ARSENIC IN THE GROUNDWATER OF MAJULI- THE LARGEST RIVER ISLAND OF THE BRAHMAPUTRA: PREVALENCE, EXPOSURE IMPACTS AND REMOVAL USING A NOVEL NANO ADSORBENT

**A thesis submitted in partial fulfillment of the
requirements for award of the degree of
Doctor of Philosophy**

By

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DEDICATED TO

MY PARENTS AND MAJULIANS

Abstract

Arsenic has recently become a matter of great concern due to the increased knowledge of its toxicological and carcinogenic effects on human health, causing the guideline value to be lowered from 100 μg/L to 50 μg/L and further to 10 μg/L by WHO (World Health Organization). As the source of arsenic is the Himalayan mountain and the Tibet Plateau, the flood plains of all the rivers that originated from those sources are expected to be arsenic contaminated. It is anticipated that, the groundwater As contamination is from the deposition of newer alluvium (Holocene) sediment. Groundwater of Majuli island in Assam on this basis is expected to be arsenic contaminated. Therefore, in the present study an attempt has been made to gain an understanding about the As contamination status and the health risk of the people in Majuli- the largest river island of the Brahmaputra, Assam by investigating the water and sediment chemistry as well as the urine, hair and nail of the people who are drinking arsenic contaminated water. The subsequent removal study of arsenic from highly contaminated water of Majuli island has also been undertaken in the study.

In the present study, surveys have been conducted in Majuli to understand the magnitude of contamination. Total 380 tube-well water samples were analyzed for arsenic (by FI-HG-AAS). Of the total groundwater samples analyzed, 37.6 % of samples exceeded 10 μg/L (WHO limit), 14% contained >50 μg/L (maximum arsenic concentration recorded was 468 μg/L). The relation between the depth of the tubewell and arsenic concentration has also been studied. Depth information of 303 tubewells from the Majuli island out of 380 analyzed samples, 77% of those tubewells are shallow tubewells in the depth range up to 15 m and it appears that in the Majuli island arsenic concentration gradually decreased beyond 25 m depth with few exceptions. Tube-well water samples were also analyzed for iron (n=319) and found elevated iron content (minimum=36 μg/L and maximum=22000). The correlation between iron and arsenic is poor (r = 0.23).

Bore hole sediment samples were collected from different depths during tube well installation at 7 locations. Sediment samples were digested for arsenic analysis using microwave digestion technique and measured by FI-HG-AAS. The arsenic concentration

ranged from 0.36 mg/Kg to 1.44 mg/Kg. The arsenic concentration did not show any correlation with depth.

To know the present arsenic body burden to population in Majuli 114 biological samples (40 hair, 33 nail, and 41 urine) have been collected and analyzed from the arsenic affected villages. The arsenic concentrations of urine (max = 697.5 μg/l), hair (max = 5461 μg/kg) and nail (max = 11725 μg/kg) correlated significantly, with drinking water arsenic concentrations.

Increasingly stringent legislation on the permissible concentrations of arsenic in drinking water has led to increased investigations of the removal of arsenic from drinking water. Hence, this study also addresses the water treatment approach and focuses on developing a novel arsenic removal technology that uses the surface functionalized ultrafine iron oxide nanoparticles as a new sorbent. The experiments carried out during this study address the removal of both arsenate and arsenite using surface functionalized ultrafine iron oxide nanoparticles developed through a gentle chemistry route. The nanoparticles are used under a wide range of experimental conditions and it is found that surface functionalized ultrafine iron oxide nanoparticles can absolutely remove arsenic from arsenic contaminated water. The efficiency of arsenic removal has been drastically improved by considering nanoparticles of size 10 nm and subsequent surface engineering of the nanoparticles resulting more adsorption sites being exposed to arsenic. The mechanism for adsorption was identified through electron microscopic and spectroscopic studies. The removal of As from water (synthetic water and natural groundwater) using surface functionalized ultrafine iron oxide nanoparticles is sensitive to several parameters tested, including pH, contact time, adsorbent dosage, initial arsenic concentration and the source water composition. The mechanism for high adsorption efficiency is attributed to surface conjugation of functionalized ultrafine Fe_2O_3 nanoparticles with arsenic. Equilibrium isotherms and the adsorption kinetics of arsenic onto the surface functionalized ultrafine iron oxide nanoparticles were studied experimentally for both the natural groundwater and the artificial model water in a batch system. The resulting isotherms were fitted using the Langmuir and Freundlich models and the parameters of the equation were determined. Simplified models such as pseudo-first order and pseudo-second-order models were applied to study the kinetics of adsorption.

Finally, the simultaneous separation of arsenic sorbed nanoparticles was ensured by entrapping them in hydrophilic calcium alginate beads and thereby a pure arsenic free solution has been obtained.

DECLARATION BY THE CANDIDATE

The thesis entitled " **Arsenic in the Groundwater of Majuli- The Largest River Island of The Brahmaputra: Prevalence, Exposure Impacts and Removal using a Novel Nano Adsorbent"** is being submitted to the Tezpur University in partial fulfillment for the award of the degree of Doctor of Philosophy in Environmental Science is a record of bonafide research work accomplished by me under the supervision of Dr. Kali Prasad Sarma, Professor, Dept. of Environmental Science, Tezpur University and Dr. Pritam Deb, Co-supervisor, Associate Professor, Dept. of Physics, Tezpur University.

All helps received from various sources have been duly acknowledged.

No part of this thesis has been submitted elsewhere for award of any other degree.

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All helps received by her from various sources have been duly acknowledged.

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Abbreviations used in the thesis

MCL	Maximum Contaminant Level
BIS	Bureau of Indian Standards
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
GMB	Ganga- Meghna- Brahmaputra
GPMB	Ganga- Padma- Meghna- Brahmaputra
PHED	Public Health & Engineering Department
MMA	Monomethyl Arsenate
DMA	Dimethyl Arsenate
GSH	Glutathione
HFO	Hydrous Ferric Oxide
GFH	Granular Ferric Hydroxide
NZVI	Nanoscale Zero Valent Iron
GP	Gaon Panchayat
BH	Borehole
UV- VIS	Ultraviolet- Visible Spectroscopy
ICP- MS	Inductively Coupled Plasma Mass Spectrocopy
ICP- OES	Inductively Coupled Plasma Optical Emission Spectroscopy
FI- HG- AAS	Flow Injection Hydride Generation Atomic Absorption Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy

NOTATIONS

C_e	Equilibrium concentration (mg/L)
X_m	Mass of solute adsorbed (g)
m	Mass of adsorbent (g)
K	Freundlich constant indicative of adsorption capacity of the adsorbent(L/mg)
K_f	Adsorption capacity
n	Adsorption intensity
K_1	Pseudo- first order rate constant (1/min)
K_2	Pseudo- second order rate constant (1/min)
q_e	amount of adsorbate at equilibrium (mg/g)
q_t	amount of adsorbate at any time t, (mg/g)
h	initial sorption rate
k_{id}	rate constant for intraparticle diffusion
R_L	Equilibrium parameter
r	Regression coefficient

CHAPTER ONE

1. Introduction

1.1 Background information and research significance

Arsenic (As) has been considered as a target contaminant because of its potential health and regulatory concerns. Due to the carcinogenic effects arsenic contamination of drinking water is a major health concern. Now a days, drinking water is recognized as the major source of arsenic in its most toxic form. However, recent studies indicate additional contamination of the food chain due to irrigation with arsenic contaminated groundwater (Roychowdhury et al. 2002, Chakraborti et al. 2004, Haris et al. 2005). Considering the negative health effects on human, WHO (1993) lowered the guideline value for As in drinking water from 50 µg/L to 10 µg/L. Many countries promulgated 10 µg/L as the maximum contamination level (MCL) in drinking water (US EPA 2000). However, India and Bangladesh still adopt 50 µg/L as the MCL for arsenic in drinking water. Reported incidences of health effects due to exposure to elevated arsenic concentrations from drinking water are available from many countries throughout the world. One of the well documented exposures to arsenic through groundwater is from Taiwan, where people suffered from characteristics symptoms of arsenicosis referred as Black foot disease as a result of drinking arsenic contaminated water for many years. But of these, the most severe outbreaks of arsenic poisoning have been reported from the Bengal Delta including Bangladesh and West Bengal (Eastern India) where millions of people are at risk (Bhattacharjee et al. 1997, Chowdhury et al., 2000). Arsenic contamination in the affected districts of the Bengal Delta is potentially the greatest environmental calamity ever reported (Guha et al. 1998, Karim 2000). Extensive arsenic pollution in groundwater in the Bengal Basin affects both eastern parts of the West Bengal, India and major parts of the Bangladesh (Mandal et al. 1996, Bhattacharya et al. 1997, Dhar et al. 1997, Nickson et al. 1998, Nordstorm et al. 2000). The affected aquifers in the Bengal Basin can be correlated with the Ganga- Brahmaputra holocene stratigraphy and delta sedimentation (Acharyya et al. 2000). Occurrence of arsenic in groundwater, in excess to the permissible limit of 50 µg/L (Indian guideline) in the Ganges-Brahmaputra fluvial plains in India is considered as the world's biggest natural groundwater calamity to the mankind after Bangladesh (Chakrabarti et al. 1999, 2001, 2003, 2004, 2008c).

Arsenic in groundwater has been reported, mostly in areas formed by recent alluvial sediments, describing Holocene aquifers (<12 thousand years of age) of the Ganga-Brahmaputra fluvial plains (Singh et al. 1996, Chakraborti et al. 2004, Nickson et al. 2007). Almost all the identified arsenic affected areas in Assam and Manipur are in the flood plains of the Brahmaputra and Barak, respectively (Singh et al. 2004, Chakraborti et al 2004). The Brahmaputra alluvial basin is bounded by lower Himalayan mountains in the north and northeast. High intensity of rainfall in the catchments and plain areas has contributed to high sediment loads, which have developed the valley into a long stretch of recent and old alluvium. Majuli island of the Brahmaputra river in Assam, India, comprises both older and younger alluvium as well as active flood plain deposits of recent age. The stratigraphy of the Majuli island is similar to the stratigraphy of the Brahmaputra Valley on the southern bank of the Brahmaputra as it comprises both older alluvium and newer alluvium at many places. Ironically, all the rivers in the Ganga-Meghna-Brahmaputra (GMB) flood plains that originated from the Himalayas are expected to be arsenic contaminated (Chakraborti et al. 2004). Keeping in mind these aspects a study has been carried out in the Majuli island to know the groundwater arsenic contamination status of this riverine island. The potential source of arsenic in the groundwater requires an understanding of the sediments. Therefore, it is felt necessary to study the borehole sediment samples of the island to find out the chemistry involved in leaching out of arsenic and the mode of occurrence and origin.

Arsenic is a tasteless, odourless and colourless element. The detection of the element is only possible through chemical analysis. Similarly, exposure to low levels of arsenic can not be detected visually since it takes more than 10 years for the common symptoms to develop. The most important biomarkers commonly used to identify or quantify arsenic exposure are total arsenic in hair or nails, and total or speciated metabolites of arsenic in urine. The elimination of arsenic via urine, its concentration in hair and nail acts as reliable indicators of internal exposure. Therefore, the most direct way of determining recent arsenic exposure is measuring its content in urine. However, the chronic arsenic exposure can be detected by measuring its concentration in hair and nails. Because arsenic has affinity for sulfhydryl groups and it accumulates in hair and nails comprising of high content of keratin (Shapiro 1976, ASTDR 1993, Mushak et al. 1995, Hakala et al. 1995, Kurttio et al. 1998). Additionally, it can give valuable information about the metabolism of arsenic species within the body. Thus, it is essential to quantify arsenic in the biological samples (urine, hair, and nail) to asses health risks associated with arsenic exposure.

The acute toxicity of arsenic poisoning can lead to rapid death, while chronic toxicity symptoms tend to appear only after several years of exposure (Smith et al. 2002). The most commonly observed symptoms of chronic arsenic poisoning are arsenical skin lesions (e.g. melanosis, keratosis), blackfoot disease, and in more severes cases, incidents of gangrene, skin cancer, and lung cancers and fetal death (Astolfi et al. 1981, Smith et al. 1992, Das et al. 1995, Karim 2000). The health effects of arsenic is a function of time of exposure and the most effective way to overcome the adverse health effects of arsenic is prevention of further exposure by providing safe drinking water. There is no effective treatment for arsenic toxicity. Due to the negative health effects of drinking arsenic contaminated water, more stringent standards have been introduced for arsenic. Therefore, the treatment of arsenic from drinking water has attracted growing interest. A lot of research has been carried out with the specific aim of developing cost-effective technology for the removal arsenic from water. Numerous investigations have examined the removal of arsenic from potable water through treatment processes such as precipitation-coagulation, reverse osmosis and ion exchange. The focus of research has now shifted to solve the problem using suitable sorbents to achieve low level of arsenic in drinking water for communities. Adsorption has emerged as one of the most practical methods because it can easily be used in small scale systems. Many researchers are looking into using iron oxides to remove arsenic from drinking water through adsorption by batch and column systems. Using iron oxides of nanosize creates an advantage over bulk iron oxides because of the increased surface area, which allows more sorption sites for removal. The mechanism for sorption of arsenic to nanoscale iron oxides can be understood by adsorption isotherms, surface complexation models, and spectroscopic studies.

1.2 Statement of the problem

Arsenic is a toxic metalloid found in the atmosphere, soils, rocks and water. It is mobilized in the environment due to both natural processes and anthropogenic activities. Naturally, arsenic is introduced into the groundwater through the dissolution of minerals and ores. Groundwater arsenic contamination has far reaching consequences including its ingestion through drinking water and food chain, which are in the form of health hazards. The acute toxicity of arsenic at high concentrations has been reported from many regions of the world including India. Long term exposure to arsenic even at low concentrations have adverse effects on human health. Extensive studies have been done on groundwater arsenic contamination throughout the world. However, limited studies have been carried out on groundwater arsenic contamination in North Eastern states of India. Many more places in North Eastern states are suspected to have possibility of arsenic in groundwater. Although groundwater has been monitored by the Public Health and Engineering Department (PHED), partly in collaboration with UNICEF, in Majuli, detailed finding are yet to be published. Therefore, a more systematic and detail study is needed to asses the magnitude of groundwater contamination in the world's largest populated river island.

Following the evidences of arsenic exposure through drinking water, remediation of this problem needs the development of the technology with improved materials and systems with high efficiency. Numerous studies have been carried out with the specific aim of developing a cost-effective eco-friendly technology for the removal arsenic from water. Many researchers have looked into the adsorption of arsenic onto iron oxides due to the strong affinity of arsenic to iron oxides. Though in recent times, some attempts were made to study the efficiency of arsenic removal from drinking water using nanoparticles, for the most part these methods are effective in removing arsenic from the drinking water, but some can be expensive due to separation techniques, or produce significant amounts of waste. However, arsenic removal methods so far used requires preoxidation of As(III) to As (V) and pH adjustment to enhance the removal efficiency. However, the reported studies have limitations in terms of high adsorbent doses, high contact time period and absolute removal efficiency. These disadvantages are what continue to make developing a new improved method for arsenic removal from contaminated water. In the present research, an attempt has been made to develop a novel technology for removal of arsenic from drinking water.

1.3 Research objectives

1. To asses the groundwater arsenic contamination statues of Majuli island of Assam by analyzing the hand tubewell water samples.
2. To analyze the groundwater samples for iron and other heavy metals and to find out their correlation with arsenic.
3. To explore and identify the possible sources of arsenic contamination of the study area by analyzing the borehole sediment samples.
4. To analyze arsenic and other heavy metals in the borehole sediment samples and to find out the correlation of arsenic with other heavy metals.
5. To measure the total arsenic concentration in biological samples (hair, nail and urine) of arsenic exposed population of different age group.
6. To develop a surface functionalized ultrafine iron oxide nanoparticles and its application for removal of arsenic from artificially prepared model water and natural groundwater.
7. Separation of spent and excess adsorbents from treated water.
8. To find out probable arsenic mitigation option in the arsenic affected areas of Majuli.

CHAPTER TWO

2. Literature review

2.1 Arsenic: Occurences, sources and properites

2.1.1 Occurrence of arsenic in the environment

Arsenic is the twentieth most abundant element in the earth's crust. In natural environment it co-exists with other metals as sulfide or oxide ores. Arsenic naturally occurs in a wide range of minerals in soils in several forms of inorganic compounds. Over 200 minerals contain arsenic mostly in the form of arsenic sulfides and oxides. The highest concentration of these minerals occurs in mineralized areas with an association to various transition metals. The principal minerals are arsenopyrite, nicolite, cobaltite, tennantite, and enargite (Bhattacharya et al. 2002). The most common arsenic-containing minerals are arsenopyrite or mispickel (FeAsS), realgar (AsS), lollingite ($FeAs_2$, $FeAs_3$, and $FeAs_5$) and orpiment (As_2S_3). These minerals are usually associated with sulfide ores or other metal ores and act as a major starting point for the introduction of arsenic into the environment. Arsenic and its compounds occur in crystalline, powder, and amorphous or vitreous forms. It usually occurs in trace quantities in all rock, soil, water and air.

Arsenic can form alloys with many other metals and covalent bonds with carbon, hydrogen, oxygen, and sulfur (Tamaki et al. 1992). The four arsenic species commonly reported are arsenite [As(III)], arsenate [As(V)], monomethylarsonate (MMA) and dimethylarsinate (DMA). The inorganic forms (As^{3+} and As^{5+}) are mainly present in groundwater and in oxidizing condition As^{5+} is predominant species and in reducing condition as As^{3+} is the predominant species.

Arsenic (As) is a ubiquitous element found in the atmosphere, natural waters, soil, rocks, and organisms exhibiting both metallic and nonmetallic properties. Arsenic chemistry is associated with sulfide chemistry, that is why arsenic concentration is high in sulfide minerals. The presence of pyrite in the sediments of many rivers, lakes, oceans, and aquifers make arsenic available for release into the environment. Pyrite is stable under reducing conditions, but if exposed to aerobic situation it oxidizes and forms iron oxides that release arsenic (Bauer et al. 2006). Arsenic is known to adsorb strongly to iron oxides and other metal oxides, such as aluminum and manganese; therefore, arsenic can be taken up again by metal oxides depending on the environmental conditions. If reducing conditions occur when arsenic is sorbed to metal oxides, then the metal oxide redox chemistry is changed, allowing for mobility of arsenic into the water bodies (Ferguson et al. 1972, Smedley 2002). Anthropogenic sources of arsenic come from mining, wood preservation chemicals, feed additives for livestock, some herbicides and pesticides, and combustion of fossil fuels (Smeldy 2002, Nicholson et al. 2003, Wolz et al. 2003).

2.1.2 Sources of arsenic

The primary natural sources of arsenic are weathering of rocks, geothermal activity, and volcanic activity, rocks being major reservoirs of arsenic. Leaching of ambient arsenic in groundwater from sediment, igneous or metamorphic rocks contain arsenic bearing minerals.

Arsenic is also a by product of some anthropogenic activities including mining; smelting; petroleum refining; manufacture of semiconductors, glass and various pharmaceutical substances; combustion of fossil fuels and wastes; pulp and paper production; pesticides; landfill leaching; and wood preservation.

Arsenic is released into groundwater or surface water through erosion, dissolution and weathering. Groundwater contamination by arsenic is often a natural phenomenon attributed to subsurface sediments containing small amounts of arsenic. The sediments of alluvial deltas originate from the mountains in the upstream river catchments and have been deposited during thousands of years (Tanabe et al. 2006). Mountain erosion leads to a release of rock-forming minerals and arsenic into the hydrosphere. Eroded iron turns to rust, iron(hydr)oxide, and forms particles as well as coatings on the surface of particles such as silt and sand. These iron(hydr)oxides are capable of scavenging dissolved arsenic from water and binding it to its surface (Manning et al. 1997). Suspended particles with iron(hydr)oxide coatings and adsorbed arsenic are washed into rivers and transported downstream.

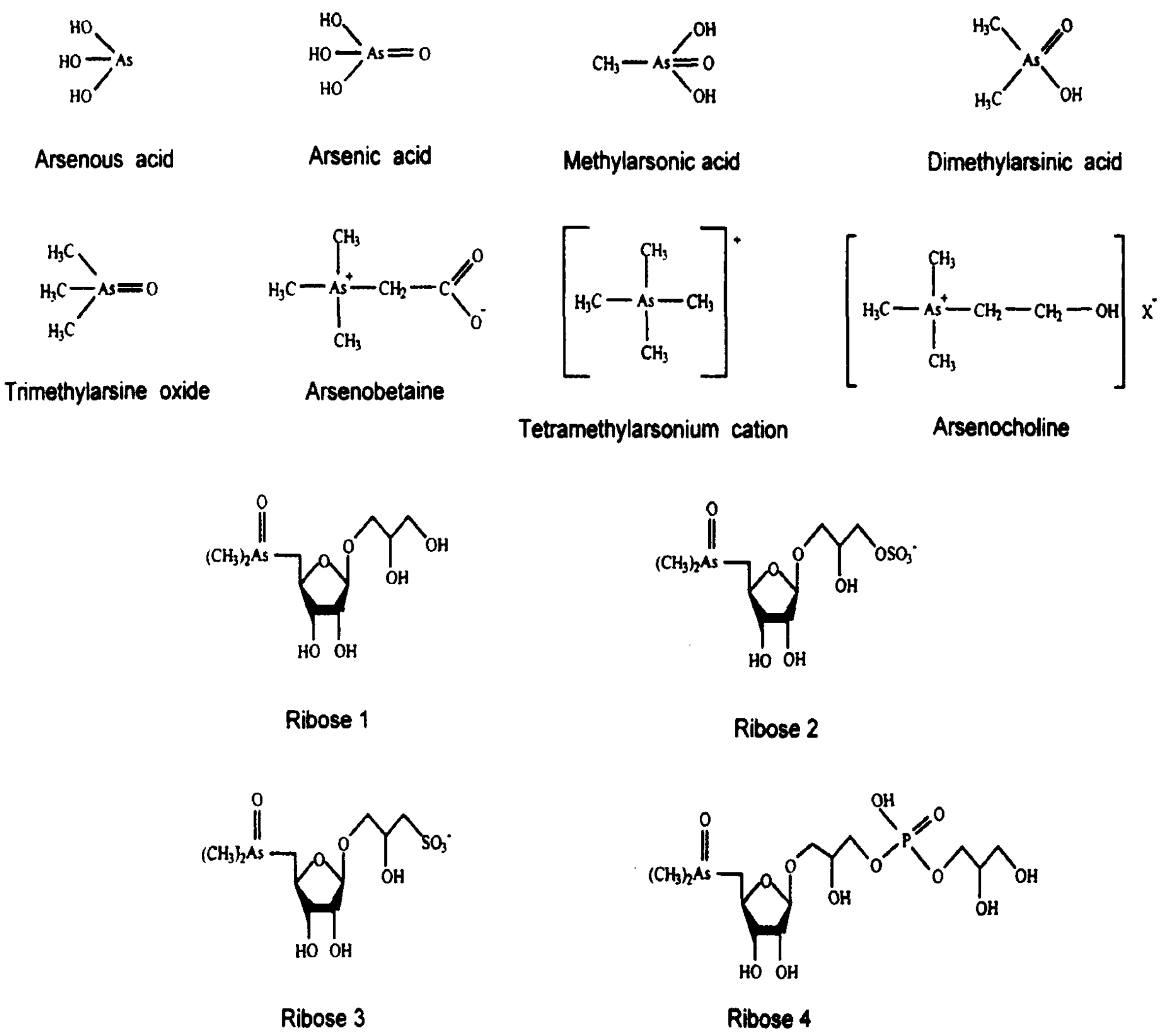
2.1.3 Chemical and physical properties of arsenic compounds

Arsenic (symbol As) with the atomic number 33 and atomic weight 74.9216 is placed in group VA of the periodic table. Arsenic and its compounds occur in crystalline, powder, and amorphous or vitreous forms. Elemental arsenic is insoluble in water. Arsenical salts exhibit a wide range of solubility depending on pH and the ionic environment. It is a component of more than 245 minerals and associated with igneous and sedimentary rocks (Murdoch and Clair 1986). Arsenic is a redox and pH sensitive element. Its occurrence, distribution, mobility and forms are dependent on pH, redox potential (Eh), and microbial activity (Wang and Mulligan, 2006). Elemental forms of arsenic occurs very rarely. Arsenate ions [As(V)] are most prevalent in oxic conditions whereas arsenite ions [As(III)] are found in anaerobic conditions.

The bioavailability and toxicity of arsenic is dependent on its chemical form. In general, the inorganic forms of arsenic are much more toxic than the organic arsenic forms. However, it has been reported that some of the organic arsenic species like MMA (III), DMA(III), which have been identified in urine are very toxic. Structures of some naturally occurring inorganic and organic arsenic species are shown in **Fig 1.1.**

2.2 Arsenic toxicity

Arsenic is of environmental concern due to its toxicity and carcinogenity (Agency for Toxic Substances and Disease Registry, 1999). Toxicology of arsenic is a complex subject, depends on arsenic species and chemical form. The toxicity of arsenite is 25-60 times higher than that of arsenate. The toxicity of arsenic decreases in the following order: arsines> arsenites [inorganic As(III)]> arsenoxides [organic As(III)]> arsenates [inorganic As(V)]> arsonium compounds > metallic arsenic (Hindmarsh et al. 1986, Subramanian 1988). Even though inorganic arsenic is more toxic than organic, but as far as chronic toxicity is concerned they are equally toxic. Trivalent arsenic is more toxic than pentavalent arsenic because it can bind strongly to sulfur groups in amino acids, the building blocks of protein. Sulfur containing amino acids include methionine, cysteine, and cystine. MMA & DMA (Organic arsenic compounds) are less toxic than inorganic arsenic, but some animal studies showed that MMA (III) is more toxic than inorganic arsenic (Aposhian et al. 1999). Arsenic toxicity may be classified into two types: (i) Acute and (ii) Chronic.



Arsenous acid

Arsenic acid

Methylarsonic acid

Dimethylarsinic acid

Trimethylarsine oxide

Arsenobetaine

Tetramethylarsonium cation

Arsenocholine

Ribose 1

Ribose 2

Ribose 3

Ribose 4

Fig 1.1 Structures of arsenic compounds

2.3 Arsenic speciation and distribution in natural water

Arsenic undergoes oxidation-reduction, ligand exchange, precipitation, and adsorption reactions in aquatic systems(Ferguson et al. 1972). In aqueous solutions, arsenic can occur in several oxidation states (-III, 0, III and V), with III and V being the most important states. The ratio of As(III) to As(V) varies in groundwater (WHO 2001). Speciation of As in natural water is a function of pH, redox potential (Eh), and microbial activity; in the pH range of most natural waters (i.e. pH 6-8), As(V) exists as a monovalent ($H_2AsO_4^-$) or divalent ($HAsO_4^{2-}$) anion, and arsenite is fully protonated and exists almost exclusively as an uncharged molecule (H_3AsO_3) (Wang and Mulligan, 2006). Redox conditions are important in influencing the speciation of As. At the high Eh values normally encountered in oxygenated waters, all four forms of the arsenic acid species are stable, whereas the arsenous acid species become stable at Eh values characteristic of mildly reducing conditions (Ferguson and Gavis, 1972). Microbial reactions may also alter As speciation (Islam, et al. 2004). Studies have shown that *Dunaliella sp*, takes up As(V) and readily reduces it to As(III) (Newman et al 1998, Islam et al. 2004).

Depending on the source of arsenic and the local geochemical environment concentrations of arsenic in natural water vary by several orders of magnitude. In most cases inorganic arsenic found in groundwater is of geological original. Arsenic concentration in ground or surface water vary from 0.01 to more than 500,000 µg/L depending on the physical and hydrogeological environment (Smedley and Kinniburgh, 2002). The baseline concentrations of arsenic in rain water is less than 0.03 µg/L (Andreae,1977). The baseline concentration of arsenic in river waters are also low in the range of 0.1-0.8 µg/L (Smedley et al. 2002). The concentration vary according to the composition of the surface recharge, the contribution of base flow and the bedrock lithology. Increased arsenic concentrations in river water can occur as a result of geothermal sources or high arsenic groundwater (Welch et al. 1988). Under natural conditions, the largest range and the highest concentrations of arsenic are found in groundwater. Higher concentrations of arsenic in groundwater are found in a variety of environments including oxidizing and reducing aquifers and in areas affected by geothermal, industrial and mining activities. Mostly the high concentration of arsenic in groundwater are the result of natural occurrences of arsenic. The most noteworthy occurrences are in parts of Argentina, Bangladesh, Chile, northern China, Hungary, India, Mexico, Romania, Taiwan and the south-west United States (Guo et al. 1994, Hopenhayn- Rich et al. 1996, Smith et al. 1998, Wyatt et al. 1998, Sun et al.1999, Gurzau et al. 2001, Bhattacharya et al. 2002, Mandal & Suzuki 2002, Smedley et al., 2002, Rahman et al. 2006, Mukherjee et al. 2006, Smedley & Kinniburgh 2002) .

2.4 Arsenic sorption/ desorption to soils and sediments

The mobilization of arsenic in natural environment is closely related to its interaction with sediments (Subramanian, et al. 1993; Harvey et al. 2002, Meharg et al. 2006). The major minerals binding arsenic in sediments are the metal oxides, particularly those of iron, aluminum and manganese. Clays can also bind arsenic due to its oxide-like character (Stuben et al. 2003; Mc.Arthur et al. 2004; Zheng et al. 2004). In the aquifer, the speciation and partitioning of arsenic between the aqueous phase and the solid mineral phase is affected by a number of competing chemical reactions. It is evidenced that arsenic is released from soils and sediments followed by the development of anoxic conditions (Wilson, et al. 1978; Azcue and Nriagu, 1995; Manning and Goldberg, 1997a; McArthur, et al. 2004). A number of factors such as pH, Eh as well as type of adsorbing mineral/solid can control the desorption and remobilization of arsenic from sediments (Schreiber, et al. 2000). The release of arsenic from sediments has long been associated with the dissolution of iron oxides (Horneman, et al. 2004). The reduction and dissolution of ferric arsenates leads to the release of arsenic is from the sediments (Deuel, et al.1972).

2.4.1 Dissolution of arsenic from anoxic sediments

Anoxic dissolution of iron(hydro)oxides is the most widely accepted geochemical theory on the presence of arsenic in groundwater. Generally, as long as the groundwater contains sufficient dissolved oxygen, the arsenic remains fixed in the sediments. However, arsenic is released from the sediments if it comes into contact with reduced groundwater conditions (Nickson et al. 2000, Smedley & Kinniburgh 2002, Harvey et al. 2002, Stuben et al. 2003, Mcarthur et al. 2004, Zheng et al. 2004, Meharg et al. 2006). During flood, high loads of river sediments covers the layers of the topsoil including its vegetation that results in the entrapment and subsequent burial of natural organic matter in the sediment. These organic matter can serve as substrate for microorganisms to survive. These microorganisms degrade the organic matter by consuming the dissolved oxygen thereby leading to the depletion of oxygen (reducing conditions) in the groundwater. Under reducing conditions, some microbes can use iron(hydro)oxides as the source of energy. Degradation of solid iron(hydro)oxide particles leads to the release of arsenic that remained attached firmly to the particle surface. Arsenic deposition with sediments in the delta region and dissolution under reducing conditions created by high levels of organic matter can hence lead to the high concentrations of dissolved arsenic in groundwater. These natural processes lead to arsenic contamination of groundwater, for example, the Bengal Delta (Bangladesh and West Bengal) (BGS & DPHE 2001, Nickson et al. 2000, Smedley & Kinniburgh 2002, Stuben et al. 2003).

2.5 Arsenic in drinking water

Of the various sources of arsenic in the environment, drinking water probably poses the greatest harm to human health. Drinking water is derived from a variety of sources depending on local availability: surface water (lakes, rivers, reservoirs and ponds), groundwater and rain water. The sources are variable in terms of arsenic risk. High concentrations of arsenic are mainly found in groundwaters. Worldwide arsenic is now recognized as the most serious inorganic contaminant in drinking water, and arsenic poisoning is a huge public health disaster in many developing countries. Following the accumulation of evidence for the chronic toxical effects of arsenic in drinking water, recommended and regulatory limits of many authorities are being reduced.

2.5.1 Arsenic standards in drinking water

Different countries have set different standards of arsenic content in drinking water. Since 1959, the World Health Organization (WHO) has been the primary authority in settling the international standards (allowable concentrations) for arsenic in drinking water. According to the last edition of the WHO (1993) guidelines for drinking water quality, the guideline value for arsenic in drinking water is less than 10 μg/L (WHO, 2004). The new guideline value was based on expanding awareness of the toxicity of arsenic, mainly its carcinogenicity; developing technology; and the use of advanced instruments that can measure the amount of arsenic more accurately. The Bureau of Indian Standards (BIS) also has notified a standard of 10 μg/L for arsenic in drinking water (BIS 2003). Given the other relative risks to life and health in India, and considering the difficulty in implementation of such a standard, the Rajiv Ghandi National Drinking Water Mission has instructed states to use 50 μg/L as the "maximum permissible limit" in the interim until the lower figure can be achieved (GOI 2004). Therefore, India has set its maximum permissible limit for arsenic to 50 μg/L.

2.6 Analytical methods for arsenic

In the past few decades, developing the technology for detecting arsenic in drinking water has become increasingly important due to the toxicity of arsenic. A variety of instrumental techniques including atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) are currently being used for the determination of arsenic in drinking water (Jain et al 2000). The US EPA currently accepts six methods for the analysis of arsenic in drinking water, which including ICP-MS; graphite furnace atomic absorption (GFAA); stabilized temperature platform graphite furnace atomic absorption (STP GFAA); electrothermal atomic absorption spectrometry (EAAS); manual hydride generation atomic absorption spectrometry; and hydride generation atomic absorption spectrometry (HG AAS) (US EPA 2003). ICP-MS is a very powerful tool for tracing extremely small amounts of elements. Now a days, this technique is in high demand for analysis of toxic elements owing to its precision and accuracy in measurement. ICP-MS can achieve the arsenic detection limit of less than 0.1 μg/L. ICP-MS has many advantages, which include a short analysis time, lower detection limits, and multianalyte capabilities. However, instrumentation is very expensive. In recent years, atomic absorption spectrometry (AAS) has become the method of choice, as it offers the possibility of selectivity and sensitivity in the detection of a wide range of metal and metalloids including arsenic. Popular methods for generating atoms for AAS are flame and electro-thermally heated graphite furnace. However, a commonly used technique for the measurement of arsenic is the highly sensitive hydride generation atomic absorption spectrometry (HG-AAS). To improve hydride generation technique, a flow infection system is coupled with hydride generation atomic absorption spectrometry. The flow injection hydride generation atomic absorption method is characterized by high efficiency, low sample volume, reagent consumption, improved tolerance of interference and rapid determination (Samanta et al. 1999).

2.7 Groundwater arsenic contamination incidences round the world

2.7.1 Arsenic contamination of groundwater: a global perspective

Arsenic contamination of groundwater sources has become a global concern. Earlier it was reported that elevated arsenic concentrations in groundwater occur in more than 20 countries worldwide (Naidu et al. 2006). For example, elevated arsnic concentrations are recorded in groundwater in Bangladesh, West Bengal (India), Inner Mongolia(China), Taiwan, Lao, Cambodia, Myanmar, Japan and Pakista (Naidu et al. 2006). However, according to recent groundwater arsenic contamination scenario 38 countries are arsenic affected **(Fig 2.1).**

Fig 2.1: Groundwater arsenic contamination situation round the world.

Before 2000, only five Asian countries were recognized of having groundwater arsenic contamination and these were Taiwan, China, West Bengal-India, Bangladesh and Thailand (Chakrabarti et al. 2002, 2004, Mukherjee et al. 2006). Millions were drinking water which contained much above the WHO guideline value (10 μg/L) of arsenic in it and thousands were suffering from arsenic related diseases. In recent years, 25 incidences generating from 13 countries in Asia are identified of having groundwater arsenic contamination and millions of people are exposed to highly toxic level of above 50 μg /L (WHO 2003, Chakrabarti et al. 2004).

2.7.2 Groundwater arsenic contamination in Ganga- Meghna- Brahmaputra (GMB) Plain

The Ganges–Brahmaputra river basin is the 13th largest river basin in the world, with an annual run-off of about 1400 billion m^3 and is home to old civilizations (Bandopadhyay et al. 2002). The Ganges River System (GRS) in North and eastern India, carries a high sediment bed load. The sediment bed load estimated at 1–2.4 billion tons per year discharges into the Bay of Bengal (Subramanian et al. 1993, Khan et al. 1994) thus making 6–16% of global annual sediment flux of about 15 billion tons (Milliman et al.1983). The Bengal Delta Plain (BDP) is drained by three important rivers – the Ganges, Meghna and Brahmaputra (GMB) – originating from the Himalayas and channelling suspended solids (1060 million tons), water (>1330 km^3) and dissolved particulates (173 million tons) to the Bay of Bengal (Milliman et al. 1995). The Bay of Bengal receives maximum amount of sediments from the GMB river system (Kuehl et al. 1989) containing several trace elements including arsenic.

Based on the study groundwater arsenic contamination in Ganga-Meghna-Brahmaputra (GMB) plain (area: 5,69,749 km^2, and population: over 500 million), it is predicted that a part of all the states in Ganga-Brahmaputra plain in India (Uttar Pradesh, Bihar, Jharkhand, West Bengal, Assam), Manipur & other North Eastern hill regions of India, Bangladesh in Padma-Meghna-Brahmaputraplain, and the Terai region of Nepal in Indo-Gangetic alluvial plain are arsenic affected (Chakraborti et al. 2004, Chakraborti et al. 2008a). Arsenic contamination in groundwater of India was first reported in 1976 from Chandigarh and different villages of Punjab, Haryana and Himachal Pradesh (Datta & Kaul 1976). In 1984 groundwater arsenic contamination in the lower Ganga Plain of West Bengal was first reported (Garai et al. 1984). Groundwater arsenic contamination in the Padma-Meghna-Brahmaputra (PMB) plain of Bangladesh was identified in 1992

(Dhar et al. 1997). During international conference held in 1995 the arsenic situation in West Bengal and consequent suffering of people came to limelight (SOES 1995). In 2001, it revealed that groundwater in the Terai region of Nepal was contaminated with arsenic (Shrestha et al. 2003). The contamination of groundwater with arsenic in Bihar lying in the middle Ganga plain and Uttar Pradesh lying in middle and upper Ganga plain was recorded in June 2002 (Chakraborti et al. 2003).

During the period of 2003-2004 arsenic contamination and its health effects have been discovered in Uttar Pradesh, Jharkhand, and Assam (Chakraborti et al. 2004). In 2007, groundwater contamination with arsenic was reported from the Manipur state, one of the seven North-Eastern Hill States (Chakrabarti et al. 2008c).

2.7.3 Present groundwater arsenic contamination status in India

Based on the surveys on groundwater arsenic contamination, it is predicted that a large portion of all the states in Ganga-Brahmaputra plain in India (West Bengal, Bihar, Uttar Pradesh, Jharkhand, Assam and Manipur) and Padma-Meghna-Brahmaputra plain in Bangladesh would be are arsenic affected (Chakraborti et al. 2008a). In these areas more than 100 million people and huge number of livestock are exposed to arsenic contaminated groundwater.

2.7.3.1 Northern India

In 1976, groundwater arsenic contamination was reported from Chandigarh and different villages of Punjab, Haryana, and Himachal Pradesh in Northern India (Datta et al. 1976). The maximum arsenic concentration was found as 545 µg/L. Studies (Datta et al., 1976) have reported high arsenic content in the liver of people who had been drinking arsenic contaminated water.

2.7.3.2 West Bengal

Groundwater arsenic contamination and its health effects in the lower Ganga Plain of West Bengal were first reported in 1984 (Garai et al. 1984). Several publications are available for the groundwater arsenic contamination and their related health effects in West Bengal (Garai et al. 1984, Saha & Poddar 1986, Chakraborty & Saha 1987, Guha

Mazumder et al. 1988, 1992, 2000, Das et al. 1996, Dhar et al. 1997, Chakraborti et al. 2002, 2004, 2009, Chowdhury et al. 2000, 2001, Rahman et al. 2001, 2003, 2005, 2005a, 2005b, 2005c, Mukherjee et al. 2005, Nickson et al. 2007). In last 20 years School of Environmental Studies (SOES), Jadavpur Universiy, analyzed 140150 hand tube-well water samples for arsenic in all 19 districts of West Bengal. Out of 140150 samples analyzed for arsenic till date, 48.1% had arsenic above 10 μg/L and 23.8% above 50 μg/L (Chakraborti et al. 2009). Importantly, 3.3% of the analyzed tubewells had arsenic concentrations above 300 μg/L, the concentration predicting overt arsenical skin lesions (Chowdhury et al. 2002). A total of 187 (0.13%) hand tube-wells were found highly contaminated (As>1000 μg/L). The maximum arsenic concentration (3700 μg/L) was found in South 24 Parganas district. This tubewell was a private one and the all the nine members of the owners' family had arsenical skin lesions and seven of them had already died who had sever arsenical skin lesions, five of them died within age range below 30 years. Based on the arsenic concentrations found in the 19 districts of West Bengal, SOES has classified them into three categories: Severely affected, mildly affected, and unaffected. Nine districts (Malda, Murshidabad, Nadia, North 24-Parganas, South 24-Parganas, Bardhaman, Howrah, Hoogly and Kolkata), where more than 300 μg/L arsenic concentrations were found in tubewells are categorized as severely affected. Based on the study, it is estimated that around 26 million people are potentially at risk of arsenic above 10 μg/L (Chakraborti et al. 2008a).

2.7.3.3 Bihar

Groundwater arsenic contamination in the Bhojpur district of Bihar in the Middle Ganga Plain was reported in June 2002 (Chakrabarti et al, 2003), which was refuted (Acharya et al. 2004). Nickson et al. (2007) also reported the groundwater arsenic contamination status in Bihar. However, SOES identified more affected areas in the other districts of Bihar state (Ahmed 2006). Investigations by Central Groundwater Board (CGWB) and Public Health Engineering Department (PHED), Bihar indicated high groundwater arsenic contamination in the surrounding villages of Bhojpur district. As per the Central Groundwater Board (CGWB, 2008) report out of 38 districts of Bihar, 15 districts are exposed to groundwater arsenic contamination above 50 μg/L.

2.7.3.4 Uttar Pradesh (UP)

Groundwater arsenic contamination in UP was first exposed in 2003 by SOES from survey of 25 villages in one district. Thereafter, with continued survey two more districts were detected for groundwater arsenic contamination (Ahmed et al. 2006). Nickson et al. (2007) and Srivastava et al. (2008), also reported the groundwater arsenic contamination status in Uttar Pradesh.

2.7.3.5 Jharkhand

During 2003-2004, SOES found groundwater arsenic contamination in the Sahibganj district of the Jharkhand state, in the middle Ganga plain (Chakrabarti et al. 2004). Later on (2006-2007), it was confirmed by CGWB through detailed investigation. Bhattacharya et al. (2005) and Nickson et al., (2007) also reported the groundwater arsenic contamination status of Jharkhand.

2.7.3.6 Chhattisgarh

SOES has also identified arsenic contamination in the groundwater from Rajnandgaon district of Chhattisgarh state (Chakrabarti et al. 1999). It is estimated that a few hundred people were suffering from arsenical skin lesions from the affected villages (Pandey et al. 1999).

2.7.3.7 Groundwater arsenic contamination in North-Eastern states

There are eight states in North Eastern region. They are Manipur, Mizoram, Assam, Tripura, Arunachal Pradesh, Nagaland, Meghalaya and Sikkim. Groundwater arsenic contamination in North-Eastern States is recent discovery (Singh et al. 2004, Chakraborti et al. 2004, Nickson et al. 2007). Singh et al. (2004) found that concentration of arsenic in groundwater exceeded the permissible level (50 μg/L) in parts of Assam (20 of 24 districts), Tripura (3 of 4 districts), Arunachal Pradesh (6 of 13 districts), Nagaland (2 of 8 districts), and Manipur (1 of 9 districts). In Tripura, arsenic was found in parts of West Tripura and Dhalai districts in the range of 65-444 μg/L. In Arunachal Pradesh, arsenic was detected in six districts (all are situated in the bordering area of Assam). Maximum level (618 μg/L) of arsenic was found in Midland block of Dibang valley district. In Nagaland, arsenic was found in seven locations in Mokokchung and five locations in Mon district. These districts where arsenic in groundwater was found are also situated near Jorhat district of Assam. In Manipur, arsenic was found only in Kakching block of Thoubal district, where the concentration of arsenic was very high (798-986 µg/L). Another recent study found that groundwater of four districts of Manipur are arsenic contaminated (Chakraborti et al. 2008c).

2.7.3.8 Groundwater arsenic contamination in Assam

The problem of arsenic in groundwater in Assam is just starting to get into the limelight. Some initial work under the project "Rapid appraisal of water quality status with respect to fluoride and arsenic in Assam,"(JPOA, 2005) was carried out during 2004-05 by PHED with the support of UNICEF. Samples were collected from government installed hand pumps from areas lying within 25 km on either side of the Brahmaputra river, areas bordering Bangladesh and were analyzed for arsenic. A study was conducted by the North Eastern Regional Institute of Water and Land Management (NERIWALM) (Singh et al. 2004) where 1500 water samples from tubewells and dug wells were taken to analyze arsenic during post monsoon in the year 2003. The NERIWALM study of groundwater shows that 20 out of 24 districts of Assam have groundwater arsenic content exceeding 50 µg/L. The very high level of arsenic was found in Jorhat, Lakhimpur, Nalbari, and Nagaon districts. In the flood plain area of Assam, viiz; Barpeta, Dhemaji, Dhuburi, Darrang and Golaghat, arsenic was found in the range of 100-200 µg/L. Another recent study of the School of Environmental Studies, Javadaur University (SOES, 2004) detected arsenic contamination in groundwater of the Upper Brahmaputra plain with maximum concentration of 490 µg/L (Chakraborti et al. 2004). SOES also detected high arsenic in two other districts of Assam, viz; Karimganj and Dhemaij, where 19.1% of the samples contain higher concentrations of arsenic (>50 µg/L), and 2.1% contain more than 300 µg/L. These studies show that the groundwater arsenic contamination is a burning issue in the state. The Public Health Engineering Department (PHED) in Assam has conducting their own study in this regard and till now 5729 samples from 22 districts of Assam were collected and analyzed for arsenic. The results reveal that, groundwater samples of 18 districts contain arsenic concentrations higher than the national level and out of which 72 blocks were severely affected (JOPA, 2005). Similarly UNICEF also reported groundwater arsenic contamination above 50 µg/L from 18 districts of Assam (Nickson et al. 2007). **Table 2.1** shows the results.

Table 2.1: Summary data on arsenic in groundwater in Assam (Nickson et al. 2007)

District	No of blocks affected	Total sources tested	Sources 10-50 µg/L	Sources >50 µg/L	% Sources >50 µg/L
Barpeta	5	130	21	7	5.4
Bongaigaon	3	100	15	6	6
Cachar	7	210	68	59	28.1
Darrang	4	254	92	9	3.5
Dhemaji	5	539	128	83	15.4
Dhubri	6	435	130	21	4.8
Goalpara	2	145	11	3	2.1
Golaghat	5	268	67	30	11.2
Hailakandi	4	159	45	11	6.9
Jorhat	6	224	96	24	23.1
Kamrup	1	261	39	1	0.4
Karimganj	6	811	150	61	7.5
Lakhimpur	5	218	50	9	4.1
Marigaon	1	271	40	2	0.7
Nagaon	1	314	55	1	0.3
Nalbari	5	148	25	14	9.5
Sibsagar	3	206	72	15	7.3
Sonitpur	3	227	34	6	2.6
Total	72	4920	1138	362	7.4

2.8 Absorption, distribution and excretion of arsenic in human

Urine is the major route of elimination of inorganic arsenic (pentavalent, As (V); trivalent, As (III)) and its metabolites (monomethylarsonic acid, MMAA, $CH_3AsO(OH)$; dimethylarsinic acid, DMAA, $(CH_3)_2$,$AsO(OH)$) from the human body (WHO 1981, Vahter 1983, Vahter 1988).

In gastrointestinal tract of humans, 70-90% of arsenic from drinking water is absorbed irrespective of the As^{3+} or As^{5+} state (Pomroy et al. 1980, Freeman et al. 1995).

Once ingested, inorganic arsenic is readily absorbed from the gastrointestinal tract and transported by blood to various organs in the human body (Karagas et al. 2001). After entering the cell, arsenate (As^{5+}) is reduced to arsenite (As^{3+}) by glutathione (GSH). Firstly, reduction of As (V) to As (III) is mediated by glutathion, acts as reducing agent and then methyl group is transfered to As (III) from S-adenosyl methionine to form MMA(V). Then MMA(V) is reduced to form an intermediate metabolite monomethylarsonous acid (MMA(III)) in methylation process and during the second methylation, MMA (III) is oxidized to DMA (V) (Le et al. 2000; Thomas et al. 2001). Glutathion and S – adenosyl methionine acts as co-substrate (Styblo & Thomas 1995). The activity of first methylation step is represented by the ratio of As / MMA, if the ratio is high which indicate poor methylation and activity of second step is denoted by the ratio of MMA / DMA, if the ratio is low which indicate good methylation (Del Razo et al. 1997, Vahter 1999).

Most of the arsenic in blood is cleared through three phases (Pomroy et al. 1980). The required time for first half is 2-3 hours; for the second and third phases, it is about 168 and 240 hours (NRC 1999, 2001). The affinity of arsenic to tissues depends on nature of tissue and the type of arsenic species. Keratin tissues like hair, nail are constituted of cysteine containing proteins with active –SH group. Due to high affinity of trivalent arsenic to -SH group cumulative deposition of arsenic occurs in these tissues (ATSDR 1990). Therefore, elevated levels of arsenic in blood and urine indicate recent arsenic exposure (NRC 1999, Vahter 1994), hair and nail are bio-indicators of chronic exposure (NRC 1999). In all keratin rich tissues the affinity for deposition of arsenic species are $As^{3+} > As^{5+} > MMA > DMA$. However, in lipid-rich organs the compounds like MMA and DMA are more prevalent (NRC 1999). This methylation process takes place mainly in liver and considered the detoxification path for more toxic inorganic arsenic. However, total ingested inorganic arsenic is not converted to DMA (V). Thus the species excreted in urine are mainly DMA(V) (70-80%) with about 10-15% MMA(V) and 15-20% inorganic arsenic (As^{3+} and As^{5+}) (Hopenhayn-Rich et al. 1998, Chowdhury et al. 2003) In humans the methylated arsenic MMA(V) and DMA(V) formed are considered less reactive to tissues and readily excreted in urine than inorganic arsenic. Children are poor methylator and good excretor in comparison to the adults. Thus children are less susceptible to arsenicism (Concha et al. 1998; Chowdhury et al. 2003).

2.9 Arsenic exposure and health effects

Humans are generally exposed to low levels of arsenic through drinking water, air, food, and beverages. Food and water are the major sources of arsenic exposure for the majority of the affected people. presently a number of populations worldwide have been exposed significantly to high arsenic levels in drinking water. In addition, people involved in the operations of mining and smelting of metals, pesticide production and application, production of pharmaceutical substances, and glass manufacturing generally have a high level of occupational exposure to arsenic.

The reports of health effect, after ingestion of arsenic contaminated groundwater, are mainly from the epidemiological study of chronic arsenic exposure. It is established fact that inorganic arsenic exposure inhibit the function of enzymes, some important anions, cations, transcriptional events in cells and causes other direct or indirect effects (Brochmoller et al. 2000). Such activities of inorganic arsenic result in numerous adverse effects, viz; (i) Dermal effects, (ii) Cardiovascular effects, (iii) Respiratory effects, (iv) Gastrointestinal effects, (v) Endocrinological effects (diabetes mellitus) , (vi) Neurological effects, (vii) Reproductive and developmental effects, (viii) cancer effects, and (ix) other effects. Symptoms of arsnicosis are primarily manifested in the form of different types of skin disorders such as skin lesions, hyper keratosis and melanosis.

The carcinogenic effect of arsenic compounds was first noted in the 19th century, when patients treated with arsenicals were found to have an unusual number of skin tumors (Hutchinson. 1887). Number of studies have been carried out to know various health effects due to chronic exposure. Ingestion of inorganic arsenic can result in both cancerous (skin, lung, and urinary bladder) and non cancerous effects (NRC 1999). Generally health effects are of two categories, depending on whether the cause was acute, such as poisoning, or chronic, which is the case for ingesting drinking water with elevated arsenic concentration over a lifetime. During the last decade, plenty of chronic arsenic exposure incidents and associated health effects have been reported from Asian countries due to intake of arsenic contaminated groundwater (Smedley et al 2000, Ehrenstein et al. 2006). There have been extensive epidemiological studies showing that chronic ingestion of high levels of inorganic As causes skin cancer (National Research Council 1999). There is documentation of As exposure also causing cancers of the nasal cavity, trachea, bronchus, lung, liver, bladder, colon, kidney, prostate, brain, and in lymphatic and hematopoietic tissues and the nervous system (Naqvi et al. 1994, Smith et al. 1998, 2006, Tsuda et al. 1995, Kurttio et al. 1999, Feng et al. 2001). In laboratory experiments, cellular effects have been shown to occur from exposure to As at levels equivalent to a human drinking 10 μg/L arsenic. Therefore if there is a threshold for As carcinogenicity it is likely below this value (National Research Council, 2001).

In India, West Bengal is one of the worst arsenic affected areas in the world arsenic scenario. During the last 25 years, more scientific and medical investigations have been carried out in this state by different government and non government organizations. Saha (2000) has ramified the chronic arsenic poisoning of contaminated drinking water into four stages, based on his experience in West Bengal. Stage one is the preclinical phase, in which arsenic is seen in blood and then in skin and hair. The second stage is clinical, and includes melanosis, spotted keratosis or diffuse keratosis on the palms and soles, and dorsal keratosis. Stage three shows complications such as a palpable liver, jaundice, and ascitis. Malignancy is the fourth stage, where lesions appear on the body (Saha, 2000).

2.9.1 Health effects on children chronically exposed to arsenic contaminated groundwater

Infants and children may be uniquely susceptible to toxic exposures and international health organizations are beginning to carefully analyze reports that arsenic may have more adverse effects in children than on adults (NRC 1999). The possibility of age-specific effects is compounded by the particularly high intake of arsenic-contaminated drinking water: the daily intake, in volume per unit of body weight (ml/kg/d) of infants is three to four times more than that of the adult and the toxic risk should increase accordingly (NRC 1999, Sun et al. 2007).

In Asian countries, where more than 130 million people are exposed to arsenic contaminated groundwater containing more than 10 μg/L (WHO guideline value), at least 20 million children below 11 years are vulnerable (Bencko et al. 1977, Chakrabarti et al. 2004, WHO 2003). Normally, children under 11 years of age do not show arsenical skin lesions although their biological samples contain high levels of arsenic (Chakraborti et al. 2004). However, exceptions are observed when (i) arsenic content in water consumed by children is very high (> 1000 μg/L) and (ii) arsenic content in drinking water is not so high (around 500 μg/L) but the children's nutrition is poor. Although children show less severe arsenical skin lesions than adults, they are more susceptible to arsenic toxicity affecting their lungs and nervous systems (NRC 1999).

2.10 Treatment technologies for arsenic removal

A variety of physicochemical technologies have been studied for arsenic removal from drinking water (USEPA, 2002a). Numerous studies have examined the removal of arsenic from drinking water through processes such as precipitation-coagulation (Bissen et al. 2003), ion-exchange (Kim et al. 2004), reverse osmosis (Ning. 2002), oxidation filtration(Gihring et al. 2001) and membrane process (EPA 2000a). Although these methods have been widely employed, they have several drawbacks: high operating and waste treatment costs, high consumption of reagents and large volume of sludge formation. Moreover, the stiffening of regulations generates strong demand to improve methods for removal of arsenic from water and controlling water treatment residuals. Therefore, the focus of research has now shifted to solve the problem using suitable sorbents to achieve low level arsenic in drinking water for communities with high raw water arsenic concentration. In contrast, adsorption methods are considered to be very important because of their treatment stability, easy operation and compact facility. Compared to other techniques, adsorption usually does not need a large area or additional chemicals for treatment.

Adsorption on iron based adsorbents is an emerging treatment technique for arsenic removal from drinking water. Iron oxide is a particularly interesting sorbent to consider for this application. Its magnetic properties allow relatively routine dispersal and recovery of the adsorbent into and from groundwater or industrial processing facilities. In addition, iron oxide has strong and specific interactions with both As(III) and As(V). Finally, this material can be produced with nanoscale dimensions, which enhance its capacity of removal.

The physico-chemical techniques presently used for arsenic removal can be described as below.

1. **Coagulation–precipitation**. In these processes dissolved contaminants are transformed into an insoluble solid by using chemicals. The solid is then removed from the liquid phase by clarification or filtration. Dissolved arsenic may also be adsorbed on the surface and co precipitated with other precipitating species. Suspended/colloidal arsenic may also be separated by coagulation and flocculation. The pH of the process highly influences the efficiency of removal. Commonly used chemicals in this technique are activated alumina, ferric salts, alum, manganese sulphate, ammonium sulphate, copper sulphate, etc.

2. **Lime softening**. It is similar to precipitation where limes are used for the removal of contaminants.

3. **Ion exchange**. In this method ions are exchanged from solution that are held electrostatically on the surface of a solid with ions of similar charge. The ion exchange medium is usually packed into a column. Arsenic contaminated water is passed through the columns and the contaminants are removed.

4. **Membrane filtration**. In this technique arsenic is separated from water by passing it through a semi permeable barrier or membrane. The membrane allows some constituents to pass, while blocking others. Pressure difference is the driving force for the separation. The removal efficiency depends on the pore size in the membrane and the particle size of arsenic species. Pre oxidation step improves the removal efficiency.

5. **Adsorption**. This method concentrates solutes at the surface of an adsorbent, thereby reducing their concentration in the aqueous phase. In this technique arsenic species is attached on the surface of the adsorbent by physical as well as chemical forces. The

active surface area of adsorbent, its surface energy and the pH of the solution highly influence the removal efficiency. Conventionally used adsorbents are activated alumina, activated carbon, greensand ($KMnO_4$ coated gluconite), granular ferric hydroxide, iron oxide coated sand, copper-zinc granules, etc.

2.10.1 Adsorption theory

Before studying the adsorption of arsenic using different adsorbents from drinking water, it is necessary to review the adsorption theory briefly.

Adsorption can be utilized as a treatment process to remove highly undesirable compounds from feed water. It involves the separation of undesirable compounds from the liquid phase, the binding of components to a surface, and their accumulation at the surface of the adsorptive media.

Adsorption is a mass transfer phenomenon, which involves accumulation of adsorbate onto adsorbent surface. The adsorption process is controlled by electromagnetic interactions. These interactions include as a result of binding forces between atoms, ions and molecules of an adsorbate and an adsorbent surface. Four types of adsorption are identified, exchange, physical, chemical and specific adsorption (Weber, 1972). Exchange adsorption involves electrostatic attraction of opposite charge between liquid-solid phases. Physical adsorption occurs as a result of the action of Van der Walls forces which involve intermolecular attraction. Chemical adsorption is due to reactions between adsorbate and adsorbent. Specific adsorption involves the interaction between adsorbate and adsorbent without adsorbate change (Weber, 1972).

Adsorption is significantly affected by adsorbate concentration, pH, surface charge, and presence of competitive ions (MWH 2005). The adsorbent selection is based on its surface area, affinity towards adsorbate of interest, and physical strength (shape, grain size).

2.10.1.1 Mechanisms of adsorption

Adsorption isotherms and spectroscopic studies can be used to understand the mechanisms of adsorption process.

Adsorption isotherms (Adsorption equilibrium)

The adsorption equilibrium for any particular adsorbent-adsorbate system can be called an adsorption isotherm because an isotherm is the distribution of solute between the liquid phase and the adsorbed phase at a specified temperature. Adsorption isotherms are important to explore the adsorption capacity of the adsorbent, to evaluate adsorbent feasibility and applicability.

The adsorption process can be described based on any of the several adsorption isotherms, including Freundlich, Langmuir, Brenaur, Emmet and Teller (BET), Dubinin and Raduskevich (D-R), and Polanyi. The appropriate model for a particular component depends on the characteristics of the system. The energetic heterogeneity or uniformity of the adsorptive surfaces is an important factor in finding a suitable model for a particular adsorbate.

For single-solute adsorption, the Freundlich and the Langmuir are the more common isotherm models (LeVan, 1996; Snoeyink and Summers, 1999). The following well known empirical and practical Freundlich equation explains adsorption data reasonably well:

$$q_e = KC_e^{1/n} \qquad (1)$$

The linear form is as follows:

$$\log(q_e) = \log(K) + \frac{1}{n}\log(C_e) \qquad (2)$$

where q_e (unit mass of adsorbate/ mass of adsorbent) and C_e (units of mass/volume) are equilibrium surface and solution concentrations, respectively. K and 1/n are constants for a given system; 1/n is unitless, and the units of K are determined by the units of q_e and C_e. K states the capacity of the adsorbent for the adsorbate and 1/n is a function of the strength of adsorption. For fixed values of C_e and 1/n, the larger the value of K, the larger is the capacity of q_e. For fixed values of K and C_e, the smaller the value of 1/n, the stronger the adsorption bond. As 1/n becomes very small, the capacity tends to be independent of C_e, and the isotherm plot approaches the horizontal level; the value of q_e is then basically constant, and the isotherm is termed irreversible. If the value of 1/n is large, the adsorption bond is weak, and the value of the q_e changes obviously with small changes in C_e.

The Freundlich isotherm is based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites. The Langmuir equation can be linearized as shown below.

$$q_e = \frac{q_{max} b C_e}{1 + bC_e} \quad \text{or} \quad \frac{1}{q_e} = \frac{1}{q_{max}\, bC_e} + \frac{1}{q_{max}} \qquad (3)$$

where b and q_{max} are constants. q_{max} represents the maximum value of q_e that can be achieved as C_e is increased. The constant q_{max} corresponds to the surface concentration at monolayer coverage. The constant b is related to the energy of adsorption and increases with the increase in adsorption bond strength. The basic assumption of the Langmiur isotherm is that adsorption of solutes occurs at specific homogeneous sites and forms a monolayer.

Spectroscopic studies

Spectroscopic data provides a better understanding of the adsorption mechanisms at the atomic scale and contributes to the interpretation of adsorption isotherm experiments and theoretical calculations. Surface sensitive techniques can be used to provide direct information about the mode of attachment of adsorbates to the surface adsorbents at the atomic scale. In general, electron based spectroscopy, vibrational spectroscopy, and synchrotron based X-ray techniques are among the common structural methods in use.

2.10.1.2 Kinetics of adsorption

The rate of sorption is one of the most important factors in evaluating the efficiency of sorption and in determining the size of water treatment unit processes. In adsorption studies, process kinetics describe the rate at which species are transferred from the solution to the pores of an adsorbent. The rate of adsorption determines the equilibrium condition and the detention time required for treatment. In order to estimate the rates of adsorption and to identify the behavior of the adsorption, the pseudo first-order Lagergren equation and the pseudo- second order equation are widely used (Ho and Mckay 2000). A simple kinetic analysis of adsorption is the pseudo first-order equation in the form:

$$\frac{dq_t}{dt} = k_l (q_e - q_t) \qquad (4)$$

Where k_l (1/min) is the rate constant of pseudo first-order adsorption, q_e (mg/g of dry weight) is the amount of metal ion sorbed at equilibrium, and q_t (mg/g of dry weight) is the amount of metal ion on the surface of the sorbent at any time t (min). By applying the boundary condition $q_t = 0$ at $t = 0$, equation (4) becomes-

$$\log (q_e - q_t) = \log q_e - k_1 t \qquad (5)$$

Instead of the pseudo first-order Lagergren equation, a pseudo- second order equation was recently described to explain the adsorption kinetics. The pseudo- second order equation is as follows.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

Where k_2 is the rate constant of adsorption (g/mg min) and h is the initial sorption rate (mg/g min). As time approaches zero ($t \rightarrow 0$), h can be defined as:

$$h = k_2 q_e^2 \qquad (7)$$

The initial sorption rate (h), the equilibrium sorption capacity (q_e), and the pseudo-second order rate constant (k_2) can be determined experimentally from the slope and intercept of the plot of t/q versus t.

To explain the diffusion state of adsorbate on adsorbent, the rate constant for intraparticle diffusion (k_{id}) is given by Weber and Morris (1972). The equation is as follows:

$$q = k_{id} t^{1/2} \qquad (8)$$

The steep linear portions generally represent intraparticle diffusion within pores of adsorbent, while the plateaus are attributed to the equilibrium.

2.10.2 Iron based adsorbents for arsenic removal from water

A number of studies have been done on the adsorption of arsenic onto iron oxide surfaces (Waychunas et al. 1993, Wilkie & Hering 1996, Cornell 1996, Arai et al. 2001, Katsoyiannis et al. 2002, Stipp et al. 2002, Zeng et al. 2003, Zhang et al. 2003, Thirunavukkaresu et al. 2003, Kundu et al. 2005, Lakshmipatiraj et al. 2006). Literature studies are summarized to better understand the present trend of research work and to compare our results.

It has been demonstrated that bulk iron oxides have a high affinity for the adsorption of arsenite and arsenate (Pierce et al. 1982, Raven et al. 1998, Bissen et al. 2003). Arsenic can form inner sphere monodentate or bidentate–binuclear complexes with iron oxides. Extended X-ray absorption fine structure spectroscopy has provided direct evidence for inner sphere adsorption of arsenite and arsenate on iron oxides (Waychunas et al. 1993, Fendorf et al. 1997, Manning et al. 1998). Iron compounds have been reported to be effective for the removal of metal ions. Several iron(III) oxides/oxyhydroxides, such as amorphous hydrous ferric oxide (FeOOH), poorly crystalline hydrous ferric oxide–ferrihydride (Wilkie & Hering 1996), goethite (a-FeOOH) and akaganeite (b-FeOOH) are effective sorbents for removing arsenic [both As(V) and As(III)] from aqueous solutions (Lakshmipathiraj et al. 2006, Vaclavikova et al. 2005b, Deliyanni et al. 2003, Matis et al. 1999). Other type of sorbents based on iron oxides/oxyhydroxides that has been extensively investigated include, iron oxide-coated polymeric minerals (Katsoyiannis et al. 2002), iron oxide-coated sand (Thirunavukkaresu et al. 2003), granular ferric hydroxide (Badruzzaman et al. 2004, Sperlich et al. 2005), iron oxide-coated cement (Kundu et al. 2005), iron-hydroxide coated alumina (Hlavay & Polyak 2005), Ce(IV)-doped iron oxide adsorbent (Zhang et al. 2003), silica-containing iron(III) oxide (Zeng 2003), magnetically modified zeolite (Vaclavikova et al. 2005a), natural iron ores (Zhang et al. 2004) and waste materials containing iron particles e.g. fly ash and red mud (Bertocchi et al. 2006). It has been reported that hydrous ferric oxide (HFO) such as granular ferric hydroxide (GFH), ferrihydride, goethite as well as akaganeite can adsorb arsenic species very strongly. Sperlich et al.(2005) studied the adsorption behavior of GFH for removal of arsenic. Because of the uniform pore size and the ability to adsorb molecular species zeolites are found to be ideal hosts for the accommodation of organic and inorganic molecules, polymer chains, etc. They are known to be good sorbents/ion exchangers for cations and their surface modification can create localized functional groups with a good affinity to arsenic. Several iron-treated natural materials, such as iron -treated activated carbon, Fe-treated gel beads, and iron oxide coated sand (IOCS) were evaluated for removing arsenic in drinking water. These studies showed that IOCS had a good performance in terms of As(III) and As(V) removal in batch tests, column tests, and field experiments (Yuan et al. 2002). Zero-valent iron filings are utilized for arsenic remediation whre arsenic removal was dramatically affected by oxygen content and pH. More than 99.8% of the As(V) was removed whereas 82.6% of the As(III) was removed at pH 6 after 9 h agitation (Bang et al. 2005).

2.10.3 Nanoscale iron based sorbents for arsenic removal from water

Nanotechnology is an emerging technology in groundwater treatment. Arsenic in ground water can be removed using nanotechnology and currently lot of research is going on in this field. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. The development of nanotechnology at the end of 20th century has widened the variety of adsorbents. The removal of arsenic by nanoparticles have shown promising results. Nanoparticles can also be functionalized with various chemical groups to increase their affinity towards target compounds. Several research groups are exploiting the unique properties of nanoparticles to develop highly efficient and selective sorbents for metal ions and anions (Oliveira et al. 2004, Gu et al. 2005, Machado et al. 2006, Zhang et al. 2007b). Goethite and akaganeite are found to be very much effective for arsenic removal (Matis et al. 1999). Synthetic akaganeite (β-FeOOH) has shown an uptake of 65 mg of arsenic per g of akaganeite at pH 3.5 and temperature 22°C (Vaclavikova et al. 2005b) and of 120 mg of As per g of sorbent at pH range 4.5–7 and temperature 25°C (Deliyanni et al. 2003). The higher removal capacity of akaganeite could be attributed to its higher surface area, which is an important factor for an effective sorption process. The particle size of the above mentioned iron oxyhydroxides is in the range of nanomaterials.

The preparation of two classes of iron-containing polymer-supported nanoparticles: (i) hydrated Fe(III) oxide (HFO) dispersed on a polymeric ion-exchange resin and (ii) magnetically active polymeric particles have been reported for arsenic [both As(III) and As(V)] removal. The high surface area to volume ratios of these nanoscale particles favored both sorption and reaction kinetics (Cumbal et al. 2003). As(V) removal by akaganeite β-FeO(OH) nanocrystals was also reported (Solozhenkin et al. 2003) where arsenic removal increased with increasing temperature. Kanel et al. (2005, 2006) synthesized nanoscale (1–120 nm diameter) zerovalent iron (NZVI) for rapid As(III) and As(V) removal. This removal rate was about 1000 times faster than that of micron-sized iron. Batch experiments determined the feasibility of using NZVI for remediation groundwater containing arsenic at different pHs (pH 3–12). The maximum As(III) adsorption capacity was 3.5 mg of As(III)/g of NZVI.

Modified nanosized zero-valent iron (Fe^0) particles such as NiFe and PdFe were synthesized by borohydride reduction of nickel and palladium salts on Fe^0 particles and used for arsenate removal. An increase in the temperature resulted increase in arsenate removal while competing sorption of phosphate and sulfate inhibited arsenate removal. (Gautham et al. 2005). A fibrous polymeric/inorganic sorbent material was synthesized and used for arsenic remediation (Vatutsina et al. 2007). The sorbent included polymer filaments inside which nanoparticles of hydrated Fe(III) oxides have dispersed. The functional groups of this weak-base anion exchanger allowed high and fairly uniform Fe(III) loading. While hydrous ferric oxide (HFO) microparticles provide a high sorption affinity toward dissolved arsenic species, the fibrous polymeric matrix shows excellent hydraulic and kinetic characteristics in fixed beds. This hybrid nano sorbent, exhibited excellent arsenic removal efficiency without any pH adjustment or pre-oxidation of the influent. In addition, As(III) sorption was not suppressed in presence of competing ions at pH typical for drinking waters.

Nanoscale iron oxides exhibit different chemical and physical properties compared to their bulk counterparts due to their extremely small size and large specific surface area (Morales et al. 1996, Yean et al. 2005). They present great potential as sorbents for a variety of ions including arsenic because of their many fold higher surface area than bulk iron oxides. Accordingly, nanometer scale iron oxides are ideal sorbents for arsenic removal from water. However, only a few studies have been conducted to understand the sorption behavior of arsenic to nanometer scale iron oxides (Wakui et al.

2002, Utsunomiya et al. 2003, Jongnam et al. 2004). Yean et al.(2005) evaluated the sorption and desorption behaviors of arsenic to magnetite(Fe_3O_4) nanoparticles, and they found that the sorption capacity is dependent on the pH value and surface area of the adsorbent. Vaclavikova et al. (2005a) presented the synthesis of magnetic iron oxide based nano-particles inside porous natural zeolite for removal of arsenic. Initial sorption experiments, have shown a sorption capacity of around 70 mg of As per g of sorbent. Moreover, the material has a porous microstructure that might make it suitable for sorption columns; fixed-bed sorption studies. A novel sorbent developed by incorporation of iron oxide based magnetic nano-particles into a zeolite structure seems to be a promising one for economic application in small systems. Arsenic adsorption on magnetite (Fe_3O_4) nanoparticles was conducted by Mayo et al. (2007). The effect of Fe_3O_4 particle size on the adsorption and desorption behavior of both As(III) and As(V)was reported. As the particle size was decreased from 300 to 12 nm the adsorption capacities for both As(III) and As(V) increased nearly 200 times. Hristovski et al. (2007) studied the arsenate removal by aggregated iron oxide nanoparticle media in packed bed columns and found high removal efficiency. In a study by Yavuz et al.(2007) magnetic separations of nanoparticles were exhibited at very low magnetic field gradients for point-of-use water purification and the simultaneous separation of complex mixtures. High surface area and monodisperse magnetite (Fe_3O_4) nanocrystals (NCs) responded to low fields in a size-dependent fashion. The particles did not act independently in the separation but rather reversibly aggregated through the resulting high-field gradients present at their surfaces. Using the high specific surface area (12 nm in diameter) of Fe_3O_4 nanocrystals, the mass of waste associated with arsenic removal from water was reduced by orders of magnitude. Sylvester et al.(2007) synthesized a hybrid sorbent consisting of nanoparticles of hydrous iron oxide distributed throughout a porous polymeric bead was utilized for arsenic remediation from drinking water. Arsenic was removed due to the interaction with the nanoscale hydrous iron oxide surfaces rather than the anion-exchange groups associated with the polymeric substrate. Anions such as sulfate, chloride, or bicarbonate did not interfere. Shipley et al (2009), found that magnetite nanoparticles were effective in removing arsenic from the potable water to below US EPA Maximum contaminant level (MCL) of 10 µg/L, with insignificant effect of pH, ionic strength and temperature. Tuutijarvi et al. (2010) investigated the suitability of maghemite nanoparticles for As(V) adsorption and found high adsorption capacity (50 mg/g) using 50 h agitation time. Chowdhury et al.(2010) used magnetite nanoparticles to treat arsenic contaminated water and found that <50% of arsenic was removed from water containing >6 mg/L phosphate. The study showed that, apart from pH, the removal of arsenic from contaminated water also depends on the contact time, the initial concentration of arsenic , the phosphate concentration in the water and the adsorbent concentration.

2.10.3 Effects of water quality parameters on Arsenic removal

The source water composition significantly affects the efficiency of arsenic adsorption on to various adsorbents. Since the effectiveness of arsenic removal process depends on the removal of soluble arsenic and of the resulting particulates, constrains with either process can limit arsenic removal (Edwards, 1994). Therefore, the impact of water quality parameters on the efficiency of removal process should be considered carefully.

2.10.3.1 pH

The predominance of arsenic(V) acid, H_3AsO_4, and arsenous(III) acid, $HAsO_2$, in natural waters is a significant issue when considering arsenic removal mechanisms. It is apparent that at pH of 7 to 8, arsenic acid is extensively ionized as divalent ion, while arsenious acid remains largely unionized. Due to ionic charge, As(V) can be removed more easily than As(III) (Ning. 2002). In aerated water, As(III) tends to be oxidized to As(V), especially at alkaline pH, and As(V) can be reduced to As(III) at low pH ranges (Pontius et al. 1994). As(III) removal is expected to be effective in the pH range of 8-11, while As(V) removal is efficient in the pH range of 4-7 (Benjamin et al. 1993, AWWA Committee Report, 1993). The literature showed that adsorption of As(V) is dependent on pH of the treated solution, as the pH increases sorption decreases. However, As(III) is independent of pH and had consistent adsorption over a wide range of pH. This observed phenomenon is due to the point of zero charge of the solid and the pH of the solute. When pH<pzc the surface of the iron oxide is positively charged and prefers the

adsorption of a charged molecule [(AsV)] compared to an uncharged molecule [As(III)]. This is the reason why at a lower pH, such as 4, As(V) usually has higher adsorption than As(III). As the pH increases there are more OH^- groups on the surface of the iron oxide; therefore, there is increased electrostatic repulsion causing less arsenate to adsorb due to its negative charge. But As(III) is neutrally charged, so it is not impacted by electrostatic repulsion, that is why increased adsorption of As(III) occurs at higher pHs (Pierce and Moore 1982, Waychunas et al. 1993, Cornell 1996, Wilkie & Hering 1996, Raven et al. 1998, Arai et al. 2001, Goldberg & Johnston 2001, Stipp et al. 2002, Al-Abadleh et al. 2003, Dixit & Hering 2003).

The pH range of the feed water is also significant for the effectiveness of iron oxide particles to remove arsenic. Arsenic removal may also occur at higher pH levels, but not as effectively as at lower pH values (Wang et al. 2003). It was also reported that better arsenic removal at low pH values is due to decreased concentration of hydroxide anion, which is an excellent ligand that strongly competes with arsenic for adsorption sites (Ghurye et al. 2004). Arsenate adsorption has been shown to decrease with increasing pH in the range of 4-9 (Wickramansinghe et al. 2004) and the decrease is more pronounced at pH values above 8.0 (Gulledge & O'Connor 1973).

2.10.3.2 Dose and initial arsenic concentration

It is reported that the initial arsenic concentration significantly affects the removal of arsenic (Sorg & Logsdon. 1978). For initial As(V) concentrations to about 1000 µg/L, with an adsorbent dose of 30 mg/L achieved higher than 95% As(V) removal; however, the percent removal decreased with increasing the initial concentrations. For initial As(III) concentrations greater than 100 µg/L, neither of the coagulants dose at 30 mg/L could remove As(III) below 50 µg/L without the pre-oxidation of As(III) to As(V). The effects of pH, coagulant dosage, and initial arsenic concentration was evaluated for removal of As(V) and As(III) (Edwards 1994). At coagulant doses higher than 5 mg/L, removal capacity for As(V) was a relatively strong as function of pH and lesser as a function of coagulant dose or initial arsenate concentration. In contrast, the removal of nonionic As(III) was not dependent on pH, and more strongly influenced by initial concentration of As(III) and coagulant dosage.

2.10.3.3 Effect of source water composition on uptake of arsenic

Most of the reported adsorption studies are carried out using deionized water in single anion systems. However, in real life situations arsenic is always accompanied in water by other ions. Therefore, it is important to explore the effect of source water composition on the removal efficiency of the process. With this motivation, considerable attention has been directed towards understanding the effects of various ions viz; Ca^{2+}, Mg^{2+}, PO_4^{3-}, Cl^-, and HCO_3^- (common ions in groundwater) on arsenic removal using iron oxides. It is found that all the anions tested, except Ca^{2+}, interfere with the arsenic sorption by competing with arsenate for the available surface sites. The suppression of arsenic sorption caused by HCO_3^- is much greater than that caused by Cl^- (Smedley & Kinniburgh 2002). Similar results are reported elsewhere by Matsunaga et al. (1996). The presence of Ca^{2+}, however, improves arsenic removal due to favourable electrostatic effects, as it increases the number of positively charged surface sites for the adsorption (Wilkie & Hering, 1996, Genç et al. 2003). Natural waters are multi-component systems consisting of various cations and anions and they can only be described properly if competitive reactions are considered (Nilsson et al. 1996). Arsenic in groundwater originates from natural iron oxides in aquifers (BGS 2001). An important factor that may enhance or suppress the arsenic concentration of natural groundwater is the co occurrence of elements. While adsorption on iron oxides is a relatively inexpensive process for removing arsenic from drinking water, the efficiency of this process depends on the presence of competitive anions and cations. Despite the fact that arsenic has a higher affinity for sorption sites on iron oxides, the presence of competitive ions affects the adsorption of this species. Generally, adsorption of anions on surfaces can be considered to occur through the formation of inner sphere or outer sphere surface complexes, which are analogous to complexes formed in solution. Iron oxides are adsorbents for other anions also and form similar surface complexes to those for As(III) and As(V) species. Silicate has been reported to have a strong ligand binding to iron oxides and therefore to influence arsenic adsorption on iron oxides (Meng et al. 2000, Swedlund & Webster 1999, Waltham & Eick 2002). Phosphate is another ion which strongly competes with arsenate for adsorption on iron oxides due to its similar dominant dissociation species (Zhao et al. 2001) and comparable intrinsic affinity for iron oxide surface (Pierce &

Moore 1982, Manning & Goldberg 1996, Jain & Loeppert 2000). Even at very low concentrations in solution, the ion is relatively important at the surface. Therefore, it will be a competitor for arsenic (Jain & Loeppert 2000). Sulphate also competes with As(III), and to lesser degree, with As(V) for adsorption on iron oxides at pH 4-7 (Wilkie & Hering 1996). The effect of sulphate is similar to that of phosphate (Pierce and Moore, 1982). In most of the groundwater systems, bicarbonate often is a major anion. Although carbonate may act as competitor for both types of arsenic oxyanions, the presence of significant concentration of phosphate makes the interaction bi(carbonate) insignificant. Moreover, abundantly present cations in groundwater are Ca^{2+} and Mg^{2+}. Due to their positive charge, they may promote the adsorption of negatively charged ions like As(V) (AsO_4^{3-}) (Wilkie & Hering, 1996). The presence of Ca^{2+} and Mg^{2+} in groundwater has insignificant effect on As(III) adsorption in the pH range relevant for natural groundwater (Smith et al. 2005, Liu et al. 2007a).

CHAPTER THREE

3. Materials and methods

3.1 The study area

The proposed study area is the Majuli- the largest populated river island of the world which is marked by its geological alienation from the mainstream Assam state due to lack of road linkage and insufficient water transport, severe bank erosion problem and regular floods, besides large segments of tribal illiteracy. Due to worst connectivity and frequent floods the area suffers very badly in terms of administrative and developmental works. The area needs special attention with regard to sanitation and safe drinking water as almost entire population drink and use raw ground water without knowing their water quality status and any filtration procedure.

3.1.1 Topographical and Morphological Charactersitics of Study Area

Majuli island is the world's largest populated river island of the River Brahmaputra (CGWB, 2009) inhabited by about 153,000 people (2001 Census). Majuli is one of the sub-divisions of the Jorhat district of Assam, India having no road linkage to the rest of Assam. The subdivision is divided into two blocks- Majuli and Ujoni Majuli. Each block is further divided into Gaon Panchyets (GPs). Each GP consists of several villages. There are 12 and 8 GPs (Total 20) under Majuli and Ujoni Majuli block respectively. According to Census report 2001, there are 248 villages (114 and 80 inhabited and 43 and 11 uninhabited villages in the Majuli and Ujoni Majuli block respectively) with a population of 1.5 lakh.

Majuli island is located on the middle of the mighty Brahmaputra River, regarded as the largest fresh water river island in the world (Groundwater Information Booklet 2008). The island is formed with the confluence of the Brahmaputra and Lohit rivers. The area lies within the latitudes 26° 39' 57.6" and 27° 16' 19.2" N and longitudes 93° 34' 12" and 94° 42' 3.6"E. Its elevation from the mean sea level is 84.50 metres. The island is bounded by three rivers: the Kherkutia Suti (an anabranch of the Brahmaputra), the Subansiri river (a tributary of the Brahmaputra) in the north, and the Brahmaputra River in the south (**Fig3.1**). The river Brahmaputra and its tributary, the Subansiri river forms-

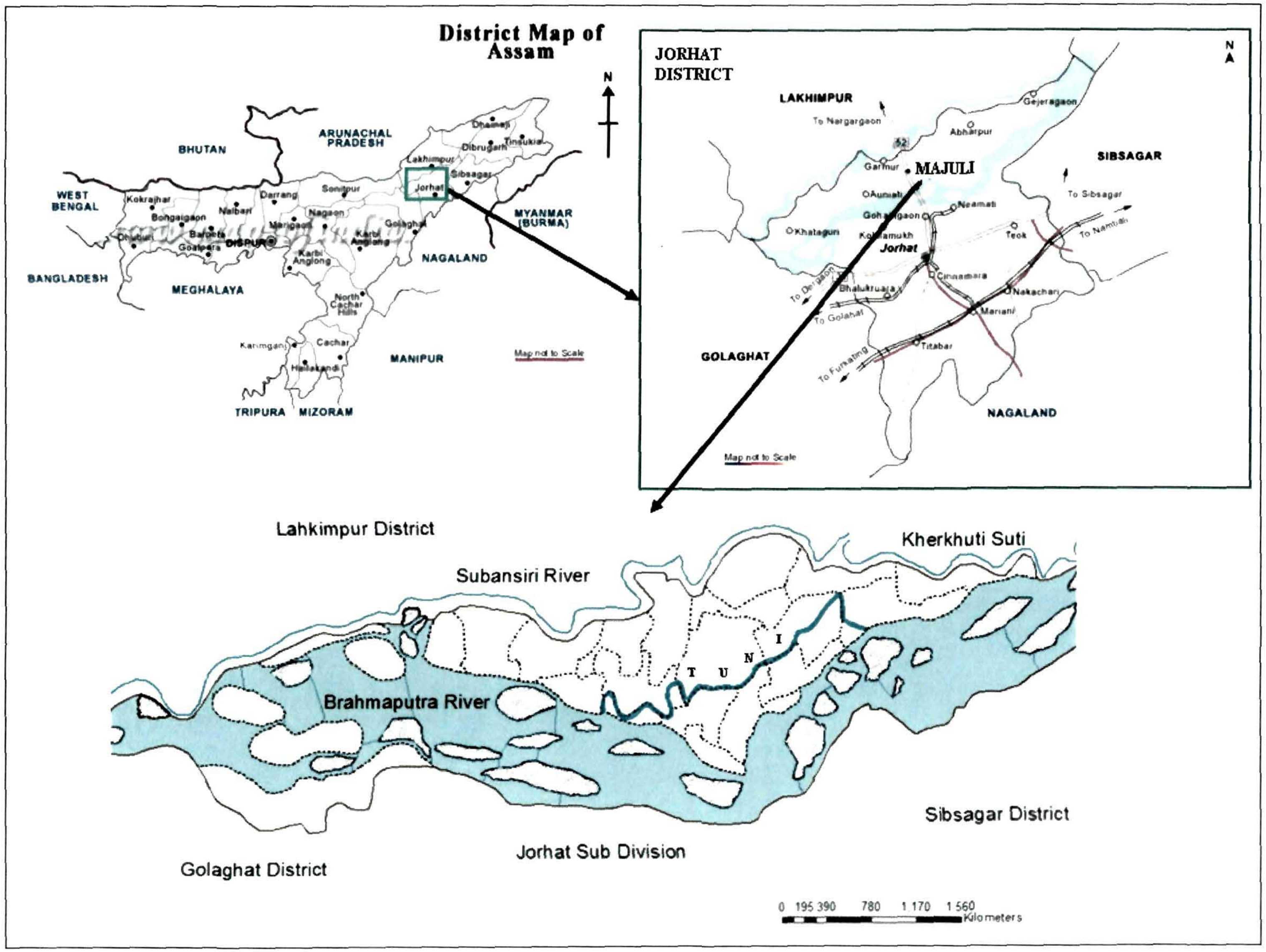


Fig 3.1: Location map of Majuli

the boundary of the island on three sides and the Kherkutia Suti, a distributory of the Brahmaputra River, forms the fourth side (**Fig 3.1**).

Majuli is home to the pristine cultural heritage of Assam and the ''Vaisnavite'' shrines, popularly known as ''Sattras''. As such, the island has been a principal place of pilgrimage for the last 400 years. But presently it is well known for having suffered from two natural hazards: severe bank erosion and flooding (Sarma et. al. 2004). The island was severely affected by erosion since the occurrence of 1950 great earthquake, that brought about astounding natural and geographical changes to the island and to the River Brahmaputra. The river bed swelled up due to deposition of silt and alluvium, resulting in severe erosion. It is reported that the original size of 1246 sq km is reduced to 924.60 sq km (1971 census) due to erosion. The studies carried out based on satellite data by ISRO and Brahmaputra board shows that about 50.27 sq km area has been eroded during 1972-1994. At present the area of the island is reported to be about 400 sq km (Sarma et al. 2004).

It is confirmed that erosion is predominant in the southern boundary of Majuli Island owing to the river Brahmaputra. The rate of erosion is more prominent in the southwestern part of the island. The rate of bank erosion is found to be dependent on bank stratigraphy and also on the presence of anabranching channels. The erosion is due more to undermining by water where there is a thick sand layer beneath the topsoil. Where cohesive silty-clay beds are present at the base of the banks, erosion is slower. The Subansiri River has been adding land to Majuli Island due to the northward migration of its channel, thereby reducing the net effects of erosion on the area of Majuli.

The island is elongated in shape like a spindle trending nearly NE–SW. Majuli has plain topography with fairly low relief. There are numerous swamps and lowlands of various sizes and shapes, which occasionally break the monotony of relief. A large number of small streams and a few big rivers flow through the island. Average altitude of the land is 85.9 m and general gradient is 1:5000 from east to west. It comprises Older and Younger Alluvium and active flood plain deposits of recent Age. The stratigraphy of the Majuli Island is similar to the stratigraphy of the Brahmaputra Valley on the southern bank of the Brahmaputra as it comprises both Older Alluvium and Newer Alluvium of Recent Age at many places such as Haldibari, Salmora, Ratnapur, Bongaon, Garmur, Kamalabari, Auniati, Goalgaon, Ahatguri to name a few (Mahanta, 2001). The soils of Majuli are alluvial fine loamy soils formed from recent river deposits.

3.1.2 Climate

The climate of the island is characterized by subtropical monsoon climate with high rainfall , high humidity and general coolness. Four distinct seasons can be identified in the region: pre monsoon, monsoon, post-monsoon and winter. Heavy rainfall is received during summer and occasional rainfall during winter. January and February are the driest months. Pre-monsoon showers are received during March and April. The heavy rainfall received during summer is influence by southwest monsoon. The annual rainfall in Majuli varies from 1494 to 2552 mm, the average annual rainfall for last ten years has been recorded to be 1922 mm. The average relative humidity in a year is 78.7 per cent. Average monthly temperature in the area vary between about 29^{o}C in summer (July-August) and 6^{o}C in winter (January).

3.1.3 Geological setting

Geologically, the Majuli island is occupied by unconsolidated alluvial sediments of Quaternary age. The island forms a part of the vast alluvial plain of Brahmaputra river valley. It was developed by foreland depression lying in between the Himalayan orogenic belt in the north and southern crystalline massifs. The sediments owe its origin and development with the different phases of upliftment, glaciations and erosion of the Himalayas and basement tectonics of crystalline massifs. The newer alluvium is generally confined to topographical lows, following the stream courses and flood banks of major rivers and alluvial terraces and forms of Brahmaputra river. These deposits are distinguishable by their characteristic grey colour and generally well sorted alternate layers of clays, silts, sands and gravels (Groundwater Information Booklet, 2008).

3.1.4 Hydrogeology

The Brahmaputra is an international river, which flows through China, India and Bangladesh for 2880 km and drains a basin of 580,000 km2. It has a large braided channel in Assam. The mean annual flow of the Brahmaputra at Bechamara in Majuli during 1975–1990 was 8829.5 m3/s (WAPCOS, 1993). The average annual suspended sediment load of the Brahmaputra as measured at Pandu, 240 km downstream of Majuli, is 402 million metric tons during the period 1955–1979 (Goswami, 1985). The Subansiri is the largest tributary of the Brahmaputra. Its total length is 520 km and it drains a basin of 37000 km2. The mean annual flow of the Subansiri during 1956–1982 was 1671 m3/s. The Subansiri carries on an average 35.48 million tons of suspended sediment annually (WAPCOS, 1993). Majuli Island is situated at the mouth of the Subansiri and 850 km upstream of the mouth of the Brahmaputra.

The area is underlain by unconsolidated alluvial sediments of the Quaternary age, which can be differentiated into Older and Younger alluvium. The Older alluvium occupies the upland areas with sediments of oxidized and relatively compact nature, while the Younger alluvium occurs along the low-lying tracts of the area along the river courses. The sediments of the north side is derived from the young Himalayas while the sediments on the south side originate from the older Assam plateau. The newer alluvium is generally confined to topographical lows following the stream courses.

Based on groundwater occurrence and movement, the regional ground water condition of the area have been grouped under two categories. a) Shallow aquifer group occurring within the depth of 50 m. and b) Deeper aquifer beyond a depth of 50 m and down to 200 m below ground level (b.g.l).

3.1.4.1 a) Shallow aquifer group

The shallow aquifer occurring within a depth of 50 m from the land surface consists of a mixture of sand, clay and silt. The thickness of aquifer is about 20 m and ground water occurs under unconfined condition. Open wells and shallow tube well groundwaters generally used for domestic as well as irrigation purposes. The water table is shallow and rests within 2-4 m below ground level during pre-monsoon period. The flow of ground water follows the general topography of the area and towards River Brahmaputra.

3.1.4.2 b) Deeper aquifer group

The aquifer occurring in the depth range of 50 to 200 m below ground level is grouped in this category. The aquifers consist of fine to medium grained sand with clay intercalation. The exploration data revealed presence of four to five major aquifer zones. Ground water occurs under confined to semi-confined conditions in these aquifers.

3.1.5 Demography

The people of Majuli represent the varied ethnic groups with a total population of about 1,53,362 with a sex ratio of 92.93 as per 2001 census with a population density of 364 persons per sq.km as compared to its total population of 1,35,378 as per 1991 census with a population density of 300 persons per sq. km. During the period between 1901 and 2001 the population of Majuli has gone up from 31,219 to 1,53,362 with a growth rate of 18.04% from 1951-1971 and 60% from 1971-2001. Infact the increase in the population density is perhaps as a result of progressive decline in the size of the island reflecting increasing man-land ratio in the fragile island. The dominated tribe of the island is Mising tribe.

3.1.6 Socio-economic condition

Agriculture is the main source of livelihood of the people of Majuli. Out of the total population according to the 2001 census, a number of 45722 comprising 29.81 percent of the total population constitute the total workforce of which 80.85 percent belongs to the farmers and another 2.05 percent agricultural labour. The accelerated rate of shrinkage in the size of island has severe impact on the socio-economic, demographic and cultural dimensions of the population..

The Government of Assam (since 1967) has been periodically assessing the loss of life and property due to floods, damage to agricultural land due to deposition of sand, and depletion of land area due to erosion, all these leading to displacement of numerous families from their homes. Therefore, erosion and flood are not only environmental but also socioeconomic issues for Majuli island.

3.2 Sample collection and preservation

The fieldwork for sample collection was performed during April 2009 to September 2011. It consisted of the collection of water, sediment as well as the biological samples (hair, nail and urine).

3.2.1 Water samples

Water samples were collected from 380 sites across Majuli island. Before sample collection, arsenic field test was performed using field testing kit (Merck).

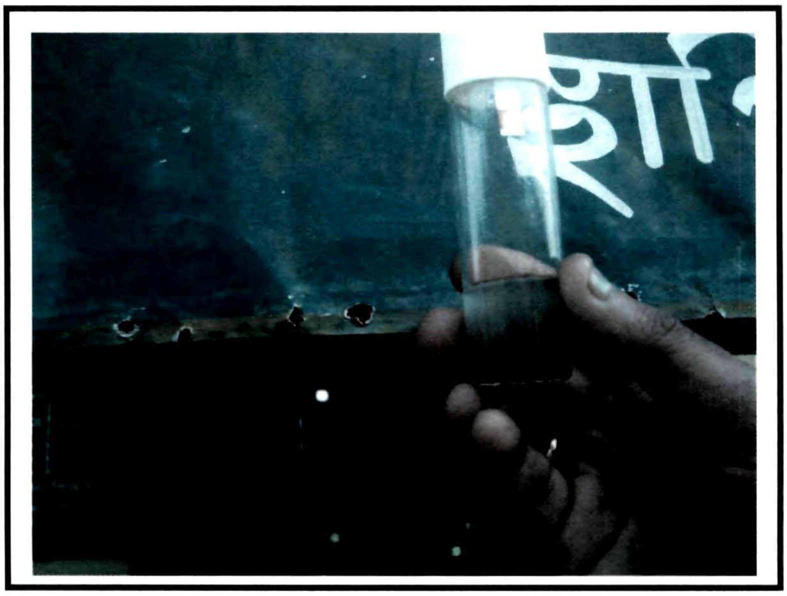


Fig 3.2: Preliminary field test of groundwater using field testing kit (Merck).

In the preliminary survey with an arsenic field kit, we could identify some hand tubewells having arsenic above 50 μg/L (**Fig 3.2**) in certain villages of the Majuli block. The villages are, village- Aalimur gaon, G.P- Dakhin Kamalabari, Village- Jogi gaon, G.P-Bongaon, Villages- Potia gaon, Hokonamukh, G.P- Rawanapar, Village- Meruwabari, Jokaibowa, G.P- Pokajora, Villages- Samoguri, Cherpaikhua, Baghgaon, Maluwal miri, Bebejia, G.P- Karatipar, Village- Barun Citdar Chuk, G.P- Chilakola, Village- Borduar Chapori, G.P- Sri Luhit, Village- Chayani miri, G.P- Ahatguri. Out of these villages the field kit indicated higher level of arsenic contamination in the hand tube wells in the Balijan, Borduar Chapori and Eri chapori village. Therefore, 55 samples from Borduar Chapori and 32 samples from Eri chapori village were collected covering most parts of the two villages. All total 286 groundwater samples had been collected from the Majuli block covering all the 12 G.Ps. Similarly, in the Ujoni Majuli block the groundwater samples from village- Muwamari in the Luit Poria G.P and Village- Abhoipuria (habitation- Bhokotiduar) in the Sri Ram G.P were found to have arsenic >50µg/L. The field kit result showed high arsenic contamination in the Bhokotiduar habitation of the Sri Ram G.P. So 55 hand tube well water samples from that habitation had been collected. All together 94 hand tubewell water samples were collected from Ujoni Majuli block covering all the 8 G.Ps of the block. All total 380 hand tubewell water samples were collected from Majuli, including both the blocks of the island covering all the 20G.Ps.Groundwater sampling locations are shown in **Fig 3.3**.

All the hand tubewell water samples were collected in pre-washed (with 1:1 HNO_3) polyethylene bottles after pumping off at least for 5 minutes. After collection, concentrated nitric acid (1.0 ml per liter) was added as preservative. Samples, which were not analyzed immediately, were kept in a refrigerator at 4°C.

3.2.2 Sediment sample

Borehole sediment samples were collected from seven boreholes at four sites . Sediments from borehole BH-1 and BH-6 were collected at Bongaon G.P, borehole sediments from BH-2 and BH-3 were collected at Luitporia G.P, sediments from BH-4 and BH-7 were collected at Rawnapar G.P, and sediments from borehole BH-5 were collected at Dakhinpat G.P (**Fig 3.4**). These boreholes provide the sediment material for the determination of arsenic, iron and other heavy and trace metals along with the mineralogical study, results of which are discussed in the next chapter. 43 core samples were collected from 7 bore holes at different depth intervals (6.1m, 18.3m, 21.3m, 24.4m, 27.4m, 30.5m and 33.5m). However, the depth interval is not uniform in all the boreholes. Because, all the samples were collected during drilling through Public Health Engineering Department (PHED), Govt. of Assam. Sediment samples were stored in plastic bags and kept in a refrigerator at in the laboratory until analyses were carried out.

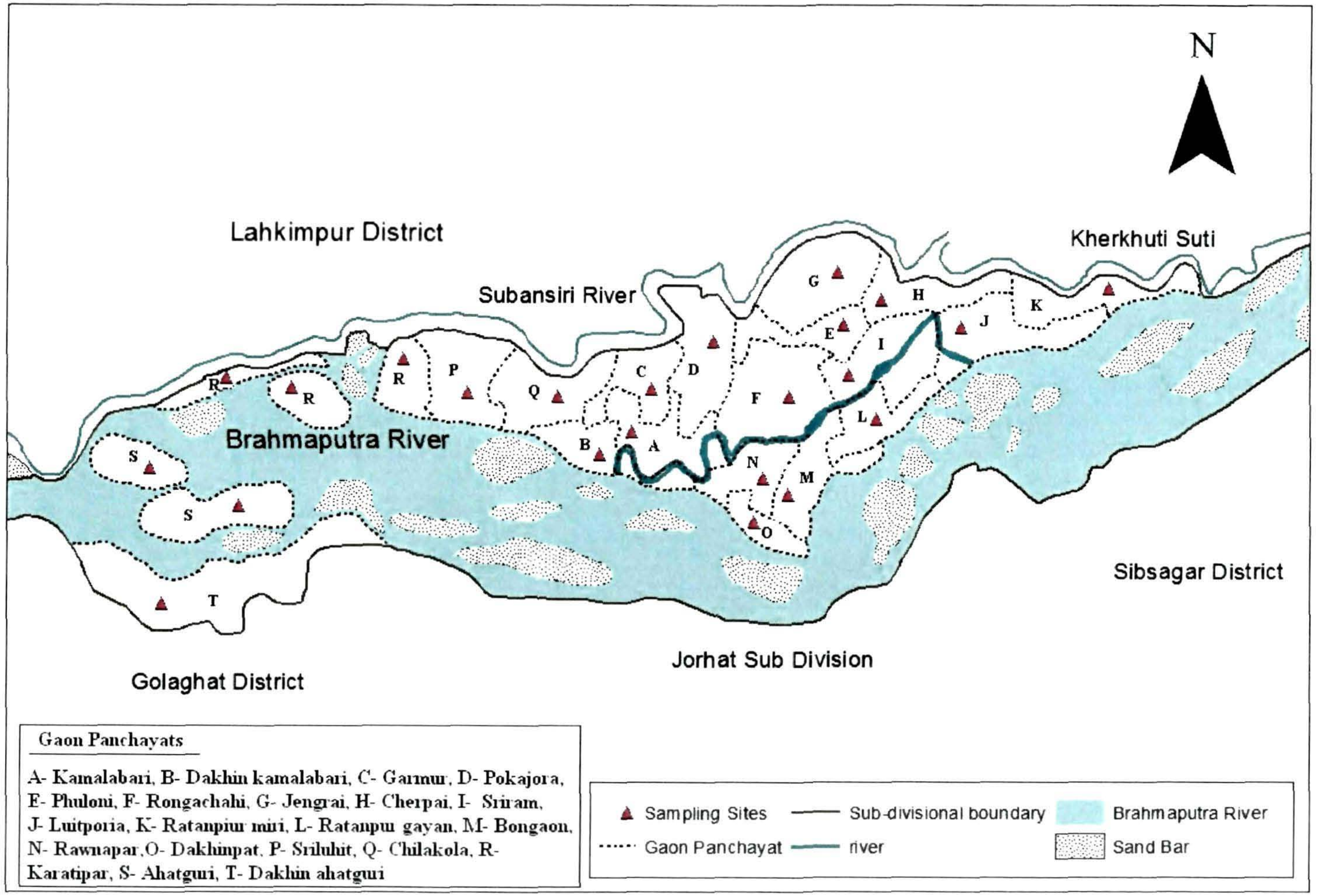


Fig 3.3: Map of Majuli showing groundwater sampling sites.

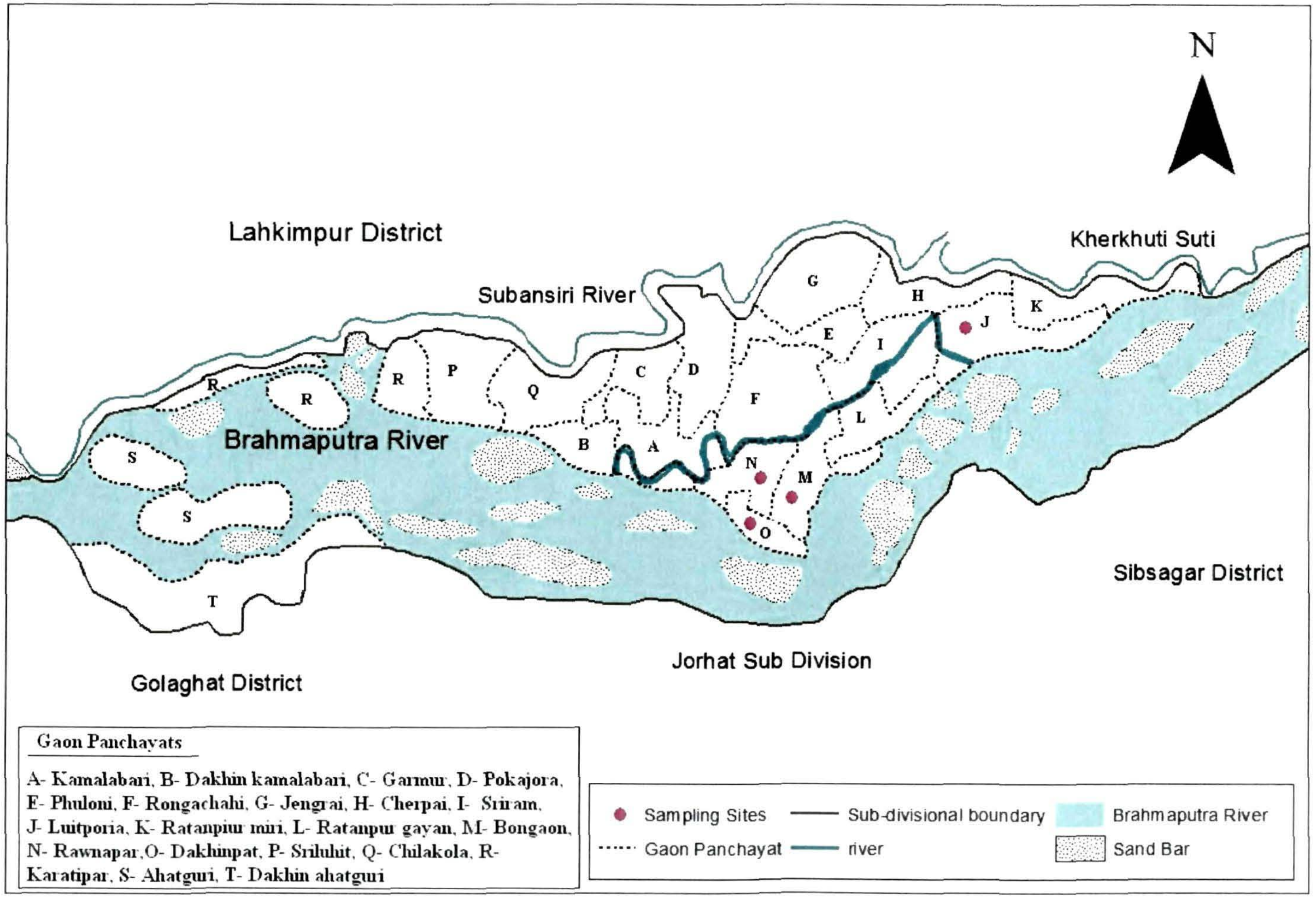


Fig 3.4: Map of Majuli showing sediment sampling sites.

3.2.3 Hair samples

The hair samples (n = 40) were collected from the people of the arsenic contaminated areas. Samples were collected mainly from close to the scalp by using stainless steel scissors (**Fig 3.5**). At first the hair samples were washed by distilled water with soap to remove the external contamination followed by micro oven heating (power level 4 and time 5 minutes) in deionized water suspension.

Fig 3.5: Collection of hair sample from the villagers of Balijan village.

Thereafter it is washed thoroughly with deionized water and finally with acetone (E. Merck, India Limited) as recommended by International Atomic Energy Agency (IAEA, 1976). Hair samples were dried in hot oven at a temperature of 50-60°C and properly stored in white and fresh paper packets with proper label for analysis.

3.2.4 Nail samples

The nail (nails from fingers and toes combined together) samples (n= 33) were collected from the people of the arsenic affected areas. After collection the samples were washed by distilled water with soap to remove the external contamination followed by micro oven heating (power level 4 and time 5 minutes) in deionized water suspension. These were washed thoroughly with deionized water and finally with acetone ((IAEA, 1976). It was then dried on a hot oven at a temperature of 50-60°C and then stored in white and fresh paper packets with proper label.

3.2.5 Urine samples

Spot urine samples were collected in pre-washed polyethylene bottles. Immediately after collection the urine samples were preserved by adding 2 drops of 50% hydrochloric acid as a preservative, and then kept in an ice-box during transport to the laboratory, where they were stored in a refrigerator at 4°C.

3.3 Chemicals & reagents and standard reference materials (SRM) used

(i) For FI-HG-AAS analysis

All reagents were of analytical grade. Distilled de-ionized water was used throughout. Standard arsenic solutions were prepared by dissolving appropriate amounts of As_2O_3 (Merck, Germany) and standard arsenic (v) Titrisol (Merck, Germany). Standard stock solutions were stored in polyethylene bottles and kept in refrigerator at 4°C. Working arsenic solutions for analysis were prepared daily. The reducing solution was sodium tetrahydroborate ($NaBH_4$, Merck, Germany) 1.5% (m/v) in 0.5% (m/v) sodium hydroxide (NaOH, Merck, India Limited). The ultrapure HCl (HCl, Merck, India Limited) concentration was 5 M.

Accuracy of the analytical method using FI-HG-AAS was verified by analyzing Standard Reference Materials (SRM). Samples analyzed were [CRM (BND 301) NPL, India water; SRM (quality control sample for trace metal analysis) from the USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio; Pond Sediment

NIES 2, from the National Institute for Environmental Studies, Japan. Standard Reference Sample, water (quality control sample for trace metal analysis), from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio; Urine SRM 2670, NIST, USA (elevated level); CRM 278 Mussel Tissue community bureau of reference, Belgium; SRM GBW 07601 human hair from the Institute of Geophysical and Geochemical Exploration, Lang fang, China.

(ii) For ICP-OES analysis

For arsenic removal experiments, stock solutions of As(III) and As(V) were prepared from arsenic (III) oxide (As_2O_3, Merck, Germany) and sodium arsenate heptahydrate ($Na_2HAsO_4.7H_2O$, Merck, Germany). The pH adjustment of the solution was accomplished with 1N NaOH (Merck, India Limited) and 6 N HNO_3 (Merck, India Limited).

3.4 Digestion of samples

3.4.1 Sediment samples

A microwave digestion system (MARS 5) with a rotor for fourteen Teflon digestion vessels HP- 500, was used for the digestion of sediment samples. For digestion, about 0.5g of dry, finely powdered sediment sample was placed in a Teflon digestion vessel. Then, 2 ml Milli Q water, 3 ml of concentrated nitric acid and 2 ml of hydrogen peroxide were added. The vessel was closed, placed into the rotor and tightened. The loaded rotor having seven vessels per single time was placed into the microwave oven. After cooling for 30 min, the vessels were opened carefully. Thereafter, each digested solution was transferred to a 50 ml volumetric flask and final volume was adjusted to 50 ml with Milli Q water. Blanks were made under identical conditions. Finally, the solutions were filtered through a milli-pore membrane (0.45 µm) and kept in polyethylene bottles for analysis.

3.4.2 Hair samples

For the digestion of hair samples, about 0.02 to 0.07 gm of hair sample was taken in a 25 ml Borosil glass beaker and to that 5 ml concentrated nitric acid was added. The covered beaker was then heated on a hot plate at temperature of 90-100°C for a few minutes. Heating discontinued and it was kept for overnight. Next day morning sample was evaporated at about 100°C in an exhaust chamber. Nitric acid was added if necessary till the colour of the solution turned into pale-yellow. On reaching a final volume of about 1 ml, heating was discontinued. The pale-yellow liquid was diluted with deionized water and filtered through a Millipore membrane (0.45μm) filtering apparatus, then adjusted to a fixed volume (2-5 ml). Blank made under the identical condition.

3.4.3 Nail samples

Nail sample of 0.02 to 0.07 gm was taken in a 25 ml Borosil glass beaker and to that 5 ml concentrated nitric acid was added. This was then heated on a hot plate with a watch glass at the top of the beaker at temperature of 90-100°C for a few minutes. Heating discontinued and it was kept for overnight. Next day morning sample was evaporated at about 100°C in an exhaust chamber. Heating was continued with time to time addition of a known volume of concentrated HNO_3 until the colour of the solution turned to almost colorless. The remaining solution was then diluted with deionized water and filtered through a Millipore membrane (0.45μm) filtering apparatus, then adjusted to a fixed volume (2-5 ml). Blank made under the identical condition.

3.4.4 Urine sample preparation for analysis

Preserved urine samples from deep Freezer (-20°C) were brought to normal temperature and for inorganic arsenic and its metabolites [sum of AS(III), As(V), MMA(V) and DMA(V)] 1:5 dilution made for FI-HG-AAS analysis. Before injection urine samples were filtered through a 0.45 μm Millipore filter (Millex-GS, sterilizing filter unit).

3.5 Analytical procedures and approached methodologies used for determination of arsenic and trace elements

3.5.1 Instrumentation

3.5.1.1 Flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS)

Arsenic in groundwater, sediment, urine, hair and nail samples was analyzed at School of Environmental Studies (SOES), Jadavpur University. A flow injection-hydride generation-atomic absorption spectrometry (FI-HG-AAS) technique has been used for analysis of arsenic in the samples. The FI-HG-AAS system was assembled from commercially available instruments and accessories. A Perkin-Elmer Model 3100 atomic absorption spectrometer equipped with a Hewlett-Packard Vectra computer with GEM software, Perkin-Elmer EDL System-2, arsenic lamp (lamp current 400 m A), and Varian AAS Model Spectra AA-20 with hollow-cathode As lamp (lamp current 10 mA) were used. The flow injection assembly consists of an injector, Teflon T-piece, tigon tubings and other parts for the FI system from Omnifit UK. The peristaltic pump (VGA-76) from Varian and Minipuls-3 from Gilson, Model M 312 (France) were incorporated into the flow injection (FI) system.

3.5.1.2 Inductively coupled plasma-optical emission spectrometry (ICP- OES)

Arsenic concentrations in the artificial model water (prepared for remediation experiments) were analyzed using Inductively Coupled Plasma-optical emission spectrometer (ICP-OES, Optima 2100 DV, Perkin Elmer) at the Department of Environmental Scienec, Tezpur University. The samples were analyzed by following standard methods (APHA 1998). The detection limit of ICP-OES is 0.1 µg/L for arsenic. In order to amplify the consistency of results, the experiments were performed in triplicate and the mean values considered. No detectable arsenic adsorbed on the walls of the tube was ascertained through the blank experiments.

3.5.1.3 Inductively coupled plasma mass spectrometry (ICP-MS)

Trace elements were determined by solution ICP-MS analysis using a Thermo Finnigan Element 2 at the trace element lab at University of South Carolina. Sediment samples were crushed in agate mortar and pestle for homogenization purpose. 30 mg of each sample was weighed into screw top Teflon beakers and dissolved with 2 ml of 3:1 distilled HF-HNO_3. After drying on a hot plate at 120°C, the samples were allowed to reflux overnight in concentrated HNO_3. Samples were then dried again and brought to a final volume of 60 ml with 2% HNO_3. The sample solutions were further diluted in the ICP vials for target concentration of 100 ppm Total Dissolved Solid (TDS). One ppb of Indium was added as internal standards and drift corrections for each analyzed mass were applied by interpolating with the internal standard.

The concentrations of trace elements were determined on a High-Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS, ELEMENT 2). An Elemental Scientific pfa nebulizer with a flow rate of 100 µl/min was used in self-aspiration mode in combination with a Teflon spray chamber and Teflon tubing.

3.5.1.4 UV-visible spectrophotometer analysis

The 1, 10-phenanthroline methods with UV-visible spectrophotometer was used for iron analysis of water samples. From solution, Fe (III) is reduced to Fe (II) by hydroxylamine hydrochloride adjusted to pH 3.2- 4.0 (pH of the sample is adjusted by adding acetic acid- acetate buffer solution). It is then treated with 1, 10- ortho Phenanthroline. The resulting orange red solution is measured at 510 nm against a reagent blank. A shimadzu (Japan) double beam spectrophotometer (Model UV- 150-02) was used for iron analysis of water samples.

3.5.1.5 Scanning electron microscopy- energy dispersive x-ray spectrometer (SEM-EDX) analysis

A qualitative elemental analysis of the sediments was carried out using the scanning electron microscopy (SEM- JEOL 6460LV). Subsequently Energy Dispersive X-ray (EDX) microanalysis was performed. A qualitative elemental analysis of the sediments was carried out using an accelerating voltage of 20 kV, a life-time of 50 s, and a magnification of 500x.

3.5.1.6 X-ray diffraction (XRD) analysis

The borehole sediment samples have also been studied using a Siemens D-5000 powder X-Ray Diffractometer (XRD), with a Cu-target and excitation conditions of 45 kV, 39 mA

3.6 Sample analysis

3.6.1 Flow injection-hydride generation–atomic absorption spectrometry (F1-HG-AAS)

In the FI-HG-AAS system the sample was injected into a carrier stream of 5M HCl by means of a six-port sample injection valve fitted with a 50 µl (or between 10 and 500 µL) sample loop. The injected sample, together with carrier solution met subsequently with a continuous stream of sodium tetrahydroborate dissolved in sodium hydroxide. Mixing with sodium tetrahydroborate generated hydride (arsine), which subsequently entered into the ice water bath and then into the gas-liquid separator apparatus, which was cooled with ice-cold water. Carrier gas nitrogen transported the arsine to the quartz tube mounted in the air-acetylene flame for AA measurement. Peak signals were recorded using a computer linked to the atomic absorption spectrophotometer (AAS) that is capable of both peak height and peak area measurement. The detection limit of the FI-HG-AAS with 95% confidence level was 3 µg/L for arsenic (the detection limit depends on the sample loop). The experimental conditions for FI-HG-AAS are given in the **Table 3.1**.

Table 3.1: Optimum-Parameters for arsenic determination by FI-HG-AAS system

Parameters	**Perkin-Elmer (Model 3100)**	**Varian (Model Spectra AA-20)**
Lamp Current	400mA (EDL power supply)	10mA (hollow cathode)
Wavelength	193.7 nm	193.7 nm
Slit	0.7 nm	0.5 nm
HCl flow rate	1.25 ml min^{-1}	1 ml min^{-1}
HCl concentration	5M	5M
$NaBH_4$ flow rate	2 ml min^{-1}	1.5 ml min^{-1}
$NaBH_4$ concentration	1.5% (w/v) in 0.5% (w/v) NaOH solution	1.5% (w/v) in 0.5% (w/v) NaOH solution
Carrier gas	Nitrogen	Nitrogen
Carrier gas flow rate	130 ml min^{-1}	50 ml min^{-1}
Flame	Air-acetylene	Air-Acetylene

Water Samples

Preserved water samples were analyzed by FI-HG-AAS against arsenite and arsenate mixture (1:1) as the standard.

Hair and nail samples

Digested samples were analyzed for total arsenic by F1-HG-AAS method against arsenate as the standard.

Urine Samples

For urine samples, only inorganic arsenic and its metabolites together [arsenite, As (III), aresenate, As (V), Monomethyl arsonic acid, MMA (V), and Dimethyl arsinic acid, DMA (V)] were measured with no chemical treatment against arsenite as the standard. In most of the cases urine samples were diluted to five folds before analysis.

Analysis of standard reference materials (SRM) for arsenic by FI-HG-AAS

To check the accuracy of the techniques various types of SRM have been analyzed for environmental and biological samples. The results are given in the **Table 3.2**. The results show good agreement with the certified values.

Table 3.2: Analysis of standard reference materials (SRM) for arsenic by FI-HG-AAS

Samples	Certified Value	Found Value
CRM (BND 301) NPL, India water	990 ±200 (μg/L)	960 ± 40 (μg/L)
SRM (QCS) Metals in Water	17.6 ± 2.21 (μg/L)	16 ± 3.5 (μg/L)
GBW 07601(Hair)	0.28 (μg/g)	0.278 (μg/g)
NIST, SRM 2670 (Urine) Elevated level	480 ± 100 (μg/L)	477 ± 30 (μg/L)
CRM 278 (Mussel Tissue)	5.9 ± 0.2 (μg/g)	6.1 ± 0.3 (μg/g)
NIES-2 (Pond Sediment)	12.2 ± 2 (μg/g)	9.85 ± 0.5 (μg/g)
Chinese River Sediment 81-101 (of 1981)	56.0 ± 10.0 (μg/g)	53.79 ± 2.0 (μg/g)

3.7 Arsenic removal experiments

3.7.1 Preparation of surface functionalized iron oxide nanoparticles

The Fe_2O_3 nanoparticle was prepared through a simple, versatile and economic gentle chemistry route. Homogeneous mixing of the initial ingredients and low temperature thermal treatment involved in this process yield uniform nanoparticles with narrow size distribution. The surface of the nanoparticles has been modified by fatty acid to improve their adsorption efficiency. First, high purity iron (III) nitrate ($FeNO_3. 9H_2O$) and stearic acid were melted to form a homogeneous solution. The homogeneous solution was then heated at 125° C for 2 hr. A reddish brown viscous mass was formed which was cooled at room temperature and then treated with tetrahydrofuran (THF).

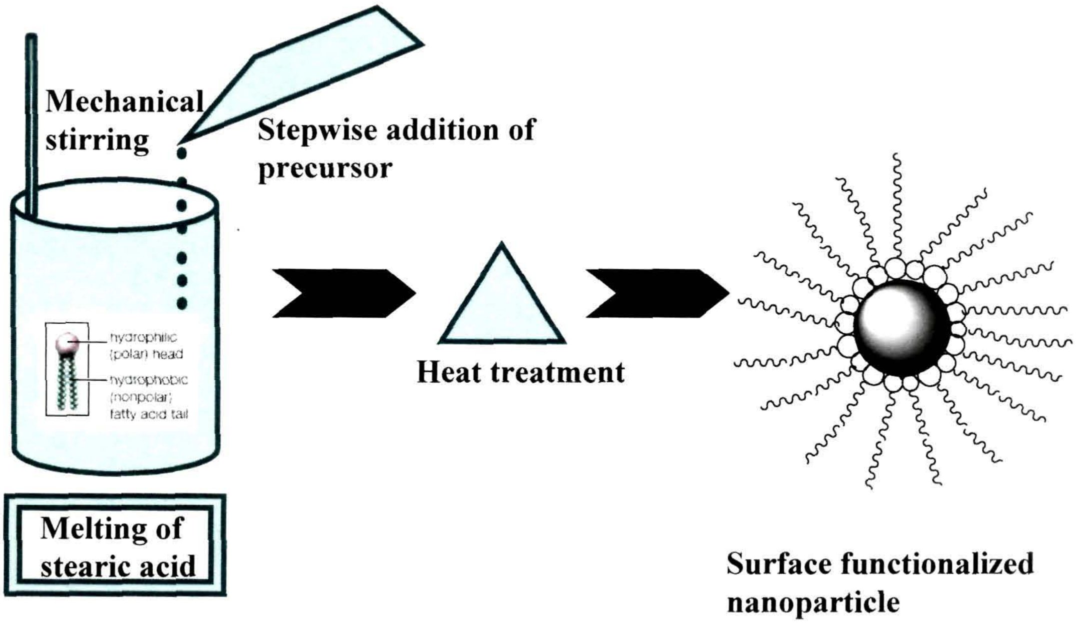


Fig 3.6: Synthesis technique of surface functionalized nanoparticles

The resulting solution was stirred intensely for 30 mins, and powdery precipitates from the solution were collected by centrifugation. The precipitates were dried in an air oven at 70° C for 36 hrs. Nanoparticles of iron oxide were obtained by heating the precipitates inside an electrical heating furnace from room temperature to 250° C and 600° C, without any holding at a heating rate of 10° C/min (Deb et al. 2006). The hydrophobic stearic acid is one way restricting the growth of the particles yielding uniform spherical ultrafine nanoparticles with surface modification by carboxyl functionalization to enhance the surface activity for adsorption. The schematic diagram of the synthesis technique of the nanoparticles is shown in **Fig 3.6.**

3.7.2 Characterization of the adsorbents

3.7.2.1 Transmission electron microscope (TEM) analysis

The ultrafine nanoparticles prepared for arsenic removal were characterized using Transmission Electron microscope (TEM). The TEM experiment was performed using a JEM-100CX II transmission electron microscope operated at 120 KV. It has a magnification from 100X to 370000X and a resolution of 0.2 nm. At first, a small amount of sample (both unheated treated and heat treated at various temperatures) was put into eppendorf filled with 95% of ethanol solution. After doing ultrasonification for 10 minute, one drop of aqueous dispersion of iron oxide nano particles were dipped onto carbon coated copper mesh and dried in an oven at 70° C for 20 minutes. Particles were imaged using a 35 mm roll film camera.

3.7.2.2 Fourier transform infrared spectroscopy (FT-IR) analysis

Fourier Transform Infrared Spectroscopy (FT-IR) was used to probe the interaction of the arsenic and the sorbent. The FT-IR was used to determine the vibration frequency changes in the sorbents due to the sorption. Virgin and arsenate-loaded sorbents were analyzed by the FT-IR spectroscopy. The samples were mixed with pure potassium bromide which acts as background at an approximate mass ratio of 1:10 (sample : KBr). The resulting mixture was pressed at 10 tons for 5 min to form a pellet. The pellet was characterized with infrared transmission spectra using a Nicolet (Impact

410) FT-IR spectrophotometer. The spectra were collected within the range of 400 and 4000 cm^{-1}. All the spectra were recorded and plotted in the same scale on the transmittance axis.

3.7.3 Batch experiment

Batch experiments were conducted using polypropylene tubes to study the removal of arsenic (both As(III) and As(V)) with iron oxide nanoparticles (bare and surface functionalized). The adsorption experiments were carried out under a nitrogen atmosphere. Arsenic concentrations were controlled at 0.1, 0.2, 0.3, 0.4 and 0.5 ppm by diluting the stock. These arsenic concentrations were chosen keeping in mind the contaminant level in drinking water in some of the high-alert zones of the world ranging from the United States to Bangladesh. The pH values were measured using a portable pH meter, calibrated using commercial pH 4.01 and 7.0 buffers. The pH values of the test solutions were adjusted to 2 to 9 (± 0.1 pH unit) using either diluted 0.1M hydrochloric acid (HCl) or 0.1 M sodium hydrochloric (NaOH). Approximately 0.0025g, 0.005g, 0.01g, 0.025g, 0.05g of adsorbent were put in contact with 50 ml of arsenic (arsenate and arsenite) solutions prepared at a predetermined arsenic concentration using deionized water, followed by rigorous stirring at room temperature until the adsorption equilibrium was reached. These parameters were varied to measure the effect of experimental conditions on arsenic adsorption to the so prepared nanoparticles. The supernatant was collected at 10 minutes interval directly from the tubes after the reaction using a 10 ml disposable syringe. Samples were centrifuged at 3000 rpm for 15 min and filtered through 0.45 μm syringe filters and analyzed for arsenic. The pH was checked at the end of each experiment to confirm that no change of pH had occurred. The adsorption capacities were calculated from the difference between the initial and the equilibrium concentrations.

3.7.4 Kinetics

Kinetic studies were also conducted at different intervals of time and concentrations in polypropylene tubes to determine the rate of arsenic removal by Fe_2O_3 nanoparticles. The same procedure was used for analysis as in adsorption experiments.

3.7.5 Entrapment study

One Gram of sodium alginate was dissolved in 50mL deoxygenated deionized water (DDW) at room temperature (25±2°C). The alginate–water mixture was stirred until complete dissolution was achieved (~20–30 min) and left at room temperature for ~30 min to allow the air/gas bubbles generated due to mixing to escape (to ensure that the alginate beads did not float in the aqueous solution). The alginate solution (2%, w/v)was gently mixed with 0.01, 0.025 and 0.05 g of surface functionalized nano powder. This mixture was dropped to 10% $CaCl_2$ solution (v/v) deoxygenated aqueous solution of $CaCl_2$ at room temperature. As soon as the alginate drops came in contact with the $CaCl_2$ solution, Ca-alginate gel beads of approximately 2 mm diameter were formed. To ensure that almost all nano powder were entrapped, the alginate solution and nano powder mixture was continuously stirred with a glass rod. The leftover nano powder (in the beaker) was accounted for by measuring them after washing them with deoxygenated water (APHA, 1998). The average amount leftover (not entrapped) was found to be 0.0001 g (out of total 0.05 g) which corresponds to an error of 0.2%. The gel beads were retained in the deoxygenated $CaCl_2$ solution for ~ 9 h for hardening and then washed with DDW. A minimum of 6 h hardening ensures that the beads allow optimal diffusion of substrates into and out of them (Aksu et al 1998, Garbayo, et al. 2002). The beads entrapping the nanoparticles were then added to the so prepared arsenic solutions followed by rigorous stirring. The supernatant was collected at certain interval until the adsorption equilibrium was reached.

CHAPTER FOUR

4. Arsenic in the groundwater of Majuli - the largest river island of the Brahmaputra: Prevalence and exposure impacts.

4.1 Introduction

Majuli island of the Brahmaputra river in Assam, is recently short listed for UNESCO World Heritage list (The Hindu, March 14, 2011). The island is bounded by three important rivers - the Kherkutia Suti (an anabranch of the Brahmaputra), the Subansiri river in the north and the Brahmaputra river in the south. The Brahmaputra is an International river, originated from eastern part of Mansarobar lake in Tibet Plateau between the Kailash range and the Himayalan range, flows through China, Bangladesh and India with large braided channel in Assam. The Subansiri - the largest tributary of the Brahmaputra, is a trans Himalayan river originating from the western part of the Mount Porom. After flowing for 190 km through Tibet, it enters India. It continues its journey through the Himalaya for 200 km and enters into the plains of Assam through a gorge near Gerukamukh (Sarma et al. 2004). Some small streams (Dehing, Looicheh, Dhekia, Kakarikata, Oraguri) and a few rivers (Tuni, the largest river of the island) flow through Majuli island (Sarma et al. 2004). The island is comprised of both older and younger alluvium and recent age active flood plain deposits (Sarma et al. 2004). As the source of arsenic is the Himalayan mountain and the Tibet Plateau, the flood plains of all the rivers that originated from those sources are expected to be arsenic contaminated (Chakraborti et al. 2004). Since, most parts of the Majuli island are formed by flood plain deposits of Brahmaputra and Subansiri river, therefore, it has anticipated arsenic contamination in the newer alluvium (Holocene) of the Majuli island.

In Bangladesh and India, the overall groundwater in the flood plains of Ganga-Meghna- Brahmaputra (GMB) rivers are mostly found to be contaminated with arsenic (Chakraborti et al. 2004). In India the first groundwater arsenic contamination and health effects were reported from Panjab and Haryana (Dutta & Kaul 1976). In 1984, arsenic contaminated groundwater was discovered in lower Ganga plain of West Bengal (Garai et al. 1984). The groundwater arsenic contamination was reported from Bihar and Uttar Pradesh in middle Ganga plain (Chakraborti et al. 2003). Groundwater arsenic contamination was reported from Jharkhand and North Eastern Hill states (Chakraborti et al. 2004; Singh et al. 2004; Nickson et al. 2007). In recent years, arsenic in groundwater has also been reported from various parts of Assam and adjoining areas (Singh et al 2004; Chakraborti et al. 2004). These areas mostly fall in the vast riverine tracts of the Brahmaputra and Barak valley areas. Although groundwater has been monitored by the Public Health and Engineering Department (PHED), partly in collaboration with UNICEF, in Majuli, detailed finding are yet to be published. Moreover, up to now there is no study on the biological samples of people exposed to arsenic. In this dissertation, for the first time an attempt has been made to study the presence of arsenic in the hair, nail and urine of a group of people mainly living in recent flood plain areas who are exposed to arsenic through contaminated groundwater. To know the potential source of arsenic in the groundwater, an understanding is required about the characteristics of the sediments. Therefore, it is felt necessary to study the borehole sediment samples of the island to find out the chemistry involved in leaching out of arsenic and the mode of occurrence and origin.

4.2 Results and discussion

Water samples have been analyzed from 380 tubewells of the estimated 28432 hand tubewells (Ground water information booklet, 2008) in the Majuli island. Of the 380 water samples analyzed for arsenic, 286(75.3%) were from Majuli and 94(24.7%) Ujoni Majuli block. The age of wells was collected from the owner of each household and ranged from less than 1–25 years. Depth of the tubewells (n = 303) indicated that they are in the range of 6-73 m, with an average of 14 m. Most of the tubewells were private except a few installed by PHED for public use.

4.2.1 Groundwater arsenic contamination status in of Majuli island

Table 4.1 shows the distribution of arsenic concentration range in the water samples collected from the affected blocks of Majuli. The distribution pattern of arsenic in groundwater shows that 37.6% of the tubewells exceeds 10 μg/L (the guideline value of arsenic concentration in drinking water set by WHO), 21.6% between 11 and 50 μg/L and 14% exceeds 50 μg/L (Indian standard of arsenic in drinking water). In addition, 2% of the tubewells had arsenic concentration more than 300 μg/L, the concentration predicting arsenical skin lesions (Rahman et al. 2001, Chakraborti et al. 2002). The distribution of arsenic concentration in 20 Gaon Panchayats (GPs) of Majuli is given in **Table 4.2**. The total sample analyzed (380) covering all the GP (**Table 4.2**), 62.4% are arsenic safe, that is, with concentration less than 10 μg/L. The most severely affected GP was Sriluhit, from Majuli block where 58.3% of the tubewell water contained >10 μg/L and 43.3% contained >50 μg/L arsenic, 10% contained >300 μg/L arsenic (**Table 4.2**). Moreover, the highest arsenic concentration (468 μg/L) was found in the groundwater of this GP. Although from table 4.2 it appears that, in the Ahatguri GP 80% samples contain arsenic >10μg/L, and 60% samples >50 μg/L, but from severity point of view this GP should not be considered as the highest affected. Because, the total number of samples collected from this GP is very less (n = 5) compared to Sri luhit GP. The least affected GP was Phuloni from Ujoni Majuli block, where none of the samples (n = 5) has arsenic >10μg/L (**Table 4.2**). Form the study it is evident that, the degree of contamination of arsenic in groundwater is higher in Majuli block as compared to the Ujoni Majuli block. A summary of the present groundwater arsenic contamination status in Majuli island is presented in **Table 4.3** and **Fig 4.1**. From **Fig 4.1**, it appears that most of the highly arsenic contaminated areas of Majuli were located in the flood depositional areas, towards north. **Fig 4.2** shows the distribution pattern of arsenic concentration against the percentage of total groundwater samples collected from Majuli. A comparison of arsenic concentrations between various places of the Ganga Meghna Brahmaputra (GMB) plain and the Majuli island is presented in **Table 4.4**. Although the number of water samples analyzed for arsenic in Majuli is much less as compared to different places of the GMB plain, however the result in respect of percent of samples having arsenic concentrations >10μg/L and >50 μg/L are similar (**Table 4.4**). The arsenic contaminated places of the GMB plain (including the river island Majuli) is shown in Fig 4.3 in which year and state wise first reporting of arsenic in ground water have been mentioned.

Table 4.1: Block wise distribution of arsenic concentration range (μg/L) in the collected groundwater samples.

Study area	<3	4-10	>10	11-50	>50	51-100	101-200	201-299	>300	301-300	>400
Majuli N=286	132 (46.2)[a]	43 (15)	120 (41.9)	65 (22.7)	49 (17.1)	19 (6.65)	24 (8.4)	3(1.05)	7 (2.5)	5 (1.8)	2 (0.7)
Ujoni Majuli N= 94	58 (61.7)	15 (16)	23(25)	17 (18)	4 (4.3)	3 (3.2)	Nil	1 (1.1)	Nil	Nil	Nil
Total N=380	190 (50)	58(15.5)	143 (37.6)	82 (21.6)	53(14)	22(5.8)	24(6.3)	4(1.1)	7(1.8)	5(1. 3)	2(0.5)

[a] Figures in parentheses are percentages.

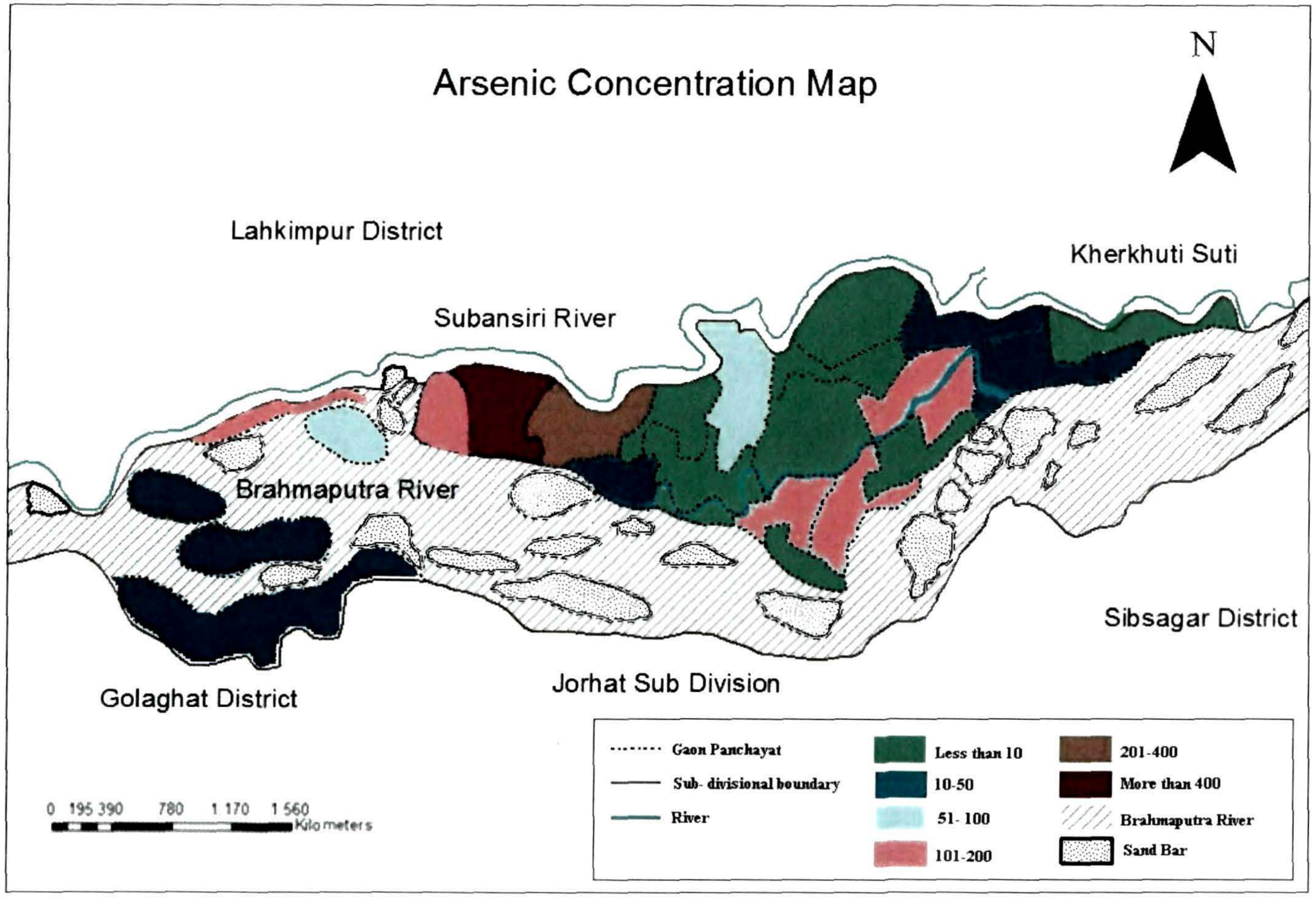


Fig 4.1: Gaon Panchayat wise arsenic concentration (µg/L) map of Majuli.

Table 4.2: Distribution of arsenic concentration range in the collected groundwater from different Gaon Panchayats (GPs) of Majuli.

		Arsenic concentration range(µg/L)							
Blocks	**GP**	**No of samples**	**<10**	**>10**	**>50**	**>100**	**>200**	**>300**	**>400**
Majuli	Kamalabari	30	19(63.3)	11(36.7)	1(3.3)	-	-	-	-
	Rawanapar	11	7(63.6)	4(36.4)	2(18.2)	-	-	-	-
	Bongaon	25	17(68)	8(32)	3(12)	2(8)	-	-	-
	Dakhin Kamalabari	14	11(78.6)	3(21.4)	1(7.1)	-	-	-	-
	Garmur	7	6(85.7)	1(14.3)	-	-	-	-	-
	Pokajora	11	6(54.5)	5(45.5)	2(18.2)	-	-	-	-
	Karatipar	56	28(50)	28(50)	8(14.3)	6(10.7)	-	-	-
	Chilakola	27	18(66.7)	9(33.3)	3(11.1)	2(7.4)	-	1(3.7)	-
	Sri luhit	60	25(41.7)	35(58.3)	26(43.3)	14(23.3)	5(8.3)	6(10)	2(3.3)
	Dakhinpat	6	4(66.7)	2(33.3)	-	-	-	-	-
	Ahatguri	5	1(20)	4(80)	3(60)	-	-	-	-
	Dakhin Ahatguri	30	20(66.7)	10(33.3)	-	-	-	-	-
Ujoni Majuli	Phuloni	5	5(100)	-	-	-	-	-	-
	Rongachahi	5	4(80)	1(20)	-	-	-	-	-
	Cherpai	9	6(66.7)	3(33.3)	-	-	-	-	-
	Luitporia	10	8(80)	2(20)	1(10)	-	-	-	-
	Sri Ram	51	39(76.5)	12(23.5)	3(5.9)	-	1(1.9)	-	-
	Jengrai	8	5(62.5)	3(37.5)	-	-	-	-	-
	Ratanpur gayan	6	4(66.7)	2(33.3)	-	-	-	-	-
	Ratanpur miri	4	4(100)		-	-	-	-	-
	Total [a]	**380**	**237(62.4)**	**143(37.6)**	**53(14)**	**24(6.3)**	**6(1.6)**	**7(1.8)**	**2(0.53)**

[a] Figures in parentheses are percentages.

Table 4.3: Summary of present groundwater arsenic contamination status in Majuli.

Parameters	Majuli
Area in Sq. km.	400
Population (in lakh)	1.5
Total number of blocks (No. of blocks surveyed)	2(2)
Total number of GPs (No. of GPs surveyed)	20(20)
Total number of villages (No. of villages surveyed)	194 (96)
Total number of water samples analyzed	380
% of samples having arsenic >10μg/L	37.6
% of samples having arsenic >50μg/L	14
% of samples having arsenic >300μg/L	1.8
Maximum arsenic concentration	468 μg/L

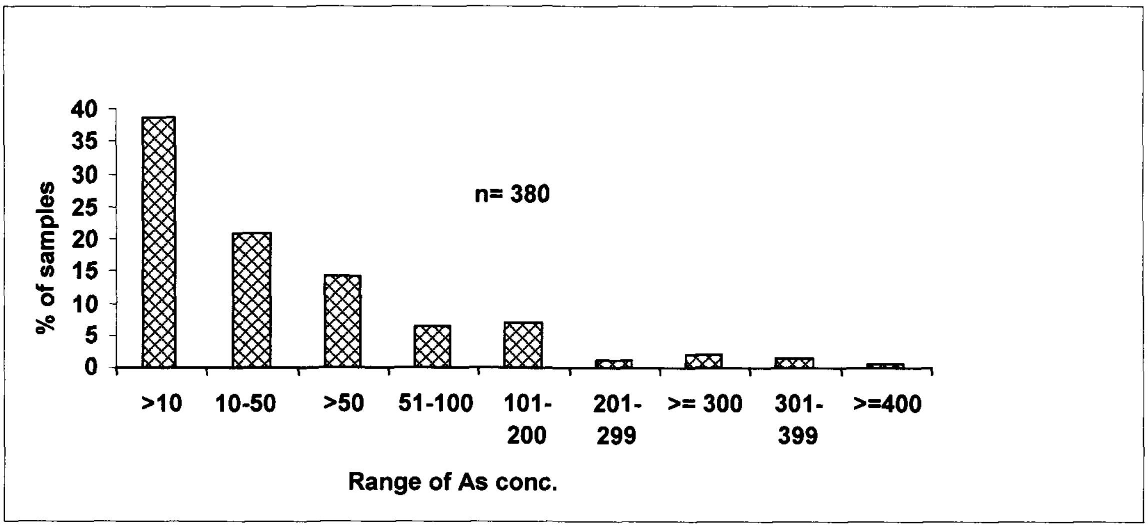


Fig 4.2 Different ranges of arsenic concentration (μg/L) verses percent of samples in Majuli island of Assam.

Table 4.4: Comparison of arsenic concentration above 10 and 50 µg/L in ground water of arsenic affected places in GMB Plain and Majuli island.

Places in GMB Plain	**Total samples analyzed for As**	**% Samples above 10µg/L**	**% Samples above 50µg/L**	**Maximum arsenic concentration µg/L**	**Reference**
Uttar Pradesh	4,780	46.5	27.7	3,191	Ahamed et al. 2006a
Bihar	19,961	32.7	17.8	2,182	Ahamed 2006
Jharkhand	3,354	35.0	15.0	1,018	Ahamed et al. 2008
West Bengal	140,150	48.1	23.8	3,700	Ahamed et al. 2008
Bangladesh	50,808	40.3	26.3	4,730	Ahamed et al. 2008
Majuli	**380**	**37.6**	**14**	**468**	**Present study**

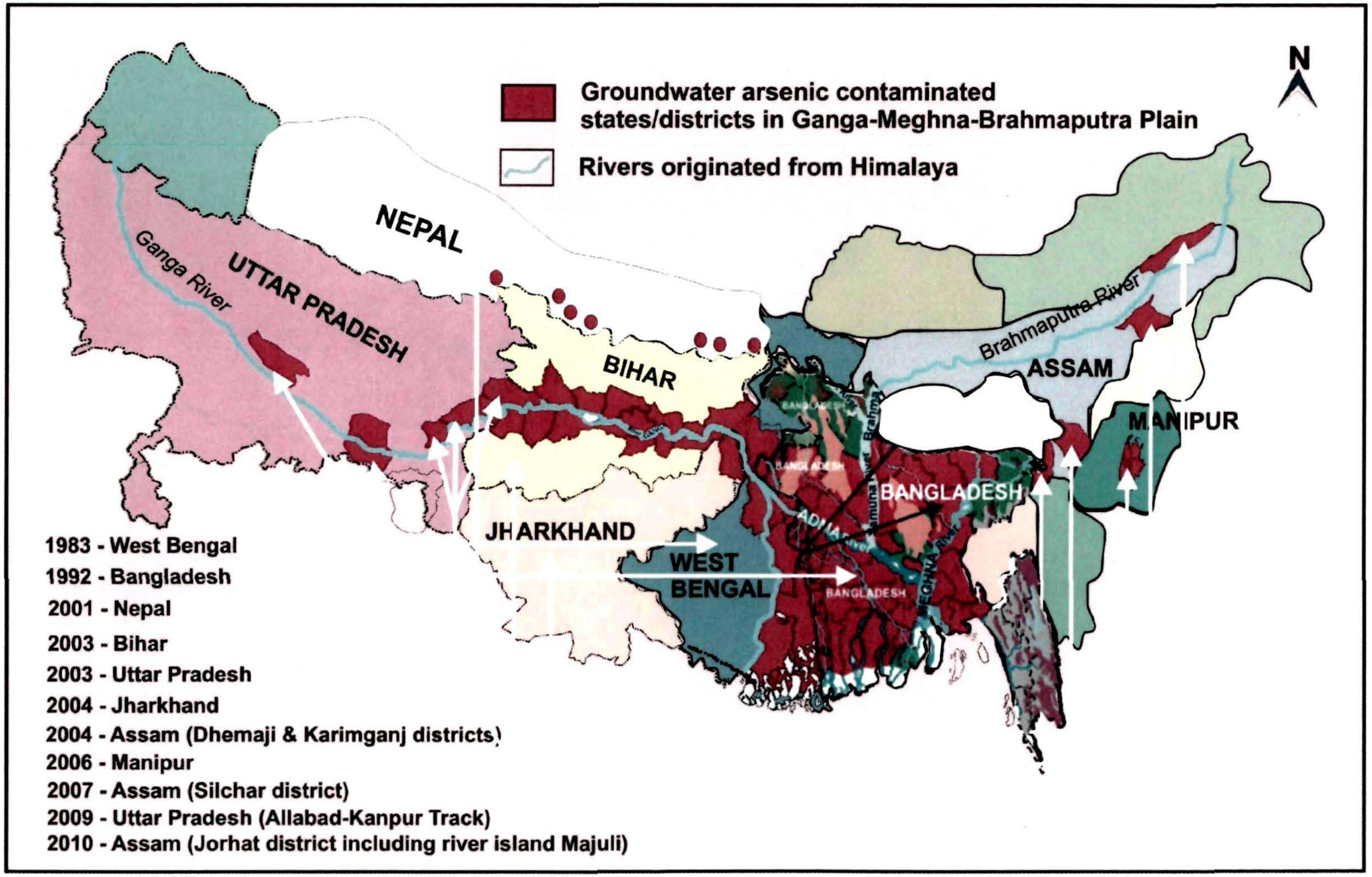


Fig 4.3: Arsenic contaminated places in GMB Plain (not to the scale)

4.2.1.1 Variation of arsenic concentration with tubewell depth

During the field survey it is possible to collect the information regarding the depth of 303 numbers of tubewells out of total 380. Of these, 77% tubewells are shallow in the depth upto 15 m. It appears from **Fig. 4.4** that the concentration of arsenic gradually decreased beyond 30 m depth with few exceptions. The depth of one tubewell is as high as 73 m, which is free from arsenic. The correlation between groundwater arsenic concentration and depth of the tubewell was very poor (r =0.02) suggesting that there is no systematic variation between groundwater arsenic concentration and tubewell depth in Majuli. However, Chakraborti et al. (2004) found strong relation between the arsenic concentration and depth in the GMB plain. Thus, we expect if the villagers of Majuli island install deep tubewells of more than 70 m they may get arsenic free water.

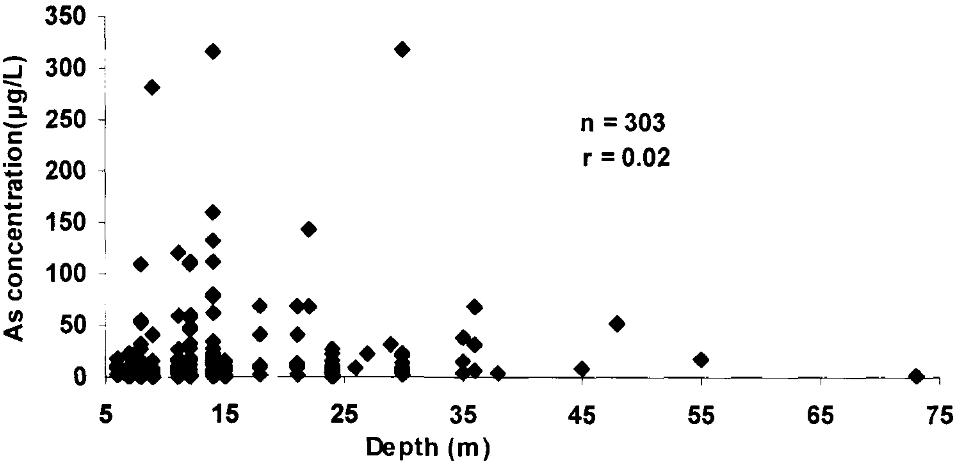


Fig 4.4: Distribution of arsenic concentration against depth of tube-wells .

4.2.1.2 Correlation of iron concentration with arsenic and tubewell depth

Water samples from 319 tube wells in Majuli were analyzed for iron. Iron concentrations in the samples ranged from 36 to 44280 µg/L, with a median of 1245 µg/L and a mean of 3168 µg/L (standard deviation 4217 µg/L). Almost 86.5% of the groundwater samples of Majuli were found above the limit (300 µg/L) as given by WHO. Generally, iron is a common element found in arsenic contaminated ground waters (Welch et al. 2000, Chakraborti et al. 2001, Meng et al. 2001). Being a highly reactive element , iron oxides serves as a control on the spread of arsenic and other heavy metals (Cornell et al. 1996). Statistically, a poor positive correlation (r = 0.36) between the concentration of iron and arsenic was observed in the present study (**Fig. 4.5**). Similar poor relationship was observed between As and Fe (r = 0.24) in West Bengal groundwater (Chakraborti et al. 2009). The probable reason for the poor relationship between arsenic and iron is that there are many processes by which iron may be released from groundwater and that some of these may not also involve arsenic (Harvey et al. 2002).

Iron concentration in tubewells in Majuli island was similar to those of the GMB plains (**Table 4.5**). **Table 4.5** shows the comparison of iron concentrations in tubewells in the Majuli island and the various places of GMB plain. The percentage of samples having iron concentration above 10,000 µg/L (7.8%), 15,000 µg/L (4.07%) and 20,000 µg/L (1.25%) is found to be highest in Majuli compared to other places of GMB plain (**Table 4.5**).

The relation between iron concentrations with depth of the tubewells has been studied and found that, higher iron concentration recorded in tubewells having less depth, ranging between 8-35 m (**Fig 4.6**). Beyond the depth of 35 m iron concentration gradually get decreased but the concentrations are still higher than WHO guideline value (300 µg/L).

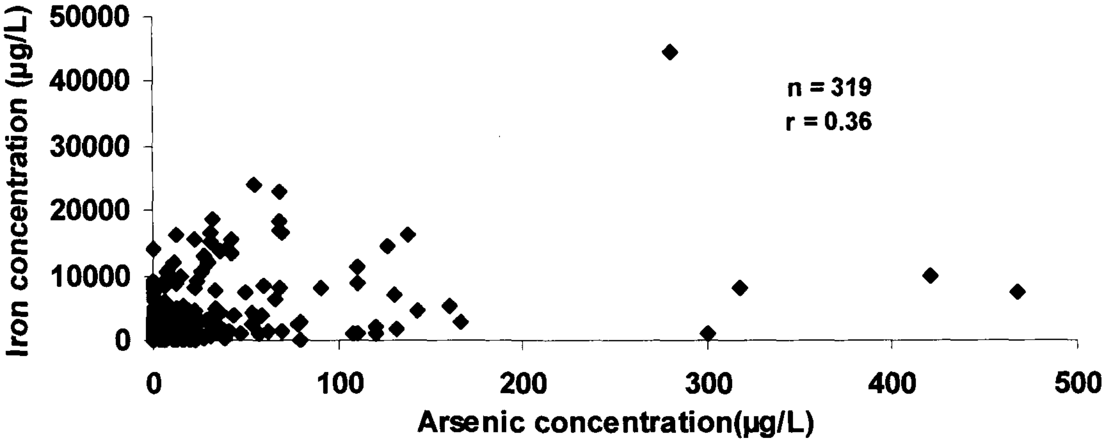


Fig 4.5: Correlation between arsenic and iron in Majuli ground water.

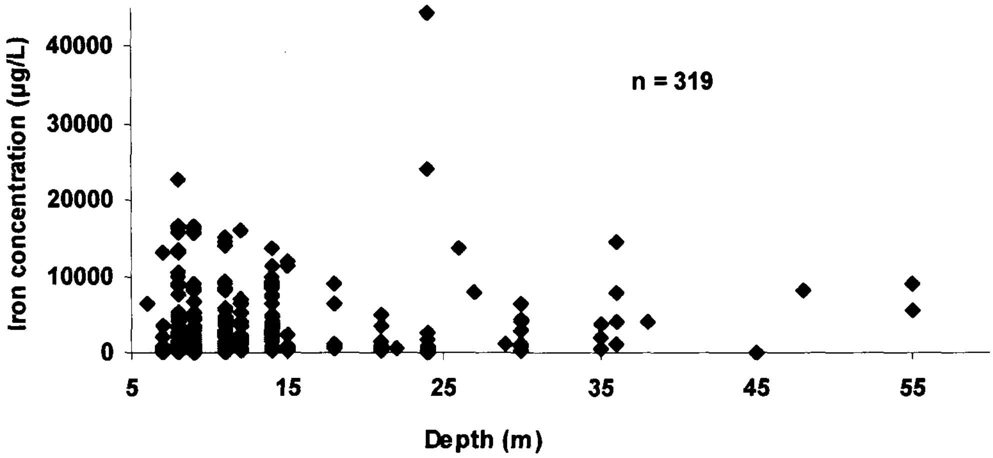


Fig 4.6: Distribution of iron concentration against depth in hand tube-wells of Majuli island, Assam

Table 4.5: Comparison of iron concentrations in hand tubewells of arsenic affected places in GMB Plain and Majuli island

Places in the GMB plain	**Total samples analyzed**	**% of samples >300 µg/L**	**% of samples >1000 µg/L**	**% of samples >5000 µg/L**	**% of samples >10,000 µg/L**	**% of samples >15,000 µg/L**	**% of samples >20,000 µg/L**	**Max. conc.**
Uttar Pradesh	583	94.5	77.9	31.9	2.6	0.5	0.3	43,575
Bihar	1,414	95	79.5	25.5	2.3	0.3	0.17	21,630
Jharkhand	559	89.3	52.6	16.6	1.6	-	-	12,589
West Bengal	17,050	93.2	75.6	28.3	4.3	0.9	0.4	77,000
Bangladesh	547	99.5	95.2	42.6	1.3	0.4	0.2	48,773
Majuli	319	86.5	61.4	21.3	7.8	4.07	1.25	44,280

4.2.2 Characterization of borehole sediments in Majuli island of Assam

Bore hole sediment samples were collected from different depths during tube well installation at different locations (described in chapter 3). After analyzing the aliquots from borehole sediment samples (n = 43) the arsenic concentration was found in the range from 0.23 mg/Kg to 1.44 mg/Kg (**Table 4.6**). The highest concentration of arsenic (1.44 mg/kg) was found for the sample BH-1 at a depth of 18.3 m. From the analysis it is observed that arsenic concentration in sediments is not dependent on depth. Although it was expected a high arsenic-rich sediment because of high abundance of arsenic in groundwater in the area, but the results showed that the sediments are not rich in arsenic. As the sediments have lower concentration of arsenic as compared to background value (5-10 mg/kg), it can be assumed that the sediment is not the only source of arsenic in the groundwater of Majuli. Therefore, hypothesis we would like to extend is that the water is getting contaminated with arsenic either in the recharge area of the aquifer or enroute. Thus, it may be assumed that the arsenic rich water may be flowing from the Himalayan head and due to the recharge of the aquifer with this water, high concentration of arsenic is found in the groundwater samples (McArthur et. al., 2004) and this is considered today as most accepted hypothesis (Kunar et. al., 2009).

Table 4.6: As concentration(mg/kg) in the borehole sediment samples at different depths.

		Bore hole nos.						
Sl.no.	**Depth(m)**	**BH-1**	**BH-2**	**BH-3**	**BH-4**	**BH-5**	**BH-6**	**BH-7**
1	6.1	—	—	—	0.92	1.21	—	—
2	18.3	1.44	0.5		1.21	0.87	0.66	0.36
3	21.3	0.34	0.54	0.42	0.8	0.55	0.85	0.75
4	24.5	0.66	0.44	0.5	0.39	0.39	0.44	0.59
5	27.5	0.51	0.33	1.37	0.78	1.29	0.62	0.23
6	30.5	0.83	0.34	BDL	0.45	0.33	0.85	0.25
7	33.5	0.33	0.35	0.29	0.48	0.29	0.58	0.25

Depth wise concentration of heavy metals in sediment samples (n = 23) is shown in **Table 4.7**. From the results it is observed that the concentration of the heavy metals does not vary with depth. Parametric presentation of arsenic and other heavy metals (mg/kg) in sediments is shown in **Table 4.8**. The mean Fe (1916388), Mn (450.1), Co (57.8), Pb (39.5), Zn (33.2) and Ni (12.7) are in higher side whereas mean Cr (0.09) and Cd (0.08) concentrations are in lower side. The concentration of Fe (range: 234702-3868028 mg/kg) and Mn (range: 172.4- 1879.1 mg/kg) was found very high in all the samples. The regression analyses were carried out between the arsenic and other heavy metals in sediment samples. The linear regressions showed poor correlation between As and Cd ($r^2 = 0.007$), As and Pb ($r^2 = 0.027$), As and Cr ($r^2 = 0.022$), As and Mn ($r^2 = 0.04$), As and Co ($r^2 = 0.025$), As and Ni ($r^2 = 0.006$), As and Cu ($r^2 = 0.029$) and As and Zn ($r^2 = 0.028$). We have not found a good correlation between As and Fe ($r^2 = 0.192$) in the sediments of Majuli. Although in Ganges aquifer sediments, good correlation has been reported between As and Fe (Nickson. 1997, Roychowdhury. 1999), a poor correlation was observed between As and Fe ($r^2 = 0.075$) in soils from an arsenic affected area of West Bengal (Roychowdhury et al. 2002a).

The statistical presentation of As/Fe ratio is given in **Table 4.9**. Identical values of the As/Fe ratio (range: 0.0000001-0.000001, std dev: 0.0000003) in the sediments have been observed in different depth ranges. The identical values of the As/Fe ratio of the borehole sediment from different depths of a single borehole or from different boreholes indicate that both iron and arsenic are coming out from a definite source (Chakraborti et al. 2001, Roychowdhury et al. 2008a).

Table 4.7: Concentration (mg/kg) of heavy metals in borehole sediment samples at different depth

Bore hole nos.	Sl. no.	Depth (m)	Concentration of heavy metals in borehole sediments (mg/kg)								
			Cd	Pb	Cr	Mn	Fe	Co	Ni	Cu	Zn
BH-1	1	18.3	0.03	17.7	0.06	267.4	2276055	52.0	6.0	8.2	14.0
	2	21.3	0.03	21.2	0.06	301.7	2166680	65.3	8.3	7.2	19.7
	3	24.5	0.02	22.6	0.04	172.4	1231680	38.7	5.3	3.1	9.1
	4	27.5	0.02	18.7	0.04	283.2	1818111	45.2	5.0	2.5	9.0
	5	30.5	0.03	34.6	0.03	338.4	2110467	57.2	6.0	3.9	13.9
	6	33.5	0.02	20.0	0.08	269.2	1896598	78.2	6.6	3.7	10.9
BH-2	7	18.3	0.02	15.4	0.05	979.6	2584362	47.3	4.6	2.3	10.3
	8	21.3	0.02	17.8	0.03	258.5	1638778	50.3	5.1	1.9	11.8
	9	24.5	0.02	16.9	0.04	269.2	1948921	47.3	4.1	2.1	9.5
	10	27.5	0.26	265.3	0.25	1879.1	1261717	138.9	29.6	22.7	78.2
	11	30.5	0.02	16.8	0.04	1106.7	2508175	46.2	4.7	3.3	10.9
	12	33.5	0.03	20.6	0.05	471.4	1797939	44.2	4.5	1.5	9.1
BH-3	13	21.3	0.02	20.3	0.07	186.9	1427433	41.5	5.6	3.0	9.4
	14	24.5	0.03	17.2	0.04	215.1	1599331	54.5	5.9	4.0	9.7
	15	27.5	0.03	18.9	0.12	573.3	2820987	53.7	49.1	5.7	13.1
	16	30.5	0.01	18.7	0.03	281.0	1563967	41.0	3.0	4.0	8.9
	17	33.5	0.06	21.2	0.04	342.1	1650037	38.9	3.1	3.6	9.1
BH-4	18	6.1	0.02	20.2	0.05	301.0	2157979	55.0	4.1	15.2	13.9
	19	21.3	0.04	19.1	0.03	435.2	2347510	47.6	5.2	18.5	10.2
	20	24.5	0.12	18.5	0.11	234.5	1131640	30.0	2.5	4.2	12.0
BH-5	21	6.1	0.02	19.8	0.05	296.8	2035836	56.1	4.0	12.3	13.2
	22	21.3	0.56	212.3	0.76	544.9	3868028	150.7	73.7	254.7	223.6
	23	24.5	0.31	33.8	0.11	345	234702	50	45.3	126.5	234

Table 4.8: Parametric presentation of arsenic and other heavy metals (mg/kg) in borehole sediments.

Element	No of sample	Mean	Min.	Max.	Median	Std.dev
As	43	0.59	0.23	1.44	0.5	0.32
Cd	23	0.08	0.01	0.56	0.03	0.13
Pb	23	39.5	15.4	265.3	19.8	63.8
Cr	23	0.09	0.03	0.76	0.05	0.15
Mn	23	450.1	172.4	1879.1	301	388.5
Fe	23	1916388	234702	3868028	1896598	703563.7
Co	23	57.8	30	150.7	50	29.2
Ni	23	12.7	2.5	73.7	5.2	18.6
Cu	23	22.4	1.5	254.7	4	56.8
Zn	23	33.2	8.9	234	10.9	63.3

Table 4.9: Statistical presentation of As/Fe ratio in borehole sediment.

Sample No.	Depth (meter)	As	Fe	As / Fe	Min	Max	Std dev.
BH-1	18	1.44	2276055	.0000010	0.0000001	0.000001	0.0000003
	21	0.34	2166680	.0000001			
	24	0.66	1231680	.0000010			
	27	0.51	1818111	.0000002			
	30	0.83	2110467	.0000003			
	33	0.33	1896598	.0000001			
BH-2	18	0.5	2584362	.0000001			
	21	0.54	1638778	.0000003			
	24	0.44	1948921	.0000002			
	27	0.33	1261716	.0000003			
	30	0.34	2508175	.0000001			
	33	0.35	1797939	.0000001			
BH-3	21	0.42	1427433	.0000002			
	24	0.5	1599331	.0000003			
	27	1.37	2820987	.0000004			
	30	0	1563967	.0000003			
	33	0.29	1650037	.0000001			
BH-5	24	1.21	2035836	.0000010			
	27	0.87	3868028	.0000003			
	30	0.92	2157979	.0000004			

4.2.2.1 SEM-EDX analysis of sediments

The sediment samples of different depth were analyzed by Scanning Electron Microscopy coupled with an Energy Dispersive X-ray Spectrometer (SEM-EDX), which provides information about major and minor elements present in various samples. The results from qualitative analysis by SEM-EDX method are presented in **Fig. 4.7** and **Fig. 4.8** respectively. In order to select an area to perform the microprobe analysis, images were taken from different regions of sediment samples (**Fig. 4.7** (a) and (b)). Oxygen, silica, iron, arsenic, manganese and bromine were detected in the samples. Moreover, trace amounts of other elements e.g. nickel, molybdenum, cadmium and lead were also detected in the sediment samples (**Fig. 4.7**). The presence of carbon was explained by the carbon coating on each sample. **Table 4.10** shows the values (% weight) of chemical analysis by EDX. The arsenic content ranging from 0.32% to 1.48%. The presence of trace elements (e.g. Pb, Cd, Cr, Mn, Ni, Zn, Fe etc.) determined using EDX analysis confirms the results obtained by ICP-MS analysis.

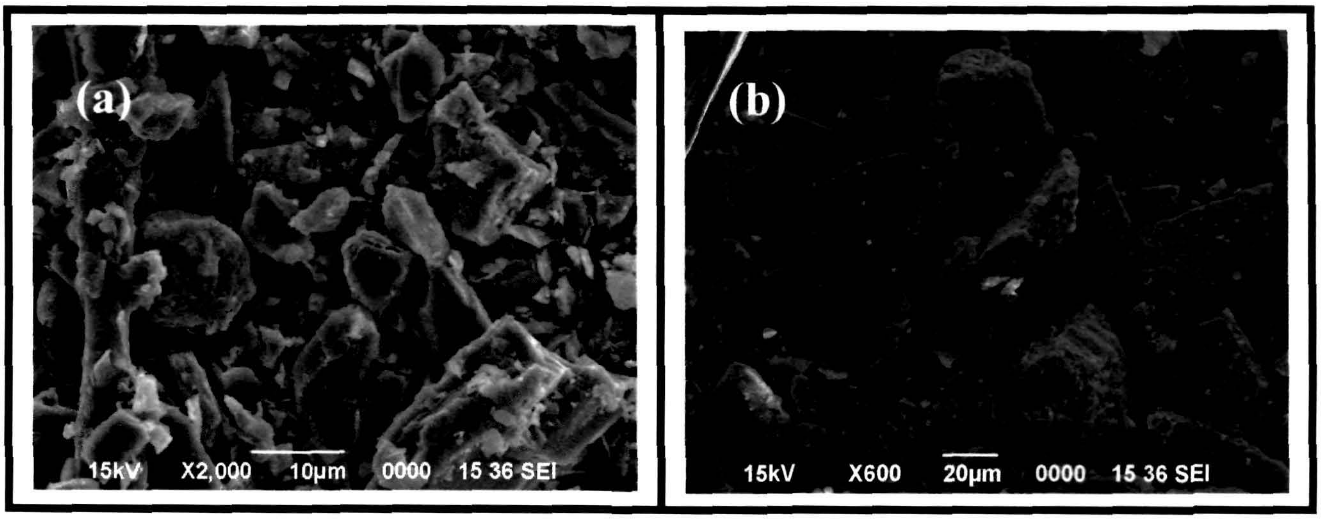


Fig 4.7: Scanning Electron Micrograph (SEM) of borehole sediment samples with highest arsenic contents. (a) BH1 (Depth 18.3 m), (b) BH3 (Depth 27.5 m).

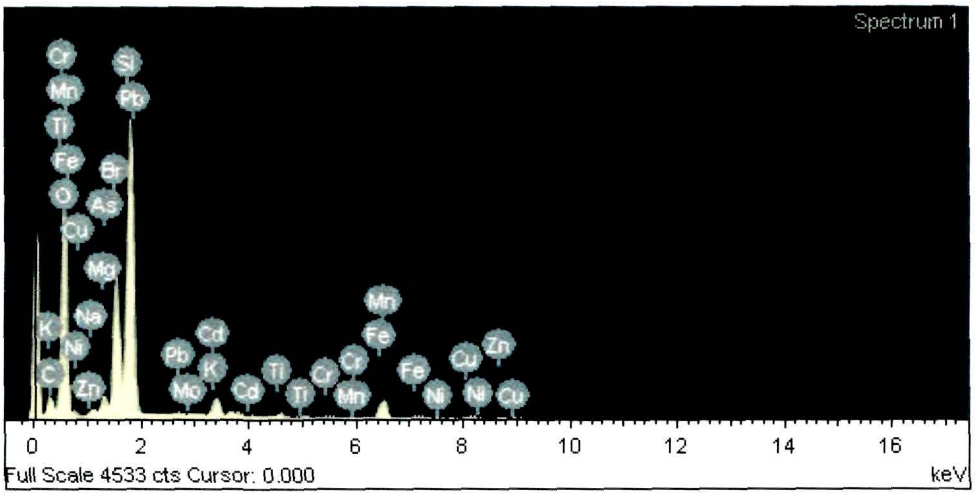


Fig 4.8: Representative EDX spectrum of dried sediments.

Table 4.10: Elemental analysis (Wt %) of sediment samples using EDX.

Element	**BH-1 (18.3m)***	**BH5 (27.5m)**	**BH3 (27.5m)**	**BH2 (27.5m)**	**BH4 (18.3m)**
C	1.82	13.17	1.19	43.35	38.89
O	35.01	48.54	53.38	50.40	40.37
Na	0.09	0.35	ND	0.62	0.49
Mg	0.49	0.63	0.70	0.07	0.46
Si	22.13	17.69	26.76	8.89	12.73
K	1.42	1.13	1.87	0.42	0.76
Ti	0.47	0.25	0.70	1.14	0.40
Cr	0.06	0.06	0.05	0.11	0.02
Mn	0.14	0.12	0.10	0.06	0.13
Fe	2.10	1.81	1.26	3.82	0.97
Ni	0.11	0.18	0.21	0.00	0.01
Cu	0.28	0.54	0.44	0.15	0.23
Zn	0.44	0.33	0.54	0.17	0.02
As	1.48	1.21	1.39	0.32	1.29
Br	17.87	13.57	12.32	4.56	4.84
Mo	0.03	0.13	ND	ND	0.15
Cd	0.52	0.39	0.60	0.14	0.06
Pb	0.14	0.19	0.15	0.15	0.02

* Figures in perentheses are depths of borehole sediments collected.
ND: Not detected

4.2.2.2 X-Ray Diffraction (XRD) study

Fig. 4.9 shows an XRD pattern of sediment sample BH-5 with depth of 27.5 m. In the figure, h,k,l values were shown in the parenthesis and peaks of the minerals were identified as hematite(1 1 3) and pyrite(2 2 0, 2 2 2). From the XRD pattern it is assumed that, the source of arsenic could be substitution of sulfur by arsenic within pyrite (Chakraborti et al. 2001).

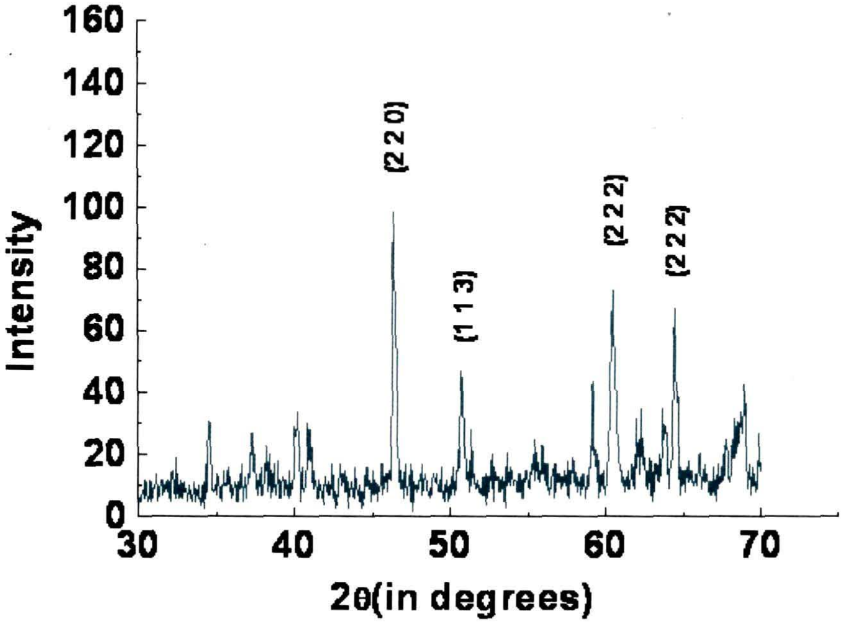


Fig 4.9: Representative XRD of borehole sediment (depth 27.5 m) showing presence of pyrite and hematite.

4.2.3 Arsenic in biological samples from exposed villagers of Majuli

Arsenic concentration in biological samples (hair, nails and urine) plays an important role in evaluating the arsenic body burden. Biomonitoring of arsenic in human currently serves as an additional diagnostic test (Povorinskaya et al. 2009). In the present study, inorganic arsenic in urine and total arsenic in hair and nail (**Table 4.11**) was measured among villagers who are exposed to high groundwater arsenic concentration (>50μg/L).

The results of arsenic analysis in different biological samples are discussed below.

Table 4.11 Statistical presentation of arsenic in urine, hair and nail samples

Parameters	**Samples from exposed population of Majuli**		
	As in urine[a] (µg/L)	**As in hair[b] (µg/kg)**	**As in nail[c] (µg/kg)**
No. of samples (n)	41	40	33
Mean	157.8	1223.1	2507.9
Median	101.8	943	1797
Minimum	20.8	224	426
Maximum	697.5	5461	11725
Standard Deviation	154.9	1039.8	2327.4
% of samples having arsenic above normal level	90	97.5	76

[a] Normal urine arsenic ranges from 5 to 40 µg/ 1.5 L/day (Farmer and Johnson , 1990).

[b] Normal hair arsenic is 80-250 µg/kg, with 1,000 µg/kg an index on toxicity (Arnold et al., 1990).

[c] Normal arsenic content of nail is 430 –1,080 µg/kg (Ioanid et al., 1961).

4.2.3.1 Arsenic in urine

Excretion of arsenic via urinary is the major pathway for the elimination of arsenic compounds from the body. Urinary arsenic is generally used as the main biomarker of recent arsenic exposure(Hakala et al.1995, Kurttio et al. 1998). In this study, inorganic arsenic and its metabolites in urine (n = 41) were measured in the sample of urine collected from the arsenic affected villages of Majuli to evaluate the extent of arsenic burden in the population who were consuming a high concentration of arsenic (average 70.5 µg/L) through drinking water. The exposed group (n = 41; 34 adults and 7 children below 12 years) was chosen from the Balijan and Borduar Chapori village of

Majuli island. Before our survey in these villages the people were not aware about the arsenic contamination of their hand tubewells.

Statistical presentation of arsenic in urine collected from the inhabitants of above mentioned villages is shown in **Table 4.11**. It is observed that 90% of urine samples had arsenic above the normal ranges. The normal levels of arsenic in hair, nail, and urine are mentioned along with references in **Table 4.11** Arsenic concentration in urine ranged from 20.8 - 697.5 μg/kg. About 53.6% and 26.8% of the urine samples contain arsenic above 100 and 200 μg/L respectively. Urinary arsenic concentration is even higher in several cases. About 12.2% of the urine samples (n = 5) with arsenic concentrations above 300 μg/L.

Table 4.12 shows the range and average arsenic concentration in urine of exposed villagers of Majuli. It appears that the average concentration of arsenic in urine (157.8 μg/L) of the exposed population are higher than the normal urine arsenic range (5 to 40 μg/ 1.5 L/day).

Table 4.12 Average arsenic concentration in urine, hair and nail of arsenic exposed population of Majuli island.

	Age(years)	**As conc. in drinking water (μg/L)**	**As in urine(μg/L)**	**As in hair (μg/kg)**	**As in nail (μg/kg)**
Average	34.73	70.5	157.8	1263.7	2515.53
Range	(5-75) (n = 41)	(50-468) (n = 41)	(20.8-697.5) (n =41)	(224-5461) (n = 40)	(426-11725) (n = 33)

The correlation between arsenic in the drinking water with arsenic in their hair, nail, and urine was determined. **Fig. 4.10** shows significant correlation (r = 0.62).

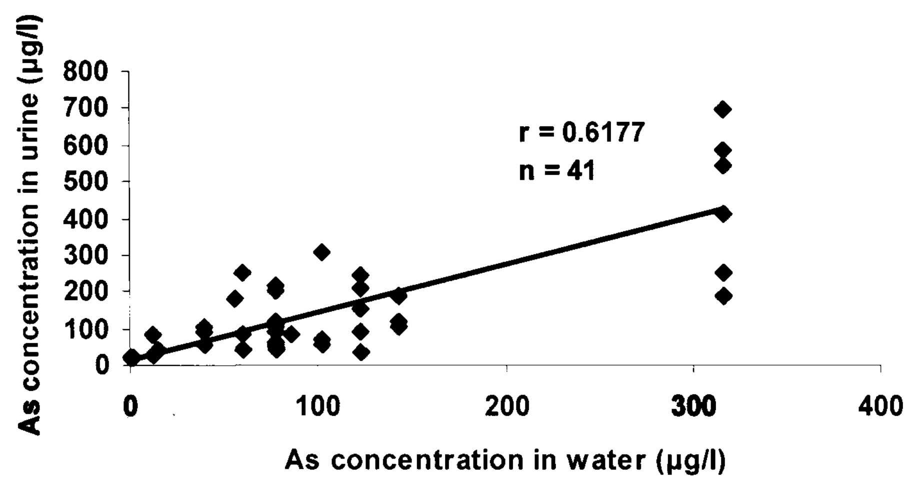


Fig 4.10:Correlation between arsenic concentration in water and urine.

4.2.3.1.1 Pattern of excretion of arsenic in urine of children compared to adults

It is generally considered that infants and children are more susceptible to the adverse effects of arsenic than adults (NRC, 1993). Many studies (Abernathy et al. 1998; Concha et al. 1998) have shown that children are at higher risk of arsenic exposure. Experimental studies have indicated that the methylation of As is influenced by the dose level, mode of administration, form of As administered, and nutritional status of the subject (Chowdhury et al. 2003, Aposhian et al. 1999). However, the influence of age is essentially unknown. To know whether the excretion of arsenic in children is higher than adults, a systematic study has been made. This study concerns the excretion of inorganic arsenic in children in the arsenic affected villages of Majuli with about >50 µg As/L in the drinking water. From the Balijan village of Majuli 7 adults and 7 children below 12 years were selected and arsenic concentration in their drinking water was knowm. **Table 4.13** shows urinary arsenic concentration (µg/L) of adult and child members of a given family exposed to same arsenic concentration in drinking water. It is interesting to note that the concentration of arsenic (average) in urine of the exposed children was much higher (339.17 µg /L), as compared to the adults (154.37 µg /L), drinking the water from the same sources. From **Table 4.13** it is evident that the concentration of arsenic in the urine of the studied children were much higher than the normal range.

From the results we may say that children retain less arsenic in their body than the adults. This may also explain why normally children do not show skin lesions compared to adults in spite of drinking same water. It is notable that, there are no statistics available on As-related health effects in the areas of the present study. Experimental studies have indicated that presence of high concentration of iron in drinking water may protect against arsenic intoxication. Further studies on the metabolism and effects of As in children are urgently needed. However, more data are needed to better understand the susceptibility of children to arsenic-induced effects.

Table 4.13: Urinary arsenic concentration (µg/L) of adults and childs, exposed to same arsenic concentration in drinking water in the same family.

Family No.	Source	Age (in years)	As conc. in drinking water (µg/L)	As in urine (µg/L)
1	Adult	31	316.8	186.1
	Child	9		413.5
2	Adult	50	278	251
	Child	11		413.5
3	Adult	40	320	241.9
	Child	7		697.5
4	Adult	45	300	216.8
	Child	11		583.4
5	Adult	48	54	59.9
	Child	5		89.7
6	Adult	35	70	64.4
	Child	10		92.4
7	Adult	50	68	60.5
	Child	11		84.2

4.2.3.2 Arsenic in hair

Chronic exposure to arsenic can be detected by measuring As in hair and was used in this study as an indicator of exposure. Statistical presentation of arsenic in hair is shown in **Table 4.11** From the results it appears that 97.5% of hair samples had arsenic above the normal ranges. Arsenic concentration in hair ranged from 224-5461 µg/kg. 100% of the hair samples contain arsenic above 200 µg/L. About 95% and 40% of the hair samples contain arsenic above 300 and 1000 µg/L, respectively. 10% of the hair samples (n =5) with arsenic concentrations above 3000 µg/L were found from Balijan village where the inhabitants consumed very high concentration of arsenic through drinking water up to the level of 468 µg/L. From the results it is found that As content in 40% of the hair samples exceeded 1 mg/kg, which is the generally accepted limit for excessive exposure (WHO 1981). Average arsenic concentration in hair of arsenic exposed population of Majuli is presented in **Table 4.12**. It is observed that the average arsenic concentration in hair (1263.7 µg/ kg) is much higher than the normal range (80-250 µg/kg). **Fig. 4.11** shows significant correlation (r = 0.53) between arsenic in the drinking water with arsenic in hair of the arsenic exposed population.

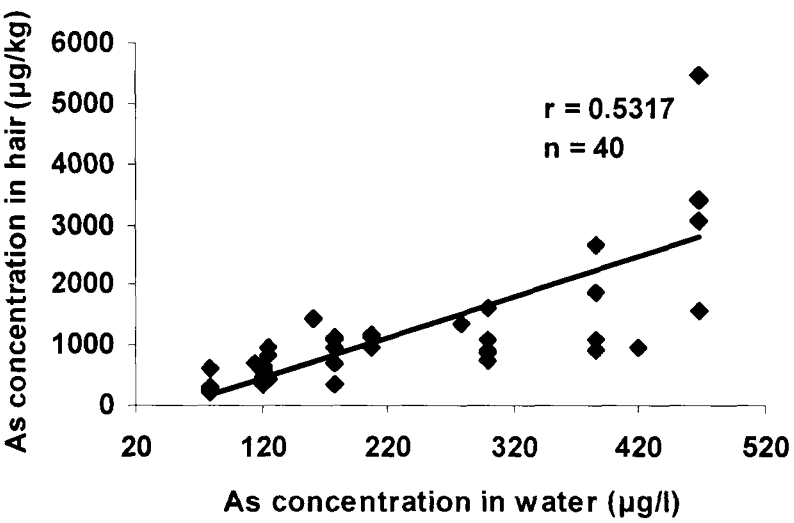


Fig 4.11: Correlation between arsenic concentration in water and hair.

Studies have shown that consumption of arsenic contaminated water is not the only reason of elevated As in hair. Washing of hair with As contaminated water may also be the another cause (Samela et al. 1981, Fergusson et al. 1983, Hindmarsh et al. 2002). There are reports that washing of hair with water containing 345 μg/L and 10 μg/L arsenic, resulted in accumulation of arsenic in hair with concentrations of 5.7 μg/g and 0.4 μg/g respectively (Fergusson et al. 1983).

4.2.3.3 Arsenic in nail

After rapid growth, nails remains isolated from other metabolic activities in the body. It is reported that after accumulation of arsenic in nails and subsequent incorporation into keratin, its mobility becomes limited (Chaudary et al. 1995, Karagas et al. 1996). Therefore, analysis of nails is considered to be a good reflection of long term exposure (Karagas et al. 1996). In this study, total arsenic in nails (n= 33) were measured in order to investigate long term exposure of residents living in areas with high environmental arsenic concentrations. **Table 4.11** shows the statistical presentation of arsenic in nails of the exposed population. It is observed that, 76% of nail samples had arsenic above the normal ranges. From the analytical results it is found that arsenic accumulation nail is higher than that of hair. Arsenic concentration in nails ranged from 426-11725 μg/kg. 100% of the nail samples contain arsenic above 400 μg/L. About 75.8% and 24.3% of the nail samples contain arsenic above 1000 and 3000 μg/L respectively. Out of the total nail samples 15.2% samples contain arsenic above 5000 μg/L. **Fig 4.12** shows significant correlation (r = 0.51) between arsenic concentration in water and nail.

The positive associations between arsenic contents measured in the urine, hair, and nails indicate the degree of severity of arsenic exposure. The arsenic concentrations in nails, hair and urine are highly correlated with the concentrations of ground water and present results agrees well with the previous reports (Chaudary et al. 1995, Karagas et al. 1996, Druyan et al. 1998, Lin et al. 1998, Chowdhury et al. 2003). Studies in highly arsenic contaminated areas of West Bengal and Bangladesh showed that arsenic concentration in body tissues increases with the increase of arsenic concentration in drinking water and hence confirms good correlation between each other (Mandal et al.

1996, Chakraborti et al 2003, Uchino et al. 2006, Roychowdhury et al. 2010). The arsenic concentrations in hair and nails were higher in comparison to urine sample. However, the concentrations arsenic were highest in nails as compared to hair and urine. A comparative study on the levels of arsenic in biological samples of the arsenic affected areas of Majuli island with worst arsenic affected places of West Bengal and Bangladesh (Mandal et al. 1997, Mandal et al. 2003, Roychowdhury et al. 2010) is shown in **Table 4.14**. Comparing the findings from Majuli with other severely affected places of West Bengal and Bangladesh, it may be concluded that Majuli is also a high risk zone, indicating severity of arsenic contamination and consequent probable health problems.

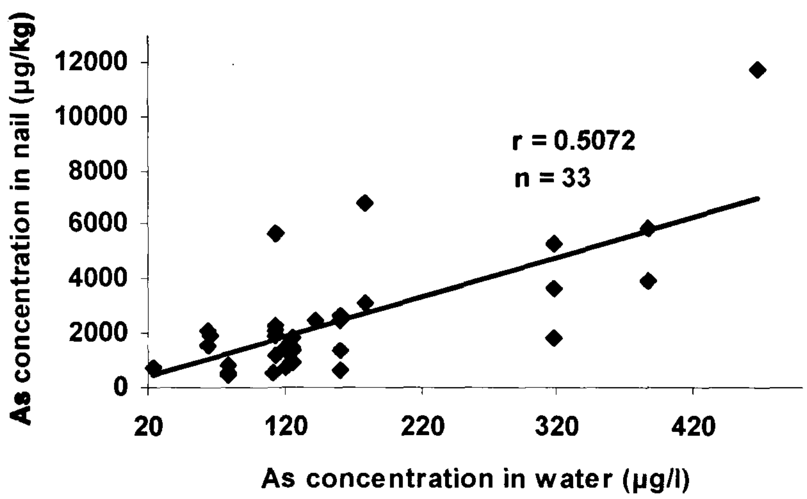


Fig 4.12: Correlation between arsenic concentration in water and nail.

Table 4.14: Comparison of arsenic in urine, hair and nail of the study group from arsenic affected locations of West Bengal and Bangladesh with that of Majuli island.

	Urine(μg/L)			Hair (μg/kg)			Nail ((μg/kg)		
Parameter	West Bengal	Bangladesh	Majuli	West Bengal	Bangladesh	Majuli	West Bengal	Bangladesh	Majuli
Sample no	9295	1043	41	7135	2942	40	7381	2940	33
Mean	181	495	157	1480	4050	1223	4560	9250	2507
Max	3147	3086	697.5	20340	28060	5461	44890	79490	11725
Min	10	24	20.8	180	280	224	380	260	426
Median	116	302	101.8	1320	2490	943	3870	6740	1797
SD	269	493	154.9	1550	4040	1039.8	3980	8730	2327.4
%*	92	99	90	57	97	97.5	83	96	76

* % of samples having arsenic above normal/ toxic level

4.2.4 Approaches for arsenic mitigation in Majuli island

After working in arsenic affected areas in Majuli island, it has been realized that arsenic mitigation strategy should be location specific. Whatever be the approach, for success at field level, without the awareness amongst the people and their wholehearted participation nothing can be achieved. During our field survey in Majuli awareness campaigns (**Fig. 4.13**) have been organized in a community level in the Balijan village where the concentration of arsenic in groundwater is very high. An attempt has been made to convince the people not to drink water from tubewells which are identified with high levels of arsenic. Probably, due to difference in sedimentary characteristics, every drinking water source in Majuli is not affected with arsenic. Since water has to come from unaffected sources only for drinking and cooking, it is possible to share an arsenic free point source such as tubewell. Therefore, we tried to make people understand about the severity of the problem and advised them to not drink the water where we found very high concentration of arsenic (>100μg/L). For this, we motivated them for sharing arsenic free- point sources where we found arsenic concentration <50 μg/L. Although, solutions based on sharing may prove only temporary, the inhabitants of Balijan village have followed our advise and started to share the sources that we have pointed out. The arsenic concentration in the drinking water was measured before and after the awareness (**Table 4.15**). It is evident that following the awareness and motivation approaches , 50 nos of people from 6 households (who were drinking highly arsenic contaminated water) changed their drinking water sources to other tubewells with arsenic <10 μg/L. From this study it was found that active people participatory appraisal appears to be one of the viable approaches to minimize or restrict the probable arsenic danger in Majuli in future.

The awareness also helped the worst affected villagers of Balijan village to have deep tubewell (about 100 ft. deep boring) installed by Rural Volunteers Centre (Okajan, Dhemaji), Majuli Unit. The villagers of the same village were helped to shift their source of drinking water from arsenic contaminated tube well to that of uncontaminated tube well suggesting them for routine groundwater monitoring and assessment need of their tube wells.

Fig 4.13: Awareness campaign in Balijan village

Table 4.15: Arsenic concentration in drinking water used by the target population before and after awareness approaches.

		Drinking water As conc.(μg/L)	
Household no	**Number of people**	**Before**	**After**
1	7	468	18*
2	7	317	5
3	10	160	10
4	8	130	4
5	11	111	5
6	7	90	10

*(newly installed tubewell)

4.2.5 Discussion

This work has attempted to understand the status of groundwater arsenic contamination in the Majuli island of Assam which is the present contender for the prestigious world heritage site tag. From the overall study on groundwater arsenic contamination in Majuli, it is found that the magnitude of arsenic calamity in the area severe. Analysis of hair, nail, and urine samples revealed that a large section of population might be sub clinically affected. Though international results show arsenical skin lesions may develop by drinking water at 100 and 200 μg/L concentration of arsenic (Astolfi et al. 1981), the present study find no such symptoms even after ingestion of >400 μg/L arsenic for a couple of years.

The island comprises both younger alluvium and older alluvium and active flood plain deposits of recent age. The morphology of the island is very dynamic in nature. Some areas have been disappeared due to erosion and some areas have newly formed due to equivalent deposition (Sarma et al. 2004). The results of the present study reveal that many of the highly arsenic contaminated areas of Majuli were formed by flood deposition of the recent Holocene age. Within our study area, Sri Luhit G.P (Lat 26°55'N to 26°58'N and Lon. 94°00'E to 94°05'E) and Chilakola G.P in Majuli block (Lat 26°55'N to 26°58'N and Lon. 94°05'E to 94°10'E) were found to have the highest arsenic concentration of 468 μg/L and 318 μg/L respectively. Due to the northward migration of the Subansiri river channel, the land mass of these contaminated areas has increased by large percentages in comparison to their original sizes. By 1990, the Subansiri river diverted the majority of its flow through the Khaboli suti, greatly diminishing the pre-existing southeasterly flowing main channel that joins with the Kherkutia suti. The bank materials of the Subansiri and Kherkutia suti, along the northern boundary of the Majuli island, are primarily channel fill materials comprising arsenic- rich sediments of the Tibetan Plateau. Similarly Luitporia G.P in Ujoni Majuli block (Lat. 27°05'N to 27°07'N, and Lon. 94°15'E to 94°20'E) containing groundwater arsenic concentration > 50 μg/l, is bounded by Kherkutia suti on the North and Tuni river on the west. Over time this area has been found to increase in total land mass due to deposition of Newer Alluvium (Sarma et al. 2004) that might be rich in arsenic. As a result, arsenic contaminated tubewell water exists in the villages situated near these river channels. The present study revealed that the quaternary alluvium deposits especially the younger regions were more arsenic-contaminated, in comparison to the older regions. The findings of the present study are in line of the earlier findings (McArthur et al. 2004, Mukherjee et al. 2006) where it was reported that the As-contaminated zones in the Ganga Padma Meghna Brahmaputra (GPMB) river basin are mostly lying within a newer alluvium plain. The middle portion of the island has considerably less arsenic contamination due to the absence of channel fill sediments in its underlying aquifers. The Brahmaputra plain is, with a few exceptions, covered by young alluvial sediments are deposited from the great sediment load carried by the river and its tributaries. The minerals on the south and north side differ a lot. The north side is fed with sediments derived from the young Himalayas while the sediments on the south side originate from the older Assam plateau (Kunte. 1988). Majuli island has been continually eroded since its formation by the shifting of the river Brahmaputra. The rate of erosion has been more prominent on the southern part of the island, resulting in the creation of several small islands from the original land mass. Due to the northward migration of the Brahmaputra, new alluvial sediment has been deposited on the southern bank, and areas formed from this arsenic rich sediment may also be contaminated.

Indeed, our preliminary survey in the city of Jorhat, located across from Majuli along the southern bank of the Brahmaputra, provides evidence of arsenic contamination. It is found that highly silty nature of sediments prevail in shallow depth (Groundwater Information Booklet, 2008) and it is a fact that inundation by flood for several times in a year is common and is responsible for high erosion and deposition in the island area. Arsenic is found high in such situations.

4.2.5.1 Probable mechanisms of arsenic mobilization

Several workers (Smedley et al. 2002, Rmalli et al. 2005, McArthur et al. 2004, Bhattacharya et al. 2006) had already proposed the mechanism of mobilization of arsenic in tubewell waters in the Gangetic delta of West Bangal, India and Bangladesh. Regarding sedimentology, the northeastern part of India, especially Assam region, has similarity with that of the Bangladesh plains (Enmark and Nordborg. 2007). Therefore, Majuli island of Assam, the site of our interest, might be expected to follow the comparable way in respect to the mobilization of arsenic in groundwater. Moreover, flood environments existing in Majuli may be one of the possible sources of arsenic in groundwater. Flooding induces reducing (anaerobic) conditions in soils. Under such conditions adsorbed pentavalent arsenic is reduced to trivalent form and is released as trivalent arsenic. Floods carry the sediments along with the contaminants (such as arsenic) that have been stored in river beds. However, the alluvial and deltaic environments are mostly characterized by reducing conditions, which can cause high arsenic concentrations in groundwater. In these environments aquifer sediments do not allow air to enter to the aquifer and reducing conditions result in increased concentrations of arsenic in solutions, which are dominated by trivalent arsenic. Therefore, flood water can carry metals that contaminate the environment.

Iron and manganese (found in high concentration in Majuli groundwater), can also play an important role in release of arsenic in groundwater. Many workers (Smedley et al. 2002, McArthur et al. 2004, and Bhattacharya et al. 2006) have proposed the importance of reductive dissolution of metal (iron) oxide/hydroxide and subsequent release of the adsorbed arsenic, in the process of its mobilization. Another factor that can affect arsenic concentration is the presence of anions such as carbonate, phosphate and sulfate in groundwater. Bicarbonate can also contribute to the mobilization of arsenic from solid. The presence of all these anions have been reported in the groundwater of Majuli (Groundwater Information Booklet, 2008). Another anion , which was found to be present in considerably high concentration in groundwater, is phosphate, which can enhance the mobilization of arsenic through competition with arsenic for the adsorption sites on solids.

The sediment in the northern region contains a high percentage of clay and organic compounds (Groundwater Information Booklet, 2008), which may retain and release arsenic in groundwater aquifer. It is believed that the weathering of sulfide associated with carbonaceous matter may have produced arsenic rich iron oxyhydroxides, which in turn released arsenic (after reduction) to the existing sedimentary environment. The process of the mobilization of arsenic might be due to the reductive dissolution of As–Fe-bearing minerals in the sediments reduced by anoxic groundwater (Singh et al. 2004). Over withdrawal of groundwater in the study region for household uses might be another strong reason for the arsenic mobilization (Bhattacharjee et al. 2005) in aquifers in Majuli island.

The groundwater of Majuli was found to contain high concentrations of As, Fe and Mn (over the WHO's drinking water guideline value). However, to find out whether Fe oxide present is the dominant source of As, more investigations are needed. Since there are no strong correlations found among trace elements in borehole sediments it is hard to get a complete conclusion about arsenic mobilization mechanism with this limited information. In addition to these, biological activity could be another trigger of high arsenic concentration in the riverine island.

4.2.6 Summary

This study presents the results of two years survey on groundwater arsenic contamination in Majuli island, Jorhat district in the Brahmaputra plain, Assam. Analyses of 380 tube-well water samples for arsenic (by FI-HG-AAS) revealed that arsenic concentrations in 37.6% exceeded 10 μg/L, in 14% 50 μg/L and in 2% above 300 μg/L limits. Maximum arsenic concentration recorded was 468 μg/L. Depth of tubewells (n=303) varied from 6- 55 m. We analyzed a total of 380 hand tubewell water samples and 265 (70%) of those tubewells are shallow tubewells in the depth range up to 15 m. From the study it appears that in the Majuli island arsenic concentration gradually decreased beyond 25 m depth with few exceptions. Before our survey, the villagers were not aware that they were drinking arsenic contaminated water. Analyses of 319 hand tube-well water samples for iron and found elevated iron content (mean = 3168 μg/L, median = 1245 μg/L, standard deviation= 4217 μg/L, minimum = 36 μg/L and maximum = 44280 μg/L). The correlation between arsenic and iron concentrations in groundwater (r = 0.23, n = 319) was poor. The borehole sediment samples were collected during drilling of wells from the Gram Panchayets (GPs) Jengrai, Rawnapar, Bongaon, Dakhinpat and Luit poria (five out of total 20 GPs). From the results it is found that arsenic concentration is not dependent on the depth. After analyzing the aliquots from borehole sediment samples (n = 43) the arsenic concentration was found in the range from 0.36 mg/Kg to 1.44 mg/Kg. We analyzed biological samples and the range of arsenic concentrations in hair, nail and urine was 224- 5461 μg/kg, 426- 11725 μg/kg, and 21- 698 μg/L respectively. The urine, hair and nail concentrations of arsenic correlated significantly (r = 0.6177, 0.5317, and 0.5072 respectively) with drinking water arsenic concentrations. Out of total two blocks, both the blocks in Brahmaputra flood plain are arsenic contaminated (namely Majuli and Ujoni Majuli). The area and population of Ganga-Meghna-Brahmaputra (GMB) plain are 569749 Km^2 and over 500 million respectively. All the states & countries in GMB plain (West Bengal, UP, Bihar, Jharkhand, Assam and Bangladesh) are affected. Millions are at risk from arsenic contamination through groundwater. To combat the situation villagers need safe water, education and awareness of the danger of arsenic toxicity. The ways to significantly reduce the risk of arsenic contamination to the population of Majuli includes further development of primary prevention i.e. the minimization or elimination of the source of contamination. There should be quality control measures of potable water, supply of special filters to remove arsenic is needful.

4.2.7 Conclusion

According to Census Report, 2001, there was 28432 tubewells present in the whole Majuli island (16012 in Majuli Block and 12420 in Ujoni Majuli block). During our preliminary survey we cover only 380 tubewells (1.34 % of the total tubewell) from the island. Deep tubewells are found to be less contaminated with compared to the shallow tubewells. Groundwater is the main source for drinking, cooking and other household purposes in Majuli. So the withdrawal of groundwater is very high. This heavy withdrawal of groundwater may be one of the reasons of high concentration of arsenic in water. The concentration of arsenic in biological samples was found much higher than the normal ranges. The studied population group including children have not shown arsenical skin lesions, still high arsenic body burden in their biological samples (hair, nail and urine). From the comparative study, it is found that children are more susceptible to arsenic poisoning. Thus a new generation could be at risk. The cause of non appearance of skin lesions, in spite of drinking highly arsenic contaminated water (>400µg/L), could be their arsenic exposure is recent. However, we may expect arsenic patients if they continue to drink arsenic contaminated water for a longer period especially in the villages where we recorded arsenic contamination above 300 µg/l. Recently it has been reported (Smith et al. 2006) that exposure to arsenic in drinking water during early childhood has pronounced pulmonary effects greatly increasing subsequent mortality in young adults from both malignant and non-malignant lung diseases. The results of the present study showed that even though the prevalence of arsenicosis in the areas studied is not seen, people had elevated levels of arsenic in hair, nail and urine samples and thus could be sub-clinically affected. It can be assumed that, the main contributor to high arsenic levels in drinking water of the studied population was the residence location. Elevated levels of arsenic in the biological samples from the villagers might be due to the fact that the samples were collected from the contaminated areas. However, we do not expect such high concentrations of arsenic in the biologic samples throughout the Majuli island.

From the overall study, it appears that the arsenic affected areas in the Majuli island in the Brahmaputra plain need immediate attention and a permanent arsenic safe water source should be arranged. Since at present there is no known medicine for arsenic poisoning, researchers in this field should consider the issue a big challenge and find out a way to save the affected population. To some extent, the problem can be minimized by increasing awareness among people, educating villagers about the techniques of water management and involving the community in maintenance of their water source. Majuli island has a plenty of surface water sources. It is not only bounded by three rivers, several small perennial river channels, swamps and water bodies are also present in the Majuli island. The island also receives an average annual rainfall of about 1922mm. Therefore, instead of using groundwater for drinking purpose, the islanders should focus on harvesting surface water resources. Alternative safe water sources such as implementation of dugwell and rainwater harvesting are needed. Only proper watershed management, careful utilization of these water bodies and education of the islanders appear to be the viable options to stop the upcoming arsenic problem in the Majuli island.

CHAPTER FIVE

5. Removal of arsenic from aqueous solution using surface functionalized ultrafine iron oxide nanoparticles

5.1 Introduction

Arsenic contamination has become one of the global environmental issues posing a series of severe health problems. As a result, the US Environment Protection Agency (USEPA) and World Health Organization (WHO) implemented the reduction of arsenic maximum contaminant level (MCL) in the drinking water from 50 to 10 μg/L. The implementation of this new MCL arsenic standard in drinking water has initiated the development of the technology to remediate this problem with improved materials and systems with high efficiency. Thus, there is a growing interest in using efficient methods and materials to remove arsenic from drinking water, before it may cause significant contamination. Materials form the basic underlying building block of nearly every advanced technology and nanoscale materials is no exception, making a significant impact on our everyday lives. Characteristics such as large surface area, potential for self assembly, high specificity and high reactivity make nanoparticles excellent candidates for water treatment applications.

The methods available for the removal of arsenic have been adequately reviewed (mentioned in chapter 2). It is generally observed that As (V) is better removed and hence in most of the arsenic removal devices, primary oxidizing- interface for converting As (III) species to pentavalent status is ensured. Moreover, under groundwater conditions, As(III) is the predominant form of arsenic, which is more toxic and mobile than As(V). Though in recent times, some attempts were made to study the efficiency of arsenic removal from drinking water using nanoparticles, but these studies have limitations in terms of high adsorbent doses, high contact time period, maximum removal efficiency and separation of nanoparticles after application.

Considering it, we intend to study here the removal efficiency of arsenic (both As(III) and As(V)) from treated water with a low adsorbent dose and less contact time period using ultrafine Fe_2O_3 nanoparticles and finally the complete separation of the arsenic adsorbed nanoparticles from treated water. Under natural condition, the surface reactivity of iron compounds plays an important role in adsorbing arsenic in the sedimentary aquifers (Hristovski. et al, 2007) and arsenic can form inner sphere monodentate or bidentate–binuclear complexes with these iron compounds (Jongnam. et al, 2004; Peggy. et al, 2004).

The main objectives of the present study are: (1) to determine the effectiveness of surface functionalized ultrafine iron oxide nanoparticles for treatment of arsenic, (2) to determine its removal efficiency with respect to adsorbent dose and contact time period, (3) to identify the mechanism for As (III) adsorption and (4) separation of spent and excess adsorbents from treated water.

5.2. Results and Discussion

5.2.1 Transmission Electron Microscope (TEM) studies

The surface morphology and size distribution of the Fe_2O_3 nanoparticles were observed by Transmission Electron Micrographic image as shown in **Fig 5.1**. Fig shows TEM photograph of the so prepared Fe_2O_3 nanoparticles. As vivid from the TEM picture that the Fe_2O_3 nano particles are almost spherical in shape.

The average particle size was estimated by calculating size of almost 50 particles from the photograph. The average particle size obtained from **Fig 5.1** is 10 nm. Also an important feature is that there is no aggregation of particles to form giant structures instead, all particles are individual and are of almost uniform size and shape. It is very interesting to observe that the sample in the photograph exhibit a very narrow size distribution. The distribution varies with the range 10-20 nm. This narrow size distribution in the sample will lead to the uniform physical property of the so prepared Fe_2O_3 nanoparticles and hence application in environmental remediation with high reliability.

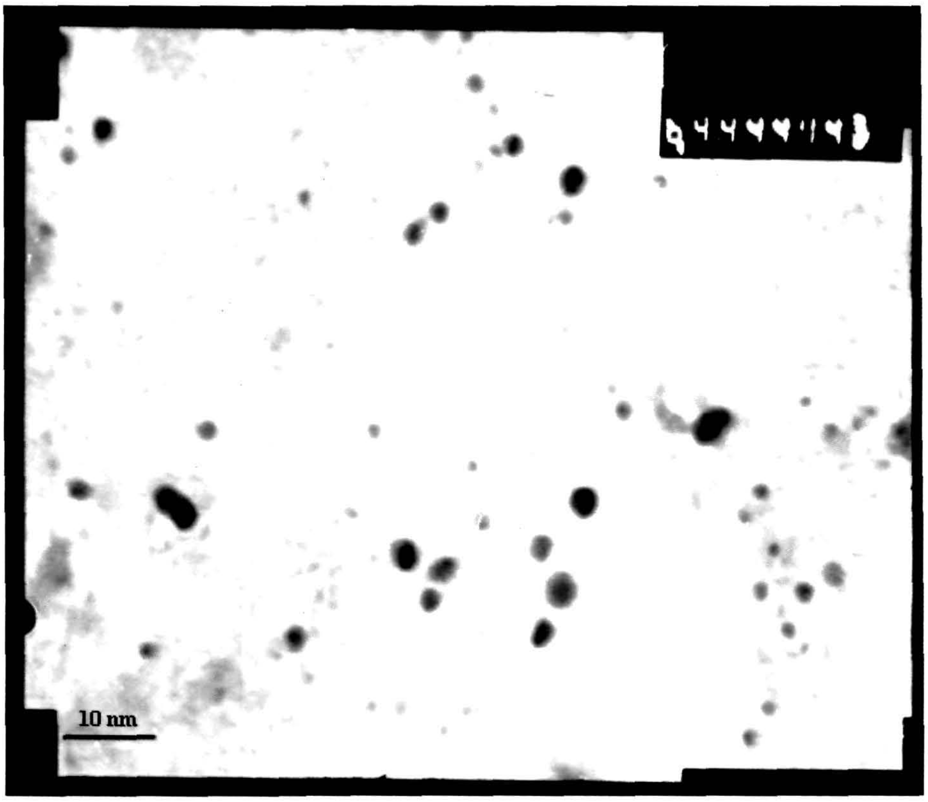


Fig 5.1: TEM image of Fe_2O_3 nanoparticles showing the particle size and distribution.

5.2.2 Batch experiment studies

Batch experiments have been carried out to investigate the sorptive characteristics of the developed sorbents. Herein, the sensitivity of the process for the reaction time, initial arsenate concentration, sorbent dosage, pH, and source water composition are tested. Adsorption isotherms are also used to determine the sorptive capacities and detailed results of these studies can be found in our earlier reports (Goswami et al.2011a, Goswami et al.2011 b). A summary is provided in the later sub-section of this thesis where batch experimental results are discussed.

5.2.2.1 Equilibrium time

In this section, adsorption experiments are carried out to find the equilibrium times for arsenic adsorption onto the surface functionalized iron oxide nanoparticles . It is found that the adsorption of arsenic onto the nanoparticles is time dependent, becoming greater with increasing time. The time dependence of arsenite(AsIII) and arsenate(AsV) adsorption onto the sorbents is given in **Fig. 5.2** and **Fig. 5.3** respectively, where it can be seen that optimal arsenate adsorption onto the nanoparticles is attained at the same equilibrium time (i.e. 80 mins). Within 80 minute of time the nanoparticles could remove arsenic (both As(III) and As(V)) absolutely(within the detection limit of the instrument) from the treated water solution.

5.2.2.2 Effect of initial concentration on arsenic removal efficiency

Initial arsenic concentration influences the percentage removal of arsenic species. Studies on the effect of initial arsenic [both As(III) and As(V)] concentration were conducted by varying it from 0.1 to 0.5 ppm keeping adsorbent dose of 0.05 g / 50 ml at neutral pH (6.5) and contact time of 80 minutes. It is evident that the percentage removal of both the arsenic species by the adsorption on iron oxide nanoparticles increases due to the decrease in initial arsenic concentration.

From **Fig. 5.2**, it is observed that so prepared surface functionalized ultrafine Fe_2O_3 nanopowder can remove arsenic(III) absolutely (100%) when the concentration of arsenic was 0.1 ppm with an adsorbent dose of 0.05g/50ml within a time period of 80 mins. When the initial concentration of arsenic increased to 0.5 ppm, the efficiency of removal was decreased, which was observed to be 98.2% at 0.3 ppm and 97.1% at 0.5 ppm. It is observed that there was a decrease in percentage of removal of arsenic corresponding to an increased initial arsenic concentration (**Table 5.1**). Moreover, the rate of this adsorptive reaction in the optimized period of contact varies directly with the concentration of the adsorbate.

Similar trend has been observed under same experimental conditions while using As(V). The sharp increase in removal efficiency at low initial concentrations observed in both the cases of As(III) and As(V). From **Fig. 5.2**, it is observed that the nano particles can also remove arsenic(V) absolutely at lowest initial concentration (0.1ppm) of the experimental set up. At initial concentration higher than 0.1ppm showed a decreasing tend in removal efficiency which was observed to be 98.5% at initial concentration of 0.3 ppm and 97.4% at 0.5 ppm (**Table 5.2**). From the tables (**Table 5.1** and **Table 5.2**) it is obvious that even at lower adsorbent doses (0.01g and 0.025g/50ml) the similar trend was observed.

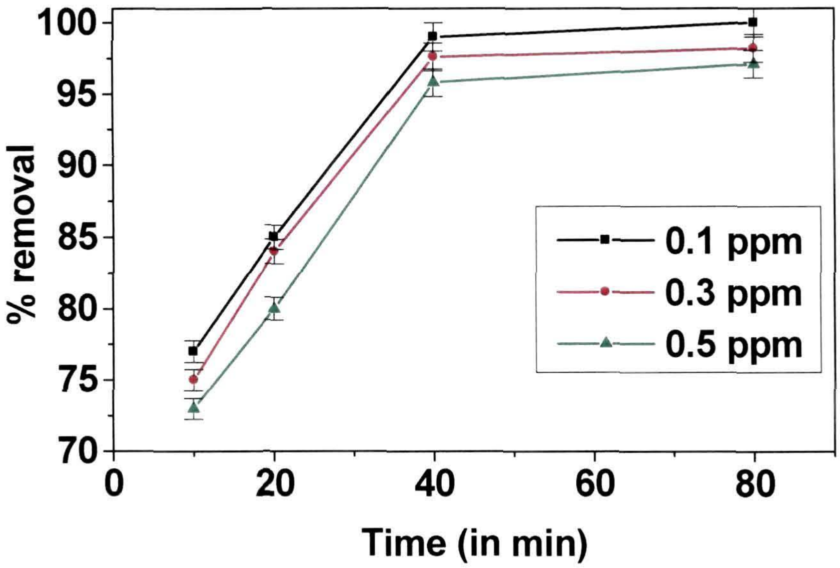


Fig 5.2: Effect of initial concentration on percent arsenic(III) removal by Fe_2O_3 nanoparticles with an adsorbent dose of 0.05 g/50 ml, pH- 6.5.

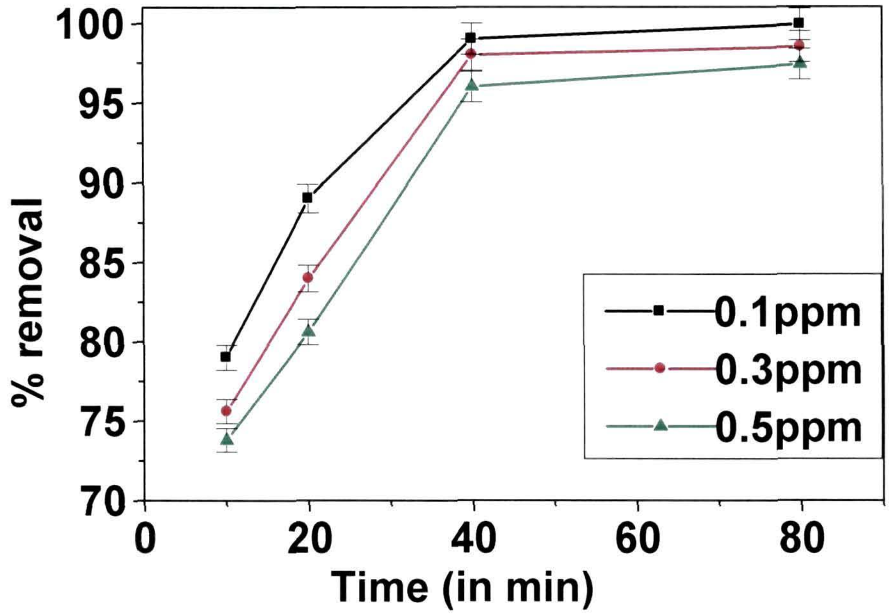


Fig 5.3: Effect of initial concentration on percent arsenic(V) removal by Fe_2O_3 nanoparticles with an adsorbent dose of 0.05 g/50 ml, pH- 6.5.

Table: 5.1 Batch experiment data for As(III) removal using surface functionalized Fe_2O_3 nanoparticles.

Initial As(III)conc.(ppm)	Mass of adsorbent(g/50ml)	% removal after			
		10 min	20 min	40 min	80 min
0.1	0.01	55	69	82	96
0.1	0.025	68	78	97	99
0.1	0.05	77	85	99	100
0.3	0.01	53	67	80.3	91.6
0.3	0.025	57	75	92.6	97.3
0.3	0.05	75	84	97.6	98.2
0.5	0.01	48.2	56.8	80.4	89.4
0.5	0.025	56.2	59.6	88.2	95
0.5	0.05	73	80	95.8	97.1

Table 5.2: Batch experiment data for As(V) removal using surface functionalized Fe_2O_3 nanoparticles.

Initial As(V)conc.(ppm)	Mass of adsorbent(g/50ml)	% removal after			
		10 min	**20 min**	**40 min**	**80 min**
0.1	0.01	59	70	85	96
0.1	0.025	70	79	97	99
0.1	0.05	79	89	99	100
0.3	0.01	56.3	68.3	81.6	93
0.3	0.025	58.3	76.6	93	97.6
0.3	0.05	75.6	84	98	98.5
0.5	0.01	51	57.8	81	90
0.5	0.025	56.2	60.2	88.2	95.4
0.5	0.05	73.8	80.6	96	97.4

The present study agrees well with earlier reports (Sorg et al. 1978; Fierro et al.2009). Sorg et al.(1978) reported that the initial arsenic concentration significantly affects the removal of arsenic. For initial arsenate concentrations to about 1 mg/L (1000ppb), a dosage of 30 mg/L of either alum or ferric sulfate achieved higher than 95% arsenate removal; however, the percent removal decreased with increasing concentrations. Mondal et al.(2008) found that the percentage removal of arsenic by the adsorption on iron based adsorbents increases due to the decrease in initial arsenic concentration, steeper slopes of decreasing trend were found when the initial arsenic concentration value lies within 0–0.5 ppm. The reason of this decreasing trend with increasing initial concentration in all these studies can be explained as follows.

It is a well-known fact that at a particular environment the percentage removal of an adsorption process depends upon the ratio of the number of adsorbate moiety to the available active sites of adsorbent. This ratio is also related to the surface coverage of the adsorbent (number of active sites occupied/number of active sites available) that increases with increase in the number of adsorbate moiety per unit volume of solution at a fixed dose of adsorbent. Less is the value of this ratio more is the percentage removal.

5.2.2.3 Effect of adsorbent dosage and contact time

The adsorbent dose is the most significant parameter for arsenic removal. The dependence of arsenic adsorption on adsorbent dosage with varying amounts of adsorbent dosages has been examined (Goswami et al. 2011) for both A(III) and As(V). It was observed that, at a constant initial arsenic concentration value, the percentage removal of arsenic increase with the increase in adsorbent dose (**Fig 5.4** and **Fig 5.5**), where the initial arsenic [As(III) and As(V)] concentration was 100 μg/L (0.1ppm). When 0.0025g/50ml adsorbent dose was used, 72.4 μg/L of As(III) and 73 μg/L of As(V) was adsorbed in 80min; however when 0.05g/50ml adsorbent dose was used 99.99 μg/L (99.99% removal) of both As(III) and As(V) was adsorbed in 80 min (**Table5.3** and **Table 5.4**). For As(III) the adsorption rate was slightly slower than As(V). When 0.05 g/50 ml adsorbent was used, the arsenite(AsIII) and arsenate(AsV) concentrations reach less than 10 μg/L (U.S. EPA MCL), for arsenate in 30 min and for arsenite in 40 min. From the plots (**Fig 5.4** and **Fig. 5.5**), it is obvious that as the adsorbent concentration increases, the sorption of arsenic increases along with the rate of adsorption. This is probably due to increase in surface area and surface adsorption reactivity and hence more active sites were available for the adsorption of arsenic. Therefore, the more adsorbent particles are able to provide more iron oxide surface-active sites for collision with arsenic molecules to accelerate the arsenic removal efficiencies. The higher arsenic removal with increasing time is due to the superior surface area of the nano particles demanding a much lower dose than that of micro scale iron (Shu, H.Y. et al. 2007).

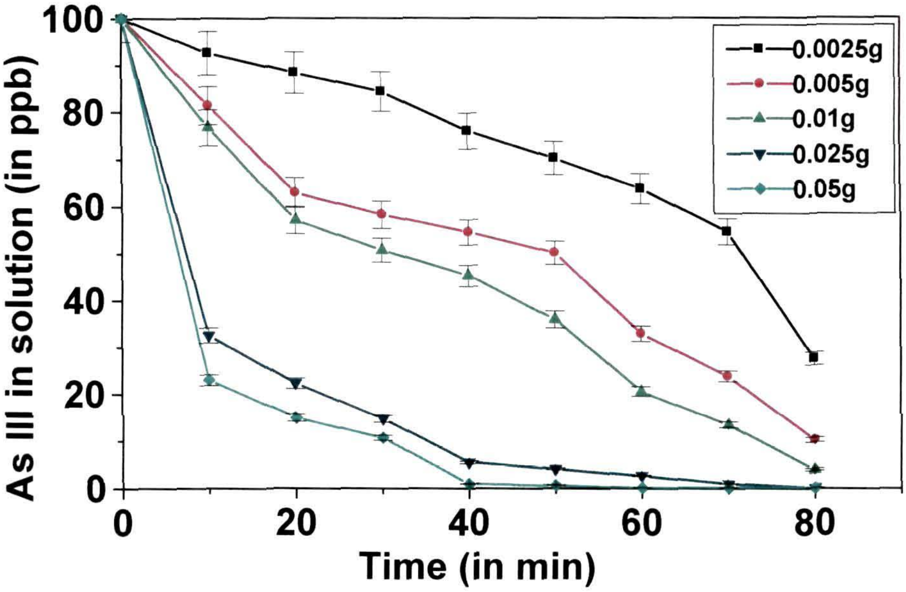


Fig. 5.4: Plots of remaining As(III) concentration (µg/L) versus time as a function of adsorbent concentration.

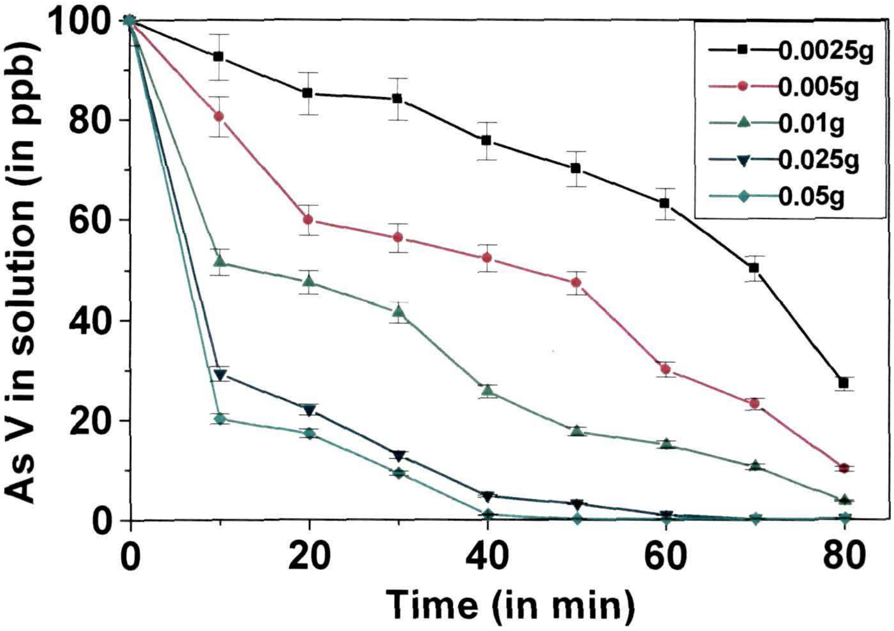


Fig. 5.5: Plots of remaining As(V) concentration (µg/L) versus time as a function of adsorbent concentration.

Table 5.3: Batch experiment data for As(III) removal using surface functionalized Fe_2O_3 nanoparticles at different adsorbent dose.

Sl.No	Contact time(min)	Dose of adsorbent(g/50ml)	Initial As(III) conc.(μg/L)	Final As(III) conc.(μg/L)	% removal
1	80	0.0025	100	27.6	72.4
2	80	0.005	100	10.3	89.7
3	80	0.01	100	4	96
4	80	0.025	100	0.2	99.8
5	80	0.05	100	0.01	99.99

Table 5.4: Batch experiment data for As(V) removal using surface functionalized Fe_2O_3 nanoparticles at different adsorbent dose.

Sl.No	Contact time(min)	Dose of adsorbent(g/50ml)	InitialAs(V) conc.(μg/L)	Final As(V) conc.(μg/L)	% removal
1	80	0.0025	100	27	73
2	80	0.005	100	10	90
3	80	0.01	100	3.7	96.3
4	80	0.025	100	0.2	99.8
5	80	0.05	100	0.01	99.99

The effect of contact time was studied for higher (0.5 ppm) arsenic concentration (**Fig. 5.6**). The plots (**Fig. 5.6**) illustrates that the aqueous arsenic concentration decrease with increasing adsorbent dose as well as with time. The absolute removal within the detection limit of the instrument was achieved with a very low adsorbent dose of 0.05 g/50 ml and less contact time period (80 min). The decrease in arsenic concentration or increase arsenic removal efficiency can be achieved by increasing the dose of the adsorbent (**Fig. 5.6**) as well as increase in contact time.

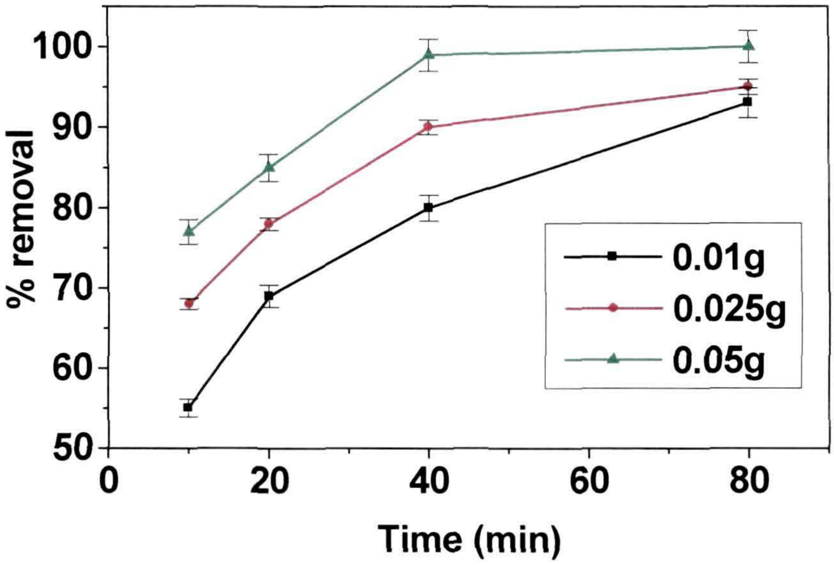


Fig 5.6: Effect of contact time on percent arsenic removal by ultrafine Fe_2O_3 nanoparticles

5.2.2.4 Effect of pH on arsenic adsorption

The pH is an important parameter in sorption based water treatment process, because proton concentration can strongly modify the redox potential of the sorbates and sorbents. The pH range of the treated water is also significant for the effectiveness of iron oxide particles to remove arsenic. It is reported that arsenate removal is efficient in the pH range of 3-7 (Streat et al. 2008). Therefore, adsorption experiments were performed at various pH levels with 100 µg/L arsenic [As(V) and As(III)] and 0.005, 0.01 and 0.05g/ 50 ml ultrafine nanoparticles at 10 minute interval up to 80 min. Analysis of pH as a function of time was conducted to determine the minimum time required to obtain arsenic adsorption equilibrium. **Fig. 5.7** displays the pH data for the 100 µg/l arsenic solutions placed in contact with 0.01g ultrafine Fe_2O_3 nanoparticles on the shaker for 80 minutes at different pH. The arsenate adsorbed at 80 min is 94 µg/L, 96 µg/L, 96.3 µg/L and 90 µg/L at pH 2.2, 3.5, 6.5 and 9.6 respectively (**Fig. 5.7**).

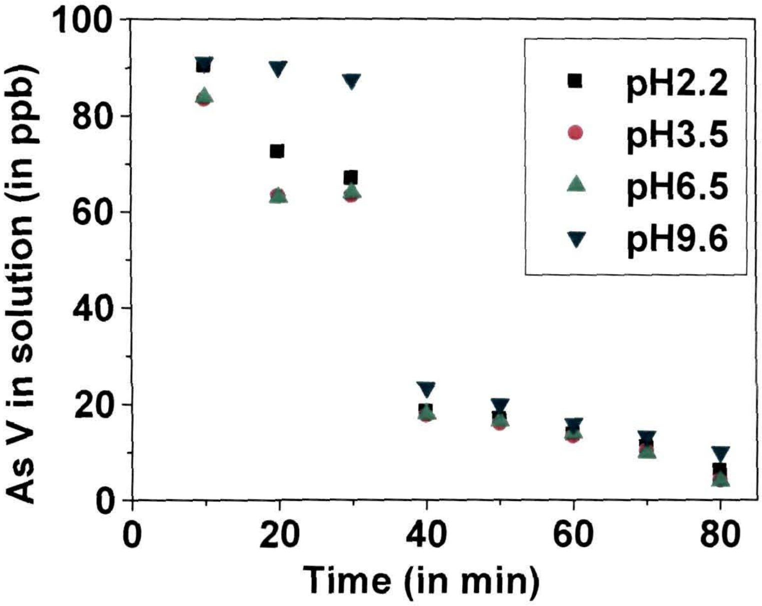


Fig. 5.7: Effect of pH on As(V) adsorption

The results demonstrate a negligible difference in arsenate adsorption at pH 2.2, 3.5 and 6.5 (~2%) and slightly higher difference at pH 9.6 (6%). From **Fig. 5.7** , it appears that the amount of arsenate adsorption increases by lowering the pH of the system from 9.6 to 6.5 by increasing the amount of sorbent. Under high acidic conditions (pH of 2.2- 3.5), As(V) adsorption by iron oxide nanoparticle was minimal and it reaches a maximum at pH 6.5 (**Fig. 5.7**). At this pH the arsenic concentration decreased from 100 µg/L to 4 µg/L (**Fig. 5.7**). This change corresponds to 96% arsenic removal. Arsenic adsorption slightly decreased as pH increased from 6.5 to 9.6.

However, the adsorption efficiency of arsenite by the iron oxide nanoparticles was observed to be more at pH > 3.5. The arsenite adsorbed at equilibrium (80 min) is 92.1 µg/L, 94 µg/L, 96 µg/L and 95 µg/L at pH 2.2, 3.5, 6.5 and 9.6 respectively. The present study reveals that the adsorption efficiency of arsenite is highest at pH 6.5 i.e. at neutral pH. The pH dependent behavior can be explained by ionization of both the adsorbate. It is worthwhile to mention here that As (III) species remain protonated as H_3AsO_3 at pH below 9.2 (Kanel et al. 2007). Below pH 9.2, H_3AsO_3 is the predominant species and presumably the major species being adsorbed. A similar pH dependence trend in As adsorption amorphous iron oxide, synthetic goethite, and magnetite has been observed (Kanel.et al. 2007). Hence, below this pH (in our study pH is 6.5) H_3AsO_3 will be the predominant phase (Kanel.et al 2005, Stachowicz et al. 2006).

The present study indicate that the nanoparticles can remove arsenic almost absolutely from contaminated water at a wide pH range (2.2-9.6). In fact, the surface engineered adsorbent material works independently of pH in the range 2.2 to 9.6, while most of the adsorbent material for arsenic removal work at low pH (Ouvrard et al.2002; Gu et al. 2005) or within a small pH range, mostly between 6.0 and 7.5 (Jain et al. 1999; Payne et al. 2005).

The results of effect of pH (2.2, 3.5, 6.5 and 9.6) on adsorption of As (III) and As (V) (100 µg /L) at different SFN dosage (0.005, 0.01 and 0.05g/50 ml) and contact time equal to 80 min is shown in **Table 5.5** to **Table 5.8**. The results showed that arsenic adsorption occurred over the whole pH range (2.2-9.6) considered.

Table 5.5: Batch experiment data for remaining As(III) (µg/L) in solution at different pH.

Initial conc. = 100 µg/L. Dose of adsorbent = 0.005g/50 ml.

Sl.No	Contact time(min)	pH			
		2.2	**3.5**	**6.5**	**9.6**
1	0	100	100	100	100
2	10	84.3	81.36	79.5	80.53
3	20	65.1	62.93	60.8	62.92
4	30	61.1	58.25	56.3	57
5	40	56.6	54.5	50.1	51.9
6	50	51.95	50.1	48.8	47.12
7	60	35.8	32.86	31.1	32.3
8	70	28.21	23.8	20.9	22.5
9	80	12	10.3	8.1	9.5

Table 5.6: Batch experiment data for remaining As(V) (µg/L) in solution at different pH. Initial conc. = 100 µg/L. Dose of adsorbent = 0.005g/50 ml.

Sl.No	Contact time(min)	pH			
		2.2	3.5	6.5	9.6
1	0	100	100	100	100
2	10	85.91	80.44	80	86.5
3	20	62.5	59.7	59.5	63.5
4	30	59.51	56.24	57	62.1
5	40	53.85	52.2	52.5	55.2
6	50	48.5	47.3	47.4	50.1
7	60	31.81	30.06	31	36.8
8	70	24.3	23.1	22.5	28.2
9	80	12	10	9.7	13.25

Table 5.7: Batch experiment data for remaining As(III) (µg/L) in solution at different pH. Initial conc. = 100 µg/L. Dose of adsorbent = 0.05g/50 ml.

Sl.No	Contact time(min)	pH			
		2.2	3.5	6.5	9.6
1	0	100	100	100	100
2	10	20.1	23	23	25
3	20	14.2	15	15	17.3
4	30	10	10.7	9.3	12.7
5	40	1.2	1	1	3.3
6	50	0.75	0.7	0.5	0.99
7	60	0.51	0.2	0.1	0.92
8	70	0.1	0.2	0.1	0.7
9	80	0.01	0.01	0.01	0.2

Table5.8 : Batch experiment data for remaining As(V) (µg/L) in solution at different pH. Initial conc. = 100 µg/L. Dose of adsorbent = 0.05g/50 ml.

Sl.No	Contact time(min)	pH			
		2.2	3.5	6.5	9.6
1	0	100	100	100	100
2	10	23.1	20.2	22.2	24.4
3	20	17.3	17.2	15.1	16.3
4	30	15.2	9.27	9	17.1
5	40	3.1	0.99	0.95	5.5
6	50	0.99	0.2	0.2	0.97
7	60	0.99	0.2	0.2	0.99
8	70	0.2	0.1	0.1	0.3
9	80	0.1	0.01	0.01	0.1

5.2.3 Entrapment study

Simultaneously, it is needed to separate the arsenic adsorbed nanoparticles from the aqueous solution. Keeping in mind this aspect, arsenic sorption was further studied by entrapping ultrafine Fe_2O_3 nanoparticles in calcium alginate beads. It is worthwhile to mention here that sodium alginate, which is water soluble and becomes a hydrogel in the presence of multivalent cations (Ca^{2+}, Ba^{2+}, Sr^{2+}), shows good permeability for small molecules (Yong et al.2005). Alginic acid has a high viscosity. Porosity in Ca-alginate allows solutes to diffuse into the beads and come in contact with the entrapped cells. Moreover, alginate is nontoxic, biodegradable, and nonimmunogenic, and produces thermally irreversible and water insoluble gels. The present research demonstrates that iron oxide nanoparticles can be effectively entrapped in this biopolymer matrix (alginate) without significant reduction in their reactivity. Ultrafine Fe_2O_3 nanoparticles entrapped in alginate beads showed 100% removal efficiency (**Fig. 5.8**). The removal efficiency increases from 96% to 100% as the dose increases from 0.01 to 0.05 g/50ml. This study reveals that the nanoparticles of Fe_2O_3 entrapped in alginate beads can also adsorb arsenic completely. Moreover, these beads entrapping arsenic sorbed Fe_2O_3 nanoparticles can be separated easily and more efficiently as compared to the arsenic sorbed bare nanoparticles (**Fig. 5.9**). In the removal of soluble pollutants from water by sorption methods, the solid/liquid separation step is very important for an efficient operation. Due to their very small sizes, nanomaterials make this separation very difficult and expensive as the common methods can not be applied. Hence, we have used ultrafine nanoparticles entrapped into the macro beads of calcium alginate for easy and efficient separation. Here, we have shown that ultrafine Fe_2O_3 nanoparticles can be effectively entrapped in Ca-alginate beads and reactivity of entrapped nanoparticles towards arsenic was comparable to that of bare nanoparticles. Alginate beads without Fe_2O_3 nanoparticles were applied to the arsenic solution with concentration 0.1 ppm in the same way. The analysis of the collected samples has shown that calcium alginate has no role in the removal of arsenic. Alginate is used only for the separation of arsenic sorbed Fe_2O_3 nanoparticles from water solution. Fe_2O_3 nanoparticles without surface functionalization were also applied in order to perform a comparative study between the surface functionlized ultrafine Fe_2O_3 nanoparticles and Fe_2O_3 nanoparticles without surface functionalization for their efficiency of arsenic removal. The experimental results showed that Fe_2O_3 nanoparticles without surface functionalization can remove maximum of 91% As(III) within 80 min of contact time with an adsorbent dose of 0.05 g/ 50 ml.

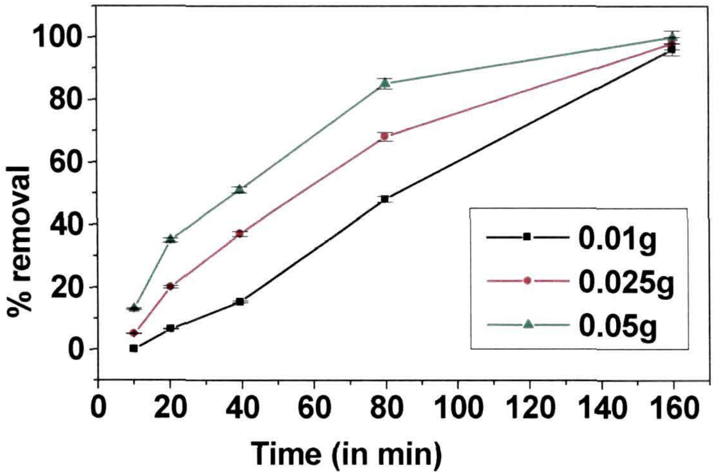


Fig. 5.8: Percent removal of arsenic using Fe_2O_3 nanoparticles entrapped in calcium alginate beads.

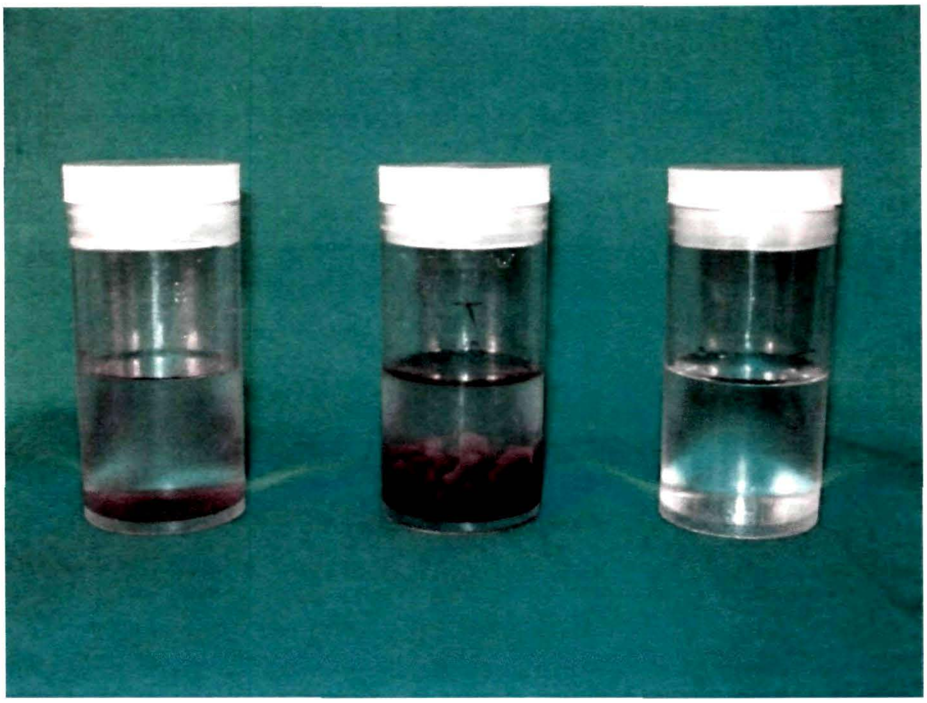


Fig. 5.9: The representative pictures of samples for Fe_2O_3 nanoparticles treated arsenic solution, arsenic solution treated with Fe_2O_3 entrapped calcium alginate beads and pure water after separation of completely adsorbed arsenic respectively (from left to right).

5.2.4 Arsenic removal mechanism

To understand the removal mechanism by this novel nanosystem, we also carried out the transmission electron microscope (TEM) investigations of the arsenic adsorbed Fe_2O_3 nanoparticles (**Fig. 5.10**). The particles are average 10 nm in diameter with size distribution of about 15%. It is also evident that the nanoparticles are well separated from each other, i.e. aggregation has not taken place. This has occurred as a result of the perturbation of electron cloud of the arsenic molecule environment during the conjugation process.

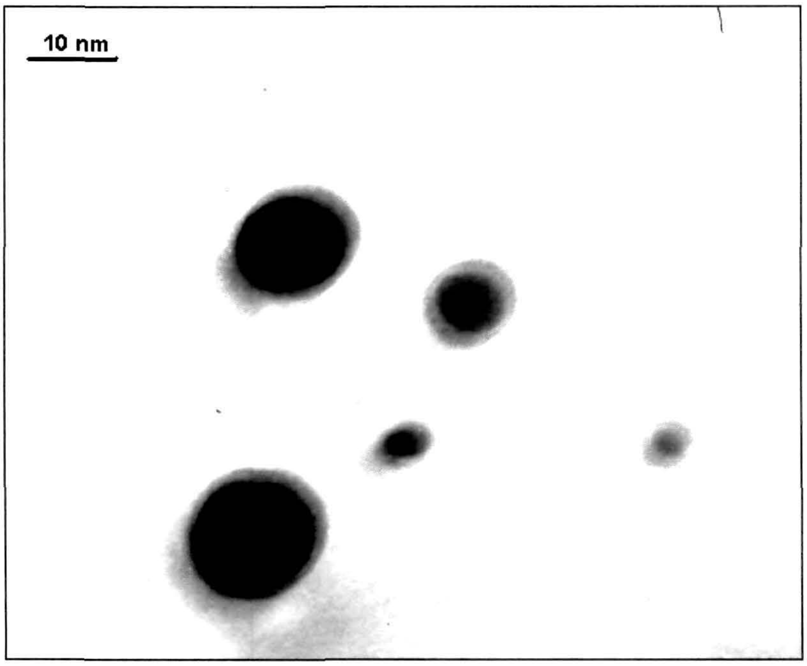
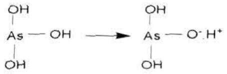


Fig.5.10: TEM micrograph of arsenic adsorbed Fe_2O_3 nanoparticles over the surface.

Fig. 5.11 shows the model of arsenic adsorption by fatty acid binding domain mediated ultrafine Fe_2O_3 nanoparticles The coupling between the arsenic and the Fe_2O_3 nanoparticles was based on functional chemistry. The ultrafine Fe_2O_3 nanoparticles were coated with strearic acid to stabilize and functionalize the nanoparticles. **Fig. 5.12** represents the schematic diagram of iron oxide nanoparticles capped with stearic acid functional group. The stearic acid capped iron oxide nanoparticles exhibit free carboxyl group on the nanoparticles surface (Deb et al. 2006; Bora et al. 2009). Due to very strong hydrophobic character of the hydrocarbon chain of stearic acid molecule, it is very difficult for the molecule to be exposed to the aqueous solution. So, the interaction of stearic acid molecule with the core iron oxide took place through the hydrocarbon segment leaving the carboxyl group towards the aqueous solution. In our study the adsorption mechanism is proposed based on the interaction between carboxyl functional groups of stearic acid capped Fe_2O_3 nanoparticles with unsaturated H_3AsO_3. It is worthwhile to mention here that As (III) species remain protonated as H_3AsO_3 at pH below 9.2 (Kanel et al.2007). Hence, below this pH (in our study pH is 6.5) H_3AsO_3 will be the predominant phase (Kanel.et al. 2005; Stachowicz et al.2006). Now, in the proposed mechanism we have assumed that the free surface functionalized COO^- end of the sorbent interact with H_3AsO_3 species releasing O^- and H^+ (Jain et al. 1999). As(III) exists as H_3AsO_3 ( $\overset{OH}{\underset{OH}{As}}{-}OH \longrightarrow \overset{OH}{\underset{OH}{As}}{-}O^-H^+$) in aqueous solution. **Fig..5.13** illustrates the chemical process occurred at the surface of iron oxide nanoparticles to conjugate with As(III) molecules and form an assembly pattern.

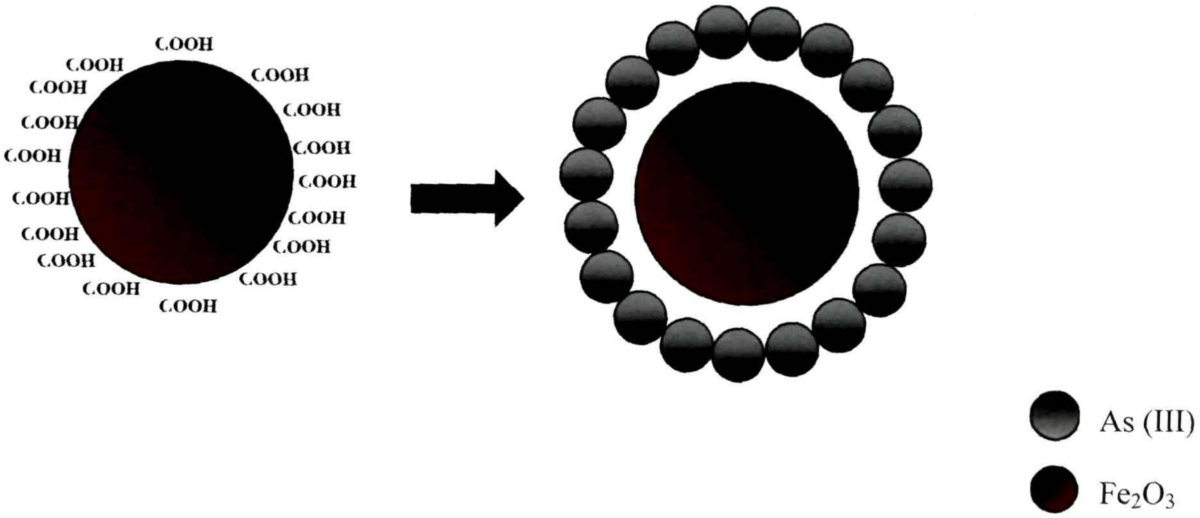


Fig.5.11: Model of arsenic adsorption over the surface of stearic acid capped Fe_2O_3.

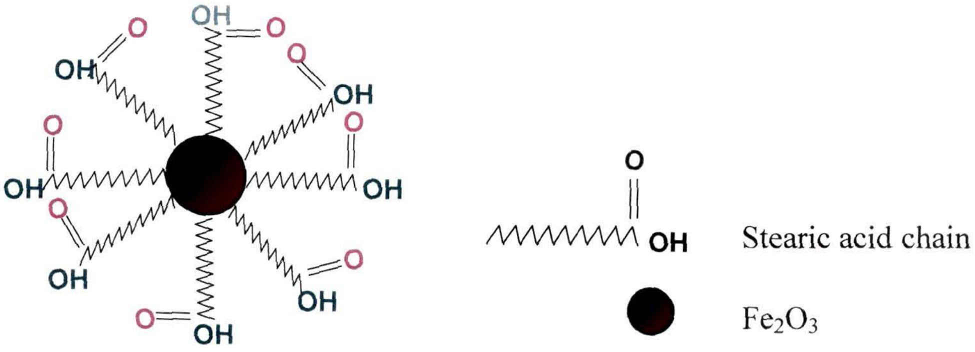


Fig. 5.12: Schematic diagram of stearic acid capped Fe_2O_3 nanoparticles.

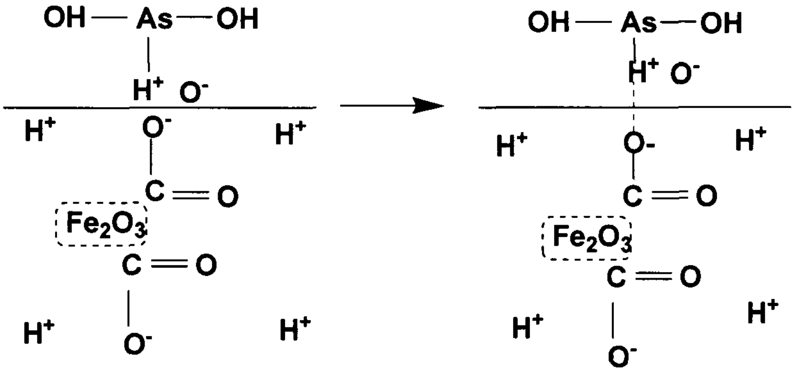


Fig.5.13: Chemical process of arsenic adsorption over the surface of stearic acid capped Fe_2O_3

5.2.5 Adsorption isotherms

The selection of appropriate correlation models for the experimental equilibrium data is important in order to optimize the design of an adsorption system for the removal of arsenic. Freundlich and Langmuir isotherm models have been demonstrated to fit the equilibrium behavior of heavy metals well (Payne et al., 2005, Yuan et al., 2006). Adsorption isotherms, which are presentation of the amount of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk solution at constant temperature were also studied. The equilibrium data obtained were fitted to Freundlich and Langmuir isotherms.

The Freundlich equation deals with physico chemical adsorption on heterogenous surfaces (indicates the adsorptive capacity or loading factor). The linearized form of Freundlich equation is given as:

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} \log C_e \qquad (1)$$

Where x is the amount of solute adsorbed, m is the mass of adsorbent used, C_e (mg/l) the equilibrium solute concentration in solution and K_f, a constant, which is a measure of adsorption capacity and n is a measure of adsorption intensity. The values of K_f and n were obtained from the slope and intercept of the plot between log (x/m) and log C_e. In the present study, values of K_f and n were found to be 72.9 mg/g and 1.92. The high K_f (72.9 mg/g) and low 1/n (0.52) indicated a high adsorption capacity. The isotherm fitted very well for the adsorbent with a correlation coefficient 0.9969. Significantly, higher values of adsorption capacity (K_f) obtained with ultrafine nanoparticles indicate that it can be effectively used for the removal of arsenic from water.

Langmuir isotherm is valid for single layer adsorption. It is based on the assumption that all the adsorption sites have equal affinity for molecules of the adsorbate and there is no transmigration of adsorbate in the plane of the surface.

Linear form of Langmuir equation is:

$$1/X = 1/X_m + (1/C_e)(1/b.X_m). \qquad (2)$$

X = x/m, where x is the amount of solute adsorbed, m is mass of adsorbent, C_e (mg/l) is the concentration of arsenic at equilibrium, X_m is the amount of solute adsorbed per unit mass of adsorbent required for monolayer coverage of the surface also called monolayer capacity and b (L mg^{-1}) is the Langmuir constant related to the affinity between the sorbent and sorbate. The plots of 1/ X against C_e for adsorption of As (III) gave a straight line. The estimated goodness of fit is $r^2 = 0.9946$ and enables applicability of the Langmuir model to As(III) adsorption on the surface functionalized nanoparticles. The Langmuir constants x/m and b for the present study are 10.47 mg/g and 0.004 respectively.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter R_L was determined (Karthikeyan et al. 2005). In the present study R_L values at different initial aresnic concentrations indicates a highly favorable adsorption (**Table 5.9**). In case of initial concentration 0.1 ppm the R_L value is 0.9996 (~1), thus indicating the linear shape of isotherm.

Table 5.9: Pseudo first order rate constants, Pseudo second order rate constants, and R_L values for As(III) adsorption on surface functionalized Fe_2O_3 nano particles at different initial concentration

As(III) (mg/l)	Pseudo first order rate constants			Pseudo second order rate constants			R_L
	K_1	q_e	r^2	K_2	q_e	r^2	
0.1	0.04	0.062	0.9859	1.466	0.096	0.9905	0.9996
0.3	0.067	0.2975	0.9821	0.27	0.324	0.9955	0.9988
0.5	0.069	0.5821	0.9756	0.119	0.566	0.986	0.998

5.2.6 Sorption kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Kinetic studies were conducted at different intervals of time and concentrations to determine the rate of arsenic removal by surface functionalized ultrafine Fe_2O_3 nanoparticles. The kinetics of As(III) adsorption on the ultrafine Fe_2O_3 nanoparticles were analyzed using pseudo first- order and pseudo second-order (Ho et al. 2000) models. The uniformity between experimental data and model predicted values was expressed by correlation coefficients (r^2 values close or equal to 1).

5.2.6.1 The pseudo first- order equation

The pseudo first- order equation is expressed as:

$$\log (q_e - q_t) = \log(q_e) - K_1 t / 2.303. \qquad (3)$$

where, q_e and q_t (both in mg/g) are the amounts of As(III) adsorbed at equilibrium and at time t respectively. K_1 is the rate constant of pseudo first- order adsorption. The plot of log (q_e-q_t) vs t gives straight line and the kinetics parameters are presented in **Table 5.9**.

The rate constant is calculated from the slope of the line using pseudo first order kinetics model is presented in **Table 5.9**. The calculated q_e values using pseudo first order kinetics model showed 0.83–38% deviation from the experimental q_e values (Table5.3.9). The kinetic plots of pseudo first- order adsorption are shown in **Fig. 5.14**.

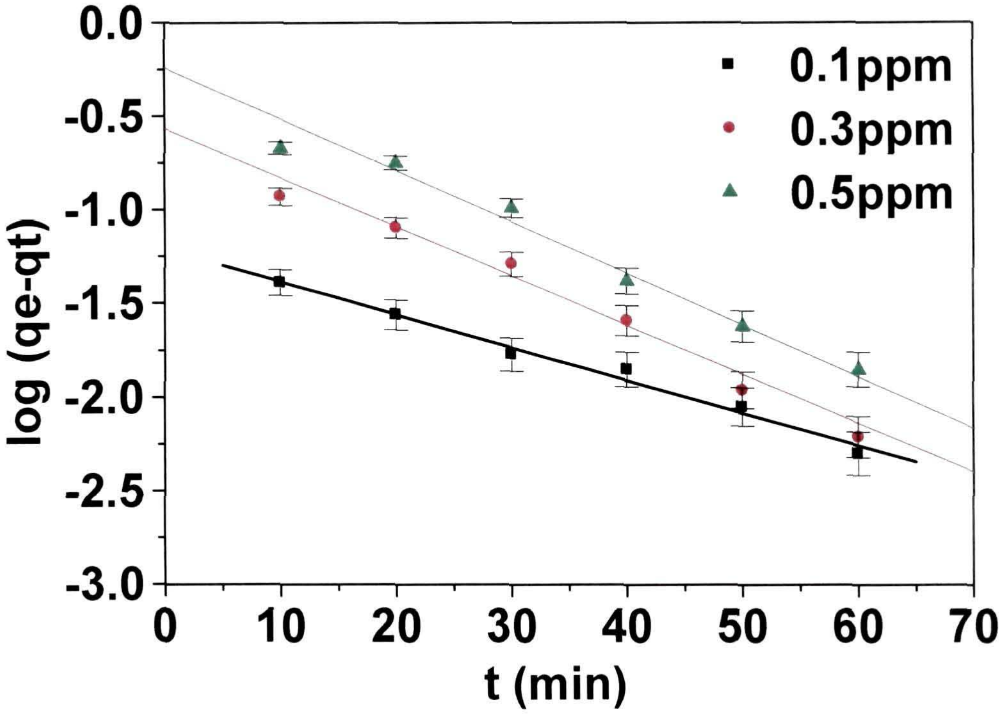


Fig.5.14: Kinetics analysis of As(III) adsorption by linear plots of pseudo first order rate equations.

5.2.6.2 The pseudo second- order equation

The linearized form of pseudo second- order kinetic rate equation is expressed as:

$$t /qt = 1/ K_2q_e^2 + t / q_e \qquad (4)$$

In addition, the initial rate of adsorption, h is $K_2\ q_e^2$.

where, q_e and q_t are the amounts of As(III) adsorbed per unit of mass of nano Fe_2O_3 at equilibrium and at time t respectively and K_2 is the rate constant of pseudo second- order adsorption. The kinetic plots between t/q_t vs t were plotted for the different initial concentrations (**Fig.5.15**) and slope and intercept values were measured to determine the value of pseudo second- order rate constant mentioned in **Table 5.9**. **Fig.5.15** and **Table 5.9** shows highly significant regression line and the data were well fitted to the pseudo second- order rate equation. The t/q_t vs t gives a straight line and depicted in **Fig.5.15**. The calculated rate constant and equilibrium concentration are presented in **Table 5.9**. The calculated q_e values using pseudo second order kinetics model is better than the pseudo first order kinetics compared to the experimental q_e values (4–13.2% deviation for second order kinetics and 0.83–38% deviation for first order kinetics. It is also observed from **Table 5.9**, pseudo second order kinetics model fits the kinetics data better than the pseudo first order kinetics model (based on R^2 value). The result shows that the goodness of fit is better in pseudo second order kinetics model as compared to pseudo first order kinetics model for the entire range of kinetics run. The straight line behavior is indicating that the process follow a pseudo second- order kinetics for various concentrations of As (III). The plots of observed and predicted values for As(III) adsorption on to the surface functionalized ultrafine Fe_2O_3 nanoparticles is presented in **Fig.5.16** and **Fig.5.17**.

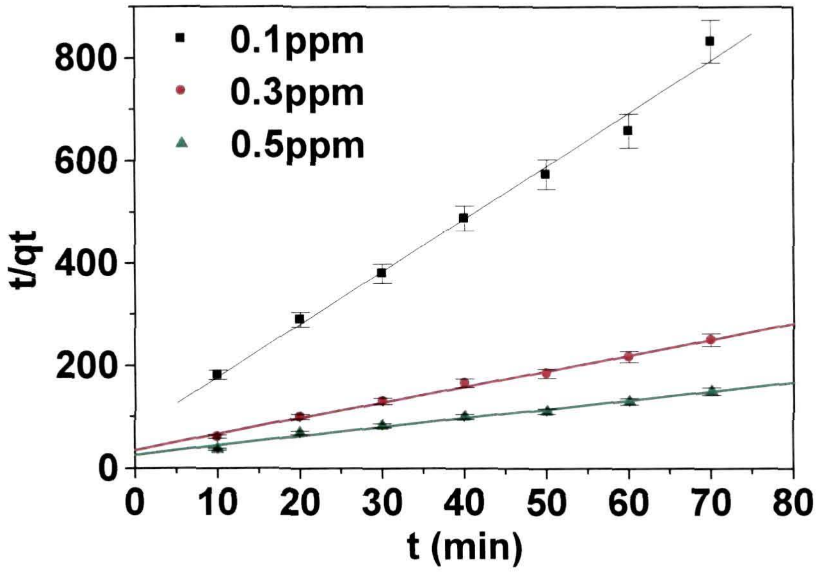


Fig.5.15: Kinetics analysis of As(III) adsorption by linear plots of pseudo second order rate equations.

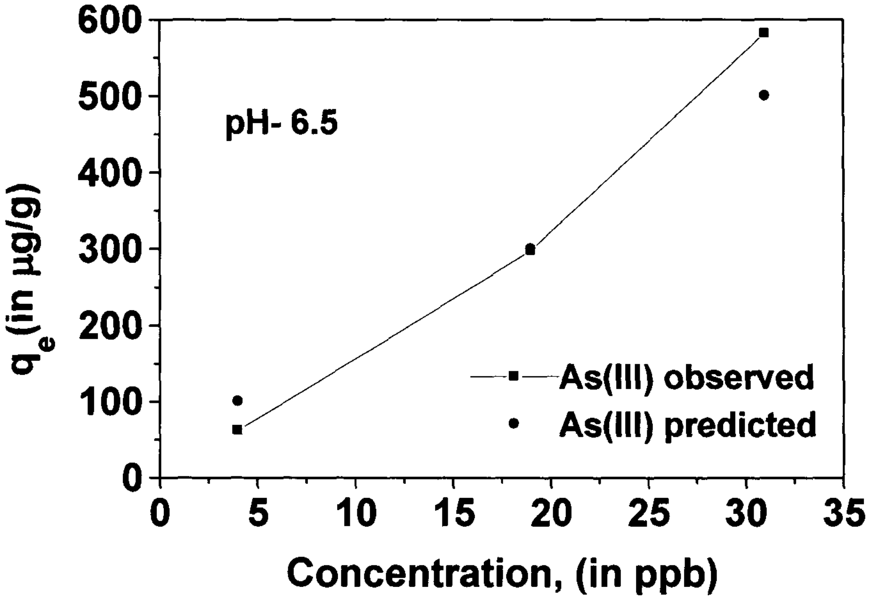


Fig.5.16: Isotherm plot (pseudo first order) for arsenic adsorption on to surface functionalized Fe_2O_3 nanoparticles.

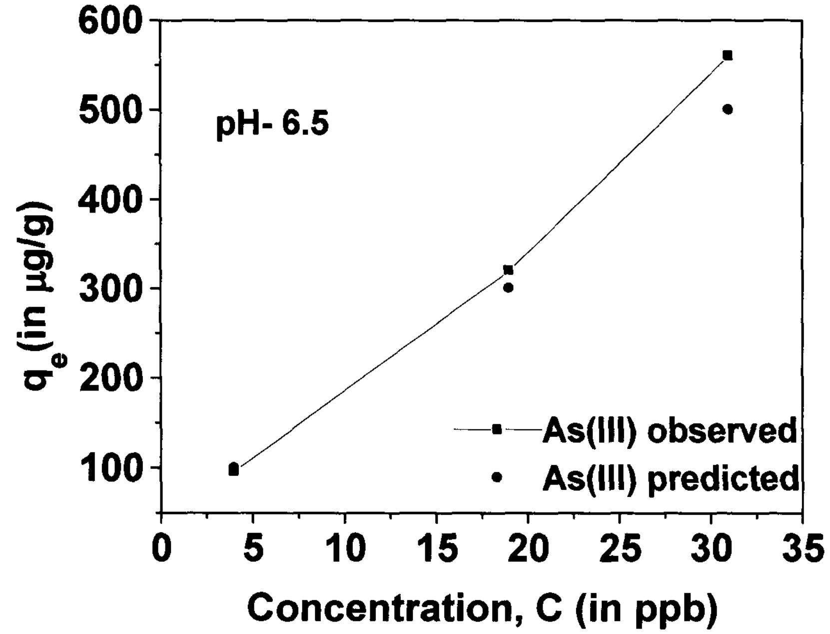


Fig.5.17: Isotherm plot (pseudo second order) for arsenic adsorption on to surface functionalized Fe_2O_3 nanoparticles.

5.2.7 FTIR study in arsenic adsorption

The FTIR spectrum is a powerful tool for analyzing the adsorption process by the adsorbate species on the adsorbent in a dilute medium. The spectra of surface functionalized nanoparticles before and after adsorbing As(III) and As(V) are shown in **Fig.5.18**. From the fig it is clear that the arsenic (III and V) adsorption leads to changes in the individual positions of the bands (**Fig.5.18** a and **Fig.5.18** c). The broad peak at 1399 cm^{-1}, disappears (M-OH bending) while loading (**Fig.5.18** b). Peaks appear at 1430 cm^{-1} (As III) (**Fig.5.18** a) and 1382 cm^{-1} (As V) (**Fig.5.18** c). The –OH peak at 3215 cm^{-1} disappear (**Fig.5.18** b) and peaks at 3413 cm^{-1} (As III) (**Fig.5.18** a) and 3429 cm^{-1} (As V) (**Fig.5.18** c) arise due to interaction with the surface –OH group. The results reveal that the arsenic is bonding to surface functionalized ultrafine nanoparticles in a surface complex.

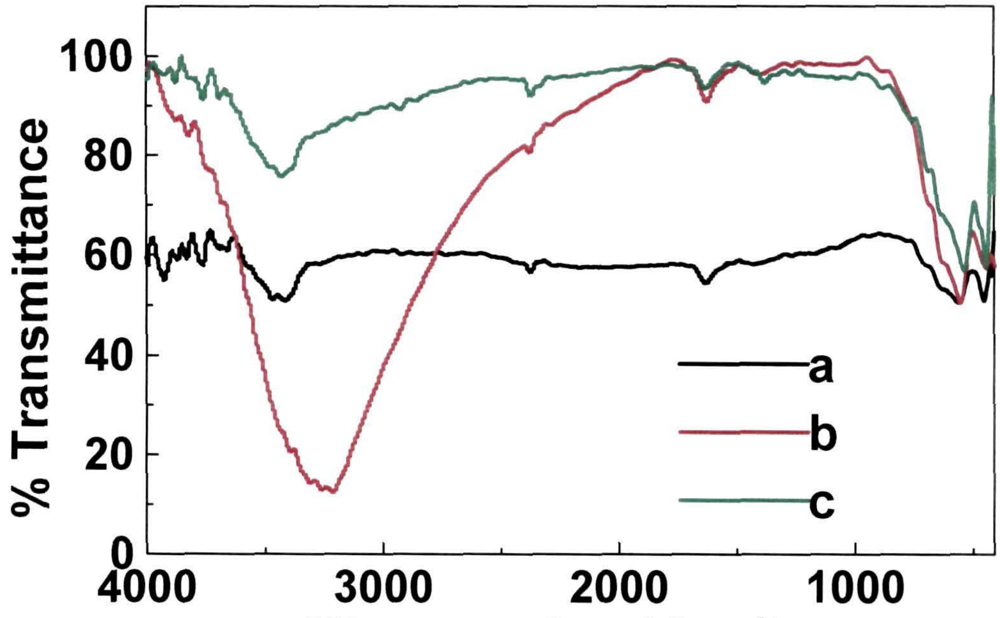


Fig.5.18: FTIR spectra of Fe_2O_3 nanoparticles (b) before sorption and after (a) As(III) (c) As(V) sorption

5.2.8 Conclusions and Future Scope

The present study demonstrated that arsenic is effectively removed up to acceptable limits prescribed by the WHO for safe drinking water using nanotechnology. Using surface functionalized Fe_2O_3 nanoparticles, arsenic adsorption is independent of pH from 2.2 to 9.6 There is no need for pH adjustment prior to water treatment, i.e. it can be carried out at neutral pH. In summary, we have demonstrated that surface functionalized ultrafine Fe_2O_3 nanoparticles can effectively remove arsenic from treated water. We have also reported the mechanism of As(III) adsorption by the surface functionalized Fe_2O_3 nanoparticles. The kinetics of the As(III) adsorption on the so prepared nano particles was found to follow the pseudo second- order rate equation. The so prepared monodisperse ultrafine Fe_2O_3 nanoparticles are capable of removing arsenic (As(III) and As(V)) from treated water with high arsenic concentration, low adsorbent dose and low contact time. Once arsenic was sorbed onto Fe_2O_3 nanoparticle surfaces, separation by hydrophilic calcium alginate beads provides a way to drag out the whole arsenic sorbed sludge out the solution.

The results of present work showed rapid reaction between surface functionalized Fe_2O_3 nanoparticles and arsenic. ultrafine nanoparticles could remove arsenic from aqueous solution at very short time (minute scale) over a wide range of pH. In addition removal efficiency has direct relation with contact time and dosage of nanoparticles. Due to the low amount of adsorbent used, the mass of produced sludge in the process was significantly low; so, the sludge may be removed by entrapment techniques, often more efficient and faster than centrifugation or filtration.

CHAPTER SIX

6. Application of technology developed with nanomaterial for removal of arsenic from contaminated groundwater of Majuli

6.1 Introduction

A decrease in the maximum contaminant level (MCL) of arsenic in drinking water from 50 to 10 μg/L causes severe problem in many states and seeks for improvement of the current techniques or a new technique to meet the current arsenic standard in a cost effective and efficient way. Moreover, studies have shown that As(V) can be more easily removed from water than As(III) due to its formation of divalent species in normal groundwater pH range (6-8) (Gupta et al., 1978; Reed et al., 2000). However, As(III) is more toxic and mobile. Thus, there is an urgent need to identify or develop efficient techniques for As(III) removal. Among the different technologies available, the application of nanomaterials in water remediation holds promise as an effective method for arsenic removal. Because of their small particle size and large surface area, nanomaterials have considerable potential for arsenic removal. From our previous studies (Goswami et al. 2011), it is found that the so prepared ultrafine iron oxide nanomaterials are very much effective in removal of arsenic (both As(III) and As(V)) from synthetic aqueous solution. In addition to optimizing the nanoparticle dimension for best removal efficiency, these nano adsorbents were surface engineered to obtain surface trap states for further adsorption sites available. This technology can be a model for removing arsenic from water treated with high arsenic concentration, low adsorbent dose and low contact time and hence obtaining a pure arsenic free water. The present study aimed to investigate the effectiveness of the so prepared nanoparticles in arsenic removal from natural groundwater containing the various competing ions. While using natural waters, arsenic removal from aqueous systems becomes complicated as there is also presence of other contaminants, e.g., competing ions (Matthess et al 1981, Meng et al. 2000, Meng et al. 2002). The presence of these competing ions makes arsenic removal from aqueous systems much more difficult. Primarily, the other ions present will compete for available adsorption sites on the adsorbent material and lower the arsenic removal efficiency. Therefore, it is felt that studies are needed to examine the effect of competition of other compounds present in real life groundwater and thus for the impact of using the technology in a more realistic setting than a water containing only arsenic. Occurrence of arsenic in groundwater of Majuli island of Assam (India) has recently explored by our group and the island is identified as an arsenic endemic area. It is worthwhile to mention that Majuli is the largest river island in Asia and a heritage site. This study tested the efficacy of the so developed surface engineered ultrafine Fe_2O_3 nanoparticles as a possible water treatment option with very high level arsenic-bearing groundwater sources of Majuli. Therefore, in this chapter arsenic adsorption kinetics is conducted with arsenic contaminated groundwater from Majuli island, using the surface functionalized ultrafine Fe_2O_3 nanoparticles. In addition to varying adsorbent dose several different exposure times were used in batch tests to obtain the equilibrium.

6.2 Experimental methods

Solutions used in the experiment were prepared from certified reagent grade chemicals and made with deionized water. Glass volumetric flasks and reactions vessels were cleaned with 10% HNO_3 and rinsed several times with deionized water before they were used. Arsenic contaminated groundwater was collected from Majuli island of Assam, India. To prevent the precipitation of the Fe-As compound, all samples were immediately acidified with 2% HNO_3 upon collection in the field and stored in plastic bottles. A comprehensive water analysis was conducted using HACH procedure in the laboratory. Heavy metals in the groundwater were determined using ICP-OES (Perkin Elmer, Optima 2100 DV).

Adsorption experiments

Arsenic adsorption was conducted in a batch experiment with arsenic contaminated groundwater from Majuli. Different doses of adsorbent (0.01g/50 ml, 0.025g/50 ml, 0.05g/50 ml, 0.07g/50 ml) of adsorbent were introduced to the reaction vessel containing the contaminated groundwater followed by rigorous stirring at room temperature until the adsorption equilibrium was reached. No attempt was made to adjust the pH during the reaction, and the pH was checked at the end of the experiment to confirm the constant pH (6.9). The supernatant was collected at 10 minutes interval directly from the tubes after the reaction using a 10 ml disposable syringe. Samples were centrifuged at 3000 rpm for 15 min and filtered through 0.45 μm syringe filter, and then acidified with trace metal grade HNO_3 to analyze arsenic and trace heavy metals with the ICP-OES (Perkin Elmer, Optima 2100 DV).

6.3 Results and discussion

Groundwater collected from two tubewells in Majuli was found to contain relatively high concentrations of arsenic (>50μg/L). The present study, therefore, examined the removal of arsenic from groundwater using surface functionalized ultrafine Fe_2O_3 nanoparticles as an adsorbent. The composition and water quality parameters of the Majuli groundwater are listed in **Table 6.1**. From **Table 6.1** it is observed that the collected water samples from Majuli consists of 100 μg/L and 318 μg/L total arsenic, and common competing ions such as sulfate, phosphate, nitrate, bicarbonate, calcium, magnesium and silica. The concentrations of trace metals in Majuli groundwater are listed in **Table 6.2**. It is observed from the results that almost all the metals are within the maximum contaminant levels, except for Pb and Mn.

Table 6.1: A summary of general groundwater analysis data from Majuli

		Sample ID	
Parameters	**units**	**W-09**	**W-11**
Total As	μg/L	100	318
pH		6.9	7.3
Conductivity	mS cm^{-1}	4.37	5.43
Ca^{2+}	mg/L	330	106.3
Mg^{2+}	mg/L	117	58.7
SO_4^{2-}	mg/L	10	30
NO_3^-	mg/L	1.59	14
PO_4^{3-}	mg/L	0.216	0.8
HCO_3^-	mg/L	116	270
Silica	mg/L	12	17.2

Table 6.2: Heavy metal concentrations (in µg/L) in Majuli groundwater

	Sample ID	
Heavy metal	W-09	W-11
Cr	17.52	99.5
Ni	5.3	9.8
Mn	148.4	131.4
Co	0.85	3.9
Cd	0.213	1.86
Pb	24.86	93.55

•Maximum contaminant level for each trace metal: Cr (100 µg/L), Ni (10 µg/L), Mn (40 µg/L), Co (Not mentioned in WHO guideline), Cd (5 µg/L), Pb (50 µg/L).

6.3.1 Arsenic adsorption kinetics

Fig 6.1 and **Fig 6.2** exhibits a decrease in arsenic concentration over time with initial groundwater arsenic concentrations of 100 µg/L and 318 µg/L respectively. From the experimental results it is found that with increasing adsorbent dose there was decrease in arsenic concentration in the solution. The arsenic concentration reach less than 50 µg/L (MCL, India) in 20 min and less than 10 µg/L (U.S EPA, MCL) in 40 min while using 0.01g/50 ml (0.2g/L) and 0.05g/50ml (1g/L) adsorbent dose respectively (**Fig 6.1**). The absolute removal efficiency was achieved within 80 min of contact time (**Fig 6.3**) that is similar as in case of our previous results described elsewhere, but the adsorbent dose for absolute removal of arsenic from real life groundwater (0.07g/50ml≈1.4g/L) was found to be slightly more than that of in the deionized model water (0.05g/50ml≈1.g/L) under similar conditions. In case of high groundwater arsenic concentration (0.318 µg/L) the rate of percent removal is slower (96%) than in case of deionized model water (98.2%) using the similar experimental conditions. For groundwater with high arsenic concentration (318 µg/L) maximum arsenic removal (98.7%) was attained using 0.07g adsorbent dose/50ml of solution (**Fig 6.4**). While in case of deionized model water the maximum removal (98.2%) was attained using less amount of adsorbent dose

(0.05g/50ml). It may be due to the presence of competing ions (**Table 6.1**) for available adsorption sites on the adsorption material.

The role of competitive sorption has been stressed by many studies. Phosphate is a well-known competitor for arsenate on Fe-oxide binding sites (Manning et al., 1996) and present in the arsenic contaminated groundwater of Majuli. Bicarbonate, also present at high concentrations in the groundwater, has likewise been implicated as a potential competitor for As (Appelo et al., 2002; Charlet et al., 2007). Silica may exert a control on the sorption of As(V) and As(III) (Swedlund et al., 1998; Rochette et al., 2000) although its effect was considered less significant for groundwater in West Bengal (Charlet et al.2007).

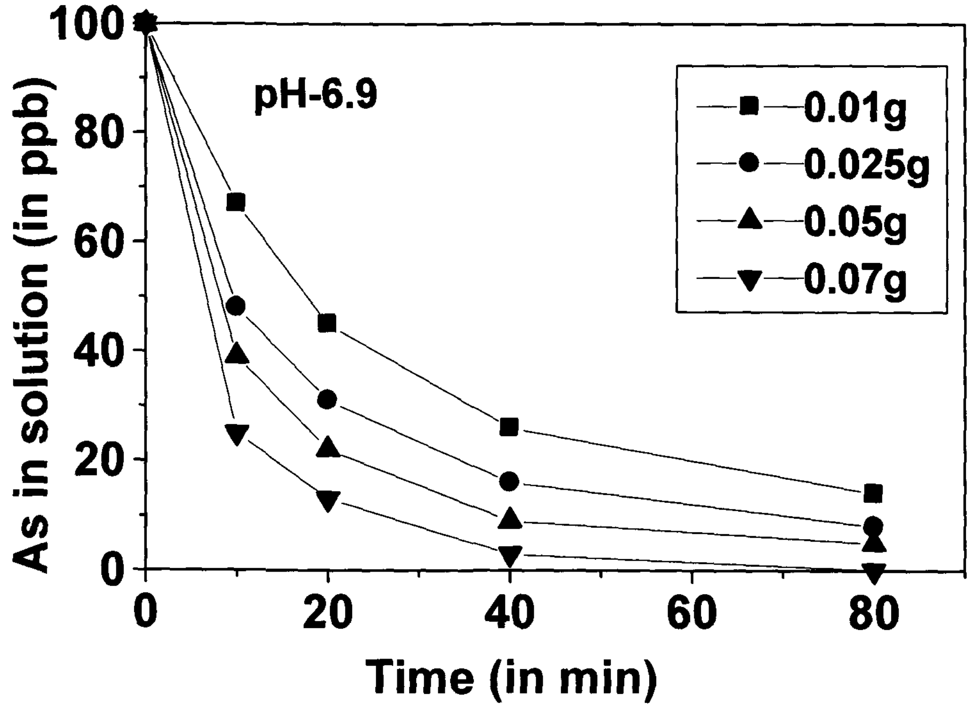


Fig. 6.1: Plots of arsenic concentration (µg/L) versus time for Majuli groundwater with initial arsenic concentration 100 µg/L, Volume of solution = 50 ml.

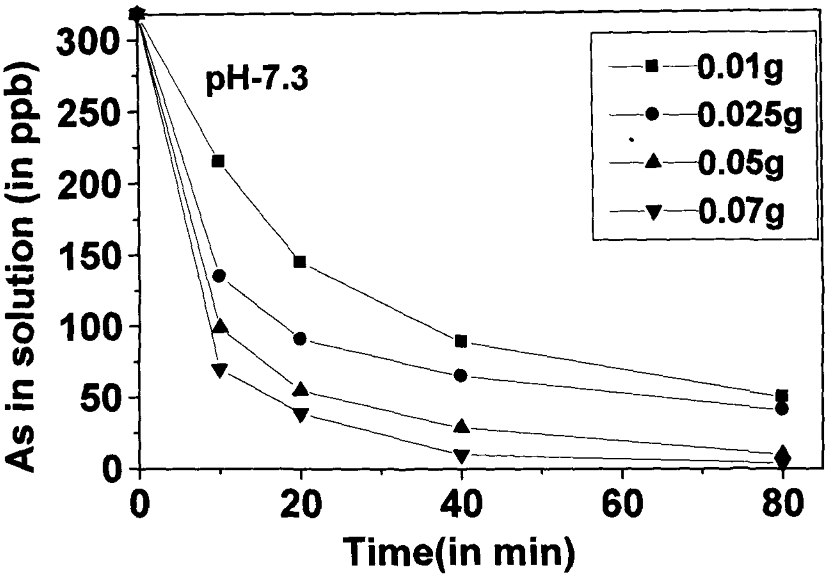


Fig. 6.2: Plots of arsenic concentration (μg/L) versus time for Majuli groundwater with initial arsenic concentration 318 μg/L, Volume of solution = 50 ml.

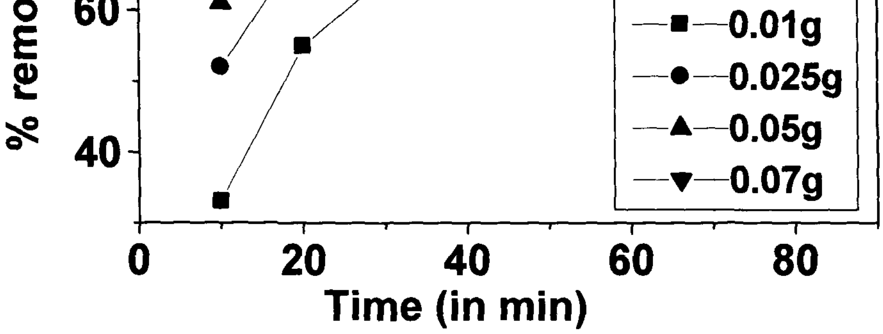


Fig. 6.3: Arsenic removal using ultrafine Fe_2O_3 nanoparticles with initial arsenic concentration 100 μg/L, pH- 6.9. Volume of solution = 50 ml.

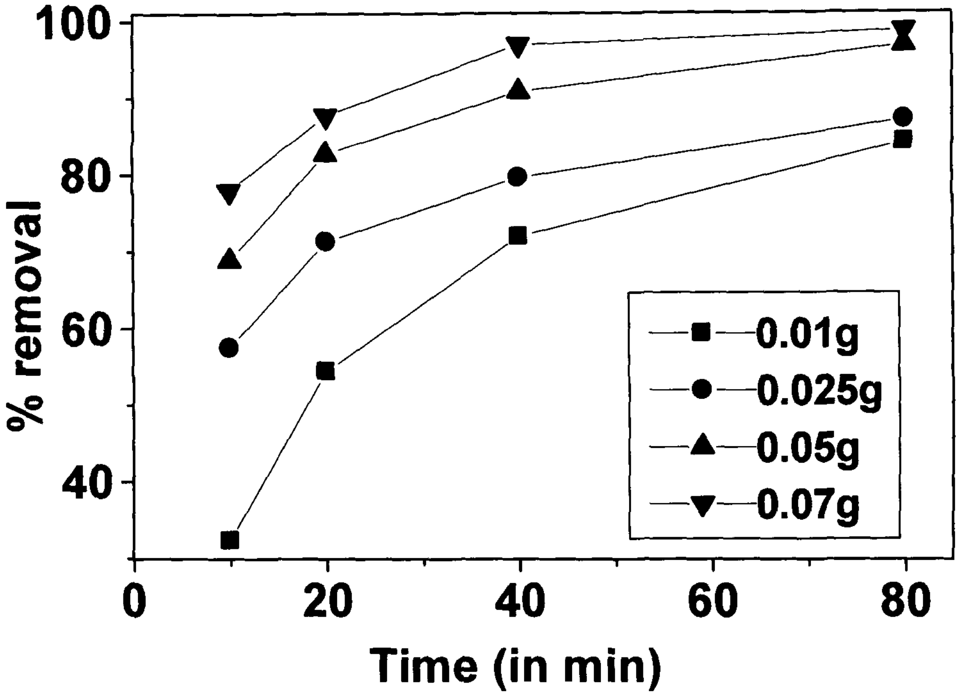


Fig. 6.4: Arsenic removal using ultrafine Fe_2O_3 nanoparticles with initial arsenic concentration 318 µg/L, pH- 7.3. Volume of solution = 50 ml.

6.3.2 Trace metal adsorption

Table 6.3 shows the changes in heavy metal concentrations over time after adding 0.2g/L (0.01g/50ml) ultrafine nanoparticles to the Majuli groundwater. The nanoparticles significantly adsorbed some of the heavy metals within minutes, such as Cr, Ni and Pb from water. However, Mn, Cd and Co concentrations were fairy constant during the reaction. The results implicate that Cr and As was eliminated from water to form inner-sphere complexes with iron oxide nanoparticles and the electrostatic forces could be attributable to explain the observations between negatively charged surface functionalized nanoparticles and positively charged Ni, Cr and Pb.

Table 6.3: Heavy metal concentrations (µg/L) in Majuli groundwater as a function of adsorbent concentration (initial As concentration= 0.2g/L)

	Concentration (µg/L)				
Heavy metal	**0 min**	**10 min**	**20 min**	**40 min**	**60 min**
Cr	17.5	10.3	9.5	4.7	1.5
Ni	5.3	2.1	0.9	0.3	0.3
Mn	148.4	148.4	148.4	151.3	149.2
Co	0.85	0.85	0.85	0.87	0.87
Cd	0.21	0.07	0.16	0.17	0.17
Pb	24.9	12.5	7.3	2.5	1.5

6.4 Conclusion

Adsorption studies were performed for the natural groundwater of Majuli in a batch system in the same fashion as those for model water, but adsorbent dose was further increased to 0.07 g to obtain maximum removal efficiency. When the nanoparticles were added to the arsenic contaminated groundwater from Majuli, an immediate decrease in arsenic concentration occurred using low adsorbent dose and less contact time period. However, arsenic concentration in water was decreased within minutes to lower than the current maximum contaminant level of arsenic in drinking water. The surface engineered ultrafine iron oxide nanoparticles could remove arsenic from natural groundwater almost absolutely without prior oxidation. The present study shows the almost absolute removal of arsenic at neutral pH, which is generally difficult to achieve and important in terms of real application. The applicability of the adsorbent at neutral pH for the removal of arsenic from real life ground water samples makes it an attractive filter for arsenic removal units. Moreover, these nanoparticles were able to efficiently treat other co occurring heavy metals simultaneously. These results show great potential in environmental applications to treat heavy metal contaminated groundwater.

CHAPTER SEVEN

.7. Conclusion and recommendation

7.1 Significance and contribution of the work

This work represented the detailed groundwater contamination status, exposure and accumulation of arsenic in bodies in the different Revenue blocks and Gaon Panchayats of Majuli island. Moreover, a novel method was developed to remove arsenic from using surface functionalized ultrafine iron oxide nanoparticles. Arsenic levels in the treated water as well as contaminated groundwater were found to be below the drinking water standards within minutes of treatment with the nano based technology. The treatment method is simple, efficient and has the possibility of house hold use provided with a cost effective dimension added to it. Moreover, the developed method has the following advantages:

- Iron oxides are readily available and most abundant and non toxic.
- Using the surface functionalized iron oxide nanoparticles, there is no need of pH adjustment prior to water treatment, i.e. it is able to remove arsenic efficiently at neutral pH.
- The method is simple, fast and efficient (arsenic can be removed absolutely within minimum time).
- The simultaneous separation of the arsenic sorbed nanoparticles can be ensured by entrapping them in hydrophilic calcium alginate beads and thereby a pure arsenic free solution can be obtained.

7.2 Approaches for arsenic mitigation

After working in arsenic contaminated areas in Majuli it is realized that arsenic mitigation strategy should be location specific. A method suitable for a specific area may not be generalized for the other affected regions due to a) geographical and sub-surface geological variations, b) differing socio-economic and literacy conditions of people. Whatever be the approach, for success at field level, it is needed to generate awareness amongst the people and their wholehearted participation. It is a fact that so far there is no available medicine for chronic arsenic toxicity. Therefore, safe water, nutritious food and vitamins are the only preventive measures to fight the chronic arsenic toxicity. A nutritive diet also plays a pivotal role in preventing and controlling arsenocosis. To do away with the arsenic menace, it is the primary responsibility of the government, aid-agencies and the researchers to educate and motivate the common masses about this issue of serious concern.

7.3 Conclusion

Water samples have been analyzed from 380 tubewells of the estimated 28432 hand tubewells of the island's twenty number of Gaon Panchayats with an average depth of 14 metres. The distribution pattern of arsenic in groundwater shows that 37.6% of the tubewells exceeds 10 μg/L (the guideline value of arsenic concentration in drinking water set by WHO), 21.6% between 11 μg/L and 50 μg/L and 14% exceeds 50 μg/L (Indian standard of arsenic in drinking water). In addition, 2% of the tubewells had arsenic concentration more than 300 μg/L, the concentration predicting arsenical skin lesions (Rahman et al. 2001, Chakraborti et al. 2002). 62.4% of the tested wells were found to be arsenic safe. It was also found that northern part of the island is mostly affected with ground water arsenic contamination compared to other parts. The ground waters of the Majuli island contain high concentrations of both arsenic and iron. Several factors are involved in the ever expanding arsenic contamination problem throughout the world, involving new aquifers that are yet to be recognized.

The present research work, for the first time in North East India, reports the arsenic accumulation in hair, nail and urine of test populations of Majuli island. The information gathered from field visits to Majuli during 2009 and 2011 indicated that physical manifestations of arsenicosis in the area has not been reported till the date. Therefore both literature and risk analysis was carried out to investigate whether the population in Majuli apparently are protected. The literature survey confirmed the findings of the field visit that the prevalence of hyperpigmentation and keratosis is not found among the population. This is probably due to the presence of high iron in the drinking water, that may affect people's water usage habits. The changes in water usage habits due to bad taste and aesthetic nuisance created by high iron would indirectly lead to reduced exposure to arsenic. The factors responsible for non prevalence of arsenicosis in this study are shorter duration of exposure, low intake of water due to excessive iron and removal of arsenic upon storage. The risk may multiply manifold in the days to come, as it has been found that 90% test population of the island never uses even any household aeration and filtration techniques and drinks water raw..

From the survey it is observed that, Majuli has already been facing two most serious water centric problems, which are gradual loss of land area due to severe bank erosion and flood inundation. In addition to that the menace of arsenic contamination in ground water of Majuli has multiplied the magnitude of silent natural calamities taking place in this remote region, which has been the forerunner for the position of World Heritage site for quite some times. Geo-physical remoteness of the region, a high illiteracy rate among the dominant missing tribes, lack of even traditional water filtration systems in their households, direct intake of ground water and the exposure impacts of arsenic contamination in ground water in terms of gradually accumulating arsenic in hair, nail and urine of the population clearly demand an well concerted effort for its awareness and technological interventions from knowledge society.

The present study develops a system which is operated as a batch type purifier for waters contaminated with arsenic, by synthesizing a iron based surface engineered novel adsorbent. Surface functionalized iron oxide nanoparticles have been studied as prospective adsorbent for removing arsenic (III and V) from drinking water under various conditions of concentration, time, dose and pH. Adsorption experiments have shown that adsorption occurs over a wide pH range (2.2-9.6). There is no need for pH adjustment prior to water treatment, i.e. good adsorption efficiency was obtained at neutral pH. The nanomaterials were also applied to the contaminated groundwater in a way of an attempt to realize the experiment in the laboratory scale using real life groundwater samples of Majuli. From the study, it is found that the nanomaterials were able to bring the concentration of arsenic to 10 μg/L (WHO limit) within 30 minutes using minimum dose and low contact time period . The method is simple, fast and very much effective (arsenic can be removed absolutely within 80 minute of contact time). The surface functionalized ultrafine iron oxide nanoparticles are found to be an ideal sorbent at normal neutral pH of groundwater, as it has shown high sorption capacity at low concentrations as well as a high binding constant. Moreover, due to the low amount of adsorbent used, the mass of produced sludge in the process was significantly low; so, the sludge may successfully be removed by entrapment techniques. The present innovation is expected to provide great contribution in improving the quality of life of millions of people who are drinking arsenic contaminated water.

7.4 Recommendations

Recommendations derived from the experiences of our research are presented below. Based on the results of present experiments, subsequent research on this topic should address the following issues.

- Deeper aquifers should be explored. Groundwater of deeper aquifers should be analyzed for assessment of arsenic content.
- Temporal study of ground water quality should be undertaken periodically, because a recently installed deep tube-well may not show arsenic contamination but in the long run it may get contaminated.
- The groundwater movements should be studied by in-depth characterization and routine verification of physical hydrogeology.
- Geophysical resistivity survey to determine the sub surface lithology may be undertaken.
- Wide coverage sampling of lithology (through manual boring) should be done to study the correlation and depositional trend of sediments.
- Arsenic in island's food chain may be assessed and roles of pesticides used for agricultural activities may be carefully observed.
- The island is known for its more than 60 number of wetlands which is also responsible for ground water recharge. Anoxic environment of the wetlands along with redox properties and high sedimentation due to frequent flood may also be the cause of ground water arsenic behind the screen. This study should be done on priority basis.
- Estimation of population at risk interms may be done to form database.
- Estimation of amount of per day water intake segregated at children and adult level, both male and female, should be studied to find out the vulnerability of population to arsenic exposure.

- Detail survey of food habits may be done to find out the vulnerable sections of the population in terms of arsenic accumulation in their bodies.
- Detail survey of filtration procedures both interms of quantity and quality may be done to find out the percentage of population at risk.
- Alternative sources of drinking water such as dug well, rainwater harvesting, surface water with proper watershed management should be studied and prioritised.
- Awareness campaigns about health hazards due to intake of arsenic contaminated water, role of better nutrition and use of safe water may be persued vigorously among the masses in vernacular languages based on our research findings including all information such as, groundwater quality, concentration of arsenic in tubewll water, impact of arsenic on human health and probable mitigation measures.
- Development of a technology for arsenic removal in a cost effective and simple way so that it can be utilized by the rural people.

CHAPTER-1

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3. **R. Goswami**, D.Chakraborti, M. Murriel, B. Das and K.P. Sarma. Arsenic in the groundwater of Majuli-the largest river island of the Brahmaputra: Prevalence, and exposure impacts. *Journal of Hydrology* (under review).

4. **R. Goswami**, D.Chakraborti, M. Murriel, B. Das and K.P. Sarma. Characterization of borehole sediments of Majuli- the largest river island of the Brahmaputra, Assam. (communicated).

Conference papers:

1. **R. Goswami**, P. Deb, R. Thakur and K.P. Sarma "Use of iron oxide and titanium dioxide nanoparticles for removal of arsenic" **(Oral), National symposium on Condensed Matter Science (CMDAYS)**, Tezpur University, **Tezpur** (29-31 Aug, **2006**).

2. **R.Goswami**, B.Devi and K.P.Sarma "Comparative study on accumulation of cadmium in three aquatic plants" (Oral) **International conference on Environmental Research and Development**, **BITS Pilani campus**, **Goa** (18-20 Dec, **2008**).

3. **R. Goswami**, P. Deb, R.Thakur, K.P. Sarma and A. Basumallick “Arsenic remediation using surface functionalized ultrafine nanoparticles” (Poster) **International Conference on Nano science and Technology (ICONSAT), IIT Bombay, Mumbai** (17-20 Feb, **2010**).

4. **R. Goswami**, P. Deb, R.Thakur, K.P. Sarma and A. Basumallick “ Preparation and application of iron oxide nanoparticles for removal of arsenic from water” (**Oral**) **National Seminar on Climate change and Sustainable Development with reference to India**, Tezpur University, **Tezpur** (1-3 April **2010**).

5. **R. Goswami**, P. Deb, R.Thakur, K.P. Sarma and A. Basumallick “Nano remediation of fluoride from aqueous solution using a novel adsorbents”(**Oral**) **National Workshop on Nuclear and Atomic Techniques Based Pure and Applied Sciences (NATPAS.-2011)**, Tezpur University, **Tezpur** 1- 3 Feb, 2011.

6. D. Chakraborti, B. Das, M. Rahman, M Sengupta, T. Roychoudhuri, **R. Goswami.** Groundwater Arsenic Contamination in Ganga-Meghna-Brahmaputra Plain: Health Effects, Arsenic in Food Chain, Social, Socio-economic Effects, Future Cancer Risk & Approach for Mitigation.. Special lecture presented to the training **workshop "Arsenic in drinking water, soil and food crops of Southeast Asia"**, Organized by the CERAR, University of South Australia, supported by Dhaka Community Hospital, Bangladesh and sponsored by Crawford Fund, **Australia**.

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Removal of As(III) from Aqueous Solution Using Functionalized Ultrafine Iron Oxide Nanoparticles

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Arsenic toxicity has become a major concern worldwide. Remediation of this problem needs the development of technology with improved materials and systems with high efficiency. We have demonstrated a simple and efficient method for the absolute removal of As(III) from high concentration As(III) treated water with a low contact time period. The process of As(III) adsorption follows pseudo-second-order kinetic model. The mechanism for high-adsorption efficiency is attributed to fatty acid binding domain-mediated surface conjugation of ultrafine Fe_2O_3 nanoparticles with As(III). We have also ensured the simultaneous separation of arsenic sorbed nanoparticles by entrapping them in hydrophilic calcium alginate beads and thereby a pure arsenic free solution has been obtained.

Keywords alginate; entrapment; mechanism; remediation; separation

INTRODUCTION

Arsenic contamination has become a worldwide epidemic, especially in some areas of India, Bangladesh, Vietnam, Chile, China, Argentina, Mexico, Hungary, Taiwan, Japan, New Zealand, Germany, and the United States, where a significant percentage of the population depends on ground water for drinking (1–5). Remediation of this problem needs the development of the technology with improved materials and systems with high efficiency. Materials form the basic underlying building block of nearly every advanced technology and nanoscale materials are no exception, making a significant impact on our everyday lives. Characteristics such as a large surface area, potential for self assembly, high specificity, and high reactivity make nanoparticles excellent candidates. It is generally observed that As(V) is better removed and hence in most of the arsenic removal devices, primary oxidizing-interface for converting As(III) species to pentavalent status is ensured. Moreover, under groundwater conditions, As(III) is the predominant form of arsenic, which is more toxic and mobile than As(V). In the proposed study, surface-functionalized ultrafine iron oxide (Fe_2O_3) nanoparticles have been developed for the removal of As(III) from aqueous solution. Though in recent times, some attempts were made to study the efficiency of arsenic removal from drinking water using nanoparticles (6–11), but these studies have limitations in terms of high-adsorbent doses (12), high contact time period (6,10, 13–15), absolute removal efficiency (12,13,15), and separation of nanoparticles after application. Considering this, we intend to study here the removal efficiency of As(III) from treated water with a low adsorbent dose and less contact time period using ultrafine Fe_2O_3 nanoparticles and finally the complete separation of the arsenic-adsorbed nanoparticles from treated water.

Under natural conditions, the surface reactivity of iron compounds plays an important role in adsorbing arsenic in the sedimentary aquifers (16) and arsenic can form inner sphere monodentate or bidentate–binuclear complexes with these iron compounds (17,18). The main objectives of the present study are:

1. effectiveness of surface-functionalized ultrafine iron oxide nanoparticles for treatment of arsenic,
2. determine its removal efficiency with respect to the adsorbent dose and contact time period,
3. identify the mechanism for As(III) adsorption and
4. separation of spent and excess adsorbents from treated water.

EXPERIMENTAL

The ultrafine Fe_2O_3 nanoparticles, with an average particle size ~10 nm, were prepared by thermal decomposition of stearic acid and iron (III) nitrate homogenous mixture followed by heat treatment at 250°C in ambient

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condition (19). The hydrophobic stearic acid is one way of restricting the growth of the particles yielding uniform spherical ultrafine nanoparticles with surface modification by carboxyl functionalization to enhance the surface activity for adsorption. Stock solution of As(III) was prepared by dissolving the corresponding arsenic oxide in deionized water with NaOH followed by rigorous stirring. To avoid As(III) oxidation the stock solution for arsenic was prepared in oxygen-free water (Milli Q water) purged with N_2 at 80°C. The adsorption experiments were carried out under a nitrogen atmosphere. The concentrations of the stock solutions were made to 0.1, 0.3, and 0.5 ppm by diluting the stock. These arsenic concentrations were chosen keeping in mind the contaminant level in drinking water in some of the high-alert zones of the world ranging from the United States to Bangladesh. Fifty ml of arsenic solution of different concentrations was taken in which 0.01, 0.025, and 0.05 g of Fe_2O_3 nano powders were introduced and rigorously stirred at room temperature. Adsorption studies were performed by the batch technique using the so-prepared nanopowder to obtain the rate of equilibrium data. In the next step, Fe_2O_3 nano powder was mixed with 2% sodium alginate solution. This mixture was poured into a 10% $CaCl_2$ solution, which leads to the formation of calcium alginate beads of approximately 2 mm in diameter. The beads entrapping the nanoparticles were then added to the so-prepared arsenic solutions followed by rigorous stirring. Arsenic concentrations in the supernatant solutions were analyzed by Atomic Absorption Spectrophotometer (AAS). A Transmission Electron Microscopy (TEM) study was carried out to confirm the adsorption of As(III) by surface functionalized Fe_2O_3 nanoparticles.

RESULTS AND DISCUSSION

The effect of major parameters like the effect of initial concentration of arsenic on the uptake of adsorbent materials, the amount of adsorbent, and the contact time and was investigated.

Effect of Initial Concentration

Studies on the effect of initial arsenic concentration were conducted by varying it from 0.1 to 0.5 ppm keeping adsorbent dose of 0.05 g/50 ml at neutral pH (6.5) and contact time of 80 minutes. From Fig. 1a, it is evident that the so-prepared surface functionalized ultrafine Fe_2O_3 nanopowder which can remove arsenic absolutely (100%) when the concentration of arsenic was 0.1 ppm with an adsorbent dose of 0.05 g/50 ml within a time period of 80 mins. When the initial concentration of arsenic increased to 0.5 ppm, the efficiency of removal was decreased, which was observed to be 98.2% at 0.3 ppm and 97.1% at 0.5 ppm. It is observed that there was a decrease in the percentage of removal of arsenic corresponding to an increased initial arsenic concentration. Moreover, the rate of this adsorptive reaction in the optimized period of contact varies directly with the concentration of the adsorbate.

Effect of Adsorbent Dose and Contact Time

The effect of the adsorbent dose was studied for higher (0.5 ppm) arsenic concentration (Fig. 1b). The figure illustrates that the aqueous arsenic concentration decrease with the increasing adsorbent dose as well as with time. The absolute removal within the detection limit of the AAS instrument (0.001 mg/L) was achieved with a very low adsorbent dose of 0.05 gm/50 ml. The decrease in arsenic concentration or increase in arsenic removal efficiency can be achieved by increasing the dose of the adsorbent (Fig. 1b) due to more availability of the surface-adsorbent sites. A similar trend has been observed with increase in contact time. Keeping the aforementioned adsorbent dose constant, absolute removal efficiency was achieved within 80 min of contact time.

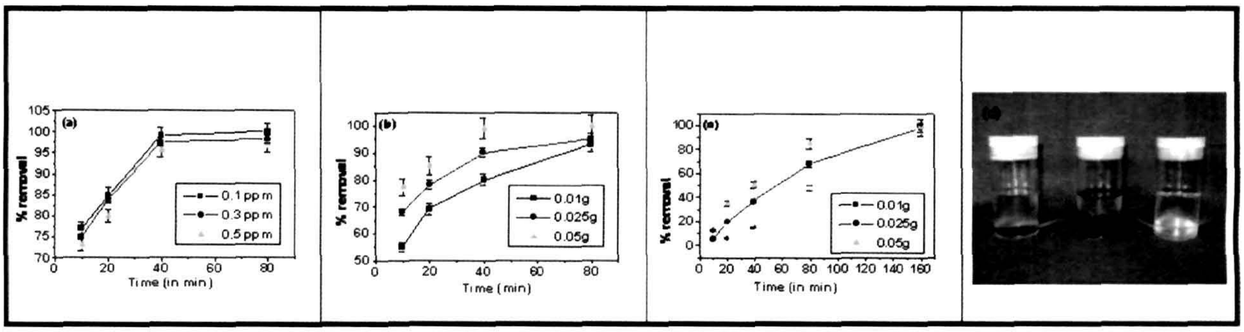


FIG. 1. Arsenic removal using ultrafine Fe_2O_3 nanoparticles. (a) Effect of initial concentration on percent arsenic removal by Fe_2O_3 nanoparticles with an adsorbent dose of 0.05 g/50 ml. (b) Effect of adsorbent dose and time on percent arsenic removal by bare Fe_2O_3 nanoparticles and (c) Fe_2O_3 nanoparticles entrapped in calcium alginate beads. 50 ml of arsenic solution with concentration 0.5 ppm was taken in which 0.01, 0.025, and 0.05 g of Fe_2O_3 nanopowder was introduced. Calcium alginate beads entrapping Fe_2O_3 nanoparticles were prepared by mixing above mentioned doses of Fe_2O_3 nanopowder in 2% sodium alginate solution. (d) the representative pictures of samples for Fe_2O_3 nanoparticles treated arsenic solution, arsenic solution treated with Fe_2O_3 entrapped calcium alginate beads and pure water after separation of completely adsorbed arsenic respectively (from left to right).

Entrapment Study

Simultaneously, it is needed to separate the arsenic adsorbed nanoparticles from the aqueous solution. Keeping in mind this aspect, arsenic sorption was further studied by entrapping ultrafine Fe_2O_3 nanoparticles in calcium alginate beads. It is worthwhile to mention here that sodium alginate, which is water soluble and becomes a hydrogel in the presence of multivalent cations (Ca^{2+}, Ba^{2+}, Sr^{2+}), shows good permeability for small molecules (20). Alginic acid has a high viscosity. Porosity in Ca-alginate allows solutes to diffuse into the beads and come in contact with the entrapped cells. Moreover, alginate is nontoxic, biodegradable, and nonimmunogenic, and produces thermally-irreversible and water-insoluble gels. The present research demonstrates that iron oxide nanoparticles can be effectively entrapped in this biopolymer matrix (alginate) without significant reduction in their reactivity. Ultrafine Fe_2O_3 nanoparticles entrapped in alginate beads showed 100% removal efficiency (Fig. 1c). The removal efficiency increases from 96% to 100% as the dose increases from 0.01 to 0.05 g/50 ml. This study reveals that the nanoparticles of Fe_2O_3 entrapped in alginate beads can also adsorb arsenic completely. Moreover, these beads entrapping arsenic sorbed Fe_2O_3 nanoparticles can be separated easily and more efficiently as compared to the arsenic-sorbed bare nanoparticles (Fig. 1d). In the removal of soluble pollutants from water by sorption methods, the solid/liquid separation step is very important for an efficient operation. Due to their very small sizes, nanomaterials make this separation very difficult and expensive as the common methods cannot be applied. Hence, we have used ultrafine nanoparticles entrapped into the macro beads of calcium alginate for easy and efficient separation. Here, we have shown that ultrafine Fe_2O_3 nanoparticles can be effectively entrapped in Ca-alginate beads and the reactivity of the entrapped nanoparticles towards arsenic was comparable to that of bare nanoparticles. Alginate beads without Fe_2O_3 nanoparticles were applied to the arsenic solution with concentration 0.1 ppm in the same way. The analysis of the collected samples has shown that calcium alginate has no role in the removal of arsenic. Alginate is used only for the separation of arsenic-sorbed Fe_2O_3 nanoparticles from water solution. Fe_2O_3 nanoparticles without surface functionalization were also applied in order to perform a comparative study between the surface-functionlized ultrafine Fe_2O_3 nanoparticles and Fe_2O_3 nanoparticles without surface functionalization for their efficiency of arsenic removal. The experimental results showed that Fe_2O_3 nanoparticles without surface functionalization can remove maximum of 91% As(III) within 80 min of contact time with an adsorbent dose of 0.05 g/50 ml.

Removal Mechanism

To understand the removal mechanism by this novel nanosystem, we also carried out the transmission electron microscope (TEM) investigations of the arsenic adsorbed Fe_2O_3 nanoparticles (Fig. 2a). The particles are an average of 10 nm in diameter with a size distribution of about 15%. It is also evident that the nanoparticles are well separated from each other, i.e., aggregation has not taken place. This has occurred as a result of the perturbation of the electron cloud of the arsenic molecule environment during the conjugation process. The coupling between the arsenic and the Fe_2O_3 nanoparticles was based on functional chemistry. The ultrafine Fe_2O_3 nanoparticles were coated with strearic acid to stabilize and functionalize the nanoparticles. The stearic acid-capped iron oxide nanoparticles exhibit free carboxyl group on the nanoparticles surface (19,21). Due to a very strong hydrophobic character of the hydrocarbon chain of stearic acid molecule, it is very difficult for the molecule to be exposed to the aqueous solution. So, the interaction of the stearic acid molecule with the core iron

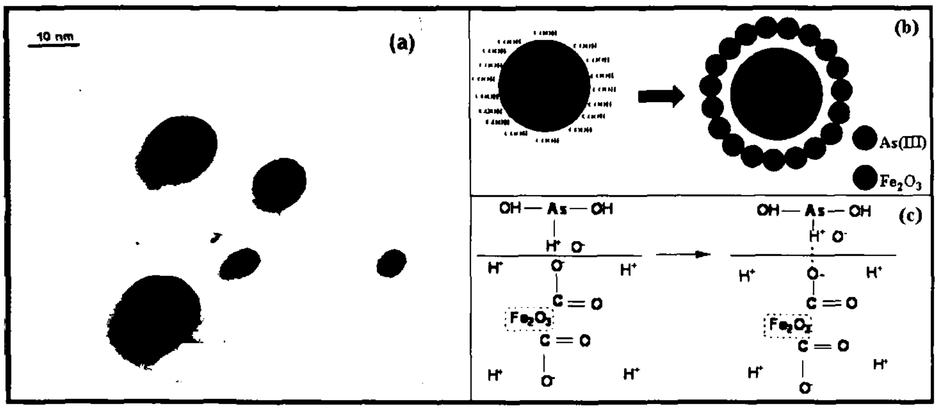
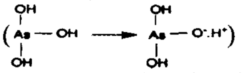


FIG. 2. Arsenic adsorption by surface functionalized Fe_2O_3 nanoparticles. (a) TEM micrograph of arsenic adsorbed Fe_2O_3 nanoparticles over the surface. (b) Mechanism of arsenic adsorption by fatty acid binding domain mediated ultrafine Fe_2O_3 nanoparticles. (c) Chemical process of arsenic adsorption over the surface of stearic acid capped Fe_2O_3.

oxide took place through the hydrocarbon segment leaving the carboxyl group towards the aqueous solution. In our study the adsorption mechanism is proposed based on the interaction between carboxyl functional groups of stearic acid capped Fe_2O_3 nanoparticles with unsaturated H_3AsO_3. It is worth mentioning here that As(III) species remain protonated as H_3AsO_3 at pH below 9.2 (22). Hence, below this pH (in our study pH is 6.5) H_3AsO_3 will be the predominant phase (23,24). Now, in the proposed mechanism we have assumed that the free surface-functionalized COO^- end of the sorbent interact with H_3AsO_3 species releasing O^- and H^+ (25). As(III) exists as H_3AsO_3  $\left(\mathrm{As(OH)_2{-}OH} \longrightarrow \mathrm{As(OH)_2{-}O^-{\cdot}H^+}\right)$ in aqueous solution. Figure 2c illustrates that the chemical process occurred at the surface of iron oxide nanoparticles to conjugate with As(III) molecules and form an assembly pattern.

Adsorption Isotherms

Adsorption isotherms, which are the presentation of the amount of solute adsorbed per unit of adsorbent as a function of equilibrium concentration in bulk solution at constant temperature, were also studied. The equilibrium data obtained were fitted to the Freundlich and Langmuir isotherms.

The Freundlich equation deals with physico-chemical adsorption on heterogenous surfaces (indicates the adsorptive capacity or loading factor). The linearized form of the Freundlich equation is given as:

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \tag{1}$$

where x is the amount of the solute adsorbed, m is the mass of adsorbent used, C_e (mg/l) the equilibrium solute concentration in solution, and K_f, a constant, which is a measure of the adsorption capacity, and n is a measure of the adsorption intensity. The values of K_f and n were obtained from the slope and intercept of the plot between $\log(x/m)$ and $\log C_e$. In the present study, the values of K_f and n were found to be 72.9 mg/g and 1.92. The isotherm fitted very well for the adsorbent with a correlation coefficient 0.9969. Significantly, higher values of the adsorption capacity (K_f) obtained with ultrafine nanoparticles indicate that it can be effectively used for the removal of arsenic from water.

The Langmuir isotherm is valid for single-layer adsorption. It is based on the assumption that all the adsorption sites have equal affinity for molecules of the adsorbate and there is no transmigration of the adsorbate in the plane of the surface.

The linear form of the Langmuir equation is:

$$1/X = 1/X_m + (1/C_e)(1/b \cdot X_m). \tag{2}$$

$X = x/m$, where x is the amount of the solute adsorbed, m is the mass of the adsorbent, C_e (mg/l) is the concentration of arsenic at equilibrium, X_m is the amount of solute adsorbed per unit mass of adsorbent required for monolayer coverage of the surface, also called monolayer capacity, and b ($L\,mg^{-1}$) is the Langmuir constant related to the affinity between the sorbent and the sorbate. The plots of 1/X against C_e for adsorption of As(III) gave a straight line. The estimated goodness of fit is $r^2 = 0.9946$ and enables applicability of the Langmuir model to As(III) adsorption on the surface-functionalized nanoparticles. The Langmuir constants x/m and b for the present study are 10.47 mg/g and 0.004 respectively.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter R_L was determined (26).

In the present study R_L values at different initial aresnic concentrations indicate a highly favorable adsorption (refer to Table 1). In case of initial concentration 0.1 ppm the R_L value is 0.9996 ($\sim$1), thus indicating the linear shape of the isotherm.

Sorption Kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of the adsorbate uptake at the solid-solution interface. The kinetics of As(III) adsorption on the ultrafine Fe_2O_3 nanoparticles were analyzed using pseudo first-order and pseudo second-order (27) models. The uniformity between

TABLE 1
Pseudo first-order rate constants, pseudo second-order rate constants, and R_L values for As(III) adsorption on nano Fe_2O_3 at different initial concentration

	Pseudo first order rate constants			Pseudo second order rate constants			
As(III) (mg/l)	K_1	q_e	r^2	K_2	q_e	r^2	R_L
0.1	0.04	0.062	0.9859	1.466	0.096	0.9905	0.9996
0.3	0.067	0.2975	0.9821	0.27	0.324	0.9955	0.9988
0.5	0.069	0.5821	0.9756	0.119	0.566	0.986	0.998

the experimental data and model-predicted values was expressed by correlation coefficients (r^2 values close or equal to 1).

The Pseudo First-Order Equation

The pseudo first-order equation is expressed as:

$$\log(q_e - q_t) = \log(q_e) - K_1 t/2.303. \qquad (3)$$

where, q_e and q_t (both in mg/g) are the amounts of As(III) adsorbed at equilibrium and at time t respectively. K_1 is the rate constant of pseudo first- order adsorption. The plot of $\log(q_e - q_t)$ vs t gives a straight line and the kinetics parameters are presented in Table 1. The rate constant is calculated from the slope of the line using pseudo first-order kinetics model is presented in Table 1. The calculated q_e values using pseudo first-order kinetics model showed 0.83–38% deviation from the experimental q_e values (Table 1).

The Pseudo Second-Order Equation

The linearized form of the pseudo second-order kinetic rate equation is expressed as:

$$t/q_t = 1/K_2 q_e^2 + t/q_e \qquad (4)$$

In addition, the initial rate of adsorption, h is $K_2 q_e^2$, where, q_e and q_t are the amounts of As(III) adsorbed per unit of mass of nano Fe_2O_3 at equilibrium and at time t respectively and K_2 is the rate constant of pseudo second- order adsorption. The kinetic plots between t/q_t vs t were plotted for the different initial concentrations (Fig. 3b) and slope and intercept values were measured to determine the value of pseudo second-order rate constant mentioned in Table 1. Figure 3b and Table 1 show a highly significant regression line and the data were well fitted to the pseudo second-order rate equation. The t/q_t vs t gives a straight line and depicted in Fig. 3b The calculated rate constant and equilibrium concentration are presented in Table 1. The calculated q_e values using pseudo second-order kinetics model is better than the pseudo-first-order kinetics compared to the experimental q_e values (4–13.2% deviation for second-order kinetics and 0.83–38% deviation for first-order kinetics. It is also observed from Table 1 that the pseudo second-order kinetics model fits the kinetics data better than the pseudo first-order kinetics model (based on R^2 value). The result shows that the goodness of fit is better in the pseudo second-order kinetics model as compared to the pseudo first-order kinetics model for the entire range of kinetics run. The straight line behavior is indicating that the process follow a pseudo second-order kinetics for various concentrations of As(III).

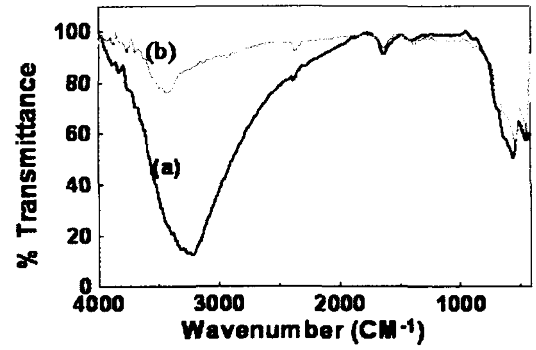


FIG. 4. FTIR spectra of iron oxide. (a) before sorption and (b) after sorption.

FTIR Study in Arsenic Adsorption

The FTIR spectrum is a powerful tool for analyzing the adsorption process by the adsorbate species on the adsorbent in a dilute medium. The spectra of surface-functionalized nanoparticles before and after adsorbing As(III) are shown in Fig. 4. From Fig. 4 it appears that the arsenic (III) adsorption leads to changes in the individual positions in the bands. The broad peak at 1399.53 cm^{-1}, disappears (M-OH bending) while loading. Peaks appear at 1430 cm^{-1} (As III). The –OH peak at 3215.10 cm^{-1} disappear and peaks at 3413.32 cm^{-1}(As III) arise due to interaction with the surface –OH group. The results reveals that the arsenic is bonding to the surface-functionalized ultrafine nanoparticles in a surface complex.

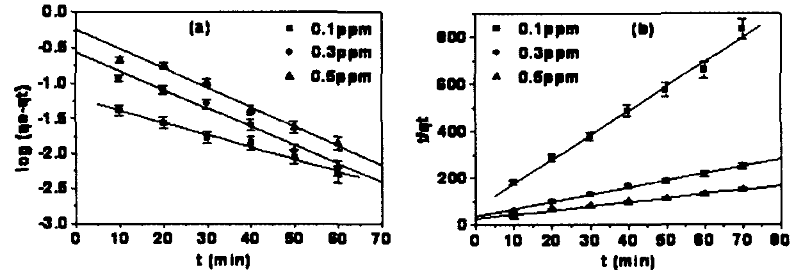


FIG. 3. Kinetics analysis of As(III) adsorption by linear plots of (a) pseudo first order, (b) pseudo second order rate equations.

CONCLUSION

In summary, we have demonstrated that the surface-functionalized ultrafine Fe_2O_3 nanoparticles can effectively remove arsenic from treated water. We have also reported the mechanism of As(III) adsorption by the surface-functionalized Fe_2O_3 nanoparticles. The kinetics of the As(III) adsorption on the so-prepared nanoparticles was found to follow the pseudo second-order rate equation. The so-prepared monodisperse ultrafine Fe_2O_3 nanoparticles are capable of removing As(III) from treated water with high arsenic concentration, low adsorbent dose, and low contact time. Once As(III) was sorbed onto Fe_2O_3 nanoparticle surfaces, separation by hydrophilic calcium alginate beads provides a way to drag out the whole arsenic sorbed sludge out of the solution.

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ARSENIC REMEDIATION USING SURFACE FUNCTIONALIZED ULTRAFINE NANOPARTICLES

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Ultrafine nanoparticles owing to their increased surface to volume ratio, coupled with the ability to tune their surface properties through molecular modification have made them ideal for their detection and remediation of broad range of environmental contaminants. Arsenic contamination has become a worldwide epidemic and remediation of this problem needs the development of technology with improved materials and systems with high efficiency. In the present study, we have demonstrated a simple and efficient method using surface functionalized ultrafine iron oxide nanoparticles for absolute removal of arsenic from arsenic treated water with low contact time period and low adsorbent dose. The efficiency of arsenic removal has been drastically improved by considering nanoparticles of size 10 nm and subsequent surface engineering of the nanoparticles resulting more adsorption sites being exposed to arsenic. The mechanism for adsorption was identified through electron microscopic and spectroscopic studies. The adsorption equilibrium data were well fitted to Freundlich isotherm.

Keywords: Arsenic; nanoparticles; surface functionalization; remediation; mechanism.

1. Introduction

Arsenic contamination has become one of the global environmental issues[1–3] posing a series of severe health problems.[4,5] As a result, the US Environment Protection Agency (USEPA) and World Health Organization (WHO) implemented the reduction of arsenic maximum contaminant level (MCL) in the drinking water from $50\,\mu\mathrm{g\,l^{-1}}$ to $10\,\mu\mathrm{g\,l^{-1}}$. The implementation of this new MCL arsenic standard in drinking water has initiated the development of the technology to remediate this problem with improved materials and systems with high efficiency. Thus, there is a growing interest in using efficient methods and materials to remove arsenic from drinking water, before it may cause significant contamination. Materials form the basic underlying building block of nearly every advanced technology and nanoscale materials is no exception, making a significant impact on our everyday lives. Characteristics such as large surface area, potential for self assembly, high specificity and high reactivity make nanoparticles excellent candidates for water treatment applications. The methods available for the removal of arsenic have been adequately reviewed.[6] Though in recent times, some attempts were made to study the efficiency of arsenic removal from drinking water using nanoparticles,[7–9] but these studies have limitations in terms of high adsorbent doses, high contact time period, and maximum removal efficiency. Considering it, we have used surface functionalized ultrafine Fe_2O_3 nanoparticles for maximum removal of arsenic from treated water with a low adsorbent dose and less contact time period.

2. Experimental Procedure

2.1. *Materials*

Stock solutions of 500 mg/L As(III) and As(V) were prepared from arsenic (III) oxide (As_2O_3) and sodium arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$). The pH adjustment of the solution was accomplished with 1 N NaOH and 6 N HNO_3.

2.2. *Preparation of surface functionalized ultrafine nanoparticles*

The ultrafine Fe_2O_3 nanoparticles, with average particle size ∼10 nm, were prepared by thermal decomposition of stearic acid and iron (III) nitrate homogenous mixture followed by heat treatment at 600°C in ambient condition.[10]

2.3. *Adsorption experiments*

The sorption experiments were conducted at room temperature using polypropylene tubes. Different doses (0.0025 g, 0.005 g, 0.01 g, 0.025 g, 0.05 g) of adsorbent were put in contact with 50 ml of arsenic (arsenate and arsenite) solutions at 100 μg/L. The pH of the suspension was adjusted to values of 2.2, 3.5 and 9.6. These parameters were varied to measure the effect of experimental conditions on arsenic adsorption to the so prepared nanoparticles. The tubes were shaken for 80 min until the adsorption equilibrium was reached. Then the samples were collected at 10 min interval upto 80 min. Samples were centrifuged at 3000 rpm for 15 min. The pH was checked at the end of each experiment to confirm that no change of pH had occurred.

Arsenic concentration in the supernatant was measured by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 2100 DV, Perkin Elmer). Transmission Electron Microscopy (TEM) study was carried out to confirm the microstructure of arsenic sorbed surface functionalized Fe_2O_3 nanoparticles. The Fourier transform infrared spectroscopy (FTIR) study was performed on nanomaterials before and after adsorption to realize the adsorption process.

3. Results and Discussion

All the experiments were conducted for both arsenic (III) and arsenic (V) in order to compare the sorption behavior of the nanoparticles onto As(III) and As(V) as a function of the adsorbent dose and pH of the solution.

3.1. *Effect of adsorbent concentration*

The pH and adsorbent dose are the most significant parameters for arsenic removal. The effect of adsorbent concentration on arsenate and arsenite adsorption was examined and found that the aqueous arsenic (arsenate and arsenite) concentrations decrease with increasing adsorbent concentration as well as with time (Figs. 1 and 2), in each experiment the initial arsenic (arsenate and arsenite) concentration was 100 μg/L. When 0.0025 g/50 ml adsorbent was used, 72.4 μg/L of arsenate was adsorbed in 80 min; however 0.05 g/50 ml adsorbed 99.9 μg/L (99.9% removal) in 80 min. For arsenite the adsorption rate was slower than arsenate. When 0.05 g/50 ml

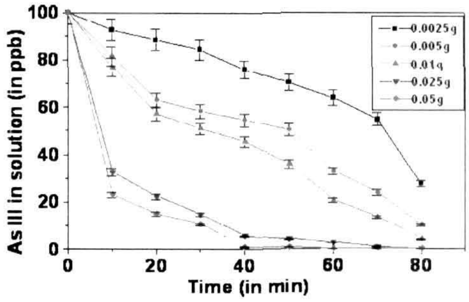


Fig. 1. Plots of remaining arsenite concentration (μg/L) versus time as a function of adsorbent concentration.

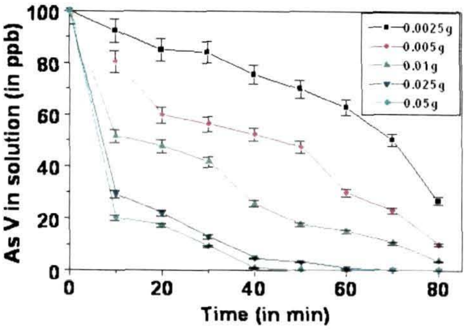


Fig. 2. Plots of remaining arsenate concentration (μg/L) versus time as a function of adsorbent concentration.

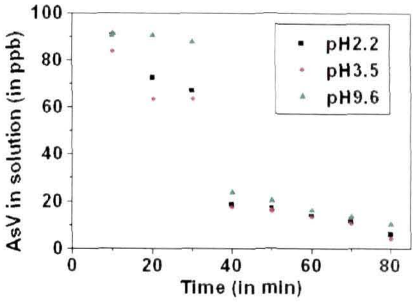


Fig. 3. Effect of pH on arsenate adsorption.

adsorbent was used, the arsenite and arsenate concentrations reach less than 10 μg/L (U.S. EPA MCL), for arsenate in 30 min and for arsenite in 40 min. From the figure, it is obvious that as the adsorbent concentration increases, the sorption of arsenic increases along with the rate of adsorption, probably due to increase in surface area and surface adsorption reactivity and hence more active sites were available for the adsorption of arsenic. The adsorption isotherm was investigated using different doses of the sorbent at pH 3.5 for both arsenate and arsenite and found that the equilibrium data were fitted very well to Freundlich adsorption model.

The two Freundlich isotherm constants (i.e., K_F and $1/n$) were obtained from fitting the experimental data to Freundlich equation isotherms. The sorption coefficient K_F was found to be 5.25 (mg/g) $(\text{L/mg})^{1/n}$ and 5.55 (mg/g) $(\text{L/mg})^{1/n}$ for arsenite and arsenate respectively. The adsorption intensity $1/n$ was 0.39 for arsenite and 0.40 for arsenate.

3.2. *Effect of pH*

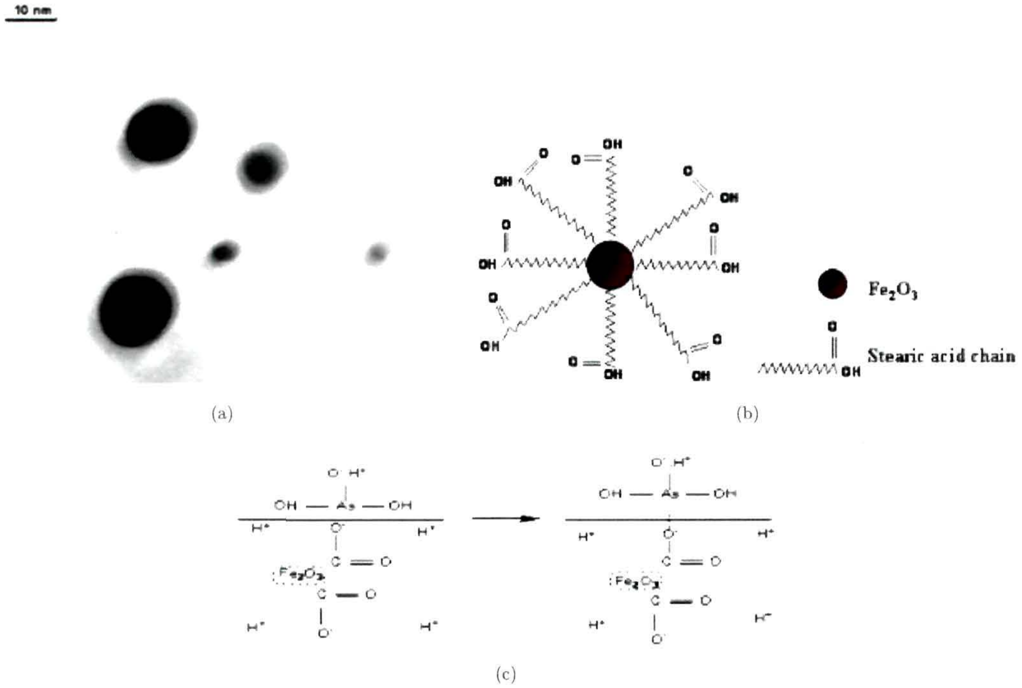
The pH is an important parameter in sorption based water treatment process,[11] because proton concentration can strongly modify the redox potential of the sorbates and sorbents. The pH range of the treated water is also significant for the effectiveness of iron oxide particles to remove arsenic. It is reported that arsenate removal is efficient in the pH range of 3–7.[11] Therefore, adsorption experiments were performed at various pH levels with 100 μg/L arsenate and 0.0025, 0.005 and 0.01 g/50 ml ultrafine nanoparticles at 10 minute interval up to 80 min.

The arsenate adsorbed at 80 min is 94 μg/L, 96 μg/L and 90 μg/L at pH 2.2, 3.5 and 9.6, respectively (Fig. 3). The results demonstrate a negligible difference in arsenate adsorption at pH 2.2 and 3.5 (2%) and slightly higher difference at pH 9.6 (6%). From Fig. 3, it appears that the amount of arsenate adsorption increases by lowering the pH (3.5) of the system and by increasing the amount of sorbent.

However, the adsorption efficiency of arsenite by the iron oxide nanoparticles was observed to be more at pH > 3.5. The arsenic adsorbed at equilibrium (80 min) is 92.1 μg/L, 94 μg/L and 95 μg/L at pH 2.2, 3.5 and 9.6 respectively. The present study reveals that the adsorption efficiency of arsenite is slightly more with increasing pH.

3.3. *Removal mechanism*

To understand the removal mechanism by this novel nanosystem, we carried out the transmission electron microscope (TEM) investigations (Fig. 4(a)) and Fourier transform infrared spectroscopy (FTIR) study (Fig. 5) of the arsenic adsorbed Fe_2O_3 nanoparticles. The particles are average 10 nm in diameter with size distribution of about 5%. The coupling between the arsenic and the Fe_2O_3 nanoparticles was based on functional chemistry. The ultrafine Fe_2O_3 nanoparticles were coated with stearic acid to stabilize and functionalize the nanoparticles. The stearic acid capped iron oxide nanoparticles exhibit free carboxyl group on the nanoparticles surface.[12] Probably, due to very strong hydrophobic character of the hydrocarbon chain of stearic acid molecule, it is very difficult for the molecule to be exposed to the aqueous solution. So, the interaction of stearic acid molecule with the core iron oxide took place through the hydrocarbon segment leaving the carboxyl group toward the aqueous solution. The conjugation of As(III) to nanoparticles surface is assigned to the formation of the covalent bond between the unsaturated arsenic and carboxyl functional groups of the arsenic hydroxide and stearic acid-capped iron oxide



(a) (b)

(c)

Fig. 4. Arsenic adsorption by surface functionalized Fe_2O_3 nanoparticles. (a) TEM micrograph of arsenic adsorbed Fe_2O_3 nanoparticles over the surface. (b) Schematic diagram of stearic acid capped Fe_2O_3 nanoparticles. (c) Chemical process of arsenic adsorption over the surface of stearic acid capped Fe_2O_3.

nanoparticles. As(III) exists as H_3AsO_3 in aqueous solution. Figure 4(b) represents the schematic diagram of iron oxide nanoparticles capped with stearic acid functional group. The proposed process of surface adsorption of arsenic over surface functionalized iron oxide nanoparticles has been depicted in Fig. 4(c).

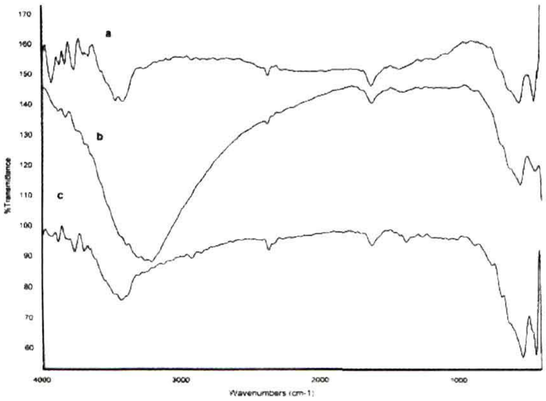


Fig. 5. FTIR spectra of Fe_2O_3 nanoparticles (b) before sorption and after (a) As(III) (c) As(V) sorption.

3.4. *FTIR study in arsenic adsorption*

The FTIR spectrum is a powerful tool for analyzing the adsorption process by the adsorbate species on the adsorbent in a dilute medium.[13]

The spectra of surface functionalized nanoparticles before and after adsorbing As(III) and As(V) are shown in Fig. 5. From Fig. 5 it is clear that the arsenic (III and V) adsorption leads to changes in the individual positions of the bands (Figs. 5(a) and 5(c)). The broad peak at 1399 cm^{-1}, disappears (M-OH bending) while loading (Fig. 5(b)). Peaks appear at 1430 cm^{-1} (As III) (Fig. 5(a)) and 1382 cm^{-1} (As V) (Fig. 5(c)). The $-$OH peak at 3215 cm^{-1} disappear (Fig. 5(b)) and peaks at 3413 cm^{-1} (As III) (Fig. 5(a)) and 3429 cm^{-1} (As V) (Fig. 5(c)) arise due to interaction with the surface $-$OH group. The results reveal that the arsenic is bonding to surface functionalized ultrafine nanoparticles in a surface complex.

4. Conclusion

We can conclude that the surface functionalized ultrafine nanoparticles can adsorb both arsenite and arsenate efficiently from the treated water solution with minimal dose and less time requirement. The maximum adsorption capacity was found to be the highest at pH 3.5. The experimental data were well fitted to the Freundlich isotherm.

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