

Chapter 1

1. Introduction and Objectives

1.1 Introduction

Arsenic is a metalloid with a name derived from the Greek word *arsenikon*, meaning potent. Toxicity of arsenic in drinking water is a global concern, as arsenic contaminated drinking water is directly linked to several types of cancers. Unfortunately, recovery from arsenic related cancers by medical treatments are not yet available, because arsenic metabolism and mechanism of carcinogenicity are not well understood, therefore, providing arsenic free drinking water is the only way to diminish the adverse health effects of arsenic (Furman, 2004). In current situation, several arsenic remediation methods are studied and proposed to provide arsenic-free drinking water. These methods suggest either the treatment of arsenic contaminated groundwater (CGW) or implemented for the alternative options (rain water harvesting, solar distillation, surface water treatment, etc). The uses of alternative water sources can only be possible after implementation of a major and costly technological shift. Thus, the treatment of CGW to the guideline values is the preferable option (Ahmed, 2003).

The elevated arsenic concentration in water and soils have been found in Bangladesh (Chakraborti et al., 2010; Selim Reza et al., 2010; Zheng et al., 2004; Alam et al., 2002; Harvey et al., 2002; Nickson et al., 1998; Das et al., 1995), China (Nga et al., 2005), Chile (Smith et al., 2000), Ghana (Smedley et al., 1996), Germany (Ruhland and Jekel, 2002), Hungary (Hodi et al., 1995), India (Bhattacharjee et al., 2005; Chatterjee et al., 1993), Mexico (Armienta and Segovia, 2008), Pakistan (Nickson et al., 2005), France (Charlet et al., 2001), USA (Litter et al., 2010), Taiwan (Tseng et al., 2003), Vietnam (Berg et al., 2001), etc. Arsenic contamination in the affected districts of the Bengal Delta (Bangladesh and West Bengal of India) is potentially the greatest environmental calamity ever reported (Karim, 2000), where an estimated total of 120 million (80 million in

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Bangladesh and 40 million in India) people are at risk to consume arsenic contaminated groundwater (Chowdhury et al., 2000). Health and socio-economic problems related to arsenic in drinking water appear to be in an unmanageable state in the southwestern part of Bangladesh (Alam et al., 2002). The situation would worsen in coming days. Thus, identification of arsenic-affected areas and supply of safe arsenic free drinking water in the affected area are needed immediately to combat the arsenic problem. Further, there is no such medical treatment method available presently for arsenic poisoning-related diseases. Therefore, the World Health Organization (WHO, 1993) has recommended a maximum contamination level (MCL) of arsenic in drinking waters of 10 $\mu\text{g/L}$. Many countries however, allow higher (maximum 50 $\mu\text{g/L}$) arsenic concentration in drinking water mainly due to higher cost associated with treatment to its lower concentration.

Treatment of arsenic contaminated water is gaining importance due to increased stringent MCL of arsenic in drinking waters introduced by WHO (1993), US EPA (2001), European Union, and many other countries. A lot of research has been carried out with the specific aim to develop cost-effective arsenic removal techniques. Several treatment methods have been proposed, but, adsorption has emerged as one of the most effective method because it can easily be used both in small and large scale system and relatively at lower cost. Further, there are ample of scopes for development of various effective adsorbents in near future.

1.1.1 Arsenic chemistry

Arsenic, a metalloid which belongs to Group VB of the periodic table, is a common dangerous toxic element in the Earth's crust. Arsenic coexists in several forms in the aqueous medium. The charge of individual species largely depends on pH-redox condition (Eh) of the aqueous system. For instance, arsenic exists in natural water mainly as oxyacid of As(V) or arsenate and As(III) or arsenite. Some organic forms of As(V) mainly monomethylarsonate (MMA) and dimethylarsinate (DMA) are uncommon in groundwater (Smedley and Kinniburgh, 2002). The methylated compounds are roughly 1% as toxic as arsenite and arsenite is about four times more toxic than arsenate (Thirunavukkarasu et al., 2002). The higher toxicity of arsenite is attributed to the fact

that arsenite (AsO_3^{3-}) exhibits a higher affinity towards sulfhydryl groups of amino acids e.g., cysteine, and after that interacts with various enzymes in the metabolism system (Fendorf et al., 1997). Only the inorganic forms of arsenic are considered in this study because organic arsenic compounds are uncommon in groundwater system (Francesconi and Kuehnelt, 2002). In reducing environment, such as groundwater, As(III) exists as uncharged species (H_3AsO_3), whereas arsenate prevails in aerated waters (oxidizing environments) and exists as monovalent (H_2AsO_4^-) and/or divalent (HAsO_4^{2-}) anions (Figure 1.1).

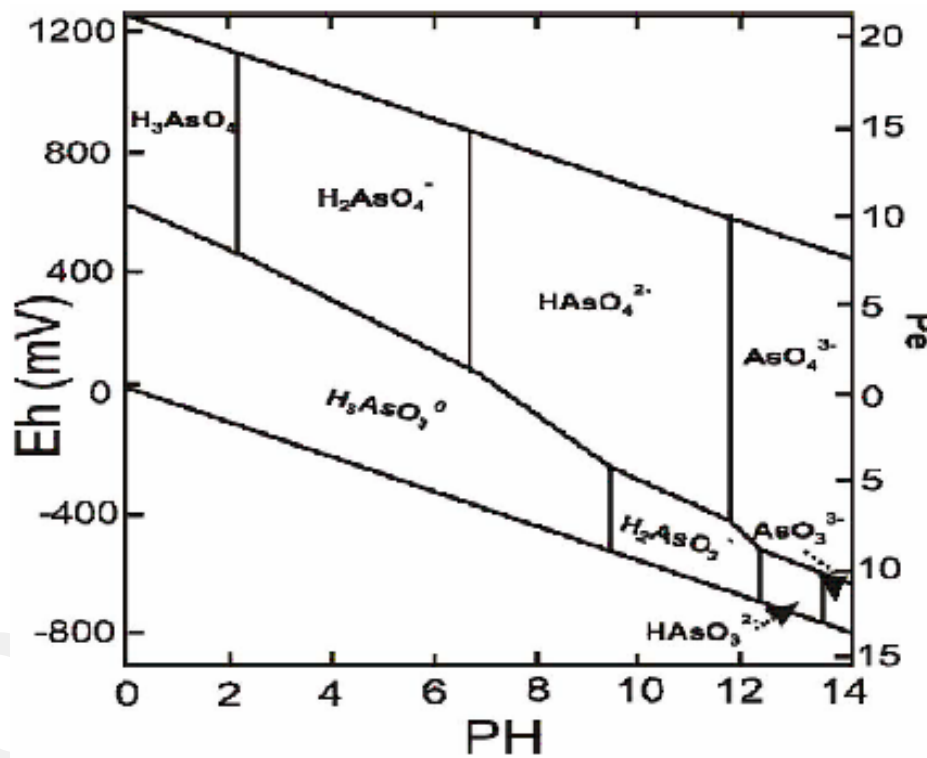


Figure 1.1: Eh-pH diagram for aqueous arsenic species in the system As-O₂-H₂O at 25 °C and 1 atm. pressure (Smedley and Kinniburgh, 2002)

However, the slow kinetic of arsenic redox transformations attributes the coexistence of both oxidation states in groundwater regardless of the redox condition (Smedley and Kinniburgh, 2002; Masscheleyn et al., 1991). Arsenic concentrations in groundwater vary widely because they are governed by mineralogy of clay of aquifers and geochemical conditions. Iron bearing minerals are considered to be important in arsenic mobilization from clay to groundwater system (Dixit and Hering, 2003). Arsenic is

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invisible and does not affect the taste or smell of the water unless concentrations are extremely high. Thus, it is called as silent killer.

1.1.2 Occurrence and mobilization of arsenic in groundwater

Arsenic naturally occurs in over 200 different minerals forms of which approximately 60% are arsenates, 20% sulfides and remaining 20% of arsenides, oxides, silicates, arsenites and elemental arsenic (Onishi, 1969). Arsenic contaminated groundwater appears in many parts of the World as mentioned above. The sub-surface mobilization of arsenic is caused by the combination of chemical, physical and microbial factors (Mondal et al., 2006; McArthur et al., 2002). Moreover, there is no such accepted general theory in literature about the arsenic mobilization by worldwide scientific communities. Three hypotheses about the natural genesis of arsenic in the groundwater are discussed in the literature. Previously, it was believed that oxidative decomposition of arsenopyrite (FeAsS) or other arsenic containing minerals in the sediments due to excessive groundwater withdrawal for agricultural purpose in the Bengal Delta region were main influential factor for arsenic release in the sub-surface water (Das et al., 1995). Consequently, aquifers recharged with increased oxygen containing water during rainy season could result in the enhanced oxidation of arsenic minerals and additional release of arsenic in water may occur (Dhar et al., 1997; Santini et al., 2000).

Secondly, due to excess use of phosphate fertilizer, the phosphate ions may enhance the release of arsenic from iron oxide based minerals (Nordstrom, 2000). However, other studies suggest that arsenic is released in groundwater as a result of microbial dissolution of arsenic minerals (Chowdhury et al., 2000; Mandal et al., 1998; Nickson et al., 1998, Cummings et al., 1999). These studies postulate that some bio-organisms, i.e. *Geospirillum barnesii* strain SES-3, may reduce both Fe(III) and arsenate, which leads to rapid arsenic release in sub-surface water. Whereas, Acharyya et al., (1999) suggests that neither of the above discussed mechanisms alone is sufficient to explain the mobilization of arsenic in groundwater and all above mechanisms together may play important role. Further, Kinniburgh et al., (2003) indicated that the release of arsenic is not associated with the oxidation of pyrite as some have suggested above. A cumulative effect may play

into major role as: (i) young sediments undergoing rapid change from an oxidizing to a reducing environment by sediment burial; (ii) arsenic release via one or more mechanisms which are poorly understood at present but which probably involve the desorption and/or dissolution of arsenic from iron oxides which are quite abundant in many of the worst-affected sediments; (iii) a very low hydraulic gradient between earth surface and aquifer throughout the Bangladesh indicates that groundwater flow is very low. This leads into slow natural flushing of the shallow aquifer allowing any released arsenic to dilute.

Groundwater is now extensively used for drinking water after 1960 in Bangladesh and India to avoid microbiological based epidemics of cholera and typhoid happened in past. Present estimates indicate that there are some 6–11 million tube wells in Bangladesh (Kinniburgh et al., 2003). The case study reveals that approximately one fourth of these wells contain arsenic at concentration exceeding the Bangladesh drinking water standard of 50 µg/L (Kinniburgh et al., 2003), and exceeded by about 42% of the WHO-guideline value of 10 µg/L. High arsenic concentrations are almost entirely restricted to groundwater from shallow aquifers (<150 m) in alluvial and deltaic sediments largely of Holocene age. The highest arsenic concentration in groundwater samples was found to be above 1000 µg/L and 5.6% of shallow wells (<150 m) samples are exceeded 300 µg/L. This study also indicates that worst-affected part of Bangladesh lies in the south-east of the country where the sediments are of Holocene age and where concentrations of arsenic are frequently exceeded 200 µg/L. Whereas, samples collected from deep tube wells (>150 m) are found to be rarely affected by arsenic contamination in Bangladesh. The details review/case study on arsenic poisoning, occurrences in water is available elsewhere (Kinniburgh et al., 2003; Mondal et al., 2006; Alam et al., 2002). Finally, Kinniburgh et al., (2003) concluded that deep wells (>150 m) in the affected area of Bangladesh have better quality water, not only in terms of arsenic, but also in terms of manganese and iron.

A study based on West Bengal by Bhattacharya et al., (1996) indicates that high arsenic groundwater is encountered in six districts of West Bengal, namely, Nadia, Bardhaman, Murshidabad, Malda, North and South 24- Parganas. This arsenic affected

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zone covers an area of around 34 000 km² and represents nearly 39% of the total area of the state. About, 35% of the total population (nearly 30-40 million or even more) in the state are affected adversely due to the consumption of high-arsenic containing groundwater for drinking and cooking purposes. Epidemiological studies (Chakraborty et al., 1987; Guha Mazumdar et al., 1988) have confirmed that nearly 92.5 percent of that population exposed to arsenic in the concentration of 200-1000 µg/L in contrast only about 6.25 per cent of the population with less than 50 µg/L.

A recent case study (Chakraborti et al., 2010) about the status of groundwater arsenic contamination in Bangladesh indicates that 27.2% and 42.1% of tube wells contain arsenic above 50 µg/L and 10 µg/L, respectively. This study also reveals that the 7.5% tubwells contain arsenic above 300 µg/L (total 52 202 water samples were tested).

1.1.3 Health hazards of arsenic

To understand the health effect of arsenic in human body, it is necessary to know the detailed metabolism of arsenic. But, few studies on arsenic metabolism are available in literature (Thomas et al., 2004; Aposhian et al., 2003; Bode and Dong, 2002) and detailed mechanism is yet not available. Therefore, medical treatments are not available for arsenicosis. It is undetectable in the primary stage, chronic poisoning occurs between 8 to 14 years, depending on the amount of arsenic ingested, rate of ingestion, excretion of arsenic compounds from the body, nutritional status, and immune response of the individual (Alam et al., 2002). The toxicity of arsenic generally classified into acute, sub-acute, and chronic types. Both acute and sub-acute are typically reversible and these poisoning results from ingestion of large quantities accidentally with lower exposure time whereas, chronic poisoning occurs due to consumption of arsenic contaminated water for a longer period. Short-term exposure has no such effect if dose is less than 0.03 mg/kg body weight per day and it is lethal at dose above 1 mg/kg body weight per day (Alam et al., 2002).

In general, there are four recognized stages of arsenicosis, or chronic arsenic poisoning (Choong et al., 2007; Romero-Schmidt et al., 2001). First stage is preclinical,

when the patient shows no symptoms, but arsenic can be detected in urine or body tissue samples. Second stage of arsenicosis is designated as clinical. Various effects can be seen on skin at this stage. Most common symptom is darkening of the skin (melanosis), often observed on the palms. Dark spot on the forehead, chest, back, limbs or gums have also been reported. Odema (swelling of hands and feet) is some time observed. A serious symptom is keratosis, or hardening of skin into nodules, often on palms and soles. WHO analysis shows that this stage requires 5-10 years of exposure to arsenic. Third stage is more complicated. Clinical symptoms become more intensified and internal organs are affected. Enlargement of liver and kidney have been reported. Final stage of arsenicosis assigns as malignancy. At this stage, tumors or cancers affect skin or other organs.

Borgono and Greiber (1972), study in Antofagasta, Chile indicates that over 12% of the population exhibiting dermatological manifestations related to arsenic due to ingestion of arsenic contaminated drinking water. Exposure to arsenic via drinking water has been documented to cause a severe disease of blood vessels leading to gangrene, known as “blackfoot disease” in Taiwan (Lu, 1990). According to some estimates, arsenic in drinking water will cause 2 00 000-2 70 000 deaths from cancer in Bangladesh alone (Smith et al., 2000). Farmer and Johnson, (1990) suggested that between 40 to 60% of the arsenic ingested is retained by the human body. Therefore, the more arsenic-containing water is consumed the greater will be the risk. In a tropical country like, Bangladesh and India, water consumption is normally high (5-6 L daily per adult person).

The normal arsenic content in hair is 0.08-0.25 mg/kg, levels higher than 1.0 mg/kg are indicative parameter of arsenic toxicity (Arnold et al., 1990). The tolerable arsenic concentration in finger nail and urine are 0.005-0.040 mg/kg (assuming the total discharge of urine in one day is 1.5 L) and 0.43-1.08 mg/kg, respectively (Dhar et al., 1997; Farmer and Johnson, 1990). A study in Bangladesh indicated that 28% of the urine specimens collected from the affected patients contained 100-1500 times more arsenic than the tolerable limit, 47% of the fingernail samples contained 8-20 times more arsenic than normal value. This survey also indicated that 98% of the skin samples contained 100 times higher arsenic than normal.

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Arsenicosis manifests different ways in various countries. In Bangladesh skin related arsenicosis are most common. Epidemiological characteristics study of arsenicosis in village Samta in Jessore (considered as most affected village in Bangladesh) indicated that almost all of 363 patients with clinical manifestations of arsenicosis showed signs of melanosis. Next, most common symptom was keratosis (69%), leukomelanosis (43%), hyperkeratosis (36%), bronchitis (24%), conjunctivitis (16%) and peripheral neuropathy (11%). The clinical manifestation of cancer was about 6% (Ahmad et al., 1999). The clinical manifestations identified by Ahmad et al., (1999) are similar to those found in patients from arsenic affected areas of West Bengal, India, except hepatopathy, which is more common among the arsenicosis patients in West Bengal. Whereas, most significant manifestation of arsenicosis in the Taiwan is “blackfoot disease” (Lu, 1990).

1.1.4 Social impact of arsenicosis

Arsenic contaminated groundwater is recognized not only for health hazards, but also for potential social problem in Bangladesh and India (Alam et al., 2002). Chronic arsenic exposures have serious implications for its victims (i.e. arsenicosis patients) and their families including social instability, social discrimination, refusal of victims by community and families, and marriage-related problems (Brinkel et al., 2009). Because of illiteracy and lack of information about symptoms of arsenicosis (Paul et al., 2004), many confuse the skin disorder with leprosy, which is considered as contagious killer by village people. As a result, patients with early symptoms of arsenicosis do not visit to doctor to avoid social ostracism.

1.2 Arsenic removal technologies

Most removal methods in literature that are discussed to remove arsenic from water containing high initial arsenic concentration (usually > 50 mg/L) but arsenic concentration in the final treated water is exceed the value of 0.01 mg/L (Mohan and Pittman Jr., 2007). In the conventional technique, first As(III) ions are oxidized by using some chemical agents like chlorine, potassium permanganate, ozone etc. In the second step, the physico-chemical methods of coagulation-precipitation, adsorption, ion

exchange, reverse osmosis, electrodialysis, membrane filtration, etc., are used to obtain arsenic free water. Although many technologies are developed but few of them are implemented in rural area to remove arsenic from contaminated groundwater. Thus, new cost effective technologies to be applicable in rural areas in small scale are in high demand. Conventional and non conventional arsenic removal technologies are well documented by Ngo et al. (2002).

The efficiency of many of these technologies reduces in presence of interfering ions, such as PO_4^{3-} , silicate, carbonate, and fluoride (Frankenberger, 2002). Selection from existing technology and/or development of new technology for arsenic removal is a big challenge for environmentalists and government policy makers. Fuhrman, (2004) has proposed a method of selection of an appropriate arsenic removal technology based on following criteria:

(a) quality of treated water

- Method must be effective enough to meet the water quality standard for arsenic ($< 10 \mu\text{g/L}$).
- It is necessary to meet other water quality standards besides arsenic. If the applied method itself be a source of unwanted contaminants to the water, a secondary treatment may be needed, hence increasing the overall cost.
- Method should be tested with natural water sample. Thus, process must perform well in the combination of potentially competing ions namely phosphate, silicate, carbonate, sulfate, etc.

(b) Operation and maintenance

- Simple operational and maintenance should be preferred in addition to minimize energy requirements.
- Method should be well effective in the pH range of groundwater (pH: 6.0 to 9.0). Thus, pH adjustment during treatment can be avoided.
- If a sorption method is applied, the regeneration of spent adsorbent becomes critical.

(c) Economy

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- The expected cost of the method in terms of set-up, operation and maintenance should be affordable.

(d) Safety and reliability

- Operation of the process should be safe, reliable, and easy.
- The method should preferably be effective in removing both arsenite and arsenate.

(d) Social acceptance

- No method would be applicable if it is not accepted by local people. Thus, before implementing any technology, the likely acceptance of the method by local residents should be evaluated.

(e) Environmental impact

- Occupational health hazard should be considered
- Method should address the proper management of toxic sludge

In the following sections, the main arsenic removal methods and their process characteristics with main advantages and disadvantages are highlighted. Among the conventional techniques the following methods have been defined as the best available technology (BAT) for arsenic removal till today (National Drinking Water Advisory Council USA, 2001). (i) anion exchange, (ii) activated alumina, (iii) reverse osmosis, (iv) modified coagulation/filtration, (v) modified lime softening and (vi) oxidation/filtration.

1.2.1 Oxidation

The rate of oxidation kinetics of As(III) species is slow by dissolved oxygen in water. Chlorine, ozone, potassium permanganate, manganese oxide, and hydrogen peroxide are widely used to increase oxidation rate of As(III) to As(V) (Kartinen and Martin, 1995). It should be noted that oxidation alone cannot serve as a sufficient technology for arsenic removal. It has been always added before the main treatment procedure to increase the efficiency of overall process. All chemical oxidants have their advantages and disadvantages. For example, chlorine is a good oxidant but it produces unwanted disinfection by-products with organic matter, and release of bad tastes and odors. On the other hand, potassium permanganate produces no harmful compounds, but may produce color.

1.2.2 Chemical coagulation-precipitation and electrocoagulation

In this process, chemicals are precipitated in a particular solution pH. Then, dissolved arsenic ions are adsorbed and co-precipitated with precipitating species. A comparative study of electrocoagulation and chemical coagulation for arsenic removal is available in literature (Lakhmanan et al., 2010). Commonly used chemicals of this technique are ferric salts, ammonium sulfate, alum, etc. The formation of these insoluble products facilitates the subsequent removal of arsenic from the water by means of sedimentation and filtration process. The pH adjustment and proper dosing are very critical to obtain higher efficiency of this process. Lime treatment is similar to coagulation but instead of trivalent metal salts the coagulated is used as hydrated lime (Ca(OH)_2) or solid form of Mg(OH)_2 . The method of lime treatment cannot serve as a major arsenic removal technique due to the low removal efficiency. The process also requires higher solution pH and chemical dose. The process has some advantages like arsenic removal efficiency is independent of the initial arsenic concentration (Li et al., 2010; Pallier et al., 2010; Wickramasinghe et al., 2004; Hering et al., 1997, Holm, 2002). Hering et al., (1997) has concluded that As(V) is removed more effectively using coagulation method compared to As(III). Thus, a pre-oxidation would be beneficial. Major disadvantage of this process is daily production of high toxic sludge. The typical characteristic of the sludge does not allow to dewater them, resulting in to large volumes of wet sludge which is difficult to dispose. Further, this method cannot be readily applied as a small purification unit.

1.2.3 Ion Exchange

For arsenic removal, anion exchange resin (Kim and Benjamin, 2004; Johnston and Heijnen, 2001; Hodi et al., 1995), usually loaded with sulfate or chloride ions at the exchange sites are replaced by negative As(V) and other ions present in water. The uncharged As(III) can not be removed by ion exchange method. The competing anion commonly present in groundwater like sulfate decreases the efficiency drastically. Because, resins are highly selective for sulfate ion. Thus, ion exchange method alone is not self sufficient to remove arsenic under MCL of $<10 \mu\text{g/L}$.

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1.2.4 Membrane Technology

Many membrane techniques namely microfiltration (Han et al., 2002), ultrafiltration (Sababtini et al., 2010; Ruipin et al., 2009), nanofiltration (Harisha et al., 2010; Nguyen et al., 2009) direct contact membrane distillation (Qu et al., 2009), clay membrane (Fang et al., 2005, Prabhu and Philip, 2001), and reverse osmosis are studied to remove arsenic from water. The process driving force for separation in membrane process is pressure difference. Source water quality and the effluent concentration to be reached are important design parameters. Membrane process functions without any chemical addition and no solid waste is produced. Besides these advantages, there are some disadvantages. High initial investment and operational cost are involved. If the water is free of suspended solids before the membrane treatment, then only the process can be effective. Other parameters like high Fe and Mn present in water are more prone to fouling due to precipitation of these ions as hydroxide. This type of fouling is irreversible in nature. It needs pre-treatment of water, monitoring of the operating pressure and also skilled operator. Guideline value of arsenic is not met in case of high initial arsenic containing water to be treated. For long term use, management of membrane fouling must be considered. Further, As(III) is not effectively removed by membrane separation method.

1.2.5 Adsorption

Adsorption process is becoming more popular, especially in small scale treatment system, such as at the house hold level (Thirunavukkarasu et al., 2003). This is an important treatment process in countries like Bangladesh and India, where the water supply systems are not centralized. Maximum water systems are owned by individual households or small group of communities. Adsorption is a process which uses solids for removing unwanted substances present in gaseous or liquid medium. Adsorption phenomena are operative in the most natural physical, chemical and biological systems. Adsorption is a mass transfer process, where substances are accumulated at the interface of fluid-solid by physical and/or chemical attractive forces. Costs associated to adsorption include pH adjustment (if needed), operation and maintenance, cost of adsorbent itself, regeneration of spent adsorbent, and safe disposal of wastes. Disadvantages of the adsorption process may be assigned to periodic regeneration of adsorbent and monitoring

of breakthrough of filter bed. On the other hand, advantages of this method can be summarized as:

- Cheaper method depending on the cost of adsorbent.
- Several low cost new adsorbents are studied, or there are endless opportunities to develop new ones.
- User friendly at the household level and it has well social acceptability.
- Additional chemical may not be needed.
- Easy to operate and maintain, no skill operators are needed.
- There is no daily sludge disposal problem
- The efficiency is not decreased drastically in presence of sulfate, as it is observed for anion exchange method.

Overall cost of adsorption process mainly depends on cost of adsorbent itself. Although adsorption by activated alumina is a widely used cost effective option for arsenic removal from contaminated water (National Drinking Water Advisory Council USA, 2001), this technique is still not affordable by the common people of developing countries (Mondal et al., 2006). Thus, in the recent days, efforts have been directed to find out efficient and cost effective arsenic removal method that uses adsorption technique. Many adsorbents with wide variety like activated alumina, carbon based materials, granular ferric hydroxide, Fe-modified porous material, Fe-modified sand, natural clays/minerals to biomass/bio-organism, etc., are investigated to remove arsenic from water. Few of these are available commercially and maximum are not yet applied to real contaminated water.

1.2.5.1 Literature review on various adsorbents used for arsenic removal studies

Activated carbons

Activated carbon is produced by carbonization employing slow substrate heating in the absence of air below 600⁰C. This removes volatiles. Then chemical or physical activation follows. Treatment with oxidizing agents (steam, carbon dioxide, or oxygen) at elevated temperature or with chemical reagents (ZnCl₂, H₃PO₄, H₂SO₄, KOH, K₂S, KCNS, etc.) completes the activation (Pollard et al., 1992). Daus et al., (2004) studied

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As(III) and As(V) adsorption onto five different adsorbents namely activated carbon (AC), zirconium-loaded activated carbon (Zr-AC), a sorption medium with the trade name 'Absorptionsmittel 3' (AM3), zero-valent iron (Fe^0), and granulated iron hydroxide (GIH). Batch and column methods were used (Daus et al., 2004). The sorption of arsenate followed the sequence $\text{Zr-AC} > \text{GIH} = \text{AM3} > \text{Fe}^0 > \text{AC}$. A different order was found for arsenite ($\text{AC} > \text{Zr-AC} = \text{AM3} = \text{GIH} = \text{Fe}^0$). Recent studies show that carbon itself is not an effective arsenic adsorbent. Thus, carbon either being coated or impregnated with iron salt has been studied for arsenic removal (Chang et al., 2010; Liu et al., 2010; Zhang et al., 2010; Fierro et al., 2009; Chen et al., 2007; Gu et al., 2005).

Highly porous commercial granular activated carbon (GAC) coated with iron using ferrous chloride was investigated as As(V) adsorbent (Chang et al., 2010). The maximum As(V) adsorption capacity of Fe-coated GAC (Fe-GAC) was as 1.95 mg/g for iron content 4.2 % (40-46 mg of As adsorbed/per g Fe on the basis of Fe content). As(V) adsorption performance of Fe-GAC was better at the acidic condition compared to the basic pH. In the other study, nanosized magnetite doped activated carbon (MAC) fiber was examined for As(V) removal from water (Zhang et al., 2010). MACF had shown higher adsorption efficiency even at an As(V) concentration lower than 10 $\mu\text{g/L}$, whereas, raw activated carbon fiber (RACF) was ineffective even at an As(V) concentration higher than 100 $\mu\text{g/L}$. Maximum Langmuir adsorption capacity for As(V) species was investigated as 4.16 mg/g and 0.5 mg/g, for MACF and RACF adsorbent, respectively. Similar enhanced arsenic adsorption was also observed for Fe_3O_4 -loaded activated carbon prepared from waste biomass (Liu et al., 2010).

Activated alumina

As(V) sorption on activated alumina (AA) occurs mostly between pH 6 and 8 where AA surfaces are positively charged. As(III) adsorption is strongly pH dependent and highest adsorption occurs at pH 7.6 (Singh and Pant, 2004). Arsenic removal efficiency of AA has been investigated by many researchers (Bullough et al., 2010; Sarkar et al., 2005, Singh and Pant, 2004 and 2006; Kim et al., 2004; Vaaramaa and Lehto, 2003). Maximum studies found that AA was more effective to remove As(V)

compared to As(III). Singh and Pant, (2004) removed arsenites from water with AA. The effect of adsorbent dose, pH, and contact time were investigated. Both Freundlich and Langmuir adsorption isotherms were fitted to the experimental data. As(III) adsorption on AA was exothermic (Singh and Pant, 2004), adsorption kinetics was governed by a pseudo first order rate equation.

Column studies were also performed and the parameters necessary for the design of fixed-bed reactors were evaluated (Singh and Pant, 2004 & 2006a). The equilibrium and kinetics of As(III) and As(V) adsorption on AA were also investigated by Lin and Wu, (2001). A pore diffusion model, coupled with the observed Freundlich or Langmuir isotherm equations, was used to interpret the experimental adsorption kinetic curve for arsenite at one specific condition. This pore diffusion model predicted the experimental data for As(III) and As(V) at different initial arsenic concentrations, activated alumina grain sizes, and pHs.

A novel mesoporous hybrid adsorbent prepared by coating an activated alumina (AA) with a mercapto-propyl-functionalized silica (AA-SH) was examined to remove As(III) from water (Hao et al., 2009 and 2009a). In fixed-bed mode, about 3200 and 320 bed volumes of spiked tap water containing 300 µg/L of As(III) were treated at breakthrough concentration of 10 µg/L by AA-SH and AA bed, respectively. The Langmuir isotherm fitted well with the experimental data. Maximum adsorption was 8.4 mg As per g of adsorbent.

Zero-valent iron (ZVI)

The use of Fe(0) to remove arsenic has been actively investigated by many groups (Wilkin et al., 2009 ; Bang et al., 2005 & 2005a ; Manning et al., 2002). The surface area exposed plays a major role in both the adsorption kinetics and capacities. Batch experiments determined the feasibility of using ZVI for As(III)/As(V) contaminated groundwater remediation versus initial arsenic [As(III) or As(V)] concentrations and pHs (pH 3–12). The maximum As(III) adsorption Freundlich capacity was 3.5 mg of As(III)/g for ZVI.

Iron coated sand

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Iron-coated sand (IOS) filter is getting recently more importance over many costly methods for water treatment (Vaishya and Gupta, 2003). Iron-coated sand extensively studied as adsorbent to remove As(III) and As(V) from arsenic spiked and contaminated groundwater (Chang et al., 2008; Hsu et al., 2008; Petrusevski et al., 2008; Vaishya and Gupta., 2006, 2004 & 2002; Gupta et al., 2005). Vaishya and Gupta, (2004 & 2002) studied As(V) and As(III) adsorption on sulfate modified iron-oxide coated sand (SMIOCS). Quartz sand was mixed with BaSO₄ flock and 0.5 M Fe(NO₃)₃ · 9H₂O solution to prepare SMIOCS. The maximum Langmuir adsorption capacity of As(V) on SMIOCS was 0.128 and 0.117 mg/g at pH 4.0 and 7.2, respectively. SMIOCS was found most suitable for As(V) and As(III) removal at acidic to near neutral pH and in the pH range of 7-9, respectively (Vaishya and Gupta, 2006).

Portland cement

Kundu et al., (2004) utilized a hardened Portland paste cement having SiO₂ (21%), CaO(63%), Al₂O₃ (7%), Fe₂O₃ (3%), MgO(1.5%), surface area (15.38 m²/g and pore volume 0.028 cm³/g as an arsenic adsorbent. Arsenate removal exceeded (~95%) that of arsenite (~88%).

Agricultural products and by-products

Agricultural wastes are by-products, some time are used as animal feed. Agricultural waste/by-products such as rice husks were used for arsenic removal from water. Maximum adsorption occurred at 0.01 mol/L of HNO₃, HCl, H₂SO₄ or HClO₄ using 1.0 g of adsorbent for 5.97×10⁻³ mol/L of arsenic for 5 min. The Freundlich isotherm was found to be satisfactory over concentration range from 8.69×10⁻⁵ to 1.73×10⁻³ mol/L arsenic. The uptake of arsenic increased with increasing temperature (Nasir et al., 1998). Untreated rice husk was utilized for aqueous arsenic remediation (Nasir et al., 1998). Complete removal (using rice husk columns) of both As(III) and As(V) was achieved under the following conditions: initial As concentration, 100 µg/L; rice husk amount, 6 g; average particle size, 780 and 510 µm; flow rate, 6.7 and 1.7 mL/min; and pH, 6.5 and 6.0, respectively. Desorption (71–96%) was also achieved with

1M of KOH. Recently, another agricultural byproduct rice polish has been successfully used to remove arsenic from water (Hasan et al., 2009).

Red mud and Calcined bauxite

Red mud is a waste material formed during the production of alumina when bauxite ore is subjected to caustic leaching. Red mud has been explored as an alternate adsorbent for arsenic (Altundogan et al., 2000). An alkaline aqueous medium (pH 9.5) favored As(III) removal, whereas the acidic pH range (1.1–3.2) was effective for As(V) removal (Altundogan et al., 2000). The capacities were 4.31 $\mu\text{mol/g}$ at the pH of 9.5 for As(III) and 5.07 $\mu\text{mol/g}$ at the pH of 3.2 for As(V). Adsorption followed a first-order rate expression and fit the Langmuir isotherm well. Li et al., (2010a) studied batch adsorption of As(V) using ferrous modified red mud (FMRM). FRMS in dosage of 0.2 to 0.3 g/L was effective to remove >90 % As(V) from its initial concentration of 0.2-0.3 mg/L. The turbidity of supernatant in disturbing water was lower than 2 NTU after 24 h. Maximum adsorption capacity of FMRM was about 0.55-0.60 mg of As per g of adsorbent. As(V) removal capacity of raw red mud showed much lower value compared to its ferrous-modified form (Li et al., 2010a). Modified calcined bauxite was also used for As(III) and As(V) remediation from ground water (Mohapatra et al., 2008; Bhakat et al., 2006) in batch and column modes. The optimum pH was ~ 7.0 for both As(III) and As(V). The adsorption was unaffected by temperature variation (Bhakat et al., 2006). No appreciable ionic effects except from SO_4^{2-} and EDTA were observed from the background ions including Ca^{2+} , Fe^{3+} , Cl^- , NO_3^- , PO_4^{3-} , and F^- .

Blast furnace slag

Steel plants generate a large volume of granular blast furnace slag. It is being used as filler or in the production of slag cement. Recently, it was converted into an effective and economical scavenger and utilized for the remediation of aqueous arsenic (Ahn et al., 2003). Zhang and Itoh, 2005 synthesized an adsorbent for aqueous arsenic removal by loading iron(III) oxide onto melted municipal solid waste incinerator slag. Loading of iron oxide on the slag increased the surface area of iron(III) oxide loaded melted slag (IOLMS) by 68% compared to FeOOH , which could be attributed to the porous structure formed in IOLMS during the synthesis process. This adsorbent effectively removed both

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arsenate and arsenite, exhibiting removal capacities for As(V) and As(III) 2.5 and 3 times of those of amorphous hydrous ferric oxide, respectively.

Fly Ash

Fly ash obtained from thermal power stations was examined for As(V) removal from water and to restrict As(V) migration in the solid wastes or the soil (Medina et al., 2010). Kinetic and equilibrium experiments were performed to evaluate the As(V) removal efficiency by lignite-based fly ash. Removal at pH 4 was significantly higher than that at pH 7 or 10.

Biosorbents

Biosorption is capable of removing traces of heavy metals and other elements from dilute aqueous solutions. Plant, Algae, fungi, derived material from biomass and bacteria are examples of biomass-derived sorbents for several metals (Lyubenova et al., 2010; Budinove et al., 2009). Such sorbents have produced encouraging results. The microbial process, in situ immobilization, by oxidation of natural occurring iron (sometime manganese), etc are reported for arsenic removal in literature. Several bacteria and other biomaterials are capable to oxidizing As(III) to As(V) thereby eliminating the need for the use of oxidants in the other treatment methods (Sahabi et al., 2009; Zouboulis and Katsoyiannis, 2005; Katsoyiannis and Zouboulis, 2004). Furthermore, biomass generated in the oxidation processes is also capable to remove arsenic from water. The sulfate reducing bacteria is capable to perform above stated purposes (Jong and Parry, 2003). *In-situ* immobilization of arsenic in natural ground water is an alternative cost effective treatment method. Unfortunately, only a few studies have examined *in-situ* immobilization (SenGupta et al., 2009). Further, future effect of immobilization on the environment is not well understood. In Bangladesh and India the ground water often contains excess Fe(II) in addition to the arsenic and this situation is taken as advantageous to remove arsenic. This dissolved Fe(II) is oxidized by aeration and/or iron oxidizing natural bacteria (*Gallionella ferruginea* and *Leptothrix ocracea*) under appropriate redox and pH conditions to form precipitated product of iron oxide containing organic matter. In the subsequent steps, the arsenic species sorption on precipitated product followed by sand filtration provides arsenic free water (Hassan et al.,

2009; Pokhrel and Viraraghavan, 2009; Zouboulis and Katsoyiannis, 2005; Katsoyiannis and Zouboulis, 2004). The recent review studies based on bio-oxidation of iron, manganese, and arsenic removal are well documented (Wang and Zhao, 2009; Zouboulis and Katsoyiannis, 2005). Although the method looks promising and may be useful for some arsenic affected area, it has major limitation because there is no fixed correlation between iron and arsenic concentrations in groundwater. Filter clogging due to *in-situ* formation of iron oxide and bacterial growth is the potential problems for long term operation of this biological filter (Pokhrel and Viraraghavan, 2009). Chitosan as biosorbent also tested to remove arsenic from water medium (Gerente et al., 2010).

All the above mentioned technologies are either expensive or not readily available to rural communities, thus cost-effective arsenic removal technique is urgently warranted. The widely available, naturally occurring Fe-Al materials namely laterite would be better option for cost-effective removal of arsenic from groundwater. Arsenic adsorption performance of adsorbents of various categories are compared in terms of their adsorption capacity, adsorption behavior at low equilibrium arsenic concentration and presented in Chapter 4.

Miscellaneous adsorbent

Drinking water treatment residuals (WTRs) were also evaluated for As(V) and As(III) removal (Makris et al., 2006). The Al-WTR effectively removed As(V) and As(III) while Fe-WTR removed more As(III) than As(V) in the pH range of 6.0–6.5. Singh et al., (1996) employed hematite and feldspar to As(V) removal from aqueous systems at different pHs, temperatures, and adsorbent particle size. Uptake followed first-order kinetics and fitted the Langmuir isotherm. The maximum removal was 100% with hematite (pH 4.2) and 97% with feldspar (pH 6.2) at an arsenic concentration of 13.35 $\mu\text{mol/L}$. Nanoparticles of titania (Han et al., 2010), porous CeO_2 (Srivastava et al., 2010) were also evaluated for arsenic removal from aqueous medium.

A low-cost ferruginous manganese ore (FMO) removed both As(III) and As(V) from groundwater without any pretreatment in the pH range of 2–8 (Chakravarty et al., 2002).

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The major mineral phases present in the FMO were pyrolusite (β -MnO₂) and goethite [α -FeO(OH)]. The FeO(OH) can directly adsorb arsenite and arsenate anions. Pyrolusite (β -MnO₂), the major mineral phase of the FMO behaved in a manner similar to hydrous manganese oxide, MnO(OH), because of the presence of chemically bound moisture. As(III) adsorbed more strongly than As(V). Once adsorbed, arsenic did not desorb in the pH range of 2–8. Bivalent cations, Ni²⁺, Co²⁺, Mg²⁺, enhanced the adsorption capability of the FMO. The cost of the FMO was ~50–56 US\$ per metric ton. This is much cheaper than the commercially available carbons. Natural siderite-hematite material as low cost arsenic adsorbent is studied in details by group of researchers (Guo et al., 2008; Guo et al., 2007). In the recent studies, Sn(II) compound (Rivas and Aguirre, 2010) and granular Fe-Ce oxide (Zhang et al., 2010a) were also investigated as arsenic adsorbent to remove arsenic from water.

1.3 Laterite and treated laterite used as adsorbent in this study

Laterite is a product of intensive chemical weathering in tropical and subtropical environments under strong oxidizing conditions. Heavy rainfall leaches out soluble ingredients of soils, leaving behind clay minerals (kaolinite), gibbsite (Al₂O₃·3H₂O), goethite (HFeO₂), lepidocrocite (FeOOH), and hematite (Fe₂O₃) (Schellmann, 1986) and is abundantly available in the many parts of the World. Laterite appears to be in nature with wide variety of yellow, brown and red residual solids of nodular gravels, as well as fine-grained and/or cemented solid (Bourman, et al., 2003; Bourman and Ollier, 2002; Schellmann, 1994; Schellmann, 1986). Furthermore, laterite may vary from loose red-sand to a massive hard rock or co-exist together. The characteristic red color appears from iron compounds present in laterite. In literature laterite refers to many ways like “laterite concretion” (Partey et al., 2008), laterite soil (Maji et al., 2008; Maji et al., 2007; Maji et al., 2007a). The “laterite concretion” is assigned to the coarse-grained vermicular concrete materials, including massive laterite (Partey et al., 2008). Whereas, “laterite soils” refers to materials of soft rocks and fine grained solid with lower concentration of Fe and Al oxides. Laterite composition widely varies with extent of laterization, parent rock and geographical location (Bourman and Ollier, 2002). Lateritization is the removal

of silicon through hydrolysis and oxidation that results in the formation of laterites and lateritic soils. The degree of lateritization is defined by the silica-sesquioxide (S-S) ratio ($\text{SiO}_2/(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$) calculated as the weight percent of the oxides (De Medina, 1972). Soils are classified by the S-S ratios into the following categories:

- An S-S ratio of 1.33 or less = laterite or laterite concretion.
- An S-S ratio of 1.33 to 2.00 = lateritic soil.
- An S-S ratio of 2.00 or greater = non-lateritic, tropical soil

The laterite formation, i.e. laterization is a complex geo-physicochemical phenomena in nature. The laterization is well described by Persons, (1970) as follows: In first step, transformation of feldspathic material into clay occurred through intense chemical weathering subsequently, leaching and re-deposition occurred in which iron and aluminum oxides remained after the removal of bases and combined silica (Persons, 1970). Next process is a dramatic change in environment: physical, such as evaporation of the remaining water: chemical, such as the reduction of groundwater temperature, ion exchange, or pH change (Persons, 1970). This results in the deposition of iron compounds and laterite formation. These laterites usually form nodules with a hard outer shell of ferrous material surrounding an inner core of softer or un-cemented materials (Persons, 1970). Laterite is also known as fercrete (iron breast plate) by French-speaking African (Persons, 1970).

Literature studies show that laterite can be used to develop cost-effective arsenic purification system for communities (Ndur and Norman, 2003; Bhattacharyya et al., 2002). The batch and fixed-bed column studies in laboratory for As(V) and As(III) removal using laterite adsorbent also indicate its high potentiality for this process (Maiti et al., 2008; Partey et al., 2008, Maji et al., 2008; Maji et al., 2007; Maji et al., 2007a). In this study, raw laterite, acid treated laterite and acid-base treated laterite are explored as arsenic adsorbent using arsenic spiked water and real contaminated ground water. Laterite soils are abundantly available in West Bengal of India and concentrated mainly in the districts of West Midnapore, Bankura and Purulia. We have collected four laterite samples, one from Kharagpur, another one from Bankura and rest of two from Purulia. These four samples are assigned as Kharagpur laterite (KRL), Bakura laterite (BRL),

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Prulia laterite-1 (PRL1), and Purulia laterite-2 (PRL2). The details characterization of laterite samples collected from different location are discussed in the subsequent section.

1.4 Approaches to improve performances of adsorbent

As the ultimate goal of this research work is to find out cost-effective arsenic removal techniques, many studies based on adsorption of arsenic using natural materials (Fe and/or Al bearing) as adsorbents are explored in details. But, natural materials are found to be less porous and adsorption capacities are limited due to presence of low specific surface area as well as low active site density per unit surface area. It is well known that iron/manganese oxide/hydroxides are most effective arsenic adsorbent. Many iron(III) oxides, such as amorphous hydrous ferric oxide (Jang et al., 2006), and goethite (Matis et al., 1997), are known for their ability to remove both arsenic species from water. But maximum of these oxides are in the form of fine powder. Those cannot be applied in fixed-bed column unless they are of granular shape. To overcome this problem of liquid/solid separation, researchers have taken different approaches to improve adsorption capacity of different materials. The natural materials (soils/clays/minerals) are obtained as hard particle (due to presence of silica) in the spherical shape. These are easy to separate from liquid medium. Different techniques are used to improve the adsorption performance namely:

- (i) Use of iron(III) oxides/oxyhydroxide coating on materials like sand (Petrusevski et al., 2008, Vaishya and Gupta, 2002, 2003, 2004, and 2006; Gupta et al., 2005), carbon (Fierro et al., 2009; Chen et al., 2007; Gu et al., 2005) cellulose bead (Guo and Chen, 2005), chitosan bead (Gang et al., 2010; Gupta et al., 2009), cement (Kundu and Gupta, 2007), activated alumina (Kuriakose et al., 2004; Singh and Pant, 2006), resin media (Moller and Sylvester, 2008), fungal biomass (Pokhrel and Viraraghavan, 2008), manganese oxide-coated alumina (Maliyekkala et al., 2009), polymer-supported hydrated iron(III) oxide nanoparticles (Cumbal and SenGupta, 2005), etc.

- (ii) Acid activation/treatment on natural materials like Greek bentonite (Wu and Li, 2009), montmorillonite (Yan et al., 2008), clays (Hart and Brown, 2004), sepiolite (Sabah, 2007), red mud (Tor and Cengeloglu, 2006), etc.
- (iii) Acid-base treatment (Li et al., 2009) is the process to concentrate the Fe and/or Al-oxyhydroxide minerals on surface of materials without adding pure iron-salt.

Arsenic adsorption capacities of adsorbents prepared from the first process of the above are limited due to decrease in surface area and original pores of base materials after coating. As the coated iron materials are loosely bound to the base materials, so regeneration of spent adsorbent using alkali media removes substantial amount of iron from adsorbent. This results into drastic reduction of adsorption capacity of regenerated filter media. Acid activation/treatment is also a common practice to increase the adsorption efficiency or catalytic activity of clay/industrial waste and carbon like materials as stated above. Still, improvement of the performance is not drastic as found to be in the case of acid-base treated adsorbent. In the third treatment process, acid is used to leach the Fe and Al ions in liquid medium and in the second step, the alkali is added to generate Fe/Al oxyhydroxide. Finally, these precipitated products form a hard surface coating on the rest solid parts of the acid treated materials.

The third treatment method for laterite has many advantages: (i) loading of iron/aluminium oxyhydroxide on the laterite surface has more surface area compared to iron/aluminium oxyhydroxide synthesized from pure salts; (ii) Fe/Al hydroxide/oxyhydroxide particles are loaded on the solid laterite surface to form bigger sized particles. In contrast, most of the Fe or Al hydroxide/oxyhydroxide particles are generally available as fine powder, which is difficult for solid/ liquid separation after adsorption step; (iii) complexation among silicate and iron/aluminium hydroxide renders the material harder compared to oxyhydroxide forms. In literature, few studies are available based on acid-base treatment to improve adsorption capacity of the natural materials (Zhang and Itoh, 2005). Recently, Li et al., (2009) has demonstrated As(V) removal using acid-base treated fly ash. But, treatment process of fly ash was not optimized by varying different process parameters. Furthermore, adsorbent performance of treated materials widely varies with process conditions used here for treatment.

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In this study, the treatment process to prepare acid-base treated laterite (TL) is optimized based on arsenic adsorption performance under various conditions like raw laterite (RL) to HCl ratio, acid concentration, time duration of acid treatment, and final pH of hydrolysis of acid treated mass using NaOH solution. Details changes in physicochemical characteristics of TL obtained under different treatment conditions are analyzed using FTIR, XRD, SEM-EDAX, HRTEM, and surface area analyzer. Batch and fixed-bed column mode adsorption of arsenic on treated materials obtained under different treatment conditions are performed using real contaminated groundwater (CGW).

1.5 Organization of experimental work

Arsenic removal by raw laterite (RL)

1. To characterize the RL samples collected from three district of West Bengal, India, namely West Midnapore (Kharagpur), Bakura (Sonamukhi), Purulia (Purulia city and Manbazar).
2. To determine the arsenic adsorption capacities of RL samples in batch mode and standardize the capacity with respect to composition of RL samples.
3. To observe the effect of operating conditions in batch mode i.e., pH of solution, adsorbent dose, contact time, arsenic concentration, temperature and speed of agitation.
4. To evaluate maximum adsorption capacity using adsorption isotherm models namely, Langmuir and Freundlich isotherm.
5. To predict the liquid phase arsenic concentration by applying shrinking core model in batch kinetic study.
6. To apply the above model to contaminated groundwater system (CGW).
7. To evaluate fixed-bed column performance of RL using As(V)/As(III) spiked distilled water and CGW.
8. To predict the breakthrough behaviors of RL fixed-bed column by applying Adams-Bohart model.
9. To perform desorption and leaching of arsenic from arsenic-loaded RL

Arsenic removal by acid activated laterite (AAL)

1. To compare the characteristics of AAL with RL
2. To see the improvement of arsenic adsorption on AAL compared to RL in batch and fixed-bed column studies.
3. To develop shrinking core model to predict the batch kinetic for AAL/arsenic system.
4. To perform fixed-bed arsenic adsorption experiments and modeling.
5. To perform desorption and leaching of arsenic from arsenic-loaded AAL.

Arsenic removal by acid-base treated laterite (TL)

1. To optimize the acid-base treatment method by varying process conditions i.e., acid: RL ratio (weight basis), acid concentration, temperature of acid treatment, duration of acid treatment, final pH of suspension after adding base, etc.
2. To characterize the treated laterite samples obtained under different treatment conditions and arsenic adsorption capacity of each treated material in batch mode.
3. To find out best treated material and explored as arsenic adsorbent using CGW as in batch and column mode.
4. To perform batch kinetic modeling for TL/arsenic system.
5. To evaluate continuous fixed-bed arsenic adsorption on TL by varying process conditions i.e., column height, flow rate, initial arsenic concentration.
6. To see the performance of TL fixed-bed for arsenic removal from CGW.
7. To design a household column filter to remove arsenic from CGW.
8. To perform desorption study of arsenic from arsenic-loaded TL in batch and column mode.
9. To define disposal protocol of spent TL adsorbent.

1.6 Aim/Objective of the current research

It is quite clear from earlier discussion that the problem of arsenic contaminated ground water is not only associated with technical barrier, but it is also related to economical barrier, i.e., most of the areas exposed to arsenic contaminated ground water

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are situated in the developing countries. Thus, exploration of cost-effective and sustainable technology for arsenic removal from groundwater in the rural areas of developing countries is the prime objective of this work. The present studies demonstrate the arsenic adsorption behavior of raw laterite (RL) collected from different geographical locations. This study has four primary aims: (1) to evaluate effectiveness of RL to remove arsenic from water; (2) to determine the proper treatment methods whether the arsenic removal capacity of RL can be improved; (3) to investigate arsenic removal performance from contaminated groundwater (CGW) using RL and treated laterite (TL); (4) to get an overview of the capacity of the RL and developed sorbents by comparing them with other adsorbents.

1.3 Organization of the thesis

In this thesis, feasibility of RL as arsenic adsorbent is explored in details with different RL sample collected from different geographical locations. The different treatment methods are applied on RL to enhance the adsorbent performance in the context of arsenic removal from CGW in continuous fixed-bed mode operation. An overview of the state of current research in these areas with objectives of the present work is presented in Chapter 1. The application of RL as arsenic adsorbent for water medium is discussed in Chapter 2. The adsorption in batch mode is performed with different operating conditions i.e., pH of solution, adsorbent dose, contact time, arsenic concentration, temperature and speed of agitation. The adsorption kinetics in stirred tank vessel is predicted by applying shrinking core model. The model is also applied to CGW/RL system. Continuous fixed-bed column performances of RL bed are also discussed in Chapter 2. In Chapter 3, the acid activation on RL in the context of characteristics changes and arsenic adsorption behavior are explored. Both batch and column mode adsorption of arsenic using acid activated laterite (AAL) is investigated under different operating conditions. Finally in the Chapter 4, acid-base treated laterite (TL) is explored as arsenic adsorbent for CGW. Similar experimental protocol as discussed above (RL/arsenic system) are used to evaluate arsenic adsorption behaviors of TL. A household column filter using TL bed has been designed and is proposed to remove arsenic from CGW.