2. Literature review

2.1 Arsenic: Occurrences, sources and properties

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$_2$S$_3$). 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.
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 ($\text{H}_2\text{AsO}_4^-$) or divalent (HAsO$_4^{2-}$) anion, and arsenite is fully protonated and
exists almost exclusively as an uncharged molecule (H$_3$AsO$_3$) (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 cover 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

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 arsenic concentrations are recorded in groundwater in Bangladesh, West Bengal (India), Inner Mongolia (China), Taiwan, Lao, Cambodia, Myanmar, Japan and Pakistan (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 m³ 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 km³) 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 km², 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 University, 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, viz; 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 Dhemaj, 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)

<table>
<thead>
<tr>
<th>District</th>
<th>No of blocks affected</th>
<th>Total sources tested</th>
<th>Sources 10-50 μg/L</th>
<th>Sources &gt;50 μg/L</th>
<th>% Sources &gt;50 μg/L</th>
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<td>3</td>
<td>227</td>
<td>34</td>
<td>6</td>
<td>2.6</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>72</strong></td>
<td><strong>4920</strong></td>
<td><strong>1138</strong></td>
<td><strong>362</strong></td>
<td><strong>7.4</strong></td>
</tr>
</tbody>
</table>

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, CH₃AsO(OH); dimethylarsinic acid, DMAA, (CH₃)₂AsO(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 As³⁺ or As⁵⁺ 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 ($\text{As}^{5+}$) is reduced to arsenite ($\text{As}^{3+}$) by glutathione (GSH). Firstly, reduction of As (V) to As (III) is mediated by glutathion, acts as reducing agent and then methyl group is transferred 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 $S – \text{adenosyl methionine}$ 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 $–\text{SH}$ group. Due to high affinity of trivalent arsenic to $-\text{SH}$ 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 $\text{As}^{3+} > \text{As}^{5+} > \text{MMA} > \text{DMA}$. 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 ($\text{As}^{3+}$ and $\text{As}^{5+}$) (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 arsenicosis are primarily manifested in the form of different types of skin disorders such as skin lesions, hyperkeratosis 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:

\[ q_e = K C_e^{1/n} \quad (1) \]

The linear form is as follows:

\[ \log(q_e) = \log(K) + \frac{1}{n} \log(C_e) \quad (2) \]

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.

\[ q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e} \quad \text{or} \quad \frac{1}{q_e} = \frac{1}{q_{\text{max}} b C_e} + \frac{1}{q_{\text{max}}} \]  

where \( b \) and \( q_{\text{max}} \) are constants. \( q_{\text{max}} \) represents the maximum value of \( q_e \) that can be achieved as \( C_e \) is increased. The constant \( q_{\text{max}} \) 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 Langmuir 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:
\[
\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (4)
\]

Where \( k_1 \) (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-

\[
\log (q_e - q_t) = \log q_e - k_1 t \quad (5)
\]

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.

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t \quad (6)
\]

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 (\( t \to 0 \)), \( h \) can be defined as:

\[
h = k_2 q_e^2 \quad (7)
\]

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:

\[
q = k_{id}t^{1/2} \quad (8)
\]

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


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 (α-FeOOH) and akaganeite (β-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 where 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 groundwater 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 ($\beta$-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 (Fe⁰) particles such as NiFe and PdFe were synthesized by borohydride reduction of nickel and palladium salts on Fe⁰ 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$_3$O$_4$) 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$_3$O$_4$) nanoparticles was conducted by Mayo et al. (2007). The effect of Fe$_3$O$_4$ 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$_3$O$_4$) 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$_3$O$_4$ 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.

2.10.4 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.

2.10.4.1 pH

The predominance of arsenic (V) acid, \( \text{H}_3\text{AsO}_4 \), and arsenous(III) acid, \( \text{HAsO}_2 \), 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).

**2.10.4.2 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.
2.10.4.3 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; \( \text{Ca}^{2+}, \ \text{Mg}^{2+}, \ \text{PO}_4^{3-}, \ \text{Cl}^{-}, \ \text{and HCO}_3^{-} \) (common ions in groundwater) on arsenic removal using iron oxides. It is found that all the anions tested, except \( \text{Ca}^{2+} \), interfere with the arsenic sorption by competing with arsenate for the available surface sites. The suppression of arsenic sorption caused by \( \text{HCO}_3^{-} \) is much greater than that caused by \( \text{Cl}^{-} \) (Smedley & Kinniburgh 2002). Similar results are reported elsewhere by Matsunaga et al. (1996). The presence of \( \text{Ca}^{2+} \), 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 \( \text{As(III)} \) and \( \text{As(V)} \) 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).