Toxicological effects due exposure to high arsenic concentration in drinking water (WHO, 1996; Khan, 1997)

Effect	Symptoms	Remarks
Blackfoot disease Arsenical dermatosis	Dermal lesion, Peripheral neuropathy, Keratosis, Hyperpigmentation	May necessitate operation
None specific	Nausea, Abdominal pain, Diarrhoea, Vomiting, Conjunctivitis, Oedema	Mainly due to acute intoxication
Pregnancy disorders	Spontaneous abortions, Miscarriages	-
Heart Disease	Coarctation of aorta, Cardiovascular disturb	Among children
Cancer	Bladder, Kidney, Skin & Lungs, Liver & Colon	-
Mortality	-	Mainly due to cancer

In a study by the National Institute of Preventive and Social Medicine (NIPSOM), arsenic related diseases (arsenicosis) have been identified in 37 districts (Ahmed et al., 1998). A total of 6000 cases were identified in 162 villages in the 37 districts, mostly in the rural areas. Three stages of manifestations of chronic arsenicosis were observed in the study (Ahmed 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.

2.7 ARSENIC, IRON AND MANGANESE CONTAMINATION IN BANGLADESH

2.7.1 Arsenic

In Bangladesh arsenic was first detected in late 1993 in groundwater samples from the district of Chapai Nawabgonj bordering the West-Bengal district of India. Since then higher levels of arsenic have been detected in many regions of the country. The British Geological Survey (BGS) in cooperation with the Department of Public Health Engineering (DPHE) (BGS/DPHE, 2001) carried out the most comprehensive study on distribution of arsenic in groundwater of Bangladesh. In this study, water samples from 3534 tubewells from 61 out of 64 districts and from 433 out of the 496 upazillas were analyzed. Recently, the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) carried out a detailed screening of tubewells and survey of arsenicosis patients in 270 arsenic affected upazillas of the country (BAMWSP, 2005). In this study, every household of these arsenic-affected upazillas was surveyed and all tubewells were tested using field test kits. A total of 4,946,933 tubewells were screened for arsenic and over 66 million people surveyed for arsenicosis.

The regional pattern of arsenic distribution obtained from the BGS/DPHE and BAMWSP surveys are very similar, with the greatest contamination in the south and south-east (except Chittagong and Chittagong Hill Tracts) region and least in the north-west and in the uplifted areas of the north central Bangladesh. Figure 2.4 shows the distribution of arsenic concentration in Bangladesh based on the nationwide survey carried out by BGS/DPHE. According to BGS/DPHE (2001) arsenic concentration exceeding the Bangladesh standard of 50 ppb was detected in 53 out of 61 districts, and in 249 upazillas out of 433 sampled upazillas. Out of 3534 samples, only 9% were from deep (>150m) tubewells and the rest were from shallow

wells. Among the shallow tubewells, 27% contained arsenic in excess of 50 ppb and 46% in excess of WHO guideline value. For the deep tubewells, the corresponding figures are 1% and 5% respectively (BGS/DPHE, 2001). The survey results revealed some 'hot spots' with high arsenic concentration in some least contaminated regions (e.g., Chapai Nawabgonj in western Bangladesh).

It was recognized that the sample density in the BGS/DPHE survey was not sufficient to ensure detection of all such 'hot spots'. An important observation from this and other arsenic surveys is the significant variation of arsenic concentration in well waters within short distances. Neighboring wells within a village have been found to contain quite different concentrations of arsenic and other water quality parameters (BGS/DPHE, 2001). In the vertical dimension, high concentrations have been detected within tens of meters of low concentrations.

Estimates of population exposed to arsenic concentration above the Bangladesh drinking water standard of 0.05 mg/L vary from about 20 million to over 36 million (DPHE/BGS/MML, 1999; EES/DCH, 2000; Begum, 2001; BGS/DPHE, 2001). According to BGS/DPHE (2001), 35 million people of Bangladesh are exposed to an arsenic concentration in drinking water exceeding the national standard of 50 $\mu\text{g/L}$ and 57 million people exposed to a concentration exceeding the WHO guideline value of 10 $\mu\text{g/L}$.

Yu et al. (2003) estimated that if consumption of contaminated water continues, the prevalence of arsenicosis and skin cancer in Bangladesh will be approximately 2,000,000 and 1,000,000 cases per year, respectively and the incidence of death from cancer induced by arsenic will be approximately 3,000 cases per year. In the nationwide screening program carried out by the BAMWSP, over 66 million people of every household of 270 arsenic-affected upazillas were surveyed for arsenicosis patients. Figure 2.5 shows the distribution of arsenicosis patients in the survey areas.

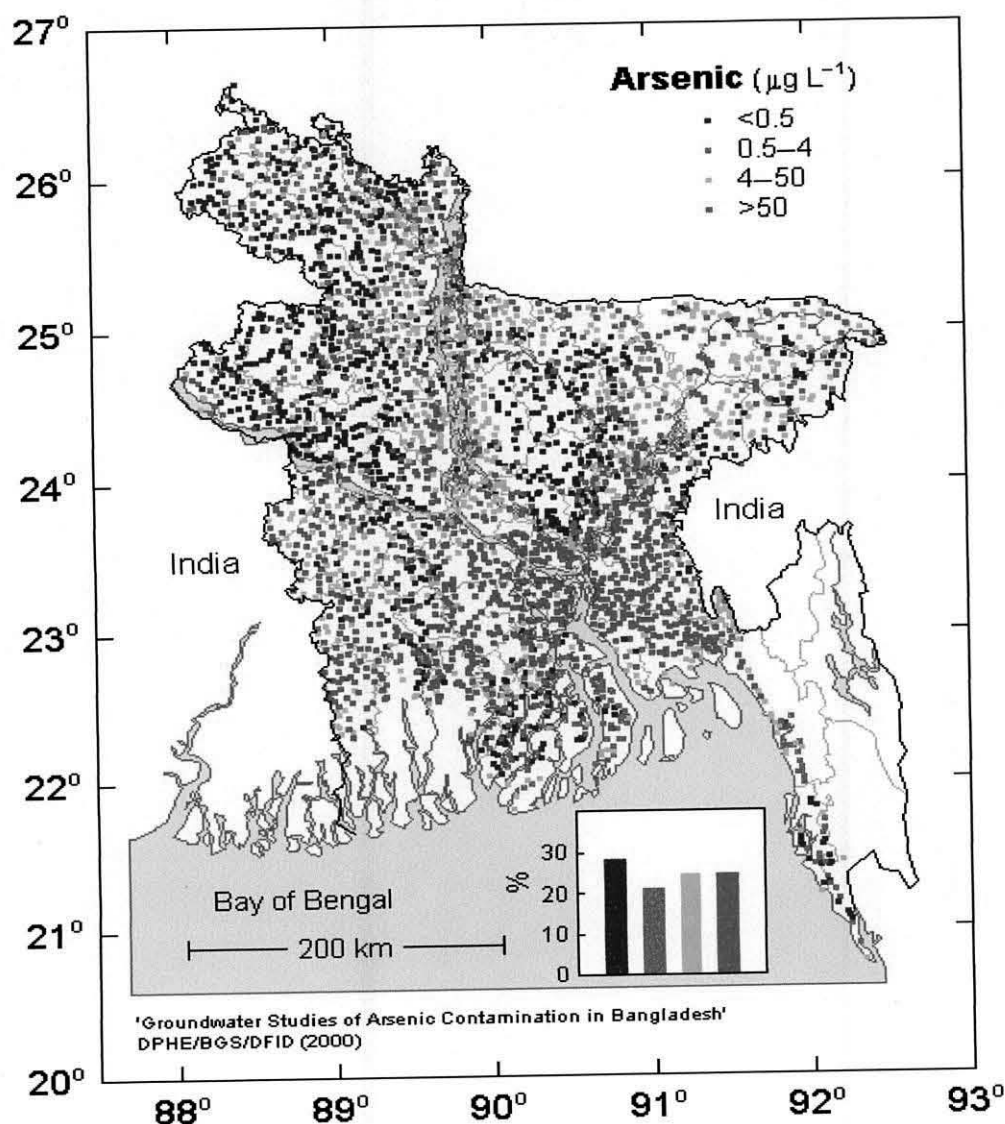


Figure 2.5 Distribution of arsenic concentration in Bangladesh based on the nationwide survey carried out by BGS/DPHE

A total of 38,430 arsenicosis patients were identified in this survey. Results from all previous surveys show poor correlation between the percentage of contaminated groundwater in a particular area and the density of patients (BGS/DPHE, 2001). Although the BAMWSP survey shows relatively low prevalence of arsenicosis, many fear it to be the 'tip of the iceberg', considering the usual delayed effect of arsenic on exposed population.

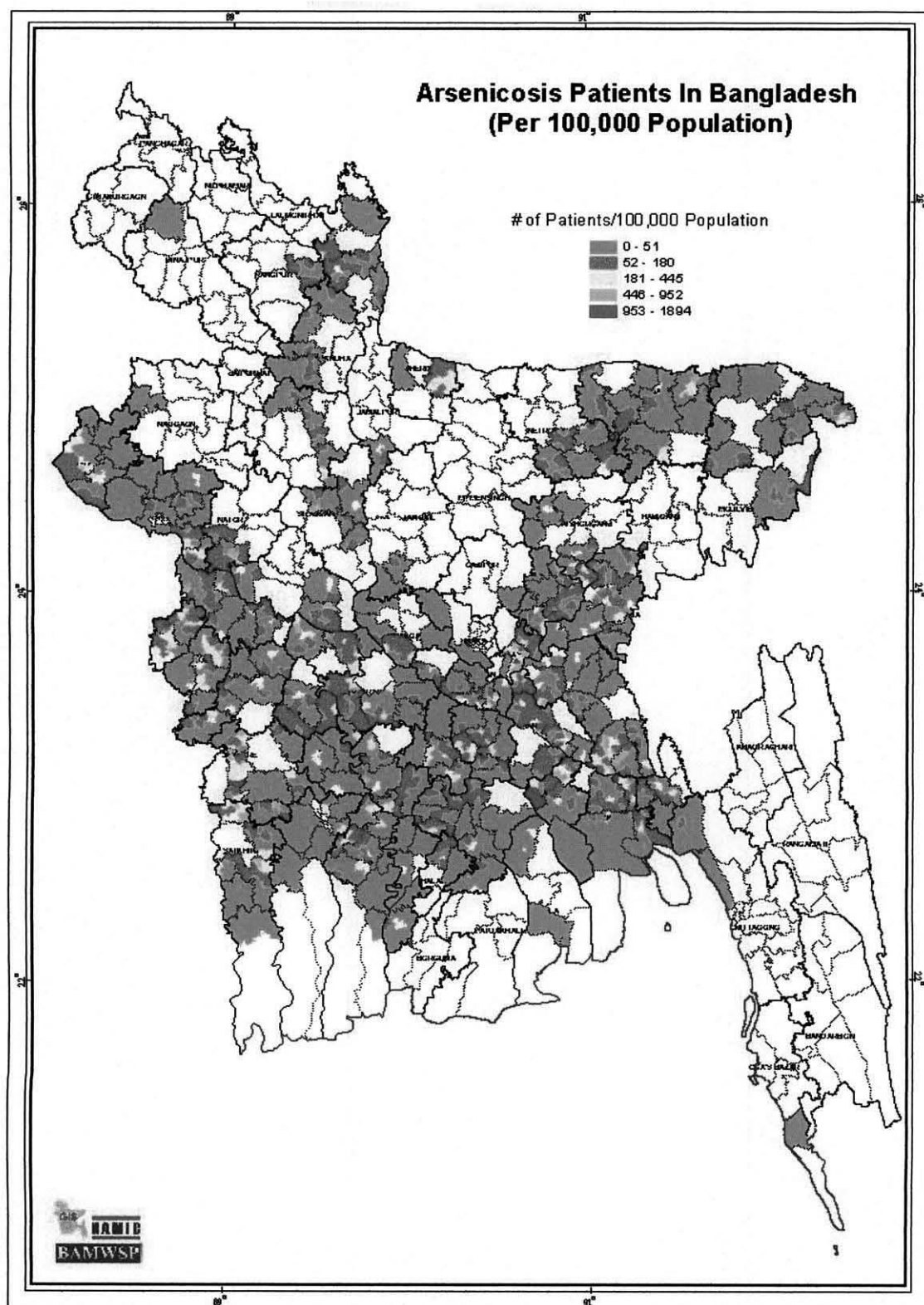


Figure 2.6 Distribution of Arsenicosis Patients in Bangladesh. (Source: BAMWSP, 2005)

2.7.2 Iron and Manganese

Occurrence in Groundwater

Bangladesh groundwaters have unusually high concentrations of both Fe and Mn by world standards (BGS, 2001). This reflects the highly reducing nature of the groundwaters and probably the presence of relatively high concentrations of poorly ordered oxides, and therefore rather soluble oxides, in the very young sediments of the delta region. While As and Fe both dissolve under reducing conditions, their chemistries are significantly different with Mn oxides tending to dissolve before Fe oxides as groundwaters become progressively more reducing. This is dictated by their relative positions in the standard redox sequence as well as kinetic factors.

It is often found that the two elements, As and Fe, can be strongly correlated, although this is by no means always the case. Indeed, on a well-by-well basis, the Fe concentration in a well water generally provides a poor predictor of the As concentration. Nevertheless, it is clear that iron oxides are closely associated with the development of high As groundwaters in Bangladesh, and the ratio can be informative. In particular, simple reductive dissolution would predict a strong relationship and, all other things being equal, should give a relatively constant As/Fe ratio.

Many groundwaters from north-western Bangladesh in particular have low arsenic but high manganese concentrations. The survey showed that 8% of samples exceeded both 50 $\mu\text{g/L}$ arsenic and 0.5 mg/L manganese, while 48% of samples were below both these criteria. Altogether, 36% of samples which had arsenic below 50 $\mu\text{g/L}$ had manganese concentrations above 0.5 mg/L.

Maps of the distribution of As and Mn are given in Figure 2.6 and Figure 2.7. The distribution of Fe shows some relationship with As, although the overall correlation is weak in some areas. Iron concentrations in the groundwater range between <0.004 and 61 mg/L, with median values of 1.4 mg/L and 0.2 mg/L in the shallow and deep waters respectively. Concentrations of manganese in Bangladesh groundwater were

measured between <0.002 mg/L and 10 mg/L. Median concentrations in the shallow and deep aquifers respectively were 0.34 mg/L and 0.03 mg/L.

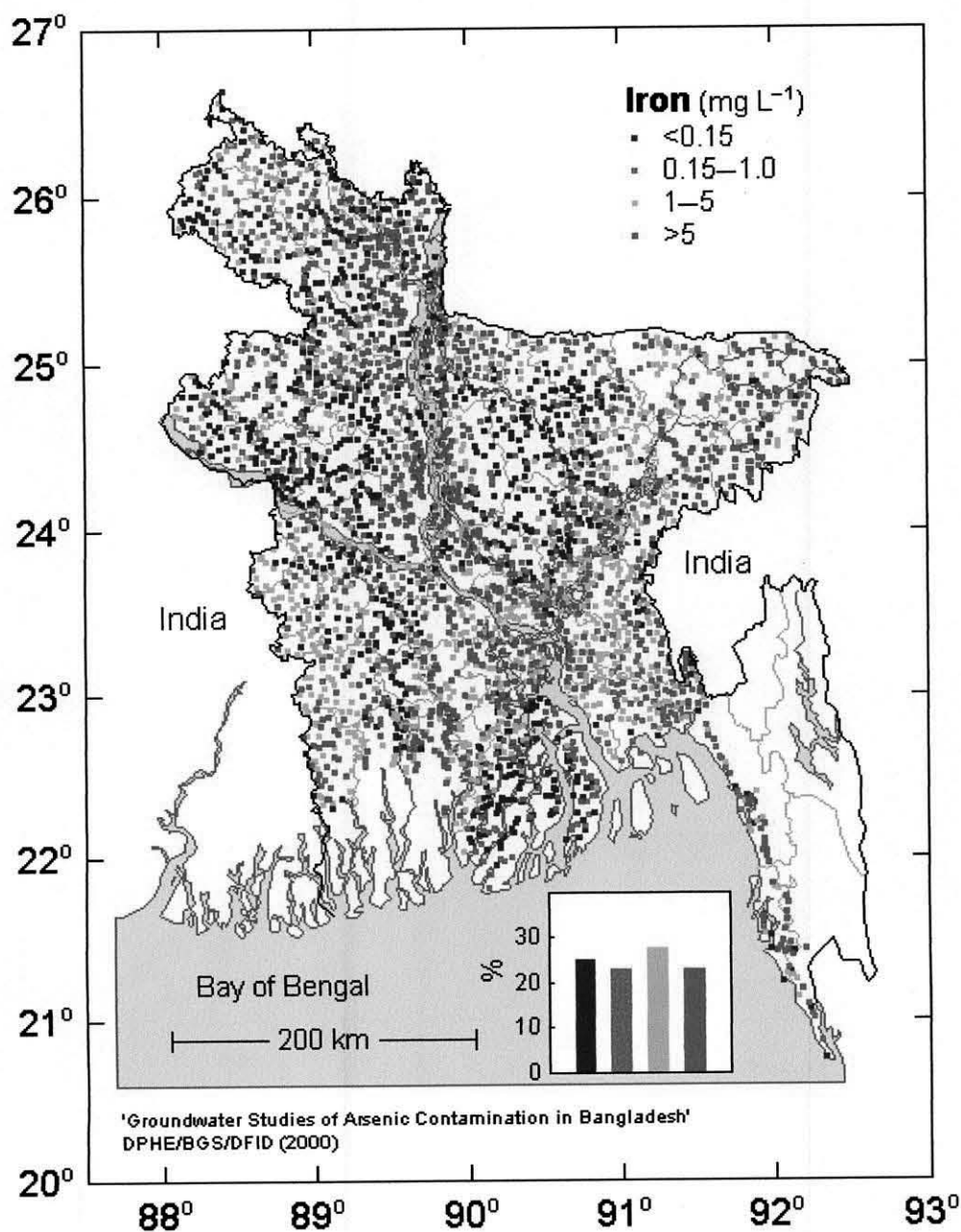


Figure 2.6 Distribution of Iron in groundwater of Bangladesh (DPHE/BGS, 2000)

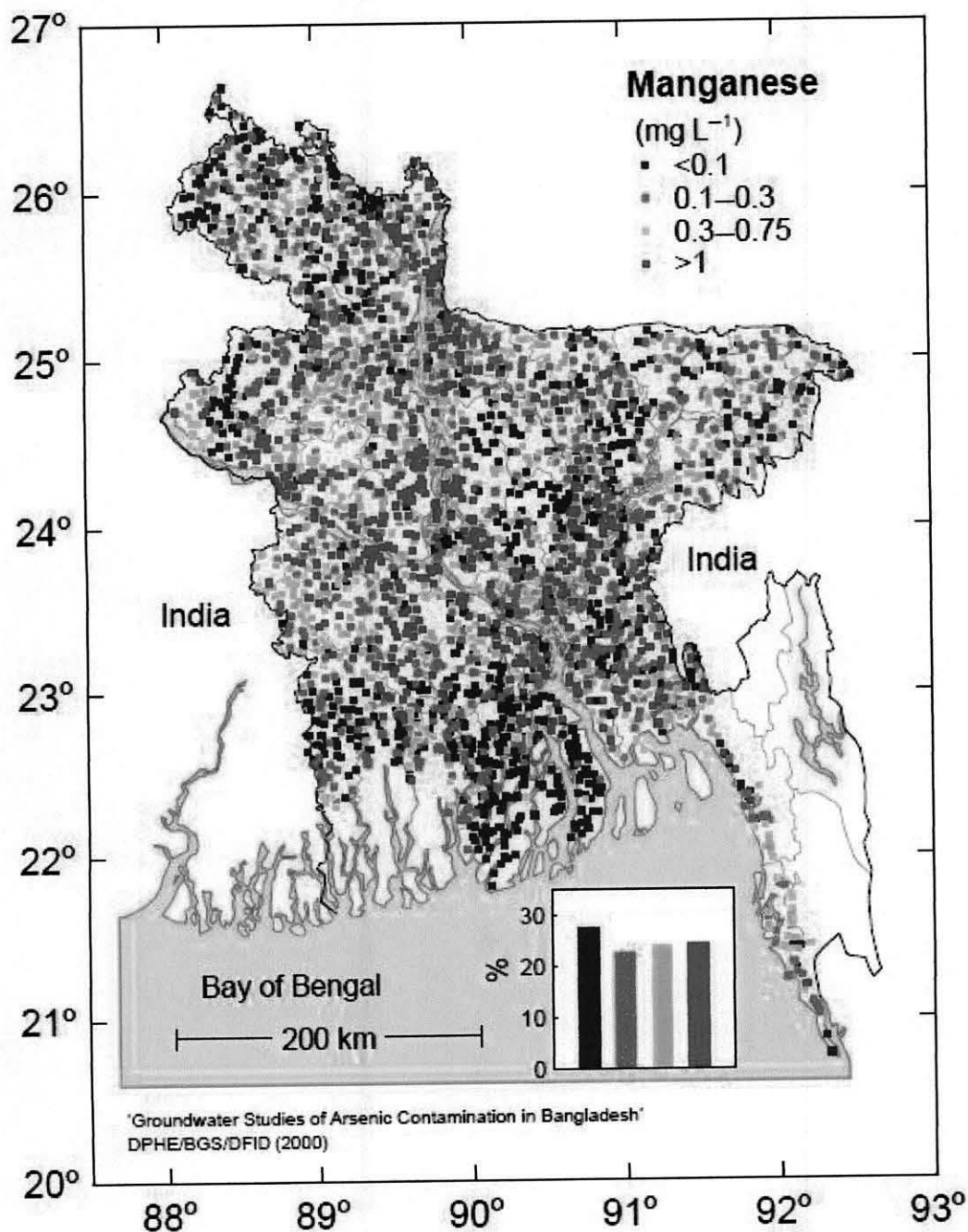


Figure 2.7 Distribution of Manganese in groundwater of Bangladesh (DPHE/BGS, 2000)

Health Effects and Guidelines in Drinking Water

Manganese is an essential element for all living organisms and occurs naturally in soil, water, and plants. The neurotoxicity of manganese after high occupational exposure by inhalation has been well documented. Manganism, a Parkinson-like

disorder was first noted in 1837 in five pyrolusite mill workers and has since been reported in hundreds of occupationally exposed workers (Cook et al., 1974; Greenhouse, 1971; Langauer-Lewowicka and Kujawska, 1974; Levy and Nassetta, 2003; Smyth et al., 1973). Manganese is often regarded as one of the least toxic metals by the oral route because homeostasis limits the gastrointestinal absorption. However, there is increasing evidence of neurotoxicity by the oral route especially in infants. They have a more sensitive nervous system than adults, and their homeostasis is not fully developed. While breast milk generally contains low manganese concentrations, significant amounts can be found in infant formula. Moreover, because infant formula is normally sold in powdered form, the manganese concentration of the water with which the formula is mixed may contribute significantly to the infant's daily manganese exposure. The World Health Organization (WHO) has recently lowered the guideline value for manganese in drinking water from 500 to 400 $\mu\text{g/L}$ (WHO, 2006).

Iron is not of health concern at concentrations normally observed in drinking-water, and taste and appearance of water are affected below the health-based value. Therefore, iron removal is needed to be assessed while developing a drinking water supply system. Usually there is no noticeable taste at iron concentrations below 0.3 mg/L, although turbidity and color may develop (WHO, 2004).

2.8 ARSENIC REMOVAL TECHNIQUES AND THEIR PERFORMANCE IN UNIT OPERATIONS

A variety of treatment technologies like co-precipitation, adsorption, ion exchange and membrane process have been demonstrated to be effective in removing arsenic from contaminated natural groundwater. However, question remains regarding the efficiency and applicability/ appropriateness of the technologies – particularly because of low influent arsenic concentration and differences in source water composition. Techniques available for removal of arsenic from contaminated water are based mainly on four principles (Das et al., 2001):

- A. Oxidation of arsenic (III) to arsenic (V) adding suitable oxidizing agent followed by coagulation- sedimentation- filtration (co-precipitation).
- B. Adsorption using Al_2O_3 , Iron filings (zero valent iron), hydrated iron oxide.
- C. Ion exchange through suitable cation and anion exchanger.
- D. Osmosis or electrodialysis (membrane filter)

Various organizations in West Bengal, India are using mostly principles A and B both for community water supply and as household device in arsenic affected areas. Several sorptive media have been reported to remove arsenic from water in India and Bangladesh. These are activated alumina, activated carbon, iron and manganese coated sand, kaolinite clay, hydrated ferric oxide, activated bauxite, titanium oxide, silicium oxide and many natural and synthetic media. The efficiency of all some sorptive media depends on the use of oxidizing agent as aids to sorption of arsenic.

Activated Alumina

Activated alumina, Al_2O_3 , having good sorptive surface is an effective medium for arsenic removal. When water passes through a packed column of activated alumina, the impurities including arsenic present in water are adsorbed on the surfaces of activated alumina grains. The activated alumina needs replacement after 3-4 regeneration. Some of the activated alumina based sorptive media used in Bangladesh include (Ahmed, 2001):

- BUET Activated Alumina
- Alcan Enhanced Activated Alumina
- ARU of Project Earth Industries Inc., USA
- Apyron Arsenic Treatment Unit

The BUET and Alcan activated alumina have been extensively tested in field condition in different areas of Bangladesh under rapid assessment and found very effective in arsenic removal (BAMWSP, DFID, WaterAid, 2001). The proponents claimed that the units installed in India and Bangladesh consistently reduced arsenic to less than $10 \mu\text{g/L}$ (Ahmed, 2001).

Granular Ferric Hydroxide

M/S Pal Trockner(P) Ltd, India and Sidko Limited, Bangladesh installed several GFH units. Granular Ferric Hydroxide (AdsorpAs[®]) is arsenic selective adsorbent developed by Technical University, Berlin, Germany. The unit requires iron removal as pre-treatment to avoid clogging of filter bed. The proponents of the unit claim to have very high arsenic removal capacity and produces non-toxic spent granular ferric hydroxide (Ahmed, 2001).

Iron Coated Sand

In Bangladesh, Joshi and Chaudhury (1996) developed a home arsenic removal unit using iron-coated sand. The unit was able to produce 600 – 700 L of water at a flow rate of 6 L/h maintaining an arsenic concentration of 0.01 mg/L for an initial arsenic concentration of 1.0 mg/L. On 11th August 2000, a household unit based on sorptive filtration through iron coated sand, and 15 ferric chloride based units were installed in a village of Adda in the Barua thana of Comilla district (Ali et al., 2001). Field testing at Adda village showed very good arsenic removal efficiency for the ferric chloride based units. Arsenic concentrations in the treated water were found to be mostly below the Bangladesh standard; while maximum arsenic concentration in the raw water was about to be 400 ppb. The clarity of treated water and easy operation and maintenance appeared to be the major factors behind ready acceptance of this type of unit. Good removal of arsenic was also achieved with the iron coated sand unit and this unit did not reach the breakpoint of 50 ppb arsenic after over seven months of operation. The major drawback of this unit was the preparation of iron-coated sand since the process is costly, time consuming and cumbersome requiring an oven with temperature control. Until an easier methodology becomes available for mass production of iron-coated sand, it would be difficult to produce such units for mass use.

Every technology has its advantages and disadvantages and may be most suitable at specific sites. Hence technical, economical, hydrological, hydro-geological, environmental and social factors must be studied carefully in selecting a technology

for providing arsenic safe water at a particular site (Jalil, 2006). In all cases, technologies should meet several basic technical criteria. The biggest challenges ahead lie however in applying the technologies in poor, rural settings, and in enabling those communities to choose safe sources of water for drinking and cooking (Johnston et al., 2001).

2.9 AN OVERVIEW ON ARSENIC REMOVAL WITH IRON-COATED BOTTOM ASH (ICBA)

Arsenic removal using iron-coated bottom ash (ICBA) is a novel process of removing arsenic from water. This process is based on using fine particles of coal bottom ash that have been coated with iron oxide. "Bottom Ash" is the ash left at the bottom of a coal-fired boiler after the combustible matter in coal has been burnt off. Arsenic removal using iron-coated bottom ash has proven effective at removing high concentrations of arsenic from drinking water in Bangladesh (Mathieu et al., 2008). During fieldwork in four sub-districts of the country, this media reduced arsenic levels ranging from 200 to 900 ppb to below the Bangladesh standard of 50 ppb. The technology is cost-effective because the substrate—bottom ash from coal fired power plants—is a waste material readily available in South Asia. In comparison to similar technologies, ICBA uses less media for arsenic removal due to its high surface area to volume ratio. Hence, less waste is produced. A number of experiments were conducted in Bangladesh to determine the effectiveness of various water treatment protocols. It was found that (1) ICBA removes more than half of the arsenic from water within five minutes of treatment, (2) ICBA, that has settled at the bottom of a treatment vessel, continues to remove arsenic for 2-3 days, (3) ICBA's arsenic removal efficiency can be improved through sequential partial dosing (adding a given amount of ICBA in fractions versus all at once), and (4) allowing water to first stand for two to three days followed by treatment with ICBA produced final arsenic levels ten times lower than treating water directly out of the well. It was proposed that the most attractive option is to use ICBA in community scale water treatment centers, installed as public-private partnerships, in Bangladeshi villages.

2.10 SUMMARY

This literature review is going to help in understanding the chemistry of arsenic under different environmental conditions while assessing its removal using Iron Coated Bottom Ash. This will also help in taking necessary actions for making the research to be effective. This would help in assessing the capacity of Iron Coated Bottom Ash in removing arsenic. However, for the purpose of effective use of ICBA, it is needed to be investigated further in different environmental conditions such as pH, temperature, DO, EC, turbidity, etc, and in the presence of competing ions such as phosphate, etc.

CHAPTER – 3

ARSENIC REMOVAL USING IRON COATED BOTTOM ASH

3.1 INTRODUCTION

Scientists at the Lawrence Berkeley National Laboratory of University of California, Berkeley have developed a simple material using bottom ash that inexpensively and effectively removes arsenic from drinking water (Gadgil et al., 2008; Patel et al., 2006). This material uses bottom ash as a substrate. Bottom ash is obtained as a finely powdered, waste material from coal-fired power plants, which are common in India. The ash is sterile because the coal has been fired at very high temperatures (close to 800 °C). To make iron coated bottom ash (ICBA), particles of bottom ash are coated with a complex consisting of oxides, hydroxides, and/or oxy-hydroxides of iron, using relatively inexpensive chemicals (ferrous sulfate and sodium hydroxide). The process is conducted at room temperature and atmospheric pressure. Thus, ICBA can be produced with relatively simple equipment at low cost (Mathieu, 2008). ICBA is mixed into the water, where it reacts with and immobilizes arsenic by adsorption and/or co-precipitation. The resulting complex can be settled out of the water with the help of a coagulant, and is safe enough for disposal in municipal landfills, per EPA standards (Mathieu, 2008). Importantly, given ICBA's large surface area to volume ratio, little material is needed to remove a given amount of arsenic, meaning that ICBA treatment produces less waste than most comparable technologies.

This chapter presents an assessment of arsenic removal capacity of Iron Coated Bottom Ash (ICBA) under several environmental conditions such as pH, presence of other competing ions, such as, phosphate, etc. Required dosages of ICBA and coagulant are also investigated in the laboratory for its use in community scale treatment systems.

3.2 CHEMISTRY OF THE ARSENIC REMOVAL PROCESS USING ICBA

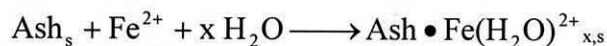
Surface Morphology: The principal ingredients of bottom ash are oxides and complexes of silicon, calcium, iron, aluminium, and magnesium. Bottom ash is the finely powdered residue left after combustion of anthracite and bituminous coal in power plant boilers. Under scanning electron microscope, the ash particles from Indian power plants were revealed to be mostly spherical with smooth glass-like surfaces. This surface morphology is consistent with the ash being heated to near its melting point during the combustion process.

Basic Unit Operations for preparation of ICBA from bottom ash (Gadgil et al., 2008)

The first stage unit operations involve preparing the arsenic removal medium. Bottom ash (residue left at the bottom of the boiler from coal fired power plants) is washed and mixed with a solution of ferrous sulfate (0.6M), and excess solution is decanted. The wet residue is mixed with a dilute solution of sodium hydroxide (0.1M). Excess solution is again decanted. The residue is dried in air, water-washed several (usually four or five) times and dried in air again. At this point, the arsenic removal medium, bottom ash coated with ferric hydroxide, is ready. The coated bottom ash is referred to as 'ICBA dust' in this chapter.

Ash is soaked in FeSO_4 solution, depositing hydrated iron(II) on the ash surface. The reactions involved are outlined below in a simplified form, using $\text{Fe}(\text{OH})_3$ to represent any of the possible hydrated ferric hydroxides or oxy-hydroxides that may be involved.

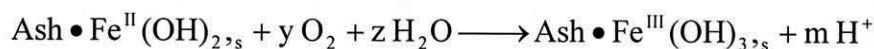
The unknown extent of hydration is indicated by x, and $\text{Ash} \cdot \text{Fe}(\text{H}_2\text{O})^{2+}_{x,s}$ represents the hydrated ferrous ion on the ash surface.



The OH^- displaces water ligands to produce ferrous hydroxide on the ash surface



During the drying process, exposure to air oxidizes the ferrous hydroxide to ferric hydroxide on the ash surface. The molar ratios of oxygen, water and H^+ are indicated below by y , z and m , respectively.



Quantities of reactants used in the first stage:

One gram of ICBA dust contains about 0.5 g of coal ash and about 0.5 g of $\text{Fe}(\text{OH})_3$ (all weights after drying in laboratory room air, in a fumehood). This leads to an estimate of 0.7 g of FeSO_4 and 0.4 g of NaOH consumed in making 1 g of ICBA dust. It was demonstrated that the decanted (and thus recovered) quantities of FeSO_4 and NaOH solutions can be reused for coating up to three successive subsequent batches of coal ash.

Figure 3.1 shows images of the uncoated and coated bottom ash.

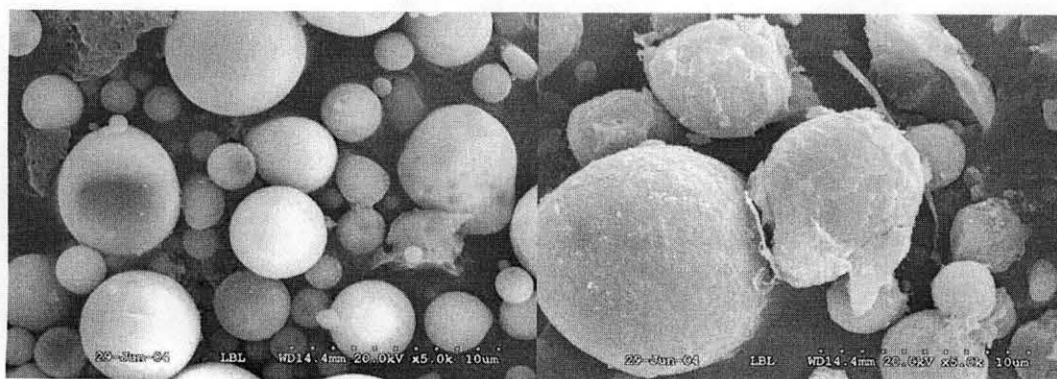


Figure 3.1 Bottom ash before (left) and after (right) coating with ferric oxide (Gadgil et al., 2008)

The second stage involves mixing the ICBA dust with arsenic-laced water. Arsenic binds to ferric hydroxide on the ash surface as insoluble adsorbed ferric arsenate. The solid residue, spent ICBA dust, is filtered out of the processed water. The chemical reactions for arsenic removal in the second stage can be described by these simple equations, but the actual mechanisms are likely to be much more complex:

The Fe^{III} on the ash surface may oxidize As^{III} to As^{V} , as indicated in this simplified reaction:

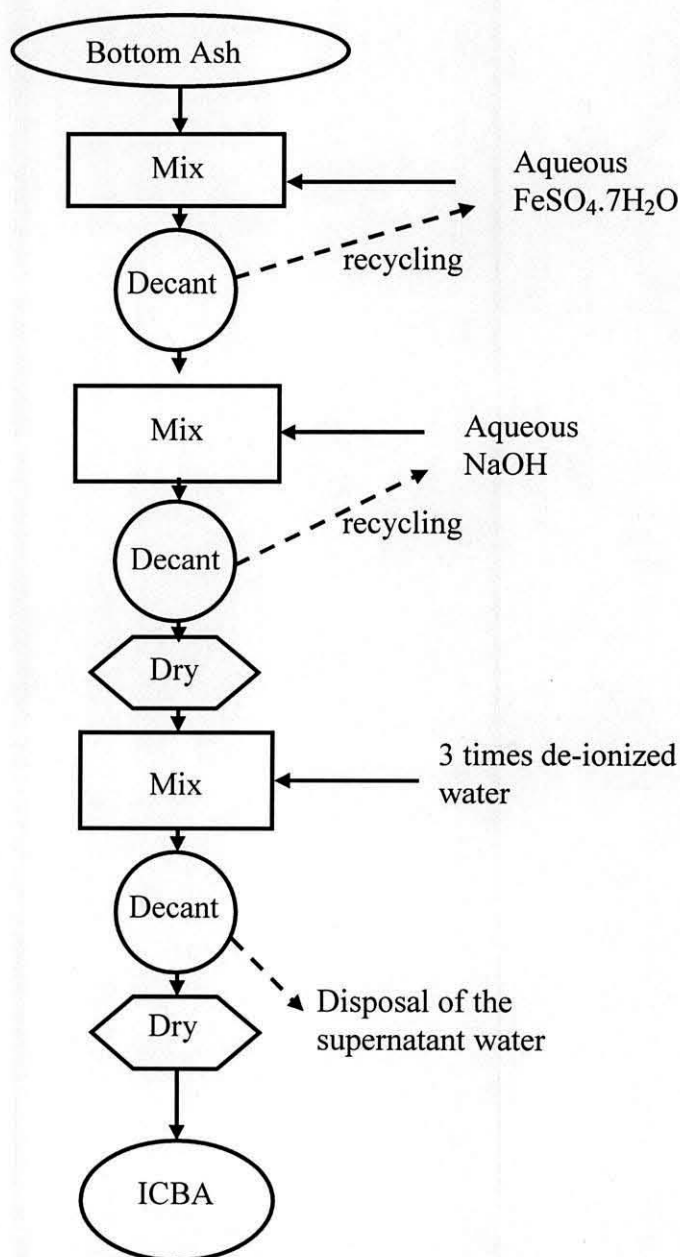
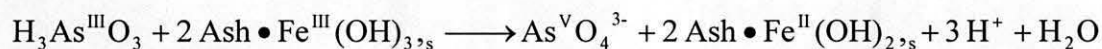
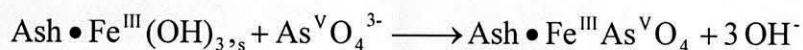


Figure 3.2 ICBA Manufacturing Process

Dissolved oxygen will also oxidize As^{III} and Fe^{II} . Formation of insoluble adsorbed ferric arsenate on the ash surface:



The flow diagram of iron-coated bottom ash production is shown in Figure 3.2.

3.3 METHODOLOGY FOR ARSENIC REMOVAL USING BOTTOM ASH

Selection of dose of the media

For the selection of ICBA dose, several experiments have been performed. The protocol in all the experiments involved mixing ICBA with arsenic spiked water (100 ml) for 30 minutes and allowing the mixture to settle for 15 minutes. Then the supernatant water was collected for determination of the final arsenic. The initial and final concentrations of arsenic were determined using Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, Shimadzu AA-6800). Arsenic spiked water samples were prepared by adding required quantities of stock solutions of As^{III} or As^{V} (concentration: 1000 mg/L) to distilled water. The initial arsenic concentration was kept 500 $\mu\text{g/L}$ in each of the samples. ICBA doses were varied from 2 to 4.8 g/L.

For each sample, a separate experiment was also performed in which ICBA was added in two steps. This was performed to evaluate whether partial dosing performs better than adding ICBA all at once. In this case, keeping the other parameters same, only ICBA mixing time was changed to two steps, each step being 15 minutes keeping no time lag between them.

Selection of the coagulant dose

For these experiments, ICBA dose was fixed at 4 g/L. A polyelectrolyte coagulant was used for settling out the ICBA and the optimum coagulant dose was determined from these batch experiments. These experiments were performed with natural groundwater collected from Sreenagar, Munshiganj whose initial pH, arsenic, iron, manganese concentrations and turbidity were 7.17, 171.1 $\mu\text{g/L}$, 5.21 mg/L, 0.047 mg/L, and 68 NTU respectively. Coagulant doses used were 0.1241 g/L, 0.2482 g/L, and 0.4964 g/L. In all cases ICBA was added to 50 ml natural groundwater sample and mixed for 15 minutes, an additional 10 minutes were used for coagulant mixing and the mixture was allowed to settle for 10 minutes. Finally, total arsenic, iron, and manganese concentration and turbidity of supernatant water were measured.

Arsenic removal capacity of ICBA in the laboratory

Arsenic removal capacity of ICBA was assessed in the laboratory for a wide range of arsenic concentrations (100 $\mu\text{g/L}$ ~ 2000 $\mu\text{g/L}$) of synthetic water prepared by adding required quantities of stock solutions of As^{III} or As^{V} (concentration: 1000 mg/L) to distilled water. The pH of the samples were observed and brought to 6.5 ~ 7 using N/44 NaOH. In all cases, ICBA and coagulant doses used were 4 g/L and 0.2482 g/L respectively. ICBA was added to 50 ml arsenic spiked sample and mixed for 15 minutes, coagulant was then added and mixed for 10 minutes and then the mixture was allowed to settle for 10 minutes. The final concentration of total arsenic of supernatant water was measured using GFAAS, Shimadzu AA-6800.

Effect of Phosphate on arsenic adsorption

Presence of phosphate in ground water can affect the arsenic removal capacity of Iron Coated Bottom Ash since phosphate competes with arsenic for adsorption sites (Manning and Goldberg, 1996; Roberts et al., 2004; Su et al., 2003; Tyrovola et al., 2006). Therefore, effect of phosphate on arsenic adsorption is needed to be determined. To do so, the phosphate removal capacity of ICBA was determined with the absence of arsenic. Then, the same determination was done with a fixed arsenic concentration in sample and varying the phosphate concentrations. Four samples having initial arsenic concentration of 500 $\mu\text{g/L}$ and phosphate concentrations of 0 mg/L, 0.1 mg/L, 0.5 mg/L, and 1 mg/L were prepared. ICBA dose was fixed at 4 g/L. The coagulant concentration was 0.2482 g/L. ICBA was mixed for 15 minutes; coagulant was mixed for 15 minutes and then the mixture was allowed to settle for 10 minutes. Finally, total arsenic and phosphate concentrations were measured using GFAAS (Shimadzu AA-6800) and UV Spectrophotometer (HACH DR-4000) respectively.

Effect of pH on arsenic adsorption

Four Arsenic spiked solutions having 300 $\mu\text{g/L}$, As^{III} and different pH conditions were prepared. 0.5N HCl and N/44 NaOH were used to vary the initial pH 3.42 ~ 8.78. ICBA was added as 4 g/L and mixed for 15 minutes, allowed to settle for 10 minutes. Coagulant was not used in these experiments so that only pH effects on ICBA capacity to remove arsenic could be understood. After settling, pH of each

sample was again measured. The final concentrations of total arsenic and turbidity of the supernatant water were measured for each sample.

3.4 RESULTS AND DISCUSSION

Selection of the dose of ICBA

The results of the two experiments described in Section 3.3 are shown in Table 3.1 and Figure 3.3. ICBA performs better with the increase in dose up to 4 g/L. However, for the higher dose 4.8 g/L, the removal goes down. The higher the dose of ICBA, the higher is its contribution in the number of colloids in the sample. Since no coagulant was used in this experiment, keeping the settling time same for each sample, for 4.8 g/L dose of ICBA, the increased number of colloids may need more time to settle down. Moreover, uncoated bottom ash can itself contain an amount of arsenic, although the exact value was not determined (Mathieu, 2008). The higher the dose, the higher is its arsenic contribution to the sample. So, the exact reason underlying this aberration could not be determined. The results show that 4 g/L performs best in lowering arsenic level by more than 66 percent. Moreover, partial dosing seems to perform better, although by a smaller degree, than addition of ICBA all at once. But it was assumed that for large scale analysis, the advantage of partial dosing would increase since it may induce better mixing conditions.

Table 3.1 Removal of arsenic (initial concentration = 500 µg/L) using different doses of ICBA

ICBA Dose, g/L	Amount of ICBA, g	Final Conc., µg/L	Percent Removal
2	0.1 + 0.1	237.7	52.5
	0.2	351.0	29.8
3.2	0.16 + 0.16	171.4	65.7
	0.32	185.6	62.9
4	0.2 + 0.2	155.6	68.9
	0.4	166.3	66.7
4.8	0.24 + 0.24	203.0	59.4
	0.48	204.8	59.0

The smaller the dose of ICBA, the difference between the percent arsenic removal of fractional and of full dosing is higher. The underlying reason of this phenomenon

could be that the effect of ICBA also depends upon the initial turbidity of the solution. For fractional dosing, the lower the first dose, the efficiency of the next dose in removing arsenic becomes better. Hence, the effect of fractional dosing also seems to flatten down with the increasing dose. Therefore, from this analysis performed, 4 g/L ICBA two step fractional dosing was decided to use for large scale analysis.

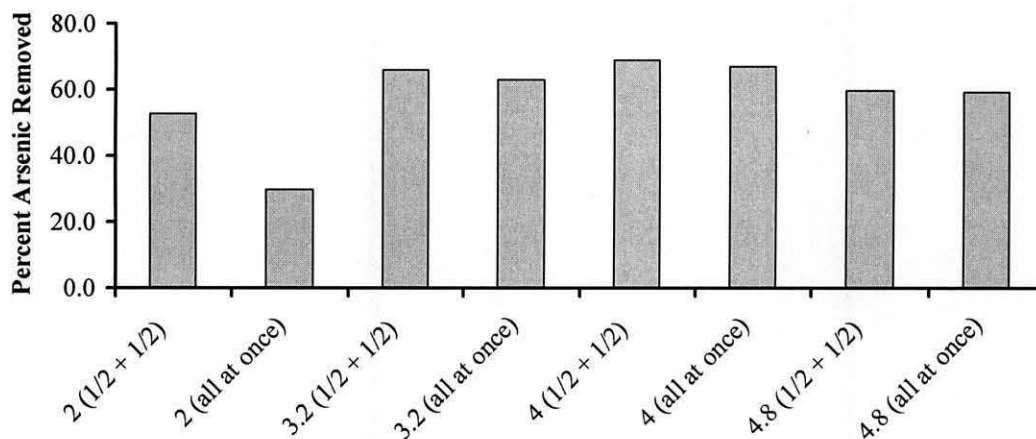


Figure 3.3 Removal of As (Initial concentration = 500 $\mu\text{g/L}$) at different doses of ICBA

Selection of the coagulant dose

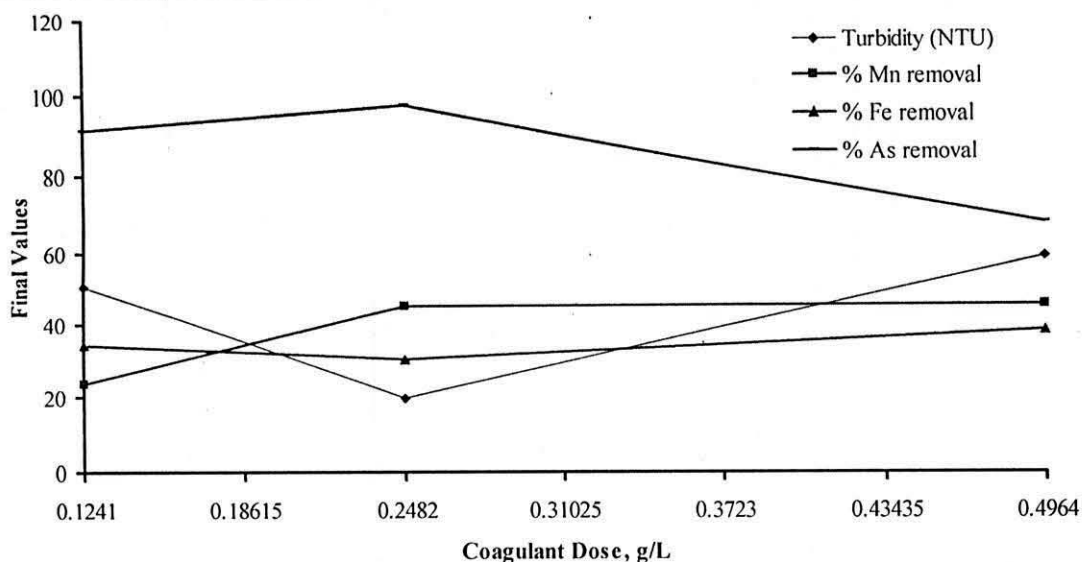
A locally available polyelectrolyte was used as coagulant aid. The results obtained from this experiment are shown in Table 3.2 and Figure 3.4 accordingly.

At the coagulant dose 0.2482 g/L, percentage removal of arsenic and manganese are higher than that of iron according to their removal trend. The turbidity of the treated water is also the lowest for the same coagulant dose. For the same coagulant mixing time, for coagulant dose 0.4964 g/L, flocs were observed to form faster but they broke down after several minutes and therefore high turbidity was observed.

A coagulant dose of 0.2482 g/L appears to result in maximum removal of two contaminants (arsenic and manganese) and although a comparative low removal of iron, it was therefore chosen for subsequent batch analysis.

Table 3.2 Initial and final concentrations of different constituents in batch experiments carried out with different doses of coagulant

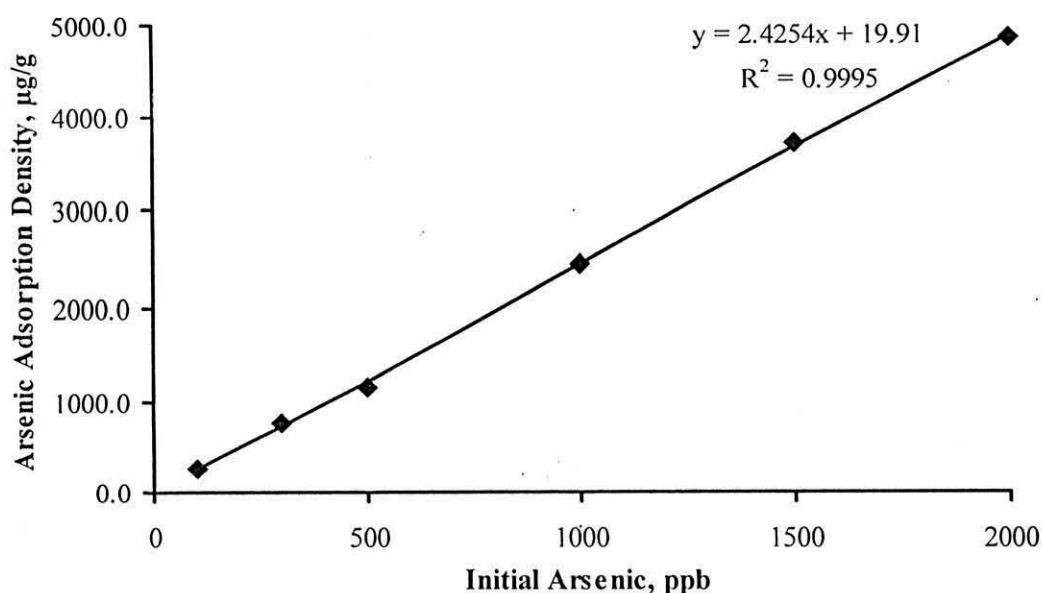
Parameters	Initial	Final Conc.		
Coagulant Dose, g/L		0.1241	0.2482	0.4964
pH	7.17			
Temp	25.7			
Mn, mg/L	0.047	0.036	0.026	0.026
Fe, mg/L	5.21	3.43	3.65	3.24
As, µg/L	171.1	14.52	4.25	55.8
Turbidity, NTU	68	50.6	19.4	58.3

**Figure 3.4** % Removal of Arsenic, Iron, and Manganese vs. Dose of Coagulant (Initial GW pH = 7.17 and T = 25.7°C, Alkalinity = 320 mg/L as CaCO₃)*Arsenic removal capacity of ICBA in the laboratory*

Adsorption capacity of ICBA is quantified as adsorbed amount of arsenic per gram ICBA added to the sample. Percent arsenic removal for each sample is also determined. The results are shown in Table 3.3 and Figure 3.5.

Table 3.3 Arsenic removal capacity of ICBA for a wide range of initial arsenic concentration (ICBA dose: 4 g/L. coagulant dose: 0.2482 g/L)

Initial, $\mu\text{g/L}$	Final, $\mu\text{g/L}$	As Adsorption density, $\mu\text{g/g}$	Percent Removal
100	33.00	269.9	67.00
300	105.00	785.7	65.00
500	210.00	1168.4	58.00
1000	393.89	2442.0	60.61
1500	581.85	3699.2	61.21
2000	795.86	4851.5	60.21

**Figure 3.5** Arsenic removal capacity of ICBA for a wide range of initial arsenic concentration (ICBA dose: 4 g/L, coagulant dose: 0.2482 g/L)

Keeping all other parameters same, arsenic removal capacity of ICBA was observed to increase with the initial arsenic concentration as shown in Figure 3.4 for a wide range of initial arsenic concentrations. A good linear regression with $R^2 = 0.9995$ was observed among the amounts of adsorbed arsenic. It also continues to reduce arsenic concentration with the increase in contact time according to the results shown in Table 3.4. An experiment was also performed to determine whether ICBA addition type changes the arsenic removal capacity with the polyelectrolyte being used as coagulant. The results are shown in Table 3.4.

Table 3.4 Arsenic removals of ICBA for different dosing types (with coagulant) and different mixing times (Coagulant dose: 0.2482 g/L)

Initial Conc., $\mu\text{g/L}$	Dosing Type	Mixing Time (mins)	Final Conc., $\mu\text{g/L}$	Adsorbed Arsenic, $\mu\text{g/g}$	% Removed
100	All at once	15	33.00	269.9	67.00
	All at once	60	12.97	350.6	87.03
	50% + 50%	30 + 30	3.51	388.8	96.49
300	All at once	15	105.00	785.7	65.00
	All at once	30	56.72	980.2	81.09
	50% + 50%	30 + 30	8.01	1176.4	97.33
500	All at once	15	129.13	1168.4	58.00
	All at once	30	210.00	1494.2	74.17

From the results shown in Figure 3.6, it can be seen that ICBA performs better with the increase in mixing time. For the increase in mixing time just 15 minutes, arsenic removal increases almost by 15 percent. For the total mixing time, 60 minutes, and also with the partial dosing, arsenic removal can be obtained as high as more than 95 percent.

From these analyses, it can be concluded that, arsenic removal increases with time. Therefore, to obtain higher removal, the mixing time of ICBA should be higher. Since, for initial arsenic concentration of 100~300 $\mu\text{g/L}$, two-step dosing of ICBA with the mixing time being 30 minutes + 30 minutes produces removal nearer to hundred percent, this mixing time has been selected for large scale analysis.

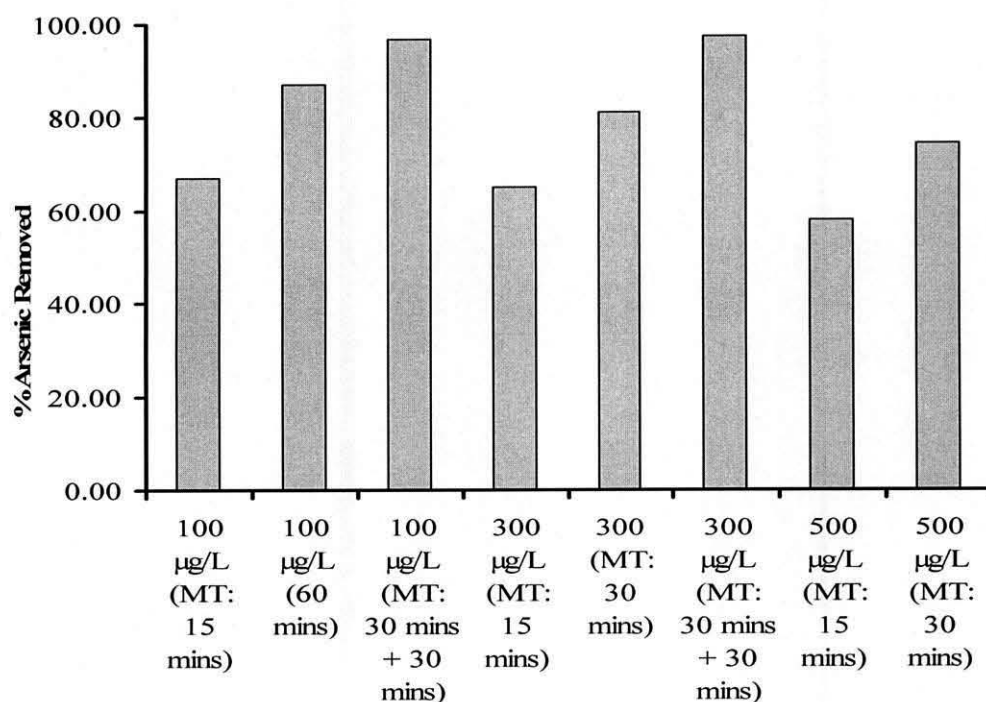


Figure 3.6 Arsenic removals with different dosing types and different mixing times

Effect of Phosphate on arsenic adsorption

The results of the experiments are presented in Table 3.6 and in Table 3.7. The phosphate adsorption capacity of ICBA increases with the increasing initial phosphate concentrations for both with and without the presence of arsenic. ICBA can remove as nearly as hundred percent of phosphate for low concentrations like 0.1 mg/L, 0.5 mg/L, and 1 mg/L. With the presence of arsenic, the phosphate removal also reduces as shown in Figure 3.8. However, an aberration was found for arsenic adsorption with the presence of phosphate. Hypothetically, phosphate interferes with arsenic for the open adsorption sites due to their similarity in structure. But, in this experiment, low level of phosphate concentration seems to help reducing arsenic concentration. However, it is also observed that the higher the initial phosphate concentration, the lower is the arsenic adsorption capacity of ICBA. Since the actual chemical process of ICBA responsible for removing arsenic is yet to be known (Mathieu, 2008), the exact reason for this kind of anomaly cannot be

determined. Therefore, further investigations are necessary to better understand the mechanism of phosphate with arsenic adsorption using ICBA.

Table 3.5 Adsorption of Phosphate on ICBA (without arsenic)

Initial PO_4^{3-} , mg/L	Final PO_4^{3-} , mg/L	Adsorbed PO_4^{3-} , mg/g
0.1	0	0.40
0.5	0.023	1.92
1	0.017	3.96

Table 3.6 Arsenic removal with and without the presence of phosphate (Initial arsenic = 500 $\mu\text{g/L}$)

Sample Types	Final As, $\mu\text{g/L}$	Final PO_4^{3-} , mg/L	Adsorbed As, $\mu\text{g/g}$	Adsorbed PO_4^{3-} , mg/g
1) Only As-spiked water	210	0.024	1168.4	-
2) As water + 0.1 mg/L PO_4^{3-}	167.7	0.033	1339.0	0.27
3) As water + 0.5 mg/L PO_4^{3-}	193.2	0.037	1236.0	1.87
4) As water + 1 mg/L PO_4^{3-}	195.6	0.134	1226.4	3.49

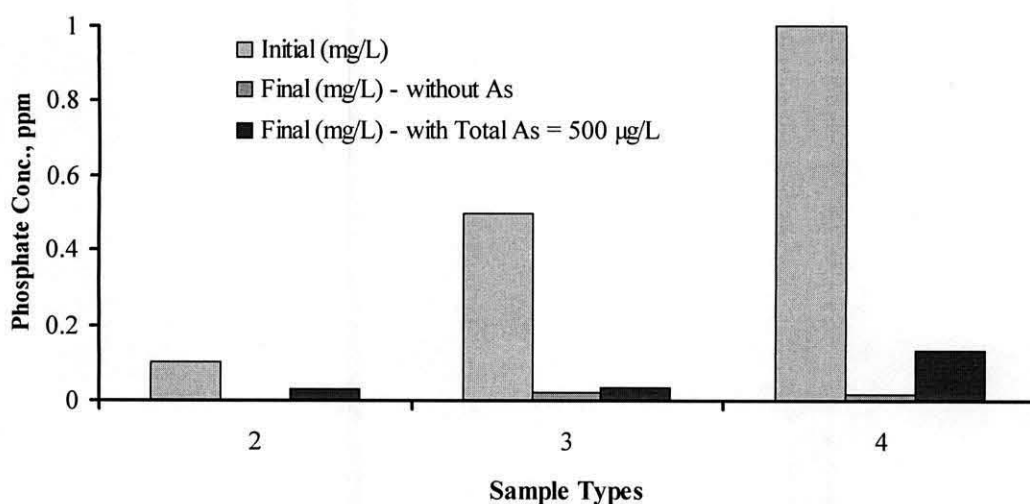


Figure 3.7 Adsorption of Phosphate on ICBA with and without the presence of Arsenic

Effect of pH on Arsenic Adsorption

Addition of Iron-Coated Bottom Ash helps As^{III} to convert to As^{V} as mentioned in section 3.2.1. Arsenic binds to ferric hydroxides on the ash surface as insoluble adsorbed ferric arsenate. Dissolved oxygen also converts As^{III} and Fe^{II} . But it also contributes hydrogen ions to the system for which pH decreases. Higher pH indicates the oxidizing conditions and relatively high presence of As^{V} in the system which can be adsorbed on the surfaces of ICBA depending upon the available sites for adsorption. From the results shown in Table 3.5 and Figure 3.7, it can be said that the higher the initial pH, the higher is the arsenic removal. This can also be understood from the turbidity of the treated water. Higher turbidity in the treated water may indicate lower removal. The arsenic removal capacity increases with increasing pH values. However, it is also important to mention that since coagulant has not been used in this experiment the arsenic concentrations in the supernatant can be affected by the possible presence of re-suspended ICBA.

At pH = 5.71, more than 50 percent arsenic seems to be removed only after 25 minutes of contact time. By increasing the contact time, the arsenic removal capacity of ICBA are expected to improve since with the increase in time, dissolved oxygen will contribute in to the removal by converting As^{III} to As^{V} .

Table 3.7 Effect of pH on Arsenic Removal of ICBA (Initial Arsenic = 300 $\mu\text{g/L}$, Temperature = 26.5°C)

pH	After pH	Turbidity (NTU)	Final As ($\mu\text{g/L}$)	Adsorbed Arsenic, $\mu\text{g/g}$	% Removal
8.78	6.23	42.5	67.18	938.0	77.61
7.55	6.05	73.5	142.4	635.0	52.53
5.71	5.41	56.2	148.67	609.7	50.44
3.42	3.42	83	282.5	70.5	5.83

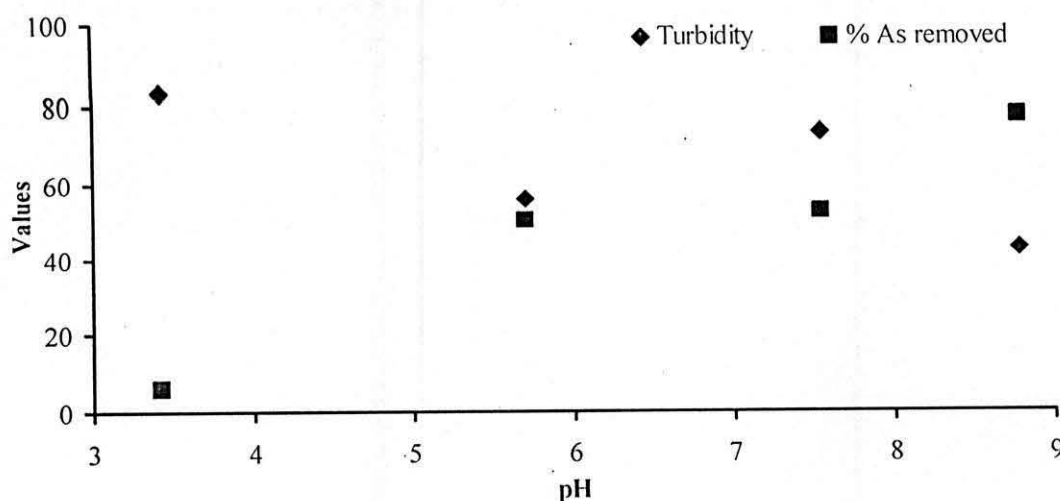


Figure 3.8 Effect of pH on arsenic removal of ICBA

3.5 SUMMARY OF PERFORMANCE OF IRON COATED BOTTOM ASH AT LABORATORY SCALE

The aforementioned analyses were performed to understand the performance of Iron Coated Bottom Ash in different environmental conditions. The findings obtained from these analyses are summarized below:

- For an initial arsenic concentration of 500 $\mu\text{g/L}$, ICBA dosage 4 g/L produces good arsenic removal and hence this dose was selected for subsequent experiments with arsenic laden water.
- ICBA seems to work better for pH levels 5.71~8.78 for synthetic groundwater samples. The higher the initial pH, the higher is the arsenic removal.
- The optimum coagulant dose under the experimental condition was fixed to be 0.2482 g/L.
- The arsenic removal capacity of ICBA increases with the increase in initial arsenic concentrations for a wide range of initial values. The dosing type of ICBA selected for large scale analysis is two-step dosing, each dose being mixed for 30 minutes. The polyelectrolyte mixing time is remained fixed as 15 minutes.
- Low phosphate concentrations seem to help increasing the arsenic removal. No exact reason for this anomaly can be found. But, the higher the

concentration of PO_4^{3-} , the higher is the interference with arsenic adsorption. However, the threshold phosphate concentration helping the arsenic removal was not determined. Further investigations are necessary to better understand the mechanism of phosphate with arsenic adsorption using ICBA.

CHAPTER – 4

PERFORMANCE OF IRON-COATED BOTTOM ASH IN REMOVING ARSENIC, IRON AND MANGANESE IN COMMUNITY SCALE SETTING

4.1 INTRODUCTION

Iron-coated bottom ash is a novel material under investigation for the purpose of treating the arsenic laden water. Many new materials are being tested for arsenic removal, from low-tech iron-coated sand and greensand to specially engineered synthetic resins. In all cases, technologies should meet several basic technical criteria. The biggest challenges lie however in applying the technologies in poor, rural settings, and in enabling those communities to choose safe sources of water for drinking and cooking.

This chapter presents development of a community based water treatment unit using Iron Coated Bottom Ash to remove arsenic with three other members (Johanna Mathieu, Kristin Kowolik and Shefah Qazi) of Berkeley Arsenic Alleviation Group (BAAG) from UC Berkeley. Then, results from the investigations performed by the author with the built prototype in removing arsenic and other contaminants such as iron and manganese are discussed in this chapter.

4.2 DEVELOPMENT OF A COMMUNITY BASED WATER TREATMENT UNIT

Several studies have outlined criteria for evaluation of arsenic removal technologies. Chowdhury et al. (2000) lists costs; ease of implementation, running and maintenance; flow rate; arsenic removal capacity; susceptibility to bacteriological contamination; and community acceptability. Ahmed (2001) lists the following

major design needs: improve arsenic removal effectiveness, reduce costs, user-friendly designs, overcome maintenance problems of household technologies, and resolve waste management problem.

The BAAG team developed eight key design strategies for designing an arsenic removal device to make the system accepted by users and scalable for dissemination through rural Bangladesh through several field surveys over the past several years. The design strategies are given in Table 4.1.

Table 4.1 Eight Key Design Strategies for Designing an Arsenic Removal Device (Mathieu, 2008)

1	Maximize effectiveness of arsenic removal technology
2	Design community-scale treatment center to minimize perceived inconvenience
3	Minimize distance between homes and water treatment center, or provide water delivery
4	Enhance perception of treated water quality
5	Build trust in technology through continuous water monitoring and guaranteeing technical efficacy
6	Minimize cost to villagers
7	Allow for ease of local water management (source monitoring)
8	Ensure feasibility of arsenic removal waste management

The BAAG team also suggested that through a three-way partnership between a local financial institution, a local NGO, and a company responsible for constructing and maintaining the water treatment centers (all working together with the local village governments), community scale water treatment plants can be constructed in Bangladesh. The structure of the proposed public-private partnership is presented in Figure 4.1.

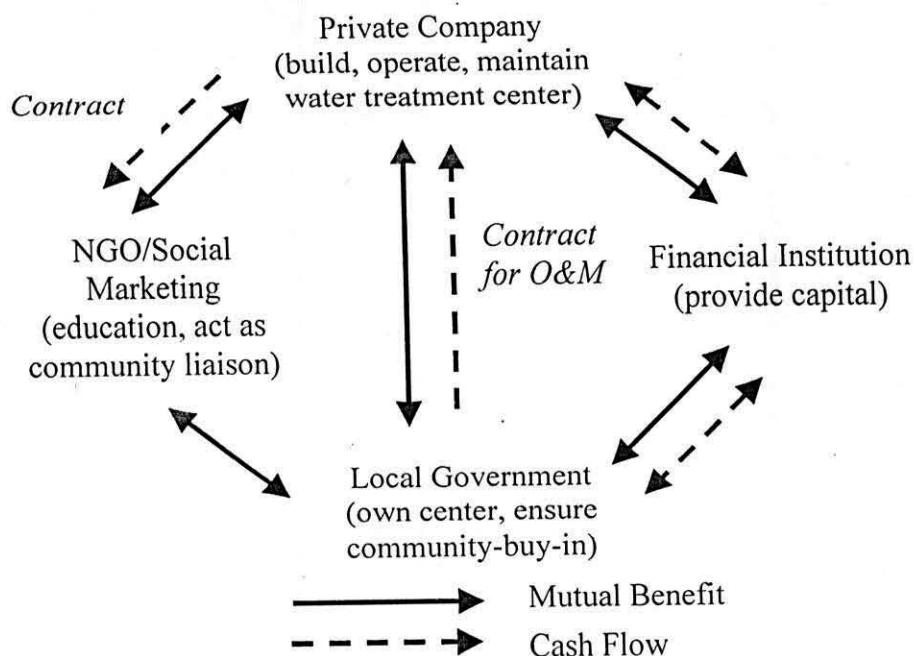


Figure 4.1 Structure of the proposed public-private partnership (Mathieu, 2008)

The author joined the BAAG team to develop a community based water treatment unit in context to Bangladesh on June 1, 2008 during their third trip (May 30, 2008 to July 3, 2008) to Bangladesh. The objective of this trip was to develop a proof-of-concept prototype of a community based water treatment system that uses Iron Coated Bottom Ash to remove arsenic, in addition of conducting a number of experiments to further understand ICBA's arsenic removal kinetics and behavior in water as water parameters change over time. The author actively contributed to the development of the prototype and hence, to the development of this novel arsenic removal technology at that time. The author worked with three other members (Johanna Mathieu, Kristin Kowolik, Shefah Qazi) of the BAAG team for the development of this prototype.

Several technical issues were also solved to bring ICBA treatment to a community scale:

- An effective way to mix Iron-Coated Bottom Ash into large volumes of contaminated water
- A low-cost method to remove the spent ICBA from treated water

An electric kitchen mixer and aeration pumps were used to mix ICBA with 20 liters of arsenic contaminated water. The kitchen mixer as shown in Figure 4.2 was observed to perform better in keeping the particles in suspension than the aeration pumps. Therefore, use of a mechanical mixer to mix ICBA into arsenic contaminated water was decided for use in larger scale prototype. Polyelectrolyte was also found to be more effective than alum in coagulating ICBA particles. Therefore, in laboratory based experiments shown in chapter 3, polyelectrolyte has been used.

A cone-shaped clarifier capable of processing 10 liters per hour was designed and built with the clarifier design rule that the particle settling rate must be greater than the flow-rate divided by the cross-sectional area ($v_t = Q/A$, where v_t is the particle settling velocity, Q is the flow rate through the clarifier, A is cross-sectional area half-way up the cone). A diagram of the 10 liter per hour prototype having 16 liters water holding capacity is shown in Figure 4.2. Since a good flow controlling valve cannot be obtained in Bangladesh, the flow rate was controlled with a valve usually used in hospitals to control the rate of fluid release from a drip bag. It was difficult to control the flow rate accurately and it was often found that the clarifier was filled faster or slower than expected.



Figure 4.2 Mixing 20 liters of contaminated water with an electric kitchen mixer (left) and then run through the ten liter per hour prototype clarifier (right)

The over-flown water was observed to have some yellowish tinge which might have been due to the presence of iron. For this, a post clarification filtration unit may be necessary. However, it was not attempted yet. But it was thought out that provided the flow rate can be maintained this system can be implemented in larger scale.

Therefore, we developed a one-hundred liter per hour prototype system based on a simplified version of the conceptual water treatment system design. The conceptual water treatment system design can be found in M.Sc. thesis of Johanna Mathieu (2008). Considering that one prototype will be able to produce 400 liters in one day, it will be able to serve drinking and cooking water need of 8 families per day, 50 liters being the average daily water need of a family consisting of 5~7 members. The idea is that if this unit becomes successful, there will be several numbers of this unit installed to serve the whole village depending upon the total number of village population. This prototype consists of a mixing tank (500 liter PVC tank), 1.5 hp motor and a stainless steel shaft/blade for mixing ICBA and coagulant with water, clarifier (1 meter cone height, 1 meter diameter), and a clean water holding tank (500 liter PVC tank). A catchment channel around the top of the clarifier has been added to direct the over-flown water to the pipe-entrance which would ultimately lead the water to the collection tank. A schematic diagram of the prototype is shown in Figure 4.3a and the built one is shown in Figure 4.3b.

This unit has been used in the subsequent batch experiments performed only by the author of this thesis. The prototype system has been modified later by adding another collection tank of 100L capacity in *Batch D* analysis, as shown in Figure 4.3c, to better understand the chlorination effects. The final flow diagram of the system is shown in Figure 4.3d.

Water is pumped into a 500 liter tank (R1) fitted with a propeller attached to a 1.5 hp motor. The ICBA is added and mixed for one hour (two-step dosing, 30 minutes being the mixing time in each step). Polyelectrolyte is added and mixed for another 15 minutes. The valve (V1) connecting the mixing tank to the clarifier is opened, a gravity flow is initiated which is controlled manually by turning the valve. Water is allowed to spill over the top of the clarifier into a catchment channel. The channel drains into the piping connecting the clarifier to the clean water collection tank (R2). As the water goes up in the clarifier due to the momentum of the flow, the top of the water experiences laminar flow. The higher the water goes it experiences the higher

cross-sectional area of the clarifier. As a result, the velocity of the flow reduces and the coagulated particles (flocs) start to settle at the sides of the clarifier due to gravity.

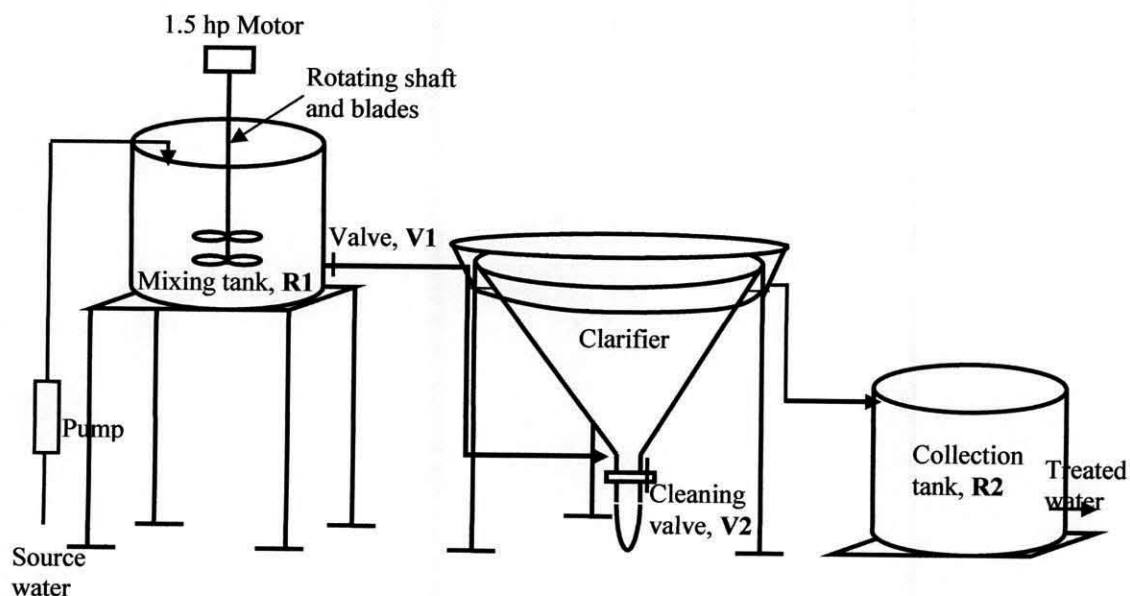


Figure 4.3a A schematic diagram of the prototype to be used for unit operation



Figure 4.3b One hundred liter per hour prototype system



Figure 4.3c One hundred liter per hour prototype system (*a 100L collection tank is added*)

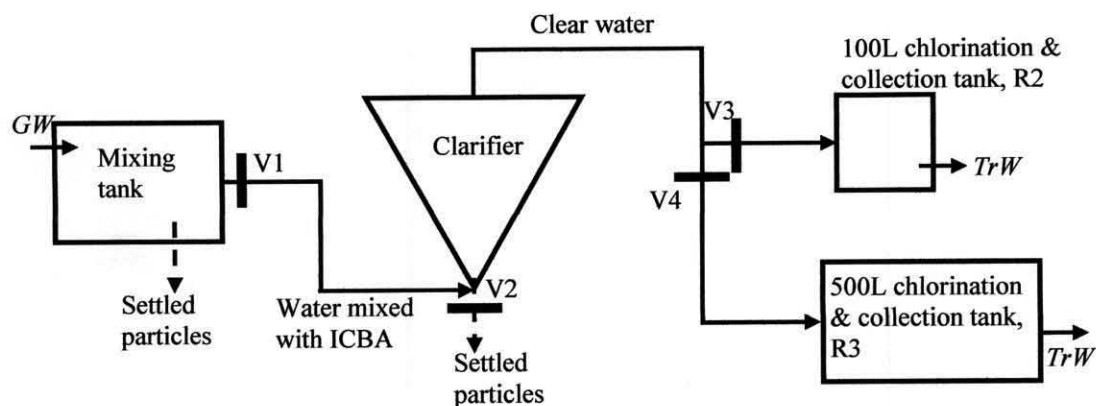


Figure 4.3d Final Flow Diagram of the Prototype Components

4.3 METHODOLOGIES USED IN THE UNIT OPERATIONS

Samples, both acidified and non-acidified, are collected from the top of the clarifier and from the tap situated at the bottom of the clean water collection tank (R2) and

are subsequently analyzed. Analyses were performed using tubewell water from Besgao village, Sreenagar, Munshiganj.

Non-acidified samples were used for determination of pH, DO, Temperature, Electric Conductivity, Alkalinity, Phosphate, Silica and Chlorine. Acidified samples were used for determination of Arsenic, Iron and Manganese. The pH, Temperature, DO, and EC were determined using respective probes. Alkalinity was determined using EDTA Titrimetric Method. Iron was determined initially by producing a red-colored iron compound, ferric thiocyanate, by the addition of potassium thiocyanate. It was later determined using FLAAS, Shimadzu AA-6800. Phosphate, silica, manganese, and chlorine were determined using UV Spectrophotometer (HACH, DR-4000). Arsenic was determined using GFAAS, Shimadzu AA-6800.

4.4 RESULTS AND DISCUSSIONS

4.4.1 Flow Rate

Maintaining the required flow rate using the locally available valve was one of the most challenging parts in this research. A small change in position of the turn of the valve can result in drastic change in the flow rate. The flow rate, 100 liters per hour, was often maintained with some deviations while running different batches. The intended investigations were continued regardless of the flow rate difficulties and the results are shown according to the timeline. The flow rate statuses of the several field visits performed are given in Table 4.2.

From the initial groundwater analysis of the tubewell, presence of Total Coliform (TC) and Fecal Coliform (FC) was observed in *Batch A* samples. Therefore, chlorination was initiated in the following batch analyses. Chlorination was performed using bleaching powder on samples from *Batch B*, however due to its low performance in removing TC/FC, Sodium hypochlorite (NaOCl) was introduced in *Batch C & Batch D* analyses. Results from the samples of the four batch analyses are presented in Appendix A.

Table 4.2 Field visits and their status

Field Visit & Batch No.	Date of performance	Flow rate	Status
A	November 22, 2008	-	Water did not spill over the clarifier due to lack of momentum
B	January 3, 2009	329 liters/hr	Small change in position of the valve has resulted in large increase in flow rate
C	April 15, 2009 (Back to back two batches were run)	1 st set: 80 liters/hr 2 nd set: 120 liters/hr	Flow rates were reasonably maintained; another manually operated valve with several turns was used
D	May 12, 2009 (Back to back two batches were run)	1 st set: 500 liters/hr 2 nd set: 178 liters/hr	The first flow rate was very high. But, the second one was considered reasonable.

4.4.2 Arsenic Removal

From the samples collected before chlorination from the top of the clarifier, it can be observed that the lower the initial arsenic concentration, the lower is the arsenic concentration in the treated water as shown in Figure 4.3. Among B-BC samples, arsenic concentration near Bangladesh drinking water standard (50 µg/L) is obtained at 24 hours of operation in B-BC-24 (51.06 µg/L). Among C-BC samples, arsenic concentration below 50 µg/L is obtained after around 71 hours of operation (C-BC-71: 31.54 µg/L) and the next sample, C-BC-72.5 shows arsenic concentration below the detection limit. Among D-BC samples, arsenic concentration can be obtained 34.95 µg/L in D-BC-25, and after several hours it again goes down to 3.47 µg/L in D-BC-109. The reason underlying the increased arsenic concentrations in samples,

from D-BC-42.5 to D-BC-91, is the re-suspension of flocs to the surface due to reducing environmental conditions. The seasonal variation in the initial arsenic concentrations was also observed as shown in Figure 4.4.

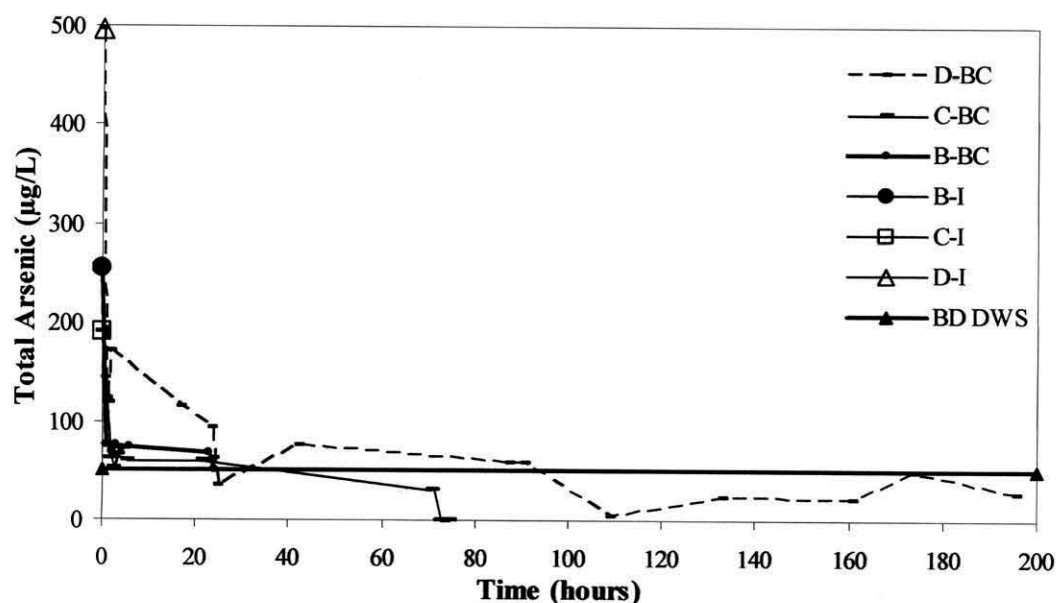


Figure 4.4 Arsenic concentrations at top of the clarifier for different batch of samples

107284 Theoretically, chlorination helps As^{III} to convert to As^V and hence subsequent more As^V adsorption on ICBA colloids should be initiated. The arsenic concentrations of the post-chlorinated samples of *Batch C* always show arsenic content below Bangladesh drinking water standard for arsenic concentration ($50 \mu\text{g/L}$). However, in samples of *Batch D*, arsenic concentrations are found to be $45.43 \mu\text{g/L}$ in D-AC2-25, but shows increasing trend after this point. It again comes down to $34.74 \mu\text{g/L}$ in D-AC1-133 and $37.96 \mu\text{g/L}$ in D-AC2-109. The D-AC samples show varying arsenic content as shown in Figure 4.5. A major draw-down of arsenic concentration was observed in D-AC samples at around 24 hours of operation. One of the many possible reasons are observed and explained in section 4.5.6.2. They also follow the similar trend as turbidity shown in Figure 4.26 which is related with the removal of colloids. The arsenic concentrations of C-BC and C-AC samples show better removal of arsenic. This can be the mutual effect of three conditions: a) low initial

arsenic concentration, b) better controlled flow rate, c) water storage time for the 2nd set was approximately 60 hours.

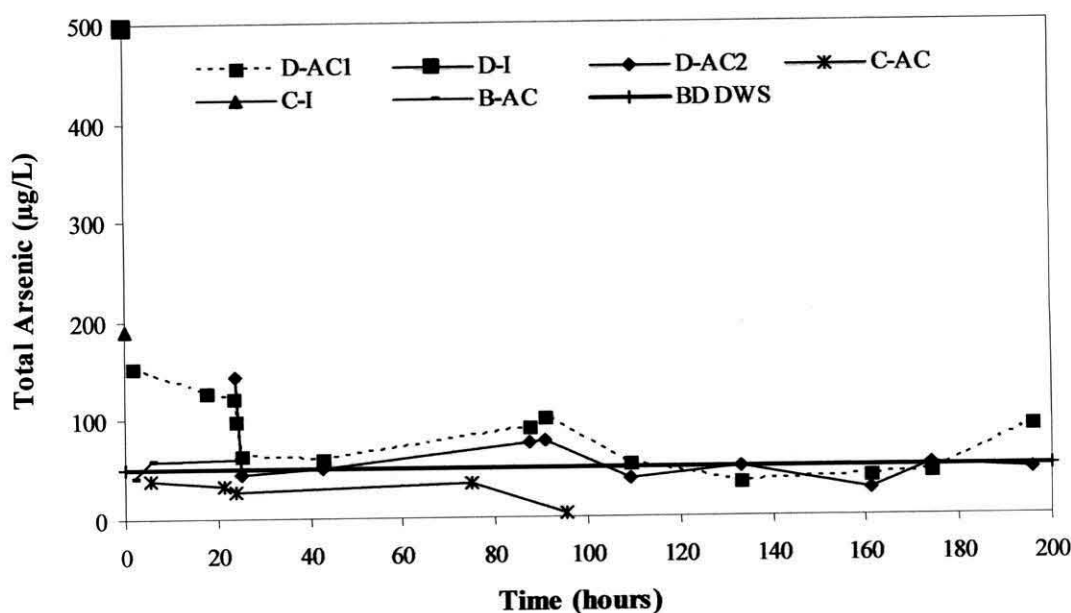


Figure 4.5 Arsenic concentrations in treated water after chlorination for different batch of samples

4.4.3 Iron Removal

Iron concentrations in the samples from three batches (B-BC, C-BC, D-BC), collected from the top of the clarifier, follow the same trend as the respective arsenic concentrations according to the results shown in Figure 4.4 and Figure 4.6. Several sudden iron releases are also observed in these samples. These are the results of either re-suspension of flocs due to momentum of flow, or reducing environmental condition leading Fe^{III} to convert to Fe^{II} . Among the post-chlorinated samples, D-AC2-25 shows iron concentration (7.05 mg/L) higher than the initial concentration (6 mg/L). Since iron coated bottom ash is being used for removal of arsenic, iron, and manganese, iron is being impregnated into the system. Also, bottom ash itself contains oxides of iron and silicon. Since an increase in silica content (28.5 mg/L to 32.6 mg/L) is also observed in this sample, it can be said that the ferric hydroxide coating on the ash surface breaks down and hence iron is released in to the system.

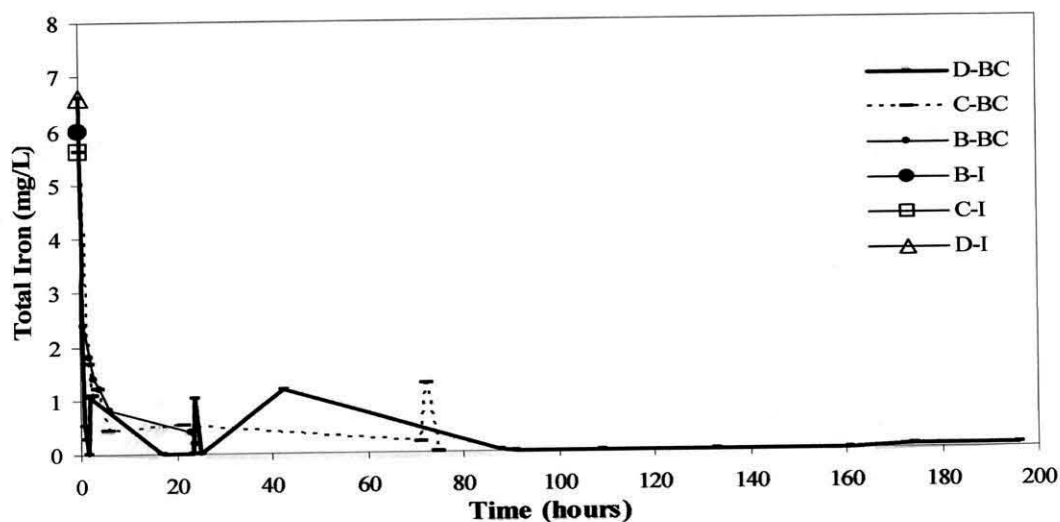


Figure 4.6 Iron concentrations at the top of the clarifier for different batch of samples

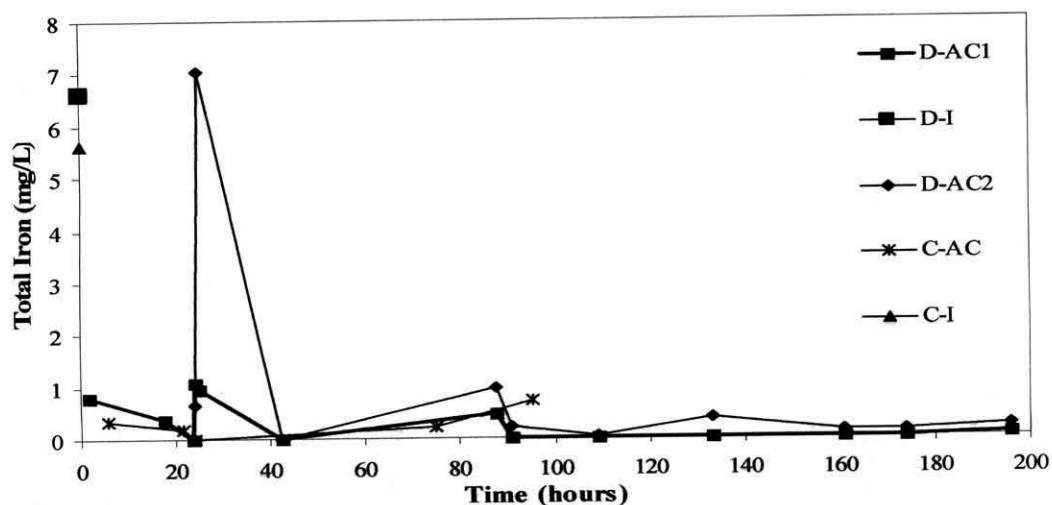


Figure 4.7 Iron concentrations in treated water after chlorination for different batch of samples

Iron concentrations are found to be below 1 mg/L in most of the samples resulting in removal of more than 85% of the initial iron. Still iron content in the treated water gives the water somewhat a brownish color as shown in Figure 4.8.

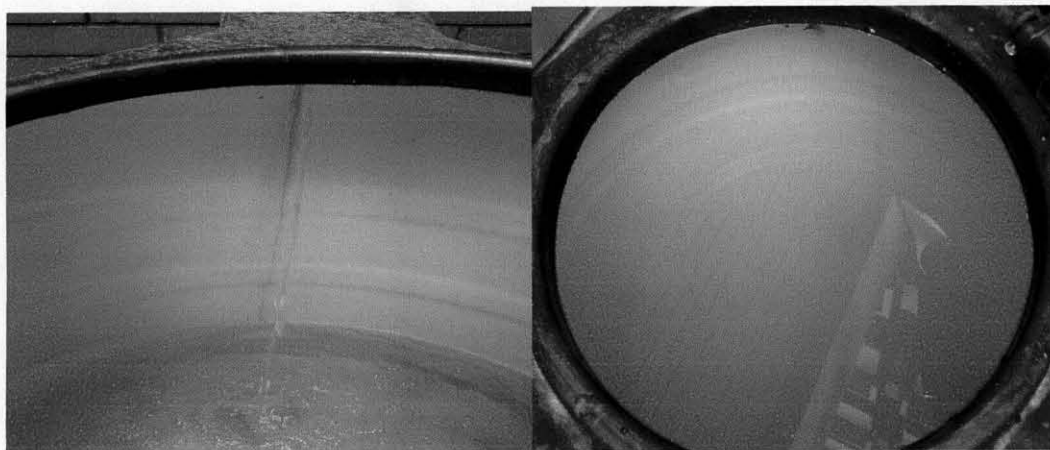


Figure 4.8 Batch D treated water before chlorination (on left-side) and after chlorination (on right-side)

4.4.4 Manganese Removal

Concentrations of manganese (0.124 mg/L to 0.15 mg/L) in initial tube well water were well below the WHO limit (4 to 5 mg/L). But, it is necessary to determine the manganese concentration levels in the samples of ICBA treated water. The effect of manganese content on removal characteristics of other components, such as arsenic, iron, etc, if there is any, can also be obtained. Manganese concentrations can be obtained below 0.075 mg/L within 2 to 3 hours of operation in all batches. Although, there are some variations in manganese concentrations in the samples collected from the top of the clarifier as well as in the treated water after chlorination, these are considered acceptable since they are well below the threshold value in the first place as shown in Figure 4.9 and Figure 4.10.

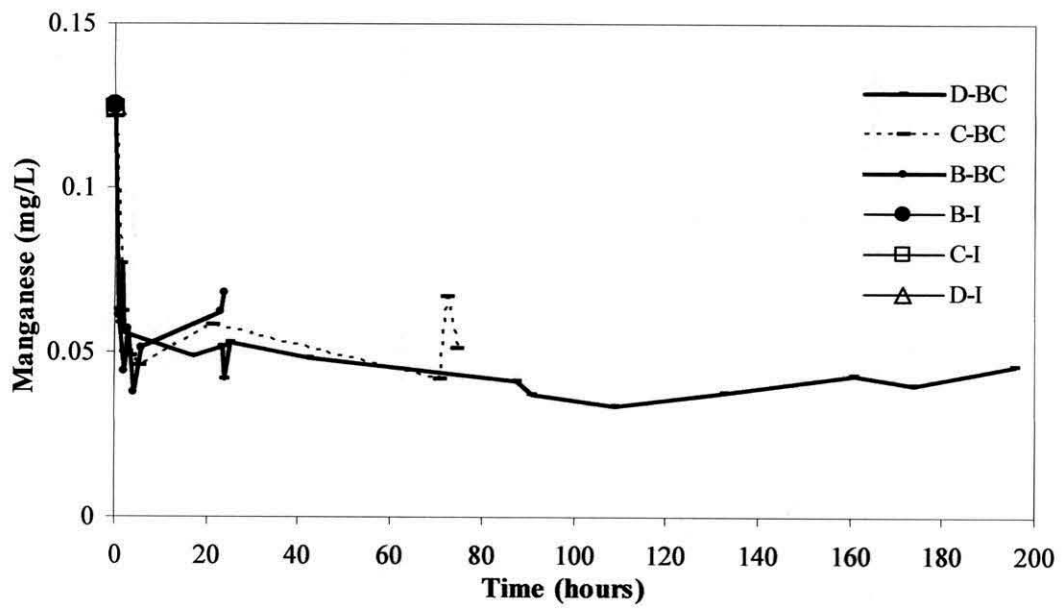


Figure 4.9 Manganese concentrations at top of the clarifier for different batch of samples

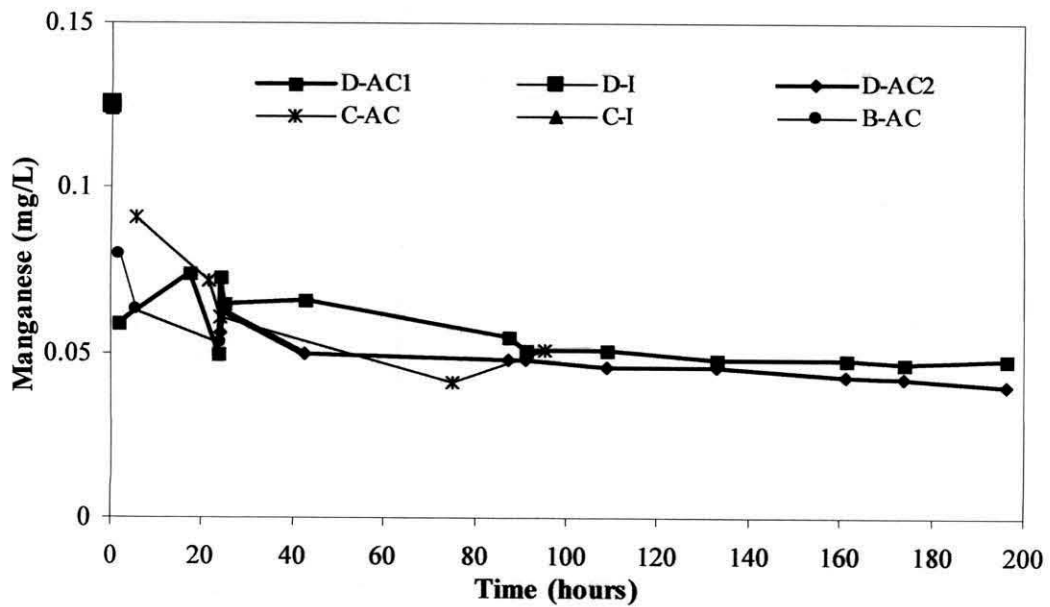


Figure 4.10 Manganese concentrations in treated water after chlorination for different batch of samples

4.4.5 Effect of Other Parameters on the Removal of As, Fe and Mn

Several other parameters such as Phosphate, Silica, pH, Dissolved Oxygen (DO), Temperature, Alkalinity, Electric Conductivity (EC), and Turbidity were measured to better understand the removal mechanism of arsenic, iron, and manganese. The phosphate content in both B-BC and B-AC samples follow a decreasing trend as that of arsenic and iron from the results observed in Figure 4.11 - 4.12, Figure 4.4 - 4.5, Figure 4.6 - 4.7 respectively. The phosphate content in C-BC samples also follow the same trend as that of arsenic, iron, and manganese, with an exception in C-BC-72.5 sample where a co-release of iron, manganese, and phosphate is observed. Among D-BC samples, a co-release of iron and phosphate is observed in D-BC-24. However, arsenic content is observed to drop down in that sample. Since the initial phosphate concentrations were around 4~6 mg/L, according to the results obtained in the laboratory in Chapter 3, they should interfere with arsenic removal.

Since Iron Coated Bottom Ash itself contributes silica, even after coagulation using polyelectrolyte, silica removals were around 5~25 percent. The silica concentrations obtained in different batch analyses are shown in Figure 4.13 and Figure 4.14.

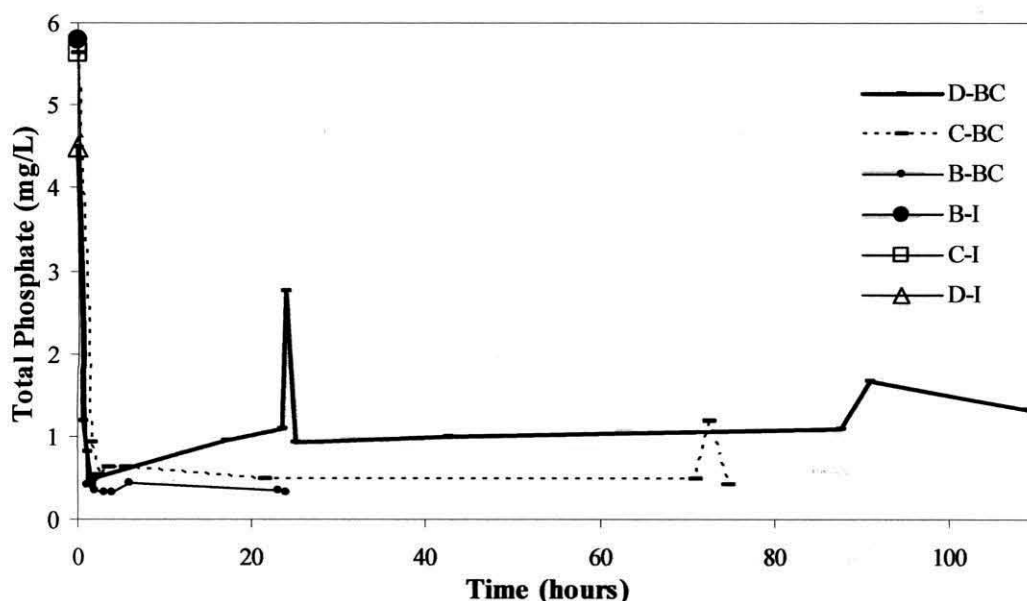


Figure 4.11 Phosphate concentrations at top of the clarifier for different batch of samples

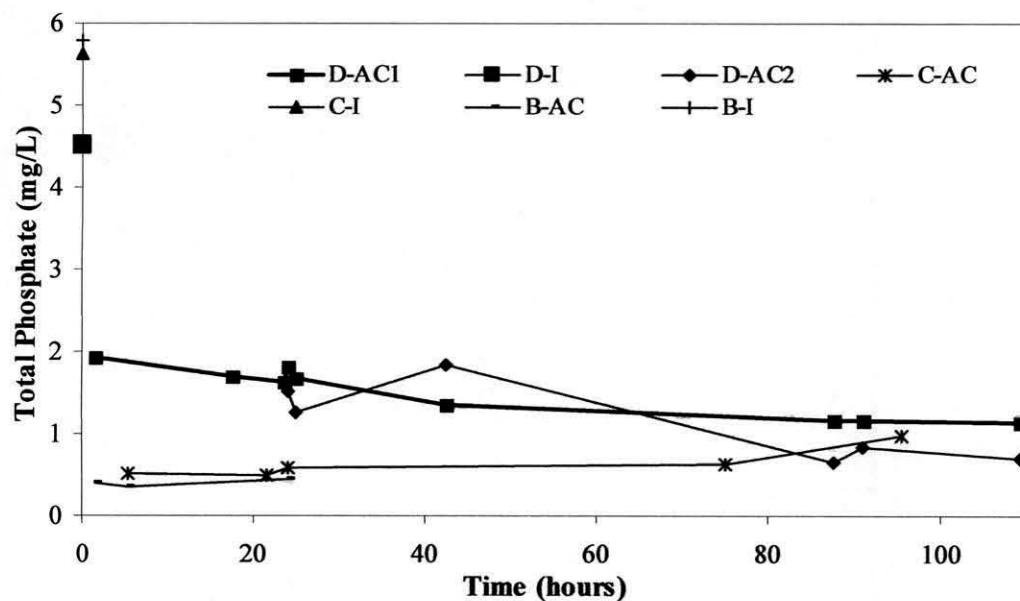


Figure 4.12 Phosphate concentrations in the treated water after chlorination for different batch of samples

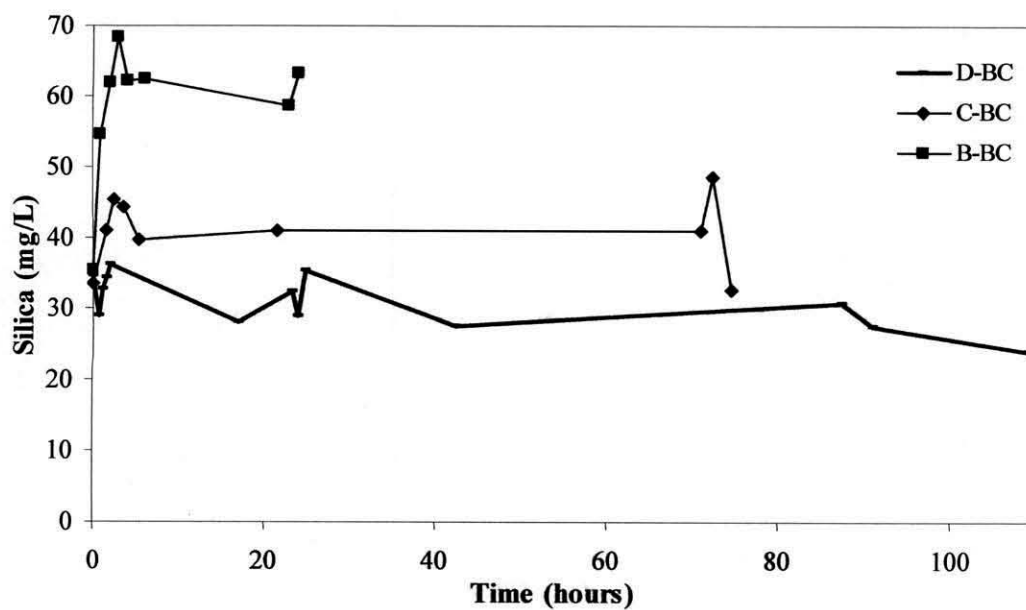


Figure 4.13 Silica concentrations at the top of the clarifier for different batch of samples

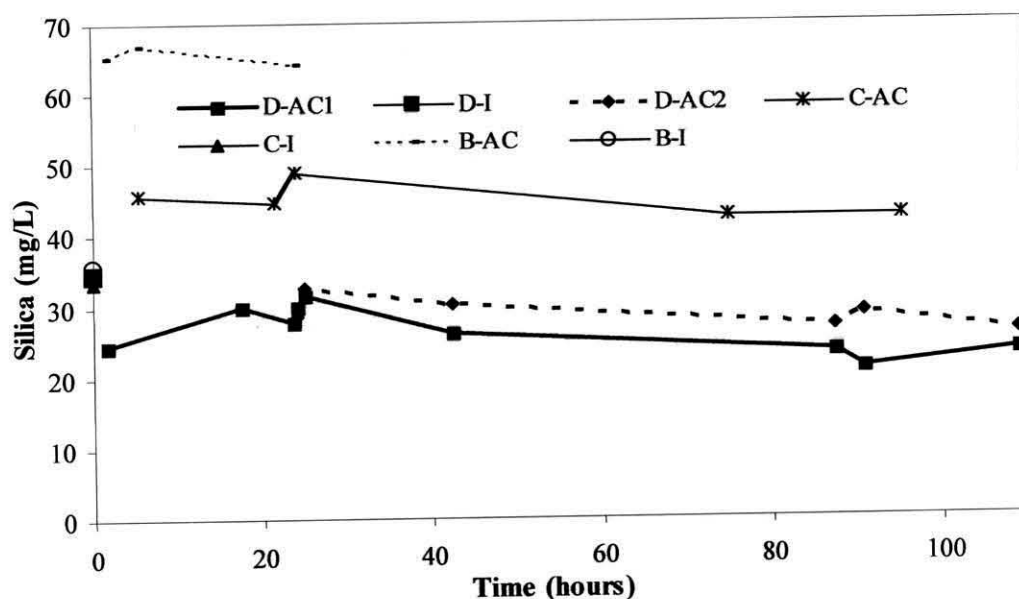


Figure 4.14 Silica concentrations in the treated water after chlorination for different batch of samples

Although pH has no direct impact on consumers, it is one of the most important operational water quality parameters (WHO, 2004). Careful attention to pH control is necessary at all stages of water treatment to ensure satisfactory water clarification and disinfection. No health based guideline value has been proposed for pH (WHO, 2004). The pH of the water immediately after the addition of ICBA decreased, but then increased with the increase in contact time and dissolved oxygen as shown in Figure 4.15 - 4.18. The pH values varied within 7~8 in B-BC, C-BC and D-BC samples. Chlorination increased the pH values slightly (equal to or greater than 8.0). No abrupt change in pH is observed in both BC and AC samples.

The dissolved oxygen content of water is influenced by the source, raw water temperature, treatment and chemical or biological processes taking place in the distribution system (WHO, 2004). Depletion of dissolved oxygen in water supplies can encourage the microbial reduction of nitrate to nitrite and sulfate to sulfide. It can also cause an increase in the concentration of ferrous iron in solution, with

subsequent discoloration at the tap when the water is aerated. No health-based guideline value is recommended. Generally, dissolved oxygen content always increases for all of the batch samples far from the initial DO content (B-I, C-I, D-I). However, DO concentrations at the top of the clarifier showed a decreasing trend after approximately 40 hours of operation for D-BC samples. A polythene cover was placed above the clarifier to keep the water free from outside debris. This might have resulted in depletion of oxygen content since water at the top of the clarifier was not in contact with air. However, there is no significant decrease in pH values in those samples. From the results shown in Figure 4.16 and Figure 4.18, it is observed that the types of variations in DO content experienced by chlorinated samples are same as those of pH values for different batch of samples respectively.

Cool water is generally more palatable than warm water, and temperature is likely to impact on the number of other inorganic constituents along with taste (WHO, 2004). High water temperature enhances the growth of microorganisms and may increase taste, odour, colour and corrosion problems. Temperature of the treated water was recorded; however, no correlation with other water quality parameters was sought (Figure 4.19 and Figure 4.20).

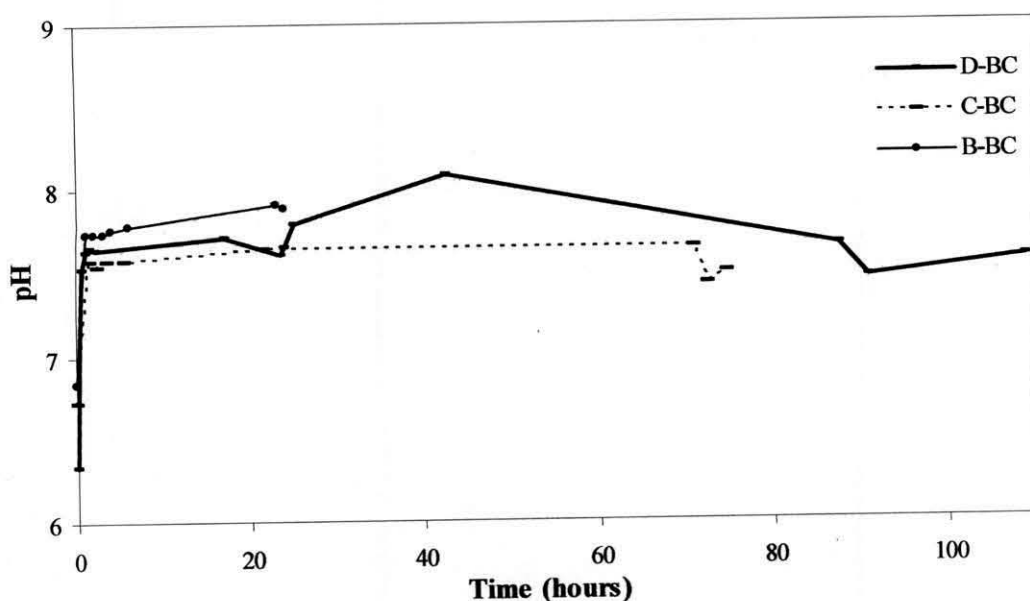


Figure 4.15 pH at the top of the clarifier for different batch of samples

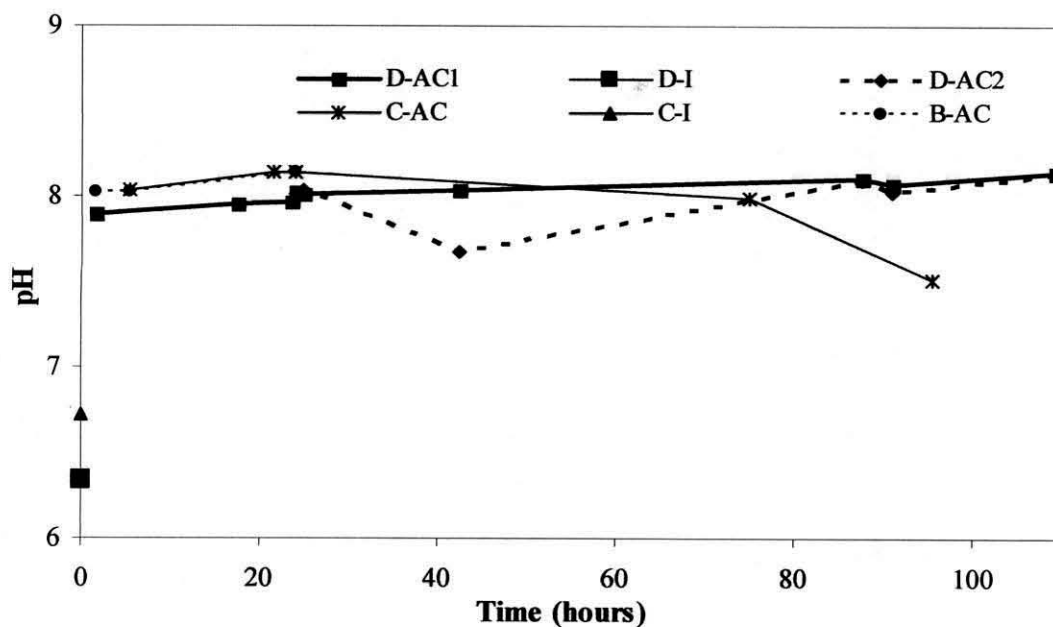


Figure 4.16 pH of the treated water after chlorination for different batch of samples

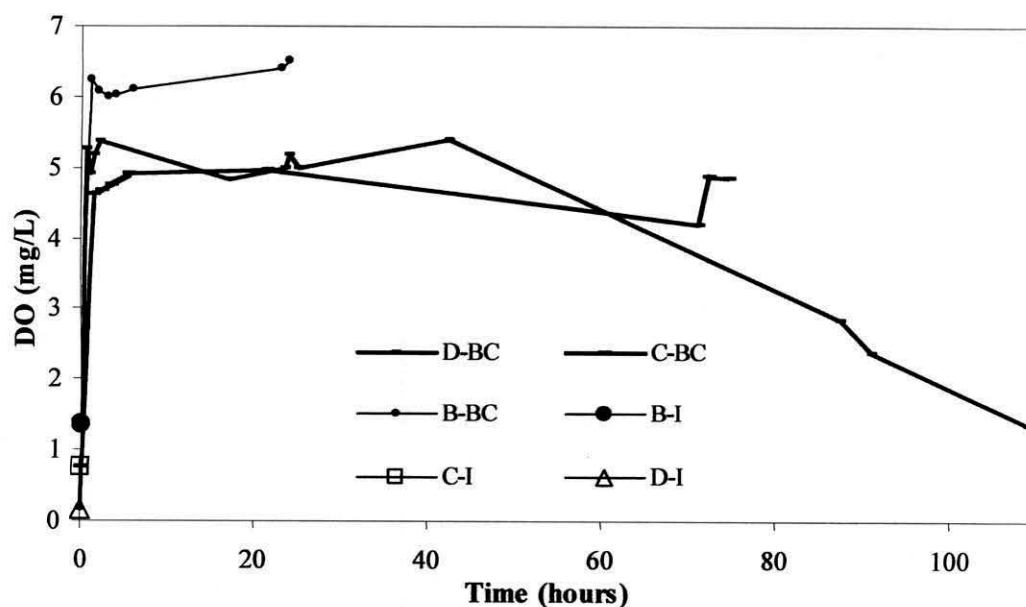


Figure 4.17 DO of the samples collected from the top of the clarifier for different batches

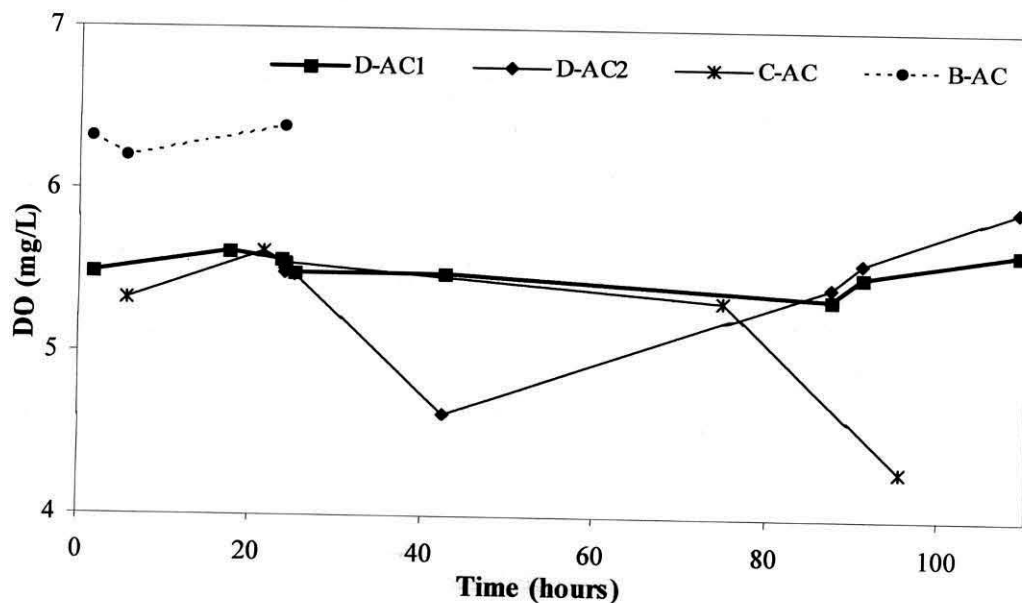


Figure 4.18 DO of the treated water after chlorination for different batches

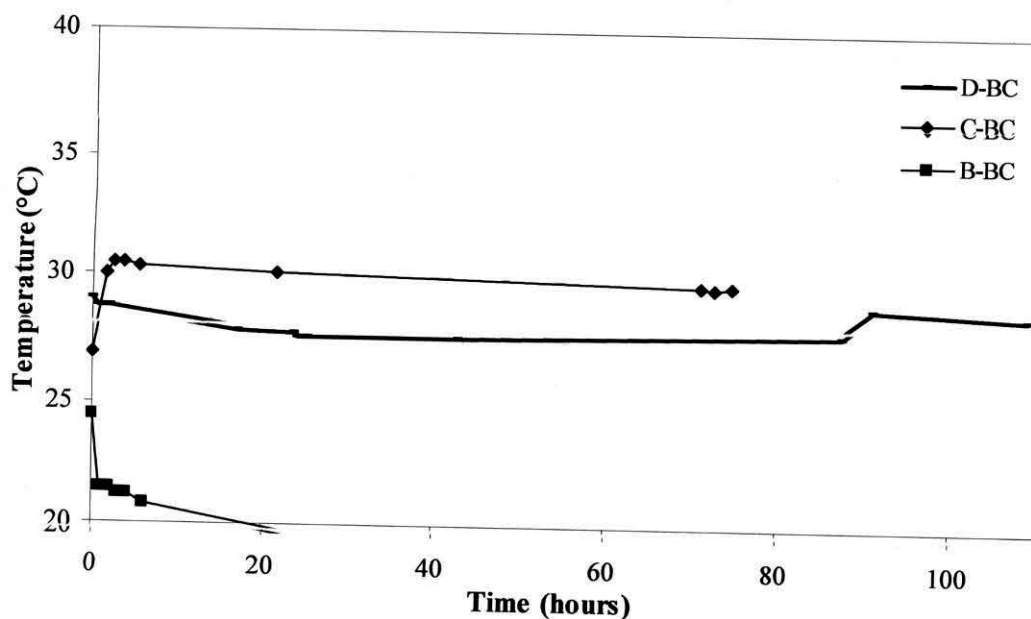


Figure 4.21 Temperature of the samples collected from the top of the clarifier for different batch of samples

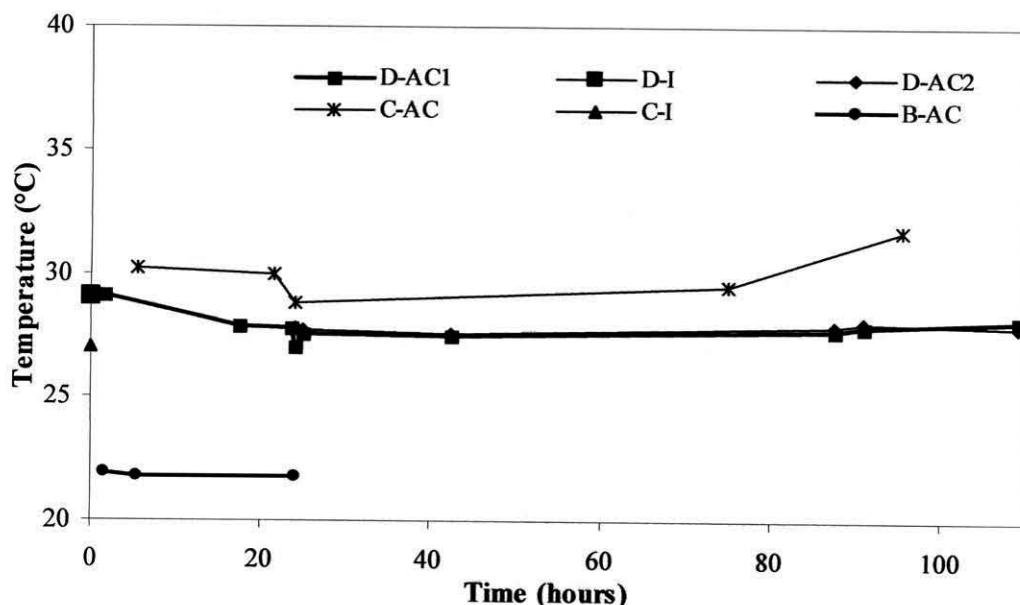


Figure 4.22 Temperature of the treated water after chlorination for different batch of samples

The average value of alkalinity in groundwater of Bangladesh, according to BGS standard, is 100-500 mg/L as CaCO_3 . Addition of ICBA reduces the alkalinity content of the groundwater as observed in Figure 4.21. After chlorination, the B-AC, C-AC, and D-AC samples do not show much variation in alkalinity content as shown in Figure 4.22. Their alkalinity content always remain between 300 ~ 400 mg/L as CaCO_3 . The conductivity values of the treated water before and after chlorination are also shown in Figure 4.23 and Figure 4.24.

Turbidity in drinking-water is caused by particulate matter that may originate from source water as a consequence of inadequate filtration or re-suspension of sediment. It may also be due to the presence of inorganic particulate matter in some ground waters or sloughing of bio-film within the distribution system. The appearance of water with a turbidity of less than 5 NTU is usually acceptable to consumers, although this may vary with local circumstances (WHO, 2004). Particulates can protect microorganisms from the effects of disinfection and can stimulate bacterial growth. In all cases where water is disinfected, the turbidity must be low so that

disinfection can be effective. The turbidity values vary with the amount of suspended particles present in the sample as shown in Figure 4.25. An abrupt increase in turbidity is observed in C-BC-72.5 sample. Re-suspension of flocs can be the likely reason underlying this situation since increased content of iron and manganese can be observed as well in the same sample (Figure 4.6 and Figure 4.9). In Figure 4.26, after approximately 80 hours of operation, it was found that in chlorinated water turbidity converged to 10~20 NTU in all batch results.

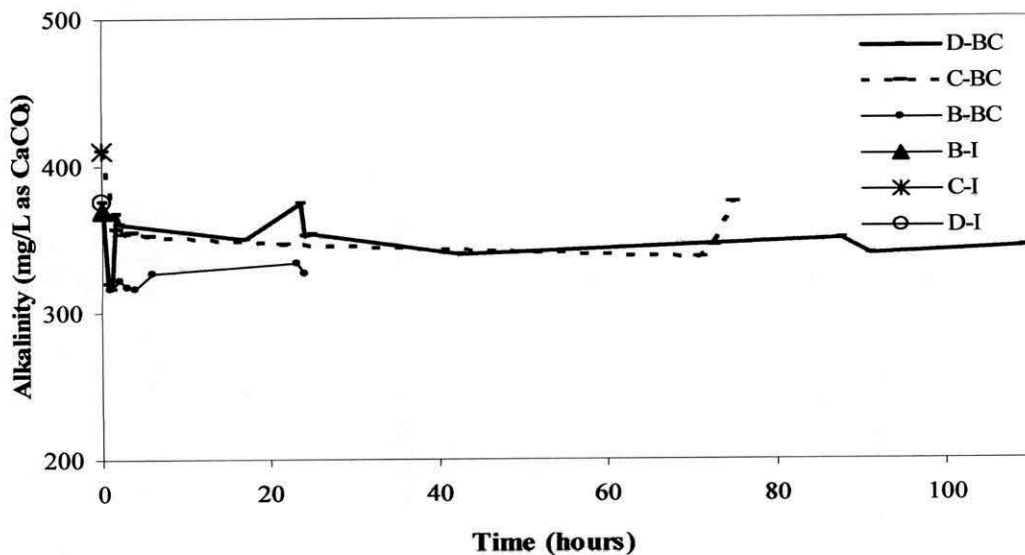


Figure 4.21 Alkalinity at the top of the clarifier for different batch of samples

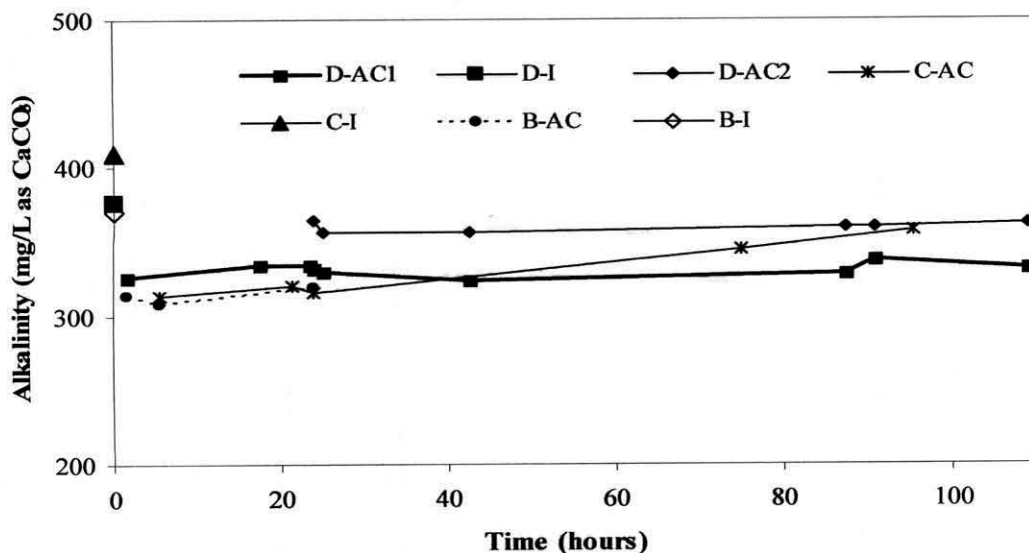


Figure 4.22 Alkalinity of the treated water after chlorination for different batch of samples

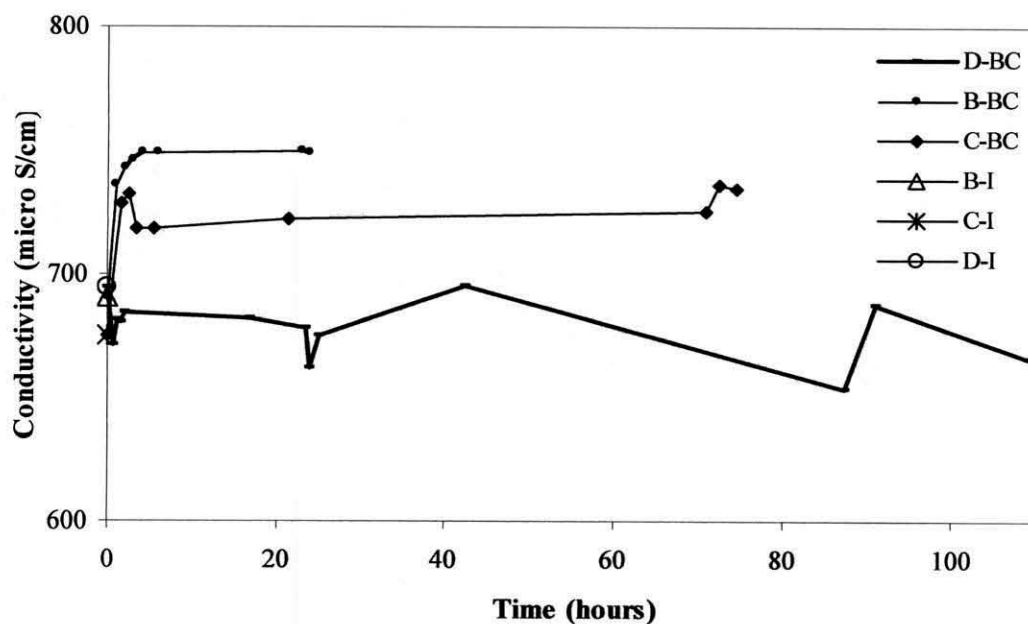


Figure 4.23 Conductivity at the top of the clarifier for different batch of samples

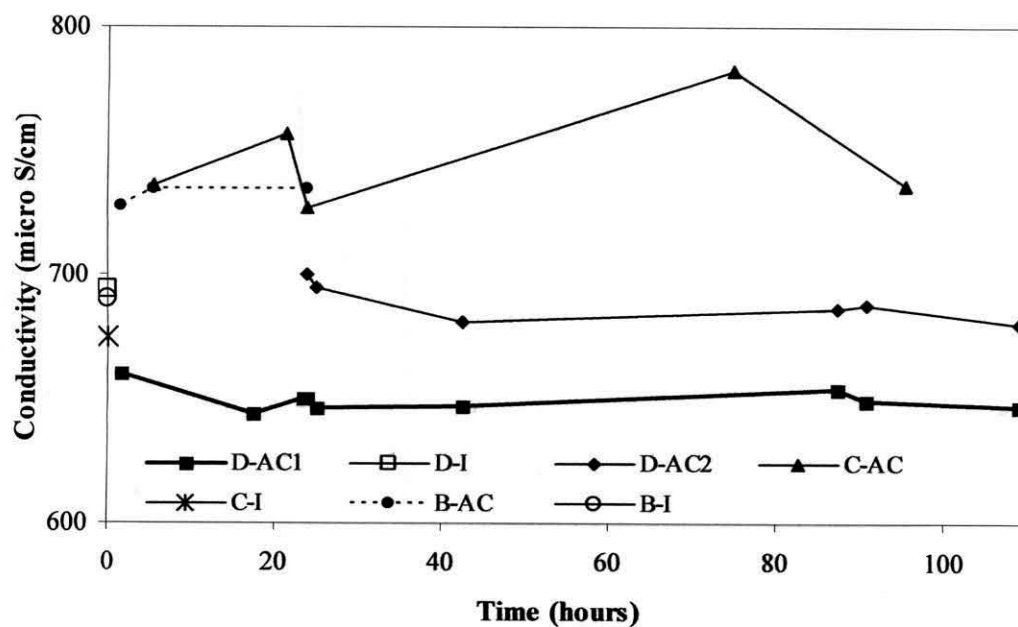


Figure 4.24 Conductivity of the treated water after chlorination for different batch of samples

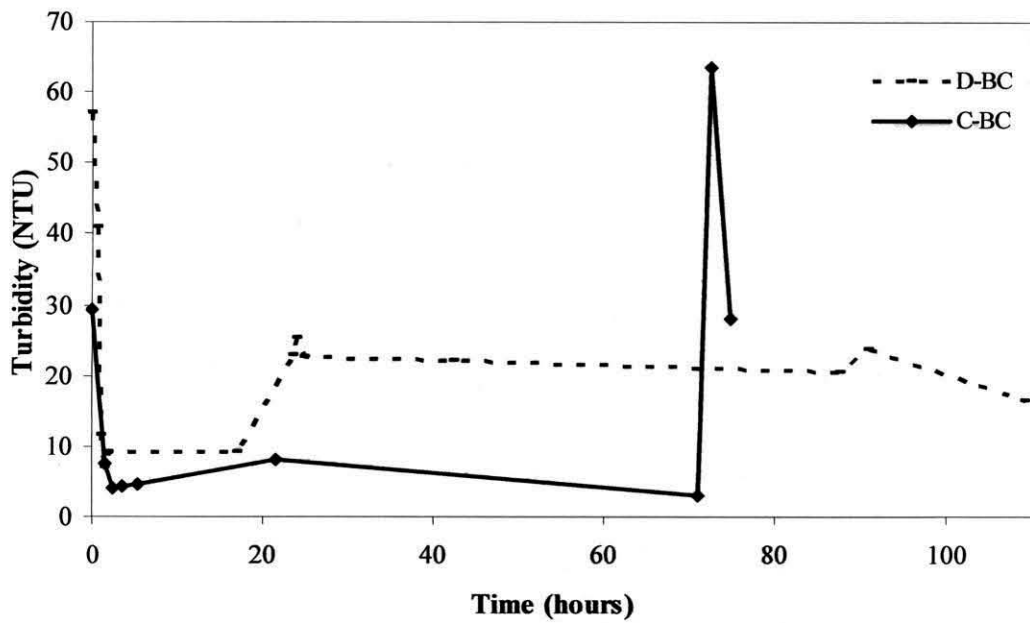


Figure 4.25 Turbidity at the top of the clarifier for different batch of samples

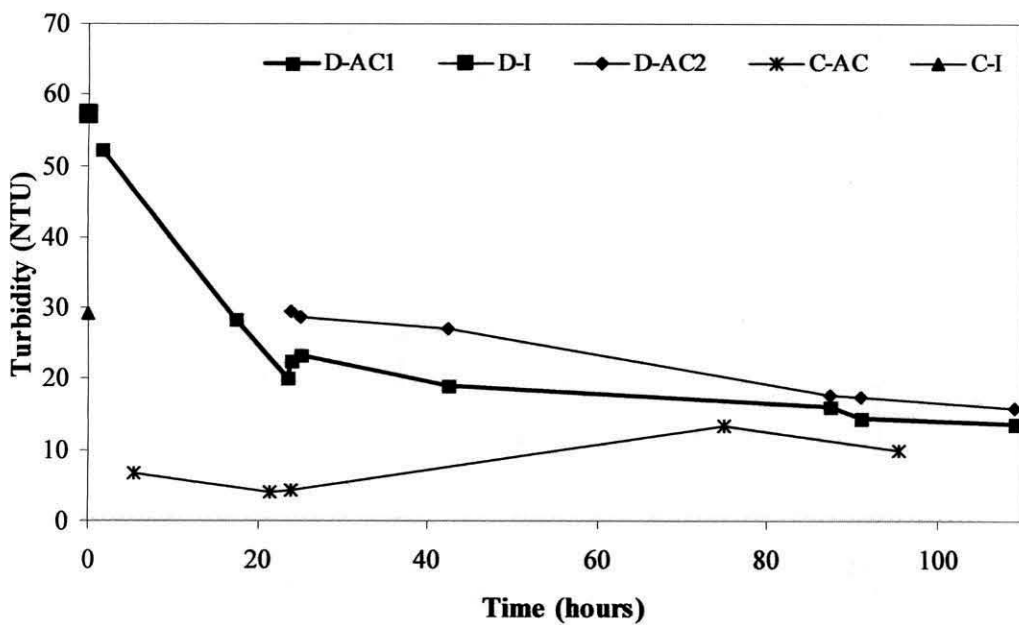


Figure 4.26 Turbidity of the treated water after chlorination for different batch of samples

4.4.6 Presence of Iron Related Bacteria (IRB)

Anaerobic groundwater may contain ferrous iron at concentrations of up to several milligrams per liter without discoloration or turbidity in the water when drawn directly from a well (WHO, 2004). On exposure to the atmosphere, however, the ferrous iron oxidizes to ferric iron, giving an objectionable reddish brown color to the water. Iron also promotes the growth of "iron bacteria", which derive their energy from the oxidation of ferrous iron to ferric iron and in the process deposit a slimy coating on the piping of water supply system.

Iron-related bacteria are difficult to enumerate because they are subdivided into several groupings (e.g., iron-oxidizing and iron-reducing bacteria). Iron related bacteria can use iron in their metabolism. Taste and odor problems and "red water" are common symptoms of problems due to iron-related bacteria. These bacteria function under different reduction-oxidation (red-ox) conditions and use a variety of substrates for growth.

As mentioned earlier, there was a sharp rise in iron concentration at around 72 hours of operation for samples of *Batch C*. This sudden increase or "spike" in iron concentration in water may have been caused by the reductive dissolution of iron resulting in de-sorption of iron from the ICBA. Usually, such dissolution is initiated by microbial activity. To assess the validity of such claim, it is imperative to determine the presence of iron reducing bacteria at around the same time as that "spike" of iron. This may be achieved by using the IRB-BARTTM method developed by HACH, USA.

IRB-BARTTM For water and wastewater

The IRB-BARTs can detect both iron-oxidizing and iron-reducing bacteria. Common iron-related bacteria include *Gallionella*, *Crenothrix*, *Sphaerotilus*, *Siderocapsa*, and *Thiobacillus ferrooxidans*. The IRB-BART method used in this analysis is enumerated in Figure 4.27.

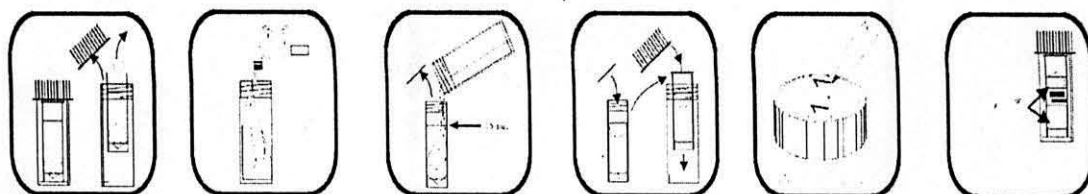


Figure 4.27 IRB-BART™ testing method for water and waste water

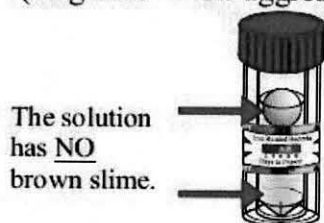
The six steps followed in this procedure are given below:

1. The inner tube is removed from the outer tube.
2. Using the outer tube from the BART, or a different sterile container, at least 20 ml of sample is collected. *The inside of the tube or lid should not be touched or contaminated. Aseptic technique should be used in collecting the samples.*
3. The inner tube is filled with sample until the level reaches the fill line.
4. The cap is tightly screwed back on the inner tube. The inner tube is returned to the outer tube and the outer cap is screwed on tightly. The medium is allowed to dissolve slowly, and the ball to rise at its own speed. *Shaking or swirling the tube is prohibited.*
5. The outer tube is labelled with the date and sample origin.
6. The BART tube is placed away from the direct sunlight and allowed to incubate at room temperature. The BART is checked visually for reaction daily.

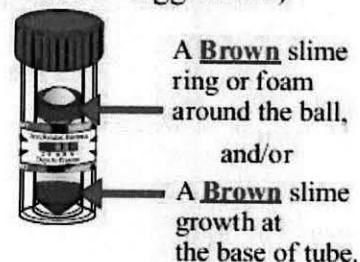
For determination of the presence or absence of IRB the descriptions in Figure 4.28, Figure 4.29, and Figure 4.30 were followed.

Present/Absent - observe daily for 8 days.

ABSENT
(Negative - Non-aggressive)



PRESENT
(Positive - Aggressive)



1. View test each day for 8 days.
2. Observe any growths/color changes.
3. Compare with descriptions.

Figure 4.28 IRB-BART method description – 1

Determination of Dominant Bacteria

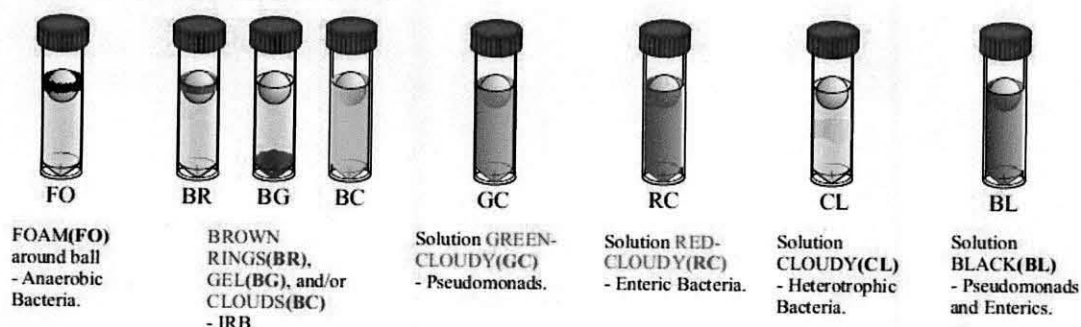


Figure 4.29 IRB-BART method description – 2

Determination of Potential IRB Population - observe daily for reaction.

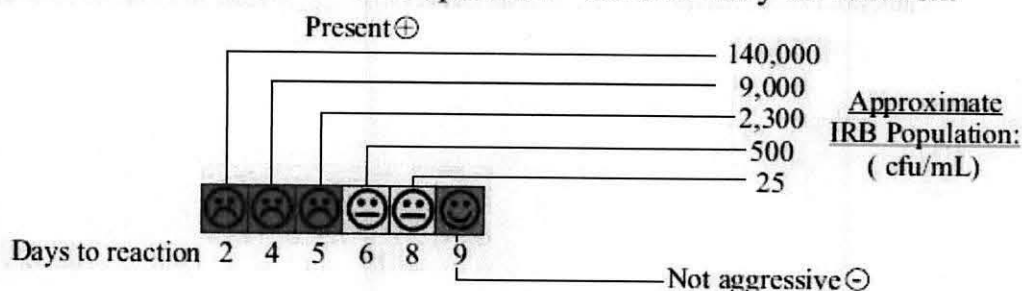


Figure 4.30 IRB-BART method description – 3

Results and Discussion

The sample from raw groundwater of *Batch C* showed brown foam around the ball at four days of reaction as shown in Figure 4.31. According to the guideline shown in Figure 4.27, it ensures the presence of some aggressive bacteria. According to Figure 4.28, the presence of anaerobic bacteria was found and the population of IRB, according to Figure 4.29, was determined to be 9,000 cfu/mL. This test was again performed for samples of *Batch D*. But this time, both raw groundwater (D-I) and treated water after chlorination (D-AC1) were tested. The observations and results in this test are given in Table 4.3 and Figure 4.32.



Figure 4.31 Presence of Anaerobic Bacteria (IRB) in raw groundwater of *Batch C*

Reduction of Fe^{3+} leads to the partial dissolution of Fe(III) oxides and the release of Fe^{2+} . This will lead to the co-release of adsorbed solutes (including As) and structural (solid solution) components (WHO, 2004). In Figures 4.4 – 4.7, for D-BC sample at 24 hours of retention, presence of Iron Related Bacteria (Anaerobic

Bacteria, and Iron Reducing Bacteria) induces reductive dissolution of iron, leaving the sites for arsenic to adsorb on the surface of ICBA. Therefore, arsenic concentration in water decreases at that time. At the same time, de-sorption of phosphate and adsorption of manganese were also observed (Figure 4.11, 4.9). However, at the same time in D-AC samples, the left out sites of iron were taken by phosphate and arsenic in a competitive way. Therefore, both arsenic and phosphate concentrations decreased, but dissolution of iron took place increasing its concentration in the system. Moreover, in D-BC samples at approximately 40 hours of operation, a co-release of arsenic and iron was observed. A gradual co-release of arsenic and iron in D-AC samples was observed at 40 to approximately 80 hours of operation. Their concentrations started to decrease after this point.

Table 4.3 Observations of IRB-BART test in *Batch D* samples

Days of observation	Observations and Results in Sample	
	Raw Groundwater	Treated Water
Day 1	Dirty brown at the bottom, color change in the middle, no change at the top	Dirty brown at the bottom, no change in the middle and at the top
Day 2	Brown slime at the bottom, brown color at the middle, and light brown at the top;	Dirty brown at bottom, very light brown color in the middle, no change at the top
Day 3	Brown slime at the bottom, foam at top; Dominant: Anaerobic bacteria; Potential IRB population: 140000 cfu/mL	Brown slime at bottom, very light brown color at top; brown cloud in the middle
Day 4	-	Brown slime at the bottom; brown cloud all over; Dominant bacteria: IRB Potential IRB population: 9000 cfu/mL



Figure 4.32 Test on IRB of *Batch D* raw water (left) and treated water (right); Number of days of reaction is shown in the picture



Figure 4.32 Test on IRB of *Batch D* raw water (left) and treated water (right) Number of days of reaction is shown in the picture (*Continued from previous page*)

4.4.7 Bacteriological Quality of Treated Water

Safe drinking-water has been recognized for centuries as a major determinant of health. It is estimated that 1.5 million people still lack access to clean water supplies (WHO, 1993). Diseases arising from the ingestion of pathogens in contaminated water have the greatest health impact worldwide (Gorchev, 1996). The health effects of these diseases are heavily concentrated in the developing world and, within the developing world, among the poorer urban and rural households of the poorer countries. An estimated 80% of all diseases and over one-third of deaths in developing countries are caused by the consumption of contaminated water and, on average, as much as one-tenth of each person's productive time is sacrificed to water-related diseases (UNCED, 1992). The use of chlorine and its compounds for the disinfection of drinking-water has played a central role in reducing the incidence of the waterborne diseases.

Several factors influence the efficiency of disinfection with chlorine. These include pH and turbidity of the water and, of course, the concentration of chlorine and contact time.

When added to water, chlorine rapidly hydrolyses, yielding hypochlorous acid (HOCl) and hydrochloric acid. Hydrolysis to HOCl is virtually complete at pH greater than 4 and at chlorine doses up to 100 mg/L. Hypochlorous acid is a weak acid that dissociates partially into hypochlorite ion (OCl⁻). At pH of about 7.5, there

is an equal distribution of HOCl and OCl⁻; at pH 6.5, 90% of the free chlorine is present as HOCl; at pH levels above 9, hypochlorite ions are the dominant species. Hypochlorous acid is a considerably more efficient disinfectant than hypochlorite ion, thus efficient disinfection is favored by lower pH (J. C. Morris, 1982).

Turbidity can have negative effects on disinfection because high levels have been shown to protect microorganisms from the action of chlorine, and to increase the chlorine and oxygen demand (WHO, 1996). Conditions for effective terminal chlorination as recommended in the WHO Guidelines for drinking-water quality are as follows (WHO, 1993; WHO, 1996):

pH	Less than 8.0
Median turbidity	Not to exceed 1 nephelometric turbidity unit (NTU)
Maximum turbidity	5 NTU
Residual concentration of free chlorine	Not less than 0.5 mg/L
Contact time	At least 30 min

These conditions are expected to ensure the absence of bacteria and viruses in treated water but not of pathogenic helminths, cysts or oocysts of protozoa. For these microorganisms, effective filtration is an essential requirement.

Chlorine, as well as other disinfectants, reacts with certain water constituents to form new compounds with potentially harmful long-term health effects. The levels of potentially toxic chlorination by-products can be reduced through appropriate treatment while maintaining the microbiological drinking water (Gorchev, 1996). Effective application of conventional treatment will reduce the levels of organic precursors before final disinfection, and avoiding pre-chlorination will result in an overall decrease in the concentrations of DBPs.

Maintaining the microbiological quality of the treated water was always challenging. The source water contained significant numbers of total and fecal coliforms (TC/FC). To remove them, bleaching powder, which is very cheap and available in the local market, was first tried in the laboratory. But it seemed to mix in the water very

slowly and required rigorous mixing to become diluted in the system. Therefore, 5.25% Sodium Hypochlorite, available in the market as 'Clotech', was tried in the subsequent batches. It seemed to perform better than bleaching powder and deemed easier to operate. Since, at the beginning, the community people are expected to carry the treated water from the system (no centralized water supply system), efforts were made to maintain the amount of free chlorine in the treated water of more than 0.5 mg/L. Sodium hypochlorite of 1.55 mg/L concentration was applied in the water (1 ml in 5 liters of water). Mixing of sodium hypochlorite was performed manually for fifteen minutes and was allowed to settle for another fifteen minutes. Then samples were started to be collected for analysis.

Free chlorine diminishes with time. In *Batch C* samples, only total chlorine measurements were possible and have been presented in Appendix A. In *Batch D* samples, due to the unavailability of chemicals for free chlorine measurement, in the laboratory and also in the local market, free chlorine content of samples till 25 hours of operation could only be measured. Free chlorine results of *Batch D* have been presented in Figure 4.32. Among D-AC2 samples, free chlorine concentrations of only two samples have been measured and therefore have not been presented in Figure 4.32. However, the results are given in Appendix A. The initial concentration of free chlorine present in raw water of *Batch D* samples is 0.5 mg/L. In D-BC samples, the free chlorine content decreases with time in first one and half hour of operation. The free chlorine content has been used in oxidizing the TC/FC of water. It has again started to increase after around 2 hours of operation. The pH of water has been observed to increase in the meantime from 6 to above 7.5. Since no extra free chlorine has been impregnated into this system, this pH increase has led to dissociation of existing chlorine content to underchloric acid (HOCl) and hypochlorite ions (OCl⁻) which may have resulted in increase in free chlorine content. However, while the pH of water has continued to remain around 7.5~8, the free chlorine content has started to diminish at 23 hours of operation.

In D-AC1 and D-AC2 samples, the free chlorine concentration immediately after chlorination has been observed to be above 0.5 mg/L. However, in D-AC1 samples,

it has changed and dropped below 0.5 mg/L after around 18 hours of operation and has again increased after approximately 24 hours of operation. A very insignificant increase in pH has been observed in these samples. Also one thing should be noted that the rate of addition of Sodium hypochlorite being same, the free chlorine concentration in D-AC2 samples after 30 minutes of contact time was greater than that in D-AC1 (results are given in Appendix A). This may have resulted from the high inflow rate (500 liters per hour) in D-AC1 samples leading to high turbidity and subsequent interference in action of chlorine.

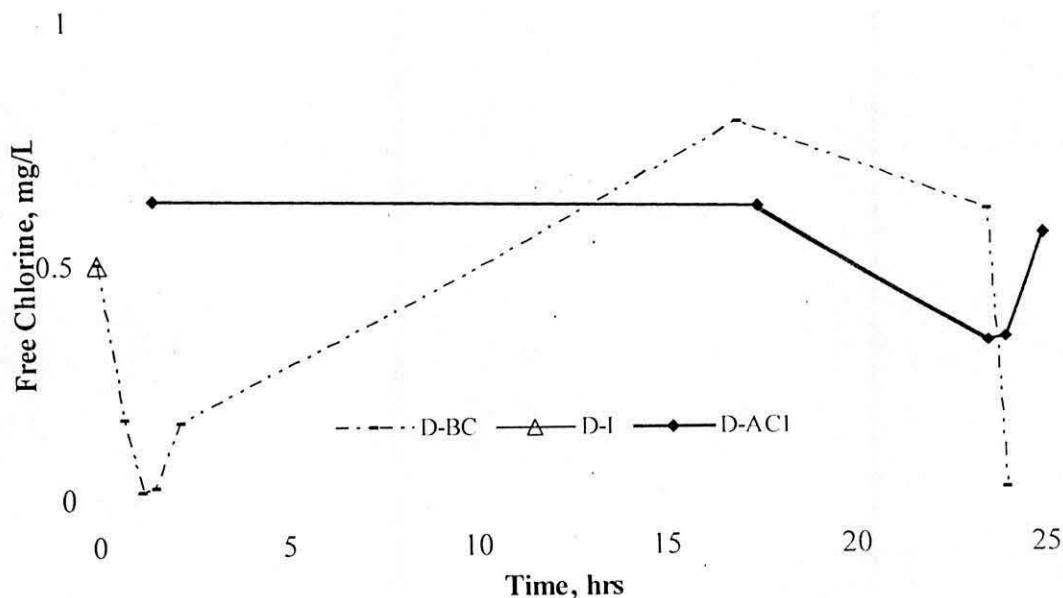


Figure 4.32 Free chlorine concentrations in samples of *Batch D*

In *Batch C* sample, fecal coliform was removed immediately after chlorination, but total coliform was still present. The results of TC/FC in *Batch C* samples are given in Appendix A. The microbiological quality in the treated water in *Batch D* was obtained after 8 days of operation. The results of TC/FC in *Batch D* samples are given in Appendix A. One thing should be noted between the initial TC/FC of these two trips is, *Batch D* contained much higher numbers of TC/FC than those of *Batch C*. Shallow tubewells can be easily contaminated with TC/FC. The tubewell under investigation in this research is situated near a mosque and madrasa. Few lavatory activities were observed to occur during the first three field visits (while collecting *Batch A, B and C* raw water samples). However, these activities were observed to be

more frequent during the last field visit (*Batch D*). This could be the one of the possible reasons for such high numbers of TC/FC (TC: 740, FC: 120) in *Batch D* raw water. Filtration is recommended for future analysis to accelerate and improve the TC/FC removal condition. Also, the turbidity for effective chlorination could not be attained due to the high flow rate. But it is believed to be attainable provided the flow rate is controlled around 100L/hr. Settled particles in the collection reservoir could also have negative effect on the proper action of chlorine. Therefore, controlled flow rate coupled with filtration is recommended for future investigation if needed.

4.5 SUMMARY

Results of this study show that maintaining the flow rate around 100 Liters per hour with the low-tech valve is not always possible. But, it is possible, that provided the flow rate is maintained, the performance of the prototype will improve significantly. The closer the flow rate to 100 L/hr, the better is the performance.

For the arsenic content in raw water around 200 µg/L and flow rates closer to 100 L/hr, if the water is stored for several hours before treatment, arsenic concentration in the treated water (after chlorination) less than 50 µg/L can be always achieved. Arsenic concentration less than 10 µg/L is also attainable after around 95 hours of operation for the same operating conditions. For raw water arsenic content around 500 µg/L, arsenic concentration less than 50 µg/L can be obtained after approximately 133 hours of operation for flow rate as high as 500 liters per hour. For the same initial concentration, but flow rate closer to 100 liters per hour (178 liters per hour), arsenic concentration less than 50 µg/L can be obtained after around 109 hours of operation.

Iron concentration in the treated water after chlorination can be reduced to 0.35 mg/L after 5.5 hours of operation, and can be further reduced to 0.18 mg/L after 21.5 hours of operation for flow rate closer to 100 liters per hour (in samples of *Batch C*). However, the iron concentration can increase around 96 hours of operation due to the presence of iron-related bacteria (anaerobic bacteria). For flow rate as high as

500 liters per hour, iron concentration in the treated water after chlorination can also be reduced to minimum in the chlorinated water after around 23 hours of operation. They also vary in subsequent samples due to the presence of iron reducing bacteria in water.

According to WHO (2006), the health-based guideline of manganese in the drinking water is 0.4 mg/L. But, the presence of manganese, at levels exceeding 0.1 mg/L, may lead to the accumulation of deposits in the water distribution system. Concentrations below 0.1 mg/L are acceptable to consumers. From these analyses, it is observed that having an initial manganese concentration of around 0.125 mg/L, Mn concentrations less than 0.1 mg/L can be always achieved in all kinds of situations in the treated water after chlorination.

Presence of iron-related bacteria can change the performance of iron-coated bottom ash by attacking at the adsorptive bond of ICBA with arsenic, iron and manganese. The number of Iron- Related Bacteria (IRB) population in the raw water is as high as 1,40,000 cfu/ml. This number can be reduced to 9000 cfu/ml after treatment with ICBA and chlorination, but cannot be completely removed.

The performance of disinfection with chlorination depends upon the initial turbidity, pH and contact time. The initial turbidity for chlorination can not be maintained if the flow rate is high. But results of *Batch C* in Figure 4.26 show that the initial turbidity for effective chlorination near 5 NTU can be maintained if the flow rate is nearer to 100 liters per hour. The time to achieve the microbiological quality of the drinking water depends upon the numbers of total and fecal coliforms present in the raw water as well. If the initial TC/FC is low (60/30), they can be removed immediately after chlorination. But as seen in *Batch D* samples, for initial TC/FC as high as 740/120, it takes around 7 days to completely remove FC and 8 days to completely remove TC. To accelerate and improve the disinfection phenomenon, filtration before chlorination can be incorporated for future investigation. Also, sanitation facilities at the source should be properly maintained.

The pH of the treated water is always close to 8, acceptable according to WHO drinking water guidelines. In D-AC2 samples, at around 40 hours after operation, the reduction in dissolved oxygen content in the treated water has resulted in pH reduction. As a result of which reductive dissolution of arsenic (from As^{V} to As^{III}) may have been initiated in the system.

CHAPTER – 5

ARSENIC LEACHING AND MAINTENANCE OF THE PROTOTYPE

5.1 INTRODUCTION

The arsenic crisis of Bangladesh has led to a massive poisoning of groundwater and disruption of public health. A large number of initiatives have been taken and different technologies have been developed in Bangladesh for arsenic removal from groundwater since 1993 when arsenic in groundwater was first detected in the district of Chapai Nawabganj. A number of studies (Badruzzaman, 2003) have been conducted to develop suitable techniques to treat arsenic laden groundwater. Most of these are aimed at developing household and small community level units.

A unit operation of arsenic removal using iron coated bottom ash for community scale use is performed for the first time in this research. All the arsenic removal units generate some form of arsenic-rich wastes, and the unit incorporated in this research is of no exception. Indiscriminate disposal of the spent media or sludge is likely to contaminate the surface water sources or may leach arsenic, which may be transported to the underlying aquifer. Therefore, concerns have been raised regarding safe disposal of wastes and possible contamination of environment from arsenic present in the wastes.

This chapter focuses on the likelihood of leaching of arsenic from the sludge generated by the treatment technologies and safe disposal of these sludges. Only the short-term leaching of arsenic is performed in this analysis. Maintenance of the arsenic removal unit is also an important aspect in order to keep the unit functioning. Thus, disposal options have also been discussed in this chapter.

5.2 ASPECTS OF LEACHING

An important issue in using coal ash as a substrate is the possibility that the ash itself might contaminate the treated water with other leachates such as heavy metals (aluminium, antimony, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium, selenium, silicon, titanium, and zinc). In fact, coal ash has been shown to contain trace levels of arsenic itself. Arsenic concentrations in fly ash have been measured to be 100-800 mg per kg where concentrations decrease with increased particle size. Bottom ash particles are smaller than fly ash particles and so we would expect arsenic concentration in the bottom ash to be lower (Mathieu, 2008). It was noted in this study that only arsenic and cadmium concentrations of the uncoated bottom ash leachates, extracted at pH 3, 6 and 10, were above the USEPA Maximum Contamination Level (MCL) for drinking water. Therefore, in this analysis only arsenic and cadmium concentrations of the TCLP extracts are determined. There has been no guideline developed so far in Bangladesh for disposal of arsenic contaminated sludge. According to USEPA (1995) surface disposal (SD) practice of sewage sludge, arsenic and cadmium contaminated sludge can be disposed off in a unit with a liner and leachate collection system. The allowable removal credits for both of the pollutants are 100,000 mg/kg dry weight basis.

5.3 METHODS OF ANALYSIS

5.3.1 Short-term leaching of arsenic

Leaching of arsenic indicates the relative stability of arsenic associated with wastes generated from the arsenic removal unit. Short term leaching is determined following TCLP of the USEPA (Method 1311). Usually, this test is used to evaluate the leaching potential of the solid waste disposed in landfill sites. This procedure involves an aggressive acetic acid leaching at a lower pH following 18 ± 2 hour agitation at a speed of 30 ± 2 rpm. In this process, arsenic rich wastes are stimulated and leaching occurs within a very short period of time. So, this type of leaching is termed as short-term leaching. These tests may not provide quantitative leach rates expected under disposal conditions but instead provide the relative reactivity of different waste products under similar conditions.

5.3.2 Toxicity Characteristics Leaching Procedure (TCLP)

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphasic wastes. Following criteria is followed in determining whether the TCLP is required or not:

- a) If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate USEPA regulatory levels could not possibly be exceeded, the TCLP need not be run.
- b) If an analysis of any of the liquid fractions of the TCLP extract indicates that a USEPA regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.
- c) If an analysis of an extract obtained using a bottle extractor shows that the concentration of any USEPA regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE (Zero Headspace Extractor) is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

Summary of the Method of TCLP

- a) For liquid wastes (i.e., those containing less than 0.5% dry solid materials), the wastes, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP extract.
- b) For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the liquid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

- c) If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

Reagents and acids

Reagent grade chemicals should be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. The following acids are essential in conducting TCLP:

- a) Hydrochloric acid (1N), HCl, made from ACS reagent grade;
- b) Nitric acid (1N), HNO₃, made from ACS reagent grade;
- c) Sodium Hydroxide (1N), NaOH, made from ACS reagent grade;
- d) Glacial acetic acid, CH₃CH₂COOH, made from ACS reagent grade.

Extraction Fluid

Extraction fluid #1 is prepared by adding 5.7ml glacial CH₃CH₂COOH to 500 ml of reagent water and 64.3 ml of 1N NaOH, and diluted to a volume of 1 liter. When correctly prepared, the pH of this fluid should be 4.93±0.05. Extraction fluid #2 is prepared by diluting 5.7ml glacial CH₃CH₂COOH with reagent water to a volume of 1 liter. When correctly prepared, the pH of this fluid should be 2.88±0.05.

These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid should be discarded and fresh extraction fluid should be prepared. TCLP extract should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portion of extracts for metallic analyte determination must be acidified with nitric acid to a pH < 2, unless precipitation occurs. Extracts should be preserved according to the guidance given in the individual analysis methods.

Preliminary Evaluation for TCLP

Preliminary TCLP evaluation is performed on a minimum of 100 gm aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include:

- a) Determination of the percent solids;
- b) Determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration;
- c) Determination of whether the solid portion of the waste requires particle size reduction;
- d) Determination of which of the two extraction fluids is to be used for the nonvolatile TCLP extraction of the waste.

Preliminary Determination of Percent Solids

Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure as described below.

If the waste obviously yields no liquid when subjected to pressure filtration (i.e., is 100% solids) the extraction procedure should be followed without delay. If the sample is liquid or multiphasic, liquid / solid separation to make a preliminary determination of percent solids is required.

If the percent dry solids are less than 0.5%, the multiphasic analysis method should be followed for nonvolatile TCLP. Otherwise, if the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, particle size reduction analysis should be performed with a fresh portion of waste. Then the appropriate extraction liquid should be determined.

Determination of Appropriate Extraction Fluid

If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents, the appropriate fluid for the nonvolatile extraction should be determined as below:

Weigh out a sub-sample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 ml beaker. Add 96.5 ml of reagent water to the beaker, cover with a watch glass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0 , extraction fluid #1 should be used. If the pH is >5.0 , add 3.5ml of 1N HCl, slurry briefly, cover with a watch glass, heat to 50°C for 10 minutes. Let the solution cool to room temperature and record the pH. If the pH is <5.0 , use extraction fluid #1. If the pH is >5.0 , use extraction fluid #2.

TCLP for Non-volatiles

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analytes required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids), weigh out a sub-sample of the waste (100 grams minimum) and extraction should be done directly as described later. Otherwise, if the sample is liquid or multiphasic, liquid / solid separation is required. This involves the filtration as described earlier in the pre-evaluation steps.

Following filtration, if required, the material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. The filtrate should be weighed. The liquid phase may now be either analyzed (as described later) or stored at 4°C until time of analysis.

If the waste contains $<0.5\%$ dry solids then it should be considered the TCLP extract and be preserved for analysis by following the instruction described later. However, if the percent solids is $>0.5\%$ then it should be determined whether particle size reduction is necessary. If not, then TCLP extraction procedure should be followed. Amount of extraction fluid needs to be added in the extraction vessels is determined by

$$\text{Wt. of extraction fluid} = (20 * \% \text{ solids} * \text{wt. of waste filtered})/100$$

This amount of appropriate extraction fluid is slowly added to the extractor vessel. It is then closed tightly, secured in rotary agitation device, and is rotated at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 during the extraction period. It is important to note that as agitation continues, pressure may build up within the extractor bottle for some types of wastes (limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

Following the 18 ± 2 hours extraction, the material in the extractor vessel should be separated into its component liquid and solid phases by filtering through a new glass fiber filter. If compatible (i.e., multiple phases will not result on combination), the filtered liquid resulting from the above step should be combined with the initial liquid phases of the waste obtained. This combined liquid is defined as the TCLP extract.

5.3.3 Collection of Sample

The arsenic removal unit is cleaned after two back to back batch studies are performed. Spent media is mainly collected from the mixing tank and from the bottom and inner surface of the clarifier. Due to the high flow rate, settled spent media is also obtained from the treated water tank but of very small amount. After the unloading of the treated water, the collection tank can be cleaned and the total sludge can be collected for later analysis. From each batch, approximately 1.6 kg of sludge is obtained since the same amount was used for the treatment.

5.3.3 Determination of Raw Arsenic Concentration in the Sample

Arsenic rich treatment waste (liquid or semi-solid and solid) collected from the treatment unit were stored in the laboratory and a portion of the sample was used for the determination of total arsenic content. For solid samples, the sample was dried in an oven at a temperature of 110°C for 24 hours to ensure that there was no moisture left in the wastes. The sample was then digested using aqua regia as described in the Standard Methods (Clesceri et al., 1998) for total extraction of heavy metals. Briefly, the sample digestion procedure consisted of the following steps: the sample was ground and 5 gram of it was taken in a volumetric flask. Then 5 ml of concentrated nitric acid and 15 ml of concentrated hydrochloric acid was added to the sample and it was kept overnight. After that, the sample was heated for 2 to 3 hours to boiling. After heating, it was allowed to cool and volume was adjusted to 500 ml by adding de-ionized water. Finally, the sample was filtered and stored. Following extraction, the amount of arsenic present in each extracted liquid was determined using a Graphite Furnace Atomic Absorption Spectrophotometer (Shimadzu Model AA-6800). The digestion procedure for the liquid sample was same as that for solid sample with the exception that in this case 50 ml of sample was taken instead of 5 gm, which was used for solid samples.

5.3.4 Carrying out TCLP

Leaching characteristics of waste collected from the arsenic removal unit have been evaluated through Toxicity Characteristics Leaching Procedure (TCLP) developed by USEPA. The procedure was described earlier in this chapter. For trip 3 & trip 4 TCLP analysis of the waste, the pH values of the extraction fluids made from Acetic acid and Sodium hydroxide were 4.93 ± 0.05 , but for trip 2 the pH of the extraction fluid was kept 11 to observe the impact of different pH condition. It is important to note that several studies have questioned the appropriateness of TCLP for assessing the leaching potential of arsenic removal wastes. Ali et al. (2003) and Badruzzaman (2003) noted that TCLP does not address leaching over time. Instead, Badruzzaman (2003) recommends that the testing should imitate the actual sludge disposal conditions in order to assess leaching in the environment. Therefore, the leachate extraction was also performed using pond water if the sludge is planned to be

disposed in to the nearby pond. The properties of the pond water used in this analysis are given in Table 5.1.

Arsenic and Cadmium concentrations in the TCLP extracts and raw wastes were measured using a Graphite Furnace Atomic Absorption Spectrophotometer (Shimadzu Model AA-6800). To determine arsenic concentrations, four standards (0 $\mu\text{g/L}$, 10 $\mu\text{g/L}$, 20 $\mu\text{g/L}$, and 30 $\mu\text{g/L}$) were prepared and for Cadmium concentrations four standards (0.5 mg/L , 1 mg/L , 1.5 mg/L , and 2 mg/L) were prepared for analysis using GFAAS.

5.4 RESULTS AND DISCUSSION

The percent dry solids in the slurry samples shown in Figure 5.1 depend upon the collection of the sample and they can vary in each collection. The results of the waste analyses in *Batch B* (January 3, 2009), *Batch C* (April 15, 2009) and *Batch D* (May 12, 2009) in this research are given in Table 5.2 to Table 5.5 of Appendix B.

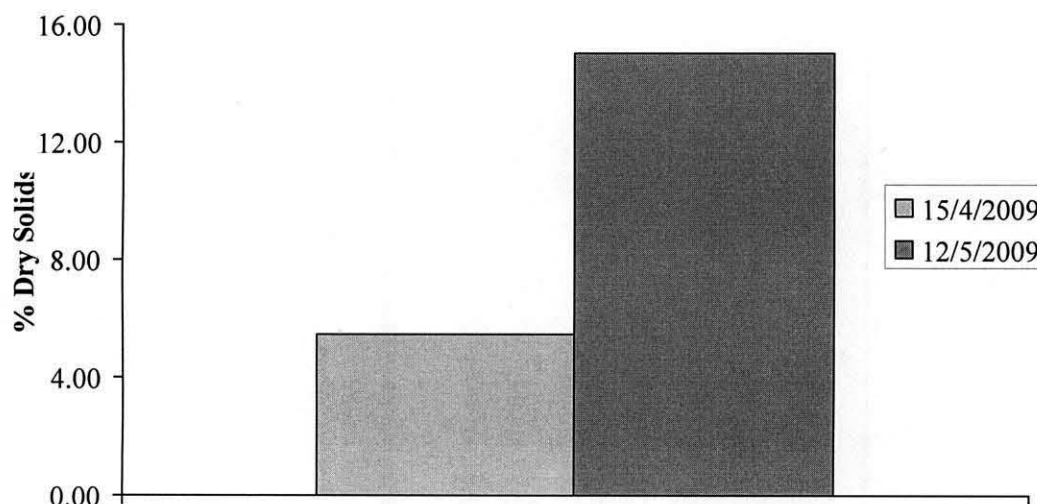


Figure 5.1 Percent Dry Solids in different batch waste

The percent of dry solids present in sludge produced in different batches has varied from 5.46 percent to 15.03 percent. The raw arsenic concentrations in the samples have varied between 393 $\mu\text{g/L}$ and 512 $\mu\text{g/L}$. For these samples, arsenic concentration in the extract has varied between <1 $\mu\text{g/L}$ and 16 $\mu\text{g/L}$.

Difference in pH in leaching fluid has been observed to impact significantly on the arsenic leaching concentrations. Arsenic concentrations in the leachates of extraction

fluid (pH = 11) of *Batch B* are much higher (278 $\mu\text{g/L}$, 418 $\mu\text{g/L}$) than those values of *Batch C* (0 $\mu\text{g/L}$) & *Batch D* (9 $\mu\text{g/L}$). Low pH (≈ 5) does not seem to affect the bond of ICBA leading to low leaching of arsenic. For leachates extracted from distilled water, there is only one aberration where concentration is higher than 10 $\mu\text{g/L}$. But very high pH triggers arsenic to leach out of the sludge.

Cadmium concentrations in the raw wastes have been observed to be less than or equal to 0.003 mg/L (USEPA drinking water guideline for cadmium concentration) and the leachates have never exceeded 0.12 mg/kg of dry waste including that in raw sludge for SD practice.

5.5 MAINTENANCE OF THE PROTOTYPE

Regular cleaning of the prototype was performed after one back-to-back batch operation. However, the number of back-to-back batches performable without the cleaning of the prototype could not be determined due to time limitation.

There are several points to be kept in mind while working with this prototype. Cleaning of tanks, mixing as well as treated water collection, can be tiring since it has to be performed at least once in two days. Although the design of the prototype was such that the coagulated flocs would settle in the clarifier sides, a major portion of the sludge also settles in the mixing tank. Moreover, when the flow rate is high, the tanks which are used for collection as well as chlorination can receive an amount of re-suspended settled sludge. The shape of the tanks also makes them difficult to clean the sludge. At least, making the lower portion of the mixing tank, somewhat conical, since it stays at high level, may improve the cleaning operation.

Since an electric motor is used to rotate the shafts and blades for mixing ICBA and coagulant with water, it has to be checked regularly and oiled when needed.

5.6 RE-USE AND DISPOSAL OF SPENT ICBA

Safe disposal of arsenic wastes poses several problems (Leist et al., 2000):

1. Incineration is limited because of the volatilization of arsenic containing compounds.

2. Recovery of arsenic is of little economic interest because of the limited number of use for the elements.

Arsenic wastes produced of a sufficient purity (approximately greater than 95%) may be economically recovered for use primarily in the manufacture of the arsenical wood preservative, chromated copper arsenate (CCA), and ammonical copper-zinc arsenate (ACZA) (Leist et al., 2000). Production of chromated copper arsenate (CCA) accounted for more than 90% of the domestic consumption of arsenic trioxide in the United States in 1998 (Reese Jr., 1998).

The most attractive option for dealing with arsenic wastes lies in encapsulating the contaminated material, usually through solidification/stabilization techniques using Portland cement, fly ash and polymeric materials and disposing of the treated wastes in secure landfills (Leist et al., 2000). However, this process is highly dependant upon the chemistry of the particular arsenic waste, not merely the varying arsenic concentrations. Fixation of the arsenic containing waste of the present study in the brick manufacturing materials can also be considered. However, in this case, there is a possibility of As(V) volatilization due to the involved high temperature in the blast furnace as in lead-zinc blast furnace investigated by De Villiers (1995).

Arsenic waste remediation could be enhanced by allowing it to undergo biochemical processes (Ali et al., 2003), such as through mixing it with cow dung or mixing with mud and domestic sewage (Badruzzaman, 2003), since toxic arsenic species are lost through biomethylation (Lee et al., 2004).

ICBA could be incorporated into concrete used in road construction with a layer of asphalt added over the top to ensure that the concrete will not crumble and turn into dust that people could inhale (Mathieu, 2008). The Chinese already incorporate arsenic removal waste into concrete (Guy Howard, personal communication, November 2008). Moreover, researchers have recently developed a new building material out of coal ash (MEM, 2008).

5.7 SUMMARY

Arsenic sludge from iron coated bottom ash in low pH environment does not allow arsenic to leach out. However, very high pH conditions (≈ 11) can cause leaching of

arsenic from the sludge. Both arsenic and cadmium contents in raw wastes and leachates are within the guideline practice for surface disposal according to USEPA (1995). However, depending upon the proposed disposal methods these guidelines can vary.

The existing prototype should be revised for better maintenance. Specially, the mixing tank should be conical based so as to allow the cleaning of settled sludge more easily. A periodic maintenance of the electric motor should be performed.

CHAPTER – 6

CONCLUSIONS

6.1 CONCLUSIONS

Arsenic occurrence in groundwater has been a major concern in Bangladesh. Although arsenic contamination of water sources has been reported from a number of countries, the contamination scenario in Bangladesh and in the West Bengal State of India appears to be the worst detected so far world-wide, both in terms of area and population affected. Arsenic pollution in groundwater is particularly challenging in Bangladesh since tube well water extracted from shallow aquifers is the major source of drinking water for most of its population. According to BGS/DPHE (2001) arsenic concentration exceeding the Bangladesh standard of 50 µg/L was detected in 53 out of 61 districts, and in 249 upazillas out of 433 sampled upazillas.

A variety of treatment technologies like co-precipitation, adsorption, ion exchange and membrane process have been demonstrated to be effective in removing arsenic from contaminated natural groundwater. Several sorptive media have been reported to remove arsenic from water in India and Bangladesh. These are activated alumina, activated carbon, iron and manganese coated sand, kaolinite clay, hydrated ferric oxide, activated bauxite, titanium oxide, silicium oxide and many natural and synthetic media. Arsenic removal using iron-coated bottom ash (ICBA) is a novel process of removing arsenic from water. This process is based on using fine particles of coal bottom ash that have been coated with iron oxide. “Bottom Ash” is the ash left at the bottom of a coal-fired boiler after the combustible matter in coal has been burnt off. Arsenic removal using iron-coated bottom ash has proven effective at removing high concentrations of arsenic from drinking water in Bangladesh (Mathieu et al., 2008).

The appropriate scale of this new technology proposed by Mathieu (2008) is a community scale system maintained by a trained technician, because of the convenience in terms of individual time spent in using and maintaining the system, over household filters. Therefore, the present research work commenced with the following objective:

1. Development of an arsenic removal unit for use in a community.
2. Assessment of the performance of Iron-Coated Bottom Ash in treating arsenic laden water in the laboratory.
3. Assessment of the community-scale water treatment unit using Iron-Coated Bottom Ash in removing As, Mn and Fe from groundwater under different environmental conditions such as presence of phosphate, silica, pH, DO, temperature, alkalinity, conductivity etc.

The conclusions from this study are summarized below:

- a) For an initial arsenic concentration of 500 $\mu\text{g/L}$, ICBA dosage of 4 g/L produces good arsenic removal and hence this dose has been selected for subsequent experiments with arsenic laden water. The optimum coagulant dose under the experimental condition was fixed to be 0.2482 g/L.
- b) ICBA seems to work better for the pH level 5.71~8.78 for synthetic groundwater samples. The higher the initial pH, the higher is the arsenic removal.
- c) Low phosphate concentrations seem to help increasing the arsenic removal. No exact reason for this anomaly can be found. But, the higher the concentration of PO_4^{3-} , the higher is the interference with arsenic adsorption. However, the threshold phosphate concentration helping the arsenic removal was not determined. Further investigations are necessary to better understand the mechanism of phosphate with arsenic adsorption using ICBA.

- d) The performance of the prototype also varies with the flow rate. It is observed that the nearer the flow rate is to 100 L/hr, the better is the performance.
- e) The lower the initial arsenic concentration (around 200 $\mu\text{g/L}$), the better is the performance of the prototype in reducing arsenic concentration in the treated water below 50 $\mu\text{g/L}$ after chlorination.
- f) Performance of this unit in removing inevitable bacteriological contamination is enhanced when there is low level of contamination. For higher TC/FC, it takes around eight days to attain the required bacteriological quality of water. Thus, it is imperative that this unit be used properly to prevent bacteriological contamination.
- g) Presence of high iron concentration in groundwater leads to presence of iron-related bacteria. These bacteria can change the performance of iron-coated bottom ash by attacking at the adsorptive bond of ICBA with arsenic, iron and manganese. During the study it was found that the number of Iron- Related Bacteria (IRB) population is as high as 1,40,000 cfu/ml in the initial groundwater. This number can be reduced to 9000 cfu/ml after treatment with ICBA and chlorination dose of 1.55 mg/L, but cannot be completely removed within a reasonable time.
- h) Arsenic sludge from iron coated bottom ash in low pH environment does not allow arsenic to leach out. However, very high pH conditions (≈ 11) can cause leaching of arsenic from the sludge.
- i) Both arsenic and cadmium contents in raw wastes and leachates are within the guideline practice for surface disposal according to USEPA (1995). However, the guidelines can vary according to the proposed disposal methods.

6.2 LIMITATIONS OF THE STUDY

Several limitations experienced by this study are as follows:

- a) Maintenance of the flow rate (around 100 Liters per hour) with the low tech valve is not always possible. The rate of flow of water may vary from 80 Liters per hour to 500 Liters per hour.

- b) Chlorination using manual mixing has been performed while running different batches. However, a mechanical mixing should have been adopted.
- c) Acceptability of this prototype system to the community could not be ascertained as the prototype has not been installed in the field for use of the community.

6.3 RECOMMENDATIONS

While this research has advanced the knowledge of using iron coated bottom ash for arsenic removal, there are several points which may be investigated in future:

- a) Installation of a low flow valve for better maintenance of the flow rate.
- b) Use of a filtration unit before chlorination to improve the efficiency of chlorination as well as to achieve better final water quality.
- c) A modification in the design of the prototype system can be carried out by making the bottom of the mixing tank somewhat conical to improve the cleaning process.
- d) Considering the final water quality of the treated water, the chlorine dose which can be applied to accelerate the attainment of bacteriological quality of treated water for high initial TC/FC can be investigated. The extent of removal of iron related bacteria with the help of this chlorination can also be investigated. However, care must be taken to assess the organic content in the treated water to avoid the formation of trihalomethanes (THMs).

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APPENDIX A

Results from Batch Experiments

Batch A: Performed on 22/11/2008; ICBA addition rate: 4 g/L; Coagulant rate: 0.1241 g/L; Flow rate: Clarifier did not overflow.

Parameters	Initial	After treatment with ICBA						
		1 Hr	2 Hrs	3 Hrs	4 Hrs	6 Hrs	18 Hrs	24 Hrs
Sample ID	A-I	A-1	A-2	A-3	A-4	A-6	A-18	A-24
pH	7.21	7.6	7.38	7.64	7.44	7.75	7.8	7.77
DO (mg/L)	1.12	0.29	0.32	0.59	0.58	3.12	3.68	3.73
Conductivity (μ S/cm)	764	735	743	740	738	735	733	731
PO ₄ ³⁻ (mg/L)	4.118	1.06	0.265	0.222	1.132	0.484	0.416	0.334
SiO ₂ (mg/L)	32.1	35.8	47.2	57.7	43.9	42.2	52.9	49.7
Mn (mg/L)	0.15	0.146	0.056	0.067	0.068	0.061	0.049	0.042
Total As (ppb)	399.73	48.74	62.16	16.18	24.8	33.42	28.16	1.75
Fe (total), mg/L	5	1.5	0	2	3	3	2	0
TC (Membrane Filter Method)	32							20
FC (Membrane Filter Method)	8							0
Alkalinity (mg/L as CaCO ₃)	360	290	270	280	278	305	336	340

Batch B: Performed on 03/01/2009; ICBA: 4 g/L, Coagulant: 0.2482 g/L; Flow rate: 329L/hr; Chlorine dose: 2mg/L, Bleaching powder was used.

Parameters	After treatment with ICBA								Disinfection			
	Initial	1 hr	2 hrs	3 hrs	4 hrs	6 hrs	23 hrs	24 hrs	0 hr	1.5 hrs	5.5 hrs	24 hrs
Sample ID	B-I	B-BC-1	B-BC-2	B-BC-3	B-BC-4	B-BC-6	B-BC-23	B-BC-24	B-AC-I	B-AC-1.5	B-AC-5.5	B-AC-24
pH	6.83	7.74	7.74	7.74	7.76	7.78	7.91	7.89		8.02	8.02	8.14
DO (mg/L)	1.35	6.24	6.07	6	6.01	6.11	6.4	6.5		6.32	6.2	6.39
Conductivity (μS/cm)	690	736	743	746	749	749	750	749		728	735	735
PO ₄ ³⁻ (mg/L)	5.802	0.409	0.352	0.314	0.321	0.429	0.346	0.319	0.943	0.405	0.347	0.453
SiO ₂ (mg/L)	35.5	54.5	61.9	68.4	62.2	62.4	58.6	63.3	64.9	65.1	66.9	64.2
Mn (mg/L)	0.125	0.061	0.044	0.057	0.038	0.051	0.062	0.068	0.09	0.08	0.063	0.053
Total As (ppb)	255	75.67	68.08	75.92	71.12	73.14	67.7	51.06	56.31	41.64	58.91	60.87
Fe (total), mg/L	6	2.4	1.8	1.4	1.2	0.8	0.4	0.2	1	0.4	0.4	1.04
TC (Membrane Filter Method)	36							30				28
FC (Membrane Filter Method)	18							14				12
Alkalinity (mg/L as CaCO ₃)	370	316	322	318	316	327	334	327	311	313	308	319
Total Chlorine (mg/L)	0.04	0.05	0.05	0.05	0	0	0	0.02	0.04	0.06	0	0
Temperature (°C)	24.4	21.4	21.4	21.2	21.2	20.8	19.7	19	21.9	21.9	21.8	21.8

Batch C: Performed on 15/04/2009; ICBA rate: 4g/L; Coagulant rate: 0.2482 g/L; Flow rate of set 1: 80 L/hr and of set 2: 120 L/hr; Chlorine dose: 1.55 mg/L, Sodium hypochlorite solution was used.

Clarifier top (after treatment with ICBA)									
Parameters	Initial	1.5 Hr	2.5 Hrs	3.5 Hrs	5.5 Hrs	21.5 Hrs	71 Hrs	72.5 Hrs	74.67 Hrs
Sample ID	C-I	C-BC-1.5	C-BC-2.5	C-BC-3.5	C-BC-5.5	C-BC-21.5	C-BC-71	C-BC-72.5	C-BC-74.67
pH	6.72	7.57	7.54	7.57	7.58	7.64	7.65	7.42	7.49
DO (mg/L)	0.76	4.6	4.66	4.74	4.9	4.97	4.21	4.89	4.87
Conductivity (μ S/cm)	675	728	732	718	718	722	725	736	734
Turbidity (NTU)	29.3	7.45	4.08	4.38	4.49	8.16	3.03	63.5	28
Phosphate	5.62	0.929	0.539	0.626	0.625	0.484	0.476	1.175	0.413
SiO ₂ (mg/L)	33.4	41	45.5	44.2	39.7	41.1	41.2	48.7	32.6
Mn (mg/L)	0.124	0.062	0.05	0.049	0.046	0.058	0.042	0.067	0.051
Total As (ppb)	190.27	62.12	51.66	65.2	60.28	60.38	31.54	0	0
Fe (total), mg/L	5.62	1.68	1.09	1.21	0.44	0.52	0.19	1.26	0
TC (Membrane Filter Method)	50								
FC (Membrane Filter Method)	35								
Alkalinity (mg/L as CaCO ₃)	410	357	353	355	352	346	337	345	374
Temperature (°C)	27	30	30.5	30.5	30.3	30.1	29.7	29.6	29.7
Free Chlorine (mg/L)	0	0.03	0						
Total Chlorine (mg/L)	0.75	0.08	0.02	0.01	0.07	0.06	0.05	0.02	0

Parameters	Samples from the bottom of the collection reservoir (after chlorination)				
	5.5 Hrs (1 st chlorination point)	21.5 Hrs	24 Hrs	74.67 Hrs (after 2 nd chlorination)	95.5 Hrs
Sample ID	C-AC-5.5	C-AC-21.5	C-AC-24	C-AC-74.67	C-AC-95.5
pH	8.03	8.14	8.14	7.99	7.51
DO (mg/L)	5.33	5.62	5.55	5.33	4.29
Conductivity (μ S/cm)	736	757	727	782	736
Turbidity (NTU)	6.59	4.11	4.38	13.5	9.99
Phosphate	0.502	0.498	0.57	0.634	0.978
SiO ₂ (mg/L)	45.9	44.6	49	42.6	42.5
Mn (mg/L)	0.091	0.072	0.061	0.041	0.051
Total As (ppb)	38.42	32.37	26.42	34.11	4.25
Fe (total), mg/L	0.35	0.18	0	0.23	0.71
TC (Membrane Filter Method)	26 : Nil (after 1 st chlorination)			16	Nil
FC (Membrane Filter Method)	20 : Nil (after 1 st chlorination)			12	Nil
Alkalinity (mg/L as CaCO ₃)	313	320	316	345	357
Temperature (°C)	30.2	30	28.8	29.5	31.7
Total Chlorine (mg/L)	0.01	0.01	0.76	2.18	0.01

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APPENDIX B

Sludge Analysis Results

Table 5.1 Pond Water Properties

DO, mg/L	4.39
pH	8.12
Temp, °C	28.2
EC, μ S/cm	393
Alkalinity, mg/L as CaCO_3	135
Hardness, mg/L as CaCO_3	122
Silica, mg/L	15.7
PO_4 , mg/L	0.094
Manganese, mg/L	0.073
Turbidity, NTU	7.78

Table 5.2 Determination of Percent Dry Solids (Pre-evaluation of TCLP)

Percent Solids	Trip 3 15/4/2009 (grams)	Trip 4 12/5/2009 (grams)
Wt. of the beaker	71.9812	89.0136
Wt. of beaker & funnel	92.9273	109.9652
Wt. of beaker, funnel & filter paper	99.0716	116.2374
Wt. of beaker, funnel, filter paper & sample	249.0232	220.9366
Wt. of beaker & filtrate	173.6581	142.2413
Wt. of waste filtered	149.9516	104.6992
After drying 24 hours in oven,		
Filter + dry sample	14.3243	22.005
Funnel	20.9461	20.9516
Filter paper	6.1443	6.2722
Filtrate	101.6769	53.2277
Dry sample	8.18	15.7328
% dry solids	5.46	15.03

Table 5.3 TCLP Data Sheet - Batch C

Serial No.	1	2	3
TCLP Extract ID	3E	3D	3P
Location	Sreenagar, Munshiganj	Sreenagar, Munshiganj	Sreenagar, Munshiganj
Type of Sample	Solid	Solid	Solid
Extraction Fluid	Extraction Fluid #1	Distilled Water	Pond Water
Time of Rotation (hrs)	18	18	18
Raw Sample	Sample Wt. (gm)	5	
	Adjusted Vol.	500	
	As Conc. (ppb)	511.6	
	As Conc. (mg/kg of dry waste)	20.46	
TCLP Extract	Sample Wt. (gm)	25	
	Adjusted Vol.	1000	
	As Conc. (ppb)	0	3.18
	As Conc. (mg/kg of dry waste)	0	0.13
			3.67
			0.15

Table 5.4 TCLP Data Sheet – Batch D

Serial No.	1	2	3
TCLP Extract ID	4E	4D	4P
Location	Srinagar, Munshiganj	Srinagar, Munshiganj	Srinagar, Munshiganj
Type of Sample	Solid	Solid	Solid
Extraction Fluid	Extraction Fluid #1	Distilled Water	Pond Water
Time of Rotation (hrs)	18	18	18
Sample Wt. (gm)	5		
Adjusted Vol.	500		
As Conc. (ppb)	485.27		
As Conc. (mg/kg of waste)	19.41		
Cadmium (mg/L)	0.003		
Cadmium (mg/kg of waste)	0.12		
Sample Wt. (gm)	25		
Adjusted Vol.	1000		
As Conc. (ppb)	9.08	15.48	2.56
As Conc. (mg/kg of waste)	0.36	0.62	0.10
Cadmium (mg/L)	0.002	0.003	0.002
Cadmium (mg/kg of waste)	0.08	0.12	0.08

