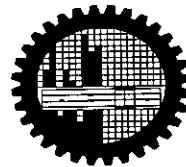
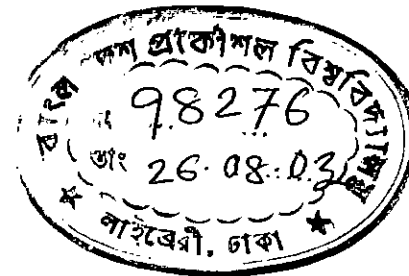


# **A Study on the Effectiveness of Activated Alumina in Removing Arsenic from Groundwater**

by

**Muhammad Azizul Hoque**



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

**MASTER OF SCIENCE IN CIVIL ENGINEERING (ENVIRONMENTAL)**

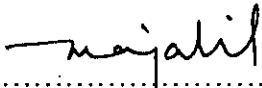
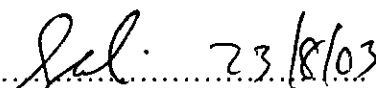
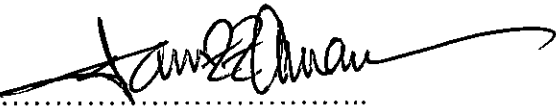
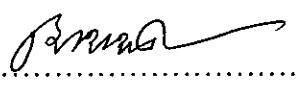
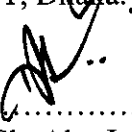
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July, 2003



.....  
Muhammad Azizul Hoque

*To*  
*My Parents*  
*&*  
*Irin*

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## ABSTRACT

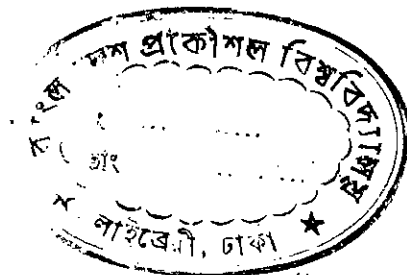
Elevated level of arsenic in ground water is a major concern for many communities in the world, because long term exposure to arsenic via drinking and cooking water leads to a wide range of health problem. The public health sector of Bangladesh is currently under serious threat from wide-spread arsenic contamination of shallow groundwater aquifers, as water abstracted from these aquifers is the prime source of drinking and cooking water. An estimated 35 million people in Bangladesh are at risk of arsenic toxicity. Providing safe water to the affected people is a viable solution of the arsenic related health problems and treatment of arsenic contaminated water is one of the options to do this.

Among the methods available for removing arsenic from water, adsorption on activated alumina is a promising one for implementing on a small-scale rural community or household levels. Various factors influence the removal efficiency of activated alumina. In this thesis work the effects of a number of parameters including oxidation state of arsenic, pH, iron, chloride, sulfate, phosphate, activated alumina size, empty bed contact time and the regeneration of spent alumina in removing arsenic by activated alumina were evaluated.

Laboratory column tests were conducted using synthetic water with different compositions and operating conditions. A method was also developed for easy and effective regeneration of spent alumina. In this method, spent alumina was taken out of adsorption column and acid wash was applied after washing with normal tap water. Then the usual base regeneration and neutralization of the alumina were carried out. The efficiency/effectiveness of activated alumina in removing arsenic were determined in terms of Empty Bed Volume (BV), quantity of adsorbed arsenic and average arsenic removal efficiency up-to 50 ppb arsenic level in the effluent.

The results of the study show that pentavalent arsenic is removed efficiently than trivalent arsenic. The bed volume of treated water decreases from 2115 to 375 with the increase of arsenic concentration from 100 ppb to 500 ppb for As(V), whereas, the bed volume decreases from 372 to 100 as the As(III) concentration increases from 100 ppb to 500 ppb. The study reveals that the presence of iron has a significant negative effect on As(V) removal efficiency and some positive effect on As(III) removal efficiency. The bed volume of treated water for As(V) changes from

5287 to 160 as the iron concentration increases from 0.0 mg/L to 5.0 mg/L, whereas, the variation for As(III) is from 25 to 316 as the iron concentration increases from 0.15 mg/L to 5.0 mg/L. As(V) removal efficiency is better within the pH range of 5.0 to 6.0, whereas, As(III) removal increases at higher pH values. Chloride has no effect on the arsenic removal efficiency but the presence of sulfate and phosphate has significant effect. The results show that the increase of phosphate from 0.68 mg/L to 345 mg/L decreases the bed volume of treated water from 2100 to 70. Arsenic removal efficiency is found better for activated alumina size 28x48 as compared with the size 14x28. The arsenic removal efficiency increases significantly with the increase of the empty bed contact time. The study also shows that the modified method of regeneration of spent alumina is very effective in removing arsenic from groundwater.



## Chapter 1

# INTRODUCTION

### 1.1 Background

It has been a long time since the rural people of Bangladesh were thriving for a dependable water supply for their domestic use. In fifties, untreated surface water from river or pond was mostly used as water sources to meet drinking and other domestic demand. As a result, the incidence of diarrhea and water-borne diseases were prevalent causing a heavy toll on human lives every year. In the context of combating water-related diseases, during sixties, groundwater was identified as a source of potable water free from pathogens. Since 1973 massive program for sinking hand pump tubewells was introduced by DPHE (Department of Public Health Engineering) with the assistance of UNICEF. Ninety seven percent of the population had access to drinking water from improved sources (tubewell, ring well, or tap). It took more than fifty years to motivate rural people to use tubewell water instead of untreated surface water (ponds/ river/ khal, etc.) for drinking to minimize water borne-diseases. Rural people now quite habituated to drink tubewell water.

Unfortunately, arsenic contamination of shallow groundwater in excess of acceptable limit has posed a formidable public health hazard having a very significant impact on people's lives, health, social and economic activities in Bangladesh. Arsenic is toxic and carcinogenic, and endangers the health of millions of people exposed to arsenic contaminated water. Groundwater contaminated by arsenic was first discovered by the Department of Public Health Engineering (DPHE) at Chapai Nawabganj in late 1993 following reports of elevated levels of arsenic in groundwater of the adjoining areas of India. Further testing in 1995 and 1996 showed that contamination extended across a large part of southern and western Bangladesh. As the source of arsenic in groundwater


is considered to be geological, the concentration in water varies from place to place within the same district and also differs on zonal basis. The analysis of data on zonal basis indicated that the Khulna and Rajshahi zones were badly affected where the Barisal and Dhaka were less affected. In Chittagong zone, some districts like Chandpur, Laxmipur & Noakhali were badly affected. Some of the large diameter production wells in the districts like Satkhira, Meherpur, Magura, Chuadanga & Chapainawabgonj are also reported to be contaminated with high arsenic (Quadiruzzaman, 1997). A study by BUET and BCSIR first indicated that groundwater in North-Eastern part of Bangladesh is also contaminated with arsenic. Arsenic was also found in deeper aquifers in that zone (Badruzzaman et. al, 1997). According to the survey report of DPHE (1997-2000), 268 upazillas are arsenic affected out of 507 upazillas in Bangladesh. Survey result shows that 27% shallow tubewells are arsenic contaminated having concentration beyond the Bangladesh standard (50 ppb) whereas, this figure increased to 46% when WHO standard (10 ppb) is considered. (DPHE / DFID / BGS, 2000 and [http://www.naisu.info/arsenic\\_2002.htm](http://www.naisu.info/arsenic_2002.htm))

In a population, drinking arsenic contaminated water, a great variety of specific as well as non-specific symptoms may be observed at a large biological variations and interactions (Mazumder et al., 1997). From practical point of view, it is very easy to identify arsenic affected people, if anybody knows about its symptoms. This is because of the primary effects, like pigmentation, keratosis and often depigmentation on palm and sole and on abdomen are directly visible and easily distinguishable for a trained health worker. On the other side, there are still no well-established guidelines about how to measure quantitatively the severity of arsenosis in a population. Thus the correlation between the severity of the disease and the contamination levels of the consumed water are yet to be established. Also a convincing correlation between the concentration of arsenic in the drinking water and the concentrations of arsenic in the urine, hair and nails are yet to be established (Mazumder et al., 1997). The population exposed to arsenic from exceeding Bangladesh and WHO drinking water standard are estimated to be



within 28-35 million and 46-57 million respectively and a total of 13,333 arsenicosis patients has been identified (DPHE / DFID / BGS, 2000; EES and DCH, 2000).

Arsenic problem is now treated as a severe problem in Bangladesh and immediate measures need to be taken to provide arsenic safe drinking water in the affected areas. There are two paths to provide arsenic safe drinking water to the consumers. One is to provide an alternative water supply to the population and the other is to remove arsenic from the existing water supply. Natural rainwater and surface water are arsenic free, but they have some limitations. The people of Bangladesh are not habituated to use rainwater for drinking purpose. Furthermore, the rainwater is not available alover the year and requires proper maintenance to keep stored water free from biological contamination. Surface water may be another option but requires proper treatment to remove physical contamination as well as biological contamination before using it for drinking purpose. So, surface water source is not a viable option from the point of view of cost effectiveness. Very shallow aquifer may contain arsenic free water and water can be abstracted through dug wells. But bacterial contamination is the main difficulty for this option. Again water may not be available in dug well in the dry season as the water table attains its lowest level at that time. Groundwater from deep tubewell appears to be arsenic free but this option is too much expensive. Also arsenic contaminated water may leach from the upper aquifers to the deep aquifer due to pressure difference during pumping. Treatment of arsenic contaminated groundwater is another promising option. Various technologies are available for removing arsenic from groundwater. A simple and cost effective arsenic removal technology is to be developed to suit the geohydrological and geochemical conditions of Bangladesh groundwater to supply arsenic safe drinking water to millions of people in the arsenic affected areas of rural Bangladesh.



## **1.2 Justification of the study**

Technologies available for removing arsenic from water include adsorption-coprecipitation with coagulation, adsorption on activated alumina or activated carbon, adsorption on iron coated medium, coarse medium bed containing iron sludge, iron exchange, reverse osmosis etc. Most of these technologies require considerable infrastructure and are expensive and difficult to operate – thus making them impracticable for small community scale water treatment system. As most of the rural populations of Bangladesh obtain their water from hand pump tubewells, as opposed to large municipal water plants, it is therefore necessity to develop a low-cost simple technology that can be implemented on a small scale rural community and household levels to remove arsenic from at least drinking and cooking water as it is extracted from tubewell. Activated alumina adsorption is an effective process for removing pentavalent arsenic from water but trivalent arsenic removal capacity is poor (AWWA, 1990). Hence, if properly designed, activated alumina process may be a viable technology to meet the requirements of removing arsenic from groundwater at household and community levels. However, there is still a need to develop design and operating criteria for an effective field deployable household/community level activated alumina adsorbent and delivery system. Various factors such as arsenic concentration, iron concentration, pH, flow rate, presence of chloride, sulfate, phosphate etc. influence the arsenic removal capacity of activated alumina and their effects have not been studied extensively in the context of Bangladesh. Quantification of the effects of these factors on arsenic removal capacity of activated alumina needs to be studied to develop design and operating criteria for an effective treatment system for use at community and household levels.

## **1.3 Objectives of the Research**

The overall objective of the research is to evaluate the effectiveness of activated alumina in removing arsenic from drinking water. The specific objectives are as follows:

- to determine the effect of initial arsenic concentration (both As(III) and As(V)) on arsenic removal efficiency by activated alumina.
- to assess the effect of pH on the As(III) and As(V) removal efficiency by activated alumina.
- to investigate the effect of iron on the performance of activated alumina bed.
- to determine the effect of contact time on arsenic removal efficiency by activated alumina.
- to study the effect of activated alumina size on the arsenic removal efficiency.
- to investigate the effect of phosphate, sulfate and chloride on arsenic removal efficiency by activated alumina.
- to assess different method of regeneration of spent activated alumina and evaluate the arsenic removal efficiency of regenerated alumina.

#### **1.4 Outline of Methodology**

A brief description of the methodology followed in conducting the study is given below:

- A number of columns were set up in the laboratory using glass tube of fixed cross-sectional area and the height of the test bed was varied. Filter column bed heights were in between 20 cm and 50 cm.

- Laboratory tap water (groundwater) was used as the source of synthetic raw water. As the tap water contained iron, two runs were conducted with distilled water to observe the performance of activated alumina bed in the absence of iron.
- To simulate with field conditions, solutions of arsenic compounds, iron and other salts were added in different amounts to the tap water. Arsenic concentration was varied from 100 ppb to 500 ppb. Iron concentration was varied from 0.0 mg/L to 10.0 mg/L.
- pH of the synthetic water was adjusted to fixed values ranging from 5.0 to 8.0 using acid (HCl) and alkali (NaOH).
- To study the removal efficiency of As(III) and As(V)
  - A large number of experiments were conducted with water having different composition, by varying arsenic concentration, pH value and iron content.
  - Similar experiments were run to investigate the effect of sulfate, chloride and phosphate in water.
- To study the size effect of activated alumina, two sizes namely 14x28 and 28x48 were used. Among 32 sets of experiments 3 sets were conducted using 28x48 mesh size. For other sets, 14x28 mesh size alumina was used.
- Spent alumina was regenerated by washing with diluted HCl first and then with distilled water, followed by NaOH treatment, and neutralization with acid (HCl) solution. Loss of alumina in the regeneration process was quantified. Arsenic removal capacity of the regenerated media was then experimentally investigated and the performance was compared to that of virgin material.

- Measurement of relevant water quality parameters was done following standard methods. Mohr method was followed to measure the chloride content of water samples. HACH DR/4000 spectrophotometer was used to determine sulphate (Salfa Ver 4 Method) and phosphate (Phos ver (Ascorbic Acid) Method) contents of water. Arsenic concentration was determined using Atomic Absorption Spectrophotometer and BUET Kit.

### 1.5 Organization of the Thesis

The thesis has been organized in five chapters. A brief description of the chapters is given below:

Introduction is the title of chapter 1 where the background of the study, its justification, the objectives of the research and outline of methodology have been presented.

Chapter 2 contains literature review and covers the sources of arsenic, its release mechanism in groundwater, presence of arsenic in atmosphere and soils, arsenic chemistry, toxicology of arsenic, treatment processes, arsenic contamination of ground water in Bangladesh and arsenic removal technologies available in Bangladesh. The activated alumina adsorption process is described in details in this chapter.

Chapter 3 is Methodology and Laboratory Procedure where description on activated alumina, experimental setup, experimental procedure, testing of water samples and parameter determining effectiveness are presented.

Experimental results and discussion are presented in chapter 4. Here the effects of different parameters (arsenic concentration, iron, pH, contact time, alumina size, chloride, sulfate and phosphate) on arsenic removal efficiency of activated alumina bed are discussed in details. Efficiency of regenerated alumina is also presented here.

Chapter 5 is the Conclusions and Recommendations chapter. It contains the major conclusions of the study and presents recommendations for further study.

## Chapter 2

# LITERATURE REVIEW

### 2.1 Introduction

Groundwater is the major source of drinking water in Bangladesh. A wide spread arsenic contamination of groundwater in Bangladesh has occurred and immediate measures need to be taken to provide safe drinking water in the arsenic affected areas of Bangladesh.

This chapter covers the sources of arsenic, its release mechanism in groundwater, presence of arsenic in atmosphere and soils, arsenic chemistry, toxicology of arsenic, treatment processes, arsenic contamination of groundwater in Bangladesh and arsenic removal technologies available in Bangladesh. The activated alumina adsorption process is described in details in this chapter.

### 2.2 Sources of Arsenic

#### 2.2.1 *Natural sources*

Arsenic bearing minerals are the primary natural sources of arsenic. There are more than 245 such minerals, mostly ores containing sulfide, along with copper, nickel, lead, cobalt and other metals, as well as some oxides. The most important ores of arsenic are arsenopyrite or mispickel ( $\text{FeAsS}$ ), realgar ( $\text{As}_4\text{S}_4$ ), orpiment ( $\text{As}_2\text{S}_3$ ), claudetite ( $\text{As}_2\text{O}_3$ ), iollingite ( $\text{FeAs}_2$ ), nicolite ( $\text{NiAs}$ ), cobaltite or cobalt-glance ( $\text{CoAsS}$ ), gersdorffite or nickel-glance ( $\text{NiAsS}$ ) and samaltite ( $\text{CoAs}_2$ ). Table 2.1 presents some arsenic-bearing minerals. Among these, arsenopyrite is probably the most common mineral (Mason and Berry, 1968). Weathering of rock converts arsenic-rich metal sulfides to arsenic trioxides, which eventually finds its way into surface water, groundwater and sediments.

Arsenic is often found to be associated with iron oxyhydroxides in sediments because of its affinity for iron oxyhydroxides; the oxidized forms of arsenic are converted back to sulfides by anaerobic processes occurring on land and in water sediments. Volatile forms of arsenic, e.g., arsine ( $\text{AsH}_3$ ) and trimethyl arsine  $[(\text{CH}_3)_3\text{As}]$  enter the atmosphere from land and water and are returned by rain and atmospheric fallout. Arsenic occurs in soil at an average concentration of about 5 to 6 mg/kg, but this varies among geographic regions. Concentrations as high as 51 mg/kg and 83 mg/kg have been reported in soils of Faridpur and Comilla districts, respectively, of Bangladesh (Ullah, 1998). A concentration varying from 1.5 to 19 mg/kg showing higher concentration in the top layers of soil has been found in samta village in Jessore (Kubota, 1999).

### 2.2.2 *Anthropogenic Sources*

Arsenic may accumulate in soil from anthropogenic activities. Arsenic is used in a variety of products. The principal arsenical compounds are herbicides, cotton desiccants, and wood preservatives and their production rates are 8000, 12000, and 10000 tons as per year respectively (Allaway, 1990). Some As bearing products are presented in Table 2.2. Arsenic may accumulate in soil through use of arsenical pesticides, dust from burning fuels, and disposal of industrial and animal wastes. It is a natural contaminant in lead, zinc, gold and copper ores and can be released during the smelting process. The stack dust and flue gases from smelters often contaminate soils with arsenic, downstream from the operation.

At the early stages of arsenic calamity in Bangladesh, wooden electric poles of Rural Electrification Board (REB) coated with arsenic preservatives was reported in the press as a probable source of arsenic in groundwater. However, as the enormity of arsenic problem became apparent, it was clear that the widespread contamination cannot possibly result from arsenic preservatives used in electric poles. Moreover, the preservatives on the wooden poles used in Bangladesh are of CCA (chromated copper arsenic) type which is not likely to permit release of arsenic into the groundwater. The

Table 2.1: Some As bearing minerals

Name	Chemical formulae
Arsenopyrite	$\text{FeAsS}$
Orpiment	$\text{As}_2\text{S}_3$
Realgar	$\text{As}_4\text{S}_4$
Claudetite	$\text{As}_2\text{O}_3$
Cobaltite	$\text{CoAsS}$
Lollingite	$\text{FeAs}_2$
Samaltite	$\text{CoAs}_2$
Niccolite	$\text{NiAs}$
Arsenogentite	$\text{Ag}_3\text{As}$
Proustite	$\text{Ag}_3\text{AsS}_3$
Chloanthite	$(\text{Ni}, \text{Co})\text{As}_{3-x}$
Domeykite	$\text{Cu}_3\text{As}$
Safflorite	$(\text{Co}, \text{Fe})\text{As}_2$
Skutterudite	$(\text{Co}, \text{Ni})\text{As}_2$
Sperrylite	$\text{PtAs}_2$
Enargite	$\text{Cu}_3\text{AsS}_4$
Tannantite	$(\text{Cu}, \text{Fe})_{12}\text{As}_4\text{S}_{13}$
Gersdorffite	$\text{NiAsS}$
Glaucodote	$(\text{Co}, \text{Fe})\text{AsS}$
Elementary arsenic	$\text{As}$

Table 2.2: Some As bearing products

Name	Chemical formulae	Use
Arsenic trioxide (White Arsenic)	$\text{As}_2\text{O}_3$	Commercial chemical
Lead arsenate	$\text{Pb}_3(\text{AsS}_4)_2$	Pesticide
Lead hydrogen arsenate	$\text{PbHAsS}_4$	Pesticide
Scheele's green	$\text{CuHAsO}_3$	Paint pigment
Paris green	$\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)\text{AsO}_3$	Paint pigment
Phenylarsenoic acid	-	Feed additive
Potassium arsenite	$\text{NaH}_2\text{AsO}_3$	Flower's solution
Arsphenamine	-	Antisymphilitic



hypothesis received no importance when analysis of soils around wooden poles did not show elevated concentration of arsenic. Wooden electric poles are no longer thought to be a source of arsenic contamination of groundwater. In fact, based on the industrial activities and use of industrial products in Bangladesh, anthropogenic sources do not appear to be contributing to the arsenic present in groundwater.

### 2.3 Mechanism of Arsenic Release in Groundwater

Among the natural sources, arsenopyrite ( $\text{FeAsS}$ ) is the most common arsenic bearing mineral. In addition, many sulfide minerals, especially pyrite ( $\text{FeS}_2$ ) is found to be rich in arsenic. Chowdhury et. al (1998) reported presence of arsenic-rich pyrite in a number of arsenic affected districts in West Bengal, India. Arsenic may leach into the groundwater as a result of arsenopyrite and arsenic-rich pyrite. Besides arsenic bearing mineral, arsenic is often present in sediment associated with iron oxyhydroxides. Arsenic derived from weathering of arsenic-rich base metal sulfides may accumulate in iron oxyhydroxides because of its affinity for the latter. This arsenic-rich iron oxyhydroxides can be a major source of arsenic in groundwater.

Thus, in Bangladesh, two most probable (natural) sources responsible for arsenic contamination of groundwater are: (i) arsenopyrite ( $\text{FeAsS}$ ) and arsenic-rich pyrite, and (ii) arsenic-rich iron oxyhydroxides. The following section presents the probable mechanisms of release of arsenic from these sources and describes the human activities that may influence release of arsenic from these sources.

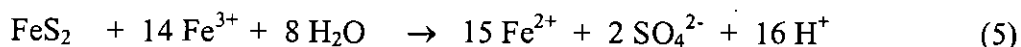
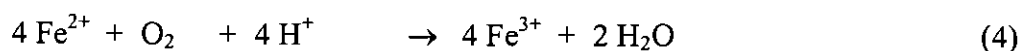
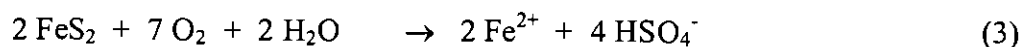
#### 2.3.1 *Arsenopyrite and Arsenic-Rich Pyrite*

Oxidation of arsenic bearing sulfide minerals [such as arsenopyrite ( $\text{FeAsS}$ ) and pyrite ( $\text{FeS}_2$ )] in aquifer can release arsenic into groundwater. The rate of oxidation of sulfide minerals is limited by the presence of an oxidizing agent, most commonly atmospheric

oxygen (as  $O_2$ ). Relatively deeper groundwater is isolated from atmosphere and the availability of oxygen in deep aquifers is limited by the amount of oxygen present in recharge water. Human activity that can significantly influence sulfide mineral oxidation and arsenic release into the aquifer is increased pumping of groundwater. Increased pumping and reducing recharge can greatly accelerate oxidation rates of arsenic bearing sulfide mineral by lowering water table and exposing mineral to atmospheric oxygen. Oxidation of arsenopyrite ( $FeAsS$ ) by oxygen and consequent release of arsenic can be expressed by the following reactions:



In the presence of oxygen, oxidation of pyrite (arsenic-rich) mineral ( $FeS_2$ ) may occur according to the following reaction (Chowdhury et al., 1998):



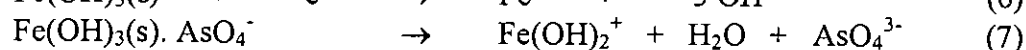
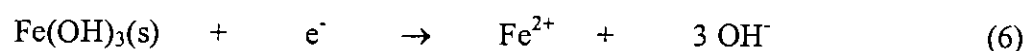
The  $Fe^{3+}$  ions formed (Eq. 4) act as a catalyst for further oxidation of pyrite (Chowdhury et al., 1998). As shown in Eqs. 3 and 5, acid ( $H^+$ ) is released during oxidation of pyrite and this acid can leach out arsenic (associated with pyrite) in soluble form in groundwater.

In the absence of oxygen, nitrate ( $NO_3$ ) can also act as an oxidizing agent and can promote oxidation of arsenic-bearing sulfide minerals. High nitrate concentrations from agricultural activities can therefore enhance arsenic release into groundwater.

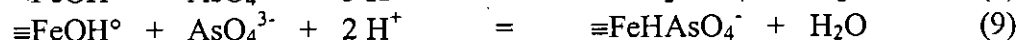
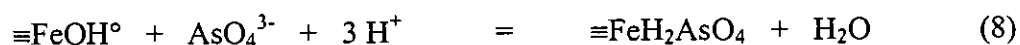
### 2.3.2 Arsenic-rich Iron Oxyhydroxide

Arsenic derived from weathering of arsenic-rich base metal sulfides are often found to be associated with iron oxyhydroxides in downstream sediments. Arsenic (both arsenate and arsenite) has high affinity for hydrous iron oxyhydroxides and become associated with them as a result of adsorption. Sediments in the Ganges delta region are known to have iron oxyhydroxide coatings on the mineral grains and at many places these coatings have been found to be rich in arsenic (Khan, 1998; Rahman and Rahman, 1998).

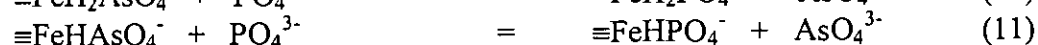
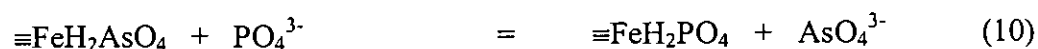
Arsenic can be released from arsenic rich iron oxyhydroxides as a result of dissolution and desorption. Dissolution of oxyhydroxides can be caused by a reducing redox environment in the subsurface. Organic matter, which is present in abundance in alluvial sediments, can be responsible for reducing environment in the subsurface. Introduction of organic waste into aquifer can also promote reducing environment. Reducing redox environment in the subsurface can promote dissolution of iron oxyhydroxides [e.g.,  $\text{Fe}(\text{OH})_3(\text{s})$ ; Eq. 6] and release of associated arsenic into groundwater. In addition, lowering of pH can also promote dissolution of iron oxyhydroxides and subsequent release of associated arsenic, as shown in Eq-7.



Possible adsorption desorption reactions of arsenate on hydrous iron oxide surface ( $=\text{FeOH}^\circ$ ) are shown in Eqs. 8 and 9 (Hering et al., 1996). At high pH values exceeding 8, adsorption of arsenic on oxide surface decreases and desorption of arsenic from iron oxyhydroxide surface can be promoted by an increase of pH. However, such high pH values are not common for groundwater in Bangladesh and this mechanism does not appear to play a major role in the release of arsenic in the subsurface.



Desorption of arsenic from iron oxyhydroxides can be promoted in the presence of a competing anion such as phosphate ( $\text{PO}_4^{3-}$ ). Possible reactions for such desorption are shown below.



Thus, application of phosphate fertilizer can potentially increase As concentration in groundwater as a result of replacement of As by phosphate ions on adsorption sites of iron oxyhydroxides.

### 2.3.3 Biological transformations

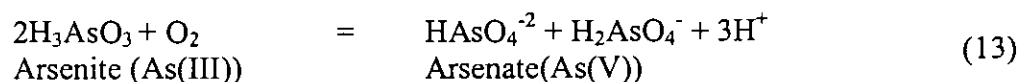
Over the past decade dissimilatory arsenate reduction involving energy conservation has been described for many arsenate respiring organisms such as: *Geospirillum arsinophilus* (Ahmann et al., 1994), *Geospirillum barnesii* (Laverman et al., 1995), *Chrysiogenes arsenatis* (Macy et al., 1996), *Desulfovibrio spp* and *Desulfomicrobium spp* (Macy et al., 2000). This reaction can be described for neutral pH by the following equation:



In *Desulfotomaculum auripigmentum* (Newman et al., 1997) the end product of arsenate reduction was found to be arsenic trisulfide ( $\text{As}_2\text{S}_3$ ). Transformation of arsenite to  $\text{As}_2\text{S}_3$

was shown to be performed by this organism in the presence of the hydrogen sulfide originated from sulfate reduction.

Certain aerobic bacteria oxidize arsenite to arsenate (Santini et al., 2000). This reaction can best be described by equation (13):



## 2.4 Presence of Arsenic in the Atmosphere

Arsenic is an environmental hazard and people are exposed to arsenic not only through drinking water but also through arsenic-contaminated air and food. Many sources emit significant amount of arsenic to the atmosphere. On a global basis, 65% of airborne arsenic is derived from the smelting of base metal ores. Most of the primary arsenic used commercially is obtained as a by-product of the benefaction of gold and base metal ores. Because As(III), the main component of smelter flue dust, is volatile, a large fraction of the arsenic in the ores is often vented to the atmosphere. It has been estimated that the Ronnskar smelter in northern Sweden used to release 50-115 tonnes of arsenic per year, a gold smelter in Yellowknife, Canada released 19-2600 tonnes of arsenic per year, and the emission from the ASARCO smelter in Tacoma, Washington was about 7-152 tonnes. A pyrite roasting plant in Barreiro/Seixal, Portugal has been known to release 1000-2000 tonnes of arsenic annually to the atmosphere (Nriagu and Pacyna, 1988).

From the observation it is found that coal combustion contributes about 11% of the arsenic emission to the global atmosphere. The coal burning type of arsenic poisoning is caused by the domestic combustion of coal containing high levels of arsenic (90-2100 mg/kg). The coal is burned inside the home in open pits for daily cooking and corn drying. These practices resulted in high arsenic concentrations in indoor air and arsenic

accumulation on the corn which was hung under the ceiling for drying, particularly in the humid harvest season in southern China. The water-arsenic concentration in that area was less than 0.005 mg/l, but the air arsenic concentration was as high as 0.04-0.13 mg/m<sup>3</sup>, i.e. 10-40 times higher than the standard. The arsenic content in the contaminated corn ranged from 1.5-110 mg/kg, which is 2-15 times higher than the proposed maximum limit value of 0.7 mg/kg (Ren, 1983).

The burning of trash cotton plants sprayed with arsenic also contributes a local scale, significant air pollution with arsenic. For example, arsenic concentrations of 600-141,000 kg/m<sup>3</sup> were reported at distance of 46-91 m downwind of burning trash from a cotton gin. It is reported that the burning of timber treated with cacodylic acid (CCA) is an important source of air borne arsenic in the United Kingdom and that the disposal of ashes of such timber contributes significantly to the arsenic burden of British soils. Microbial methylation processes can also volatilize some of the pollutant arsenic in soils and sediments. It has been estimated that 17-35% of the total annual input of arsenic into soils may be lost as methylarsines (Woolson, 1983).

## **2.5 Presence of Arsenic in Soils**

Arsenic is widely distributed in nature and classified as metalloid, which can exist both in solid and liquid states. The presence of arsenic not only found in water and atmosphere, but also in soil. Arsenic exists in soils, mostly combined with iron, nickel, gold and sulfur. Arsenic in soil may originate from the parent materials that form the soil and from industrial waste discharges or agricultural use of arsenical pesticides (Tanaka, 1988). Soil is an important natural resource for mankind, but it also serves as an important medium for the accumulation, transformation, and migration of toxicants. Arsenic can cause toxic effects to plants or may accumulate in plants and thereby enter the animal and human food chain. The total amount of arsenic in soil and its chemical forms has an important influence on plant growth and animal and human health (Nriagu and Azcue, 1990). It may cause deaths to several kinds of lives.

Arsenic pyrites, realgar, and orpiment are the most important ores of arsenic. The arsenic levels in soil enriched by these ores are often higher than in normal soil. Arsenic concentrations are considerably high in soil and shales than in earth crust because of its accumulation during weathering and translocation in colloid fractions (Zou, 1986). The parent materials of soil are usually sedimentary rocks. During the formation of these rocks, arsenic is carried down by precipitation of iron hydroxides and sulphides. Therefore, iron deposits and sedimentary iron ores are rich in arsenic (Maclean and Langille, 1981).

Human activities is another source of arsenic in soils. Arsenic may accumulate in soil through use of arsenical pesticides, application of fertilizers, irrigation water and dust from the burning of fossil fuels, and disposal of industrial and animal wastes. The anthropogenic influence on the level of arsenic in soils depends on some parameters. The pollutant dispersion pattern, the distance from the pollution sources and the intensity of the human activity are the most important parameters that influence arsenic concentration in soil.

Accumulation of arsenic in soil may be caused by irrigation water from sources such as mines. Wastewater, sewage sludge, and refuse composts have an effect on the accumulation and movement of arsenic in cultivated soil. In Japan, paddy fields polluted with arsenic from the Sasagadani mine and scattered throughout the prefectures of Miyagi, Shimane, Oita and Miyazaki. The wastes produced from the mine affected the levels of arsenic, vast amounts of which were carried by rain or wind or by the Tsuwano, Takano, and other rivers into paddy fields (Yamane, 1979).

An industrial aerosol also causes soil contamination that emitted from various industrial plants. Bituminous and sub-bituminous coals have been used as domestic fuels and by coal burning power stations, and soil may be contaminated by fly ash. Application of the material over a long period of time can lead to accumulation of arsenic in soil with consequent effects on plants. Excess amount of arsenic in soil is potentially toxic to

plants and animals (Zou, 1986). Figure 2.1 illustrates the Chemical forms of arsenic and their transformations in soils.

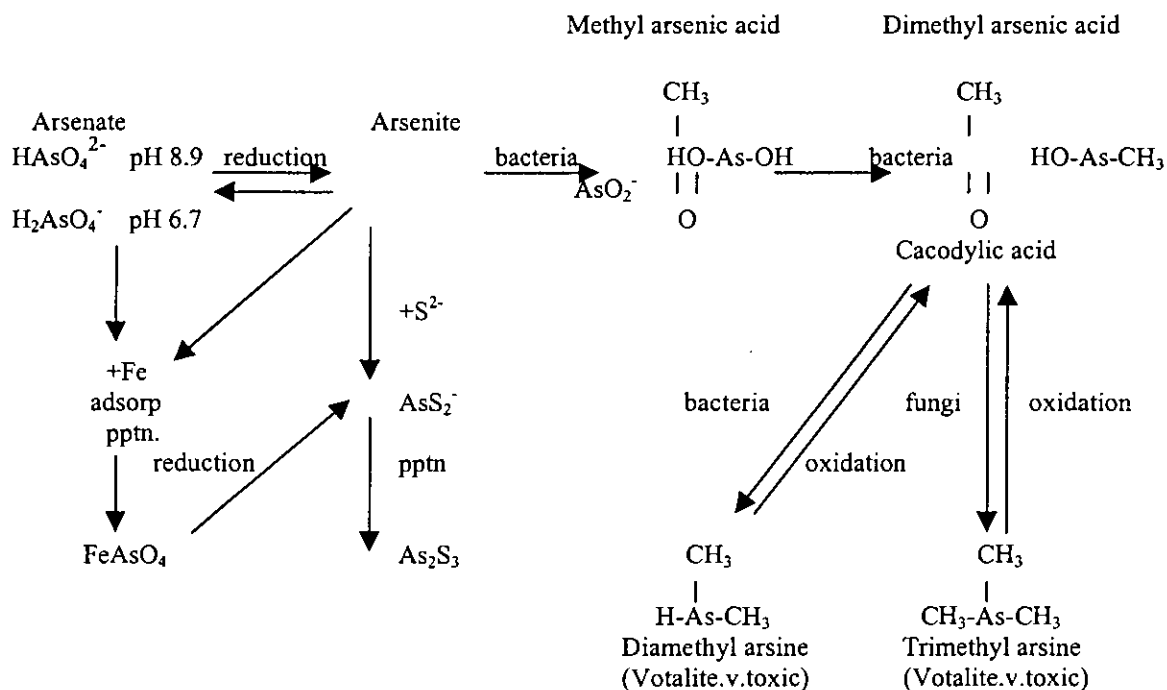


Figure 2.1: Chemical forms of arsenic and their transformations in soils (BGS, 1999)

## 2.6 Arsenic Chemistry

Arsenic chemistry in aqueous systems is quite complex because arsenic can be stable in four oxidation states. The valence and species are dependent on the oxidation-reduction conditions and pH of the water. Arsenic is usually found as an anion with acid characteristics in the trivalent and pentavalent forms. As(III) is more likely to be found in anaerobic groundwaters and As(V) in aerobic surface waters (Rajalkovic and Mitrovic, 1991).

Arsenic occurs in water in several different forms, depending upon the pH and the redox potential,  $E_h$ . Because the solubility of arsenic from elemental arsenic is extremely low,



these species may occur in the underground, which most often has low redox potential, without appearing in the groundwater. The oxides of both As(III) and As(V) are soluble in water. But as the redox potential is never high in the underground, As(III) would be the most dominant arsenic species in contaminated aquifers.

### 2.6.1 *The $E_h$ - pH Diagram*

Apart from the elementary arsenic with oxidation state of 0, arsenic is stable in the oxidation states of +5, +3 and -3. The oxidation state is closely related to the arsenic immobilization and hence the release of arsenic from its geological formations into the water bodies and the biosphere. Figure 2.2 is an  $E_h$  - pH diagram for arsenic in a system including oxygen,  $H_2O$ , and sulfur.

This diagram represents the equilibrium condition of arsenic under various redox potentials. Well-aerated surface waters would tend to induce high  $E_h$  values, therefore, any arsenic present should be in the arsenate [As(V)] form. Mildly reducing conditions, such as can be found in well water, should produce arsenite [As(III)].

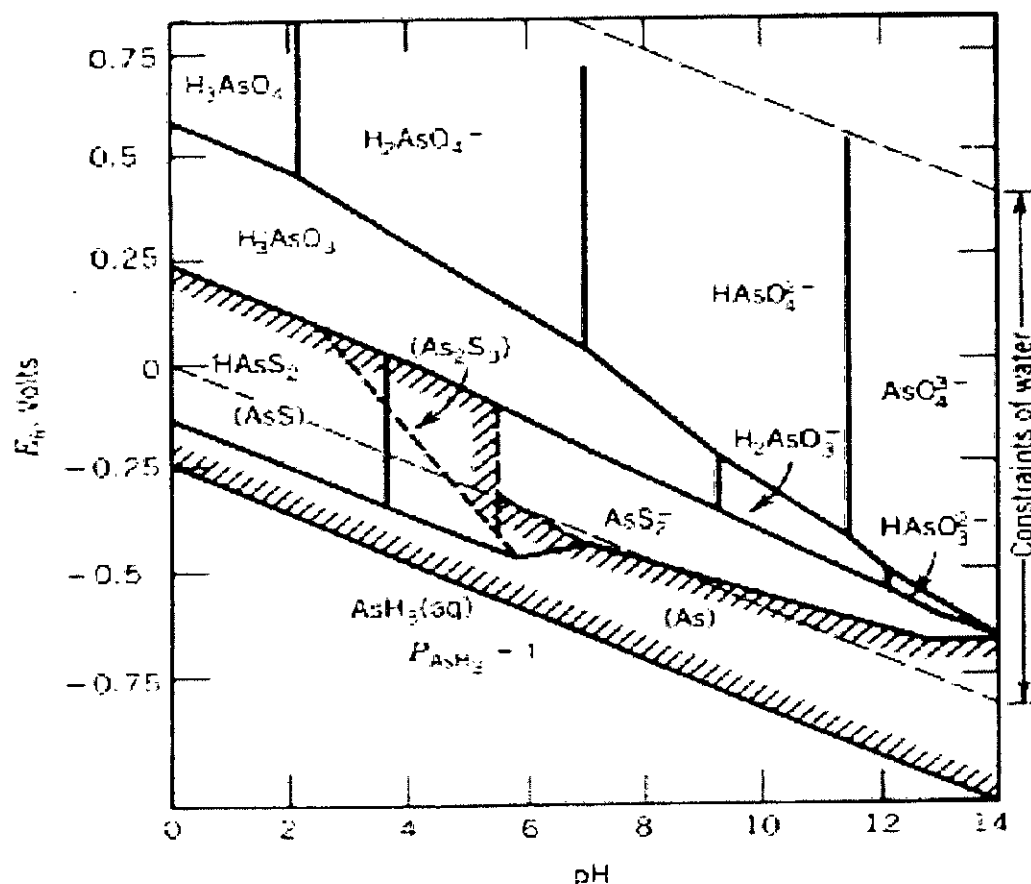


Figure 2.2: The Eh – pH diagram for As at 25 °C and 1 atm with total arsenic  $10^{-5}$  mol  $L^{-1}$  and total sulfur  $10^{-3}$  mol  $L^{-1}$ . Solid species are enclosed in parentheses in cross-hatched area, which indicate solubility less than  $10^{-5.3}$  mol  $L^{-1}$  (Ferguson and Gavis 1972).

Note the two dashed lines representing the limits that constrain water.

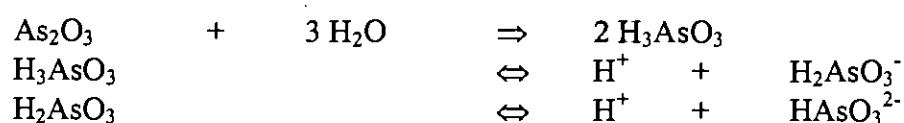
Generally speaking, both the oxidation state and the release are determined by four parameters:

- The soil and water pH.
- The redox potential  $E_h$
- The in excess occurrence of sulfide.
- The occurrence of other ions as well as solids, especially iron and manganese.

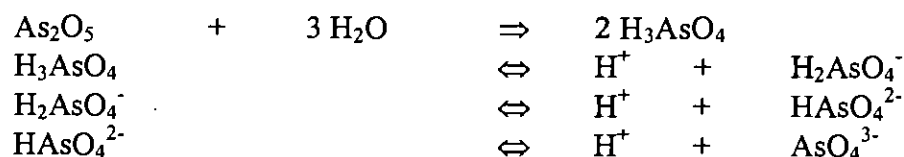
### 2.6.2 Acid – Base Reaction

The oxides of both As(III) and As(V) are soluble in water. The dissolution implies direct reaction with the water, hydration, where the oxides behaves like non-metals and exhibit acidic character. As(III) forms arsenious acid and As(V) forms the arsenic acid. The two acids dissociate to form respectively arsenite and arsenate ions:

#### Arsenious Acid Dissociation:



#### Arsenic Acid Dissociation:



Arsenic can occur in four oxidation states in water (+5, +3, 0, -3), but is generally found in only the trivalent and pentavalent states.  $\text{H}_3\text{AsO}_3$ , an un-dissociated weak acid, is predominant in the pH range of 2-9. Therefore, any As(III) present in a typical water supply would occur as  $\text{H}_3\text{AsO}_3$ . As(V) in water, on the other hand, will occur as a strong acid and dissociates according to the pH value which is shown in Figure 2.3.  $\text{HAsO}_4^{2-}$  predominates from pH 7 to 11.5, indicating that this would most likely occur in typical well water. At a pH less than 7,  $\text{H}_2\text{AsO}_4^-$  dominates. Table 2.3 shows the occurrence of arsenic species under different environmental conditions.

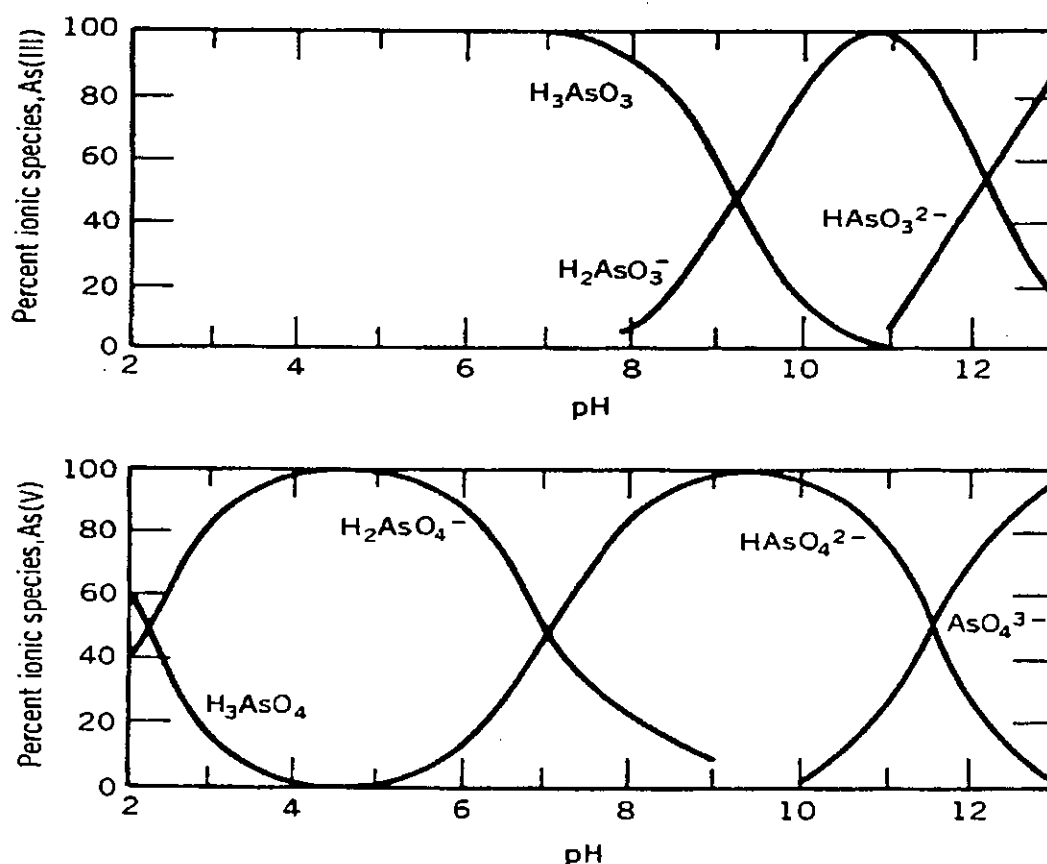


Figure 2.3: Predominance diagram for As (III) and As(V) as a function of pH (Gupta and Chen1978).

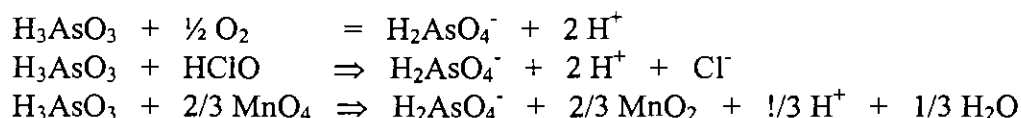
Table 2.3: Occurrence of Arsenic Species under Different Environmental Conditions

Occurrence / Species	Arsenite, As(III)	Arsenate, As(V)
<b>Occurrence</b>	Predominates in reducing conditions. Occurs as un-dissociated weak acid, Arsenious acid, $H_3AsO_3$ (pH 2-9)	Predominates in oxic conditions. Occurs as strong acid & dissociates into different species of Arsenate ion depending on pH value.
<b>Species</b>	At pH > 8.0 dissociate into $H_2AsO_3^-$ arsenite ion At pH > 11.0 dissociate into $HAsO_3^{2-}$ arsenite ion	At pH < 7.0 dissociate into $H_2AsO_4^-$ arsenate ion At pH 7.0-11.5 dissociate into $HAsO_4^{2-}$ arsenate ion At pH > 11.5 dissociate into $AsO_4^{3-}$ arsenate ion

### 2.6.3 Redox Reaction

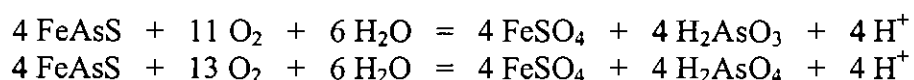
Generally speaking As(V) is dominant in oxygenated water, while As(III) is dominant in non-oxygenated ones. The reactions may be as follows:

Arsenious acid oxidation by most common oxidations:



From the above given reactions and the  $E_h$ -pH diagram, it is seen that oxygen can oxidize As(III) to As(V). Thus in principle As(III) is non-stable in atmospheric air. Any oxidizing agent like chlorine and permanganate are able to oxidize As(III) to As(V) with a very short time, e.g.  $\frac{1}{2}$  an hour or even a few minutes. This means that any chlorinating agent, like chlorinated lime, chlorine gas or sodium hypochlorite can be used for this purpose in water treatment. Similarly, any other powerful oxidizing agents like ozone; chlorine dioxide would perform the process very rapidly.

Among the most interesting redox reactions in the environment chemistry of arsenic is the oxidation of arsenopyrite. The process may be represented by the following equation (Bhumba & Keefer, 1994).



### 2.6.4 Methylation Reactions

Arsenic taken by mammals is subject to either direct excretion, direct accumulation in some parts of the body like hair, nails and skin tissue, or to biotransformation in form of methylation. Methylation is considered as the most important pathway of biotransformation. According to Vahter (1994) pentavalent arsenic can not be directly

methyated by mammals. Instead it is first reduced to tetravalent arsenic. Once the arsenic is produced it is continued to be methylated to monomethylarsenonic acid, MMA, dimethylarsonic acid, DMA, and at last to trimethylarsonic acid, TMA or trimethylarsine (Figure 2.4). Thus by analyzing urinary excreted arsenic of man, about half of the arsenic can be found to be excreted as inorganic, the other half is MMA and MMA in almost equal amounts. These proportions are subject to wide variations among mammals.

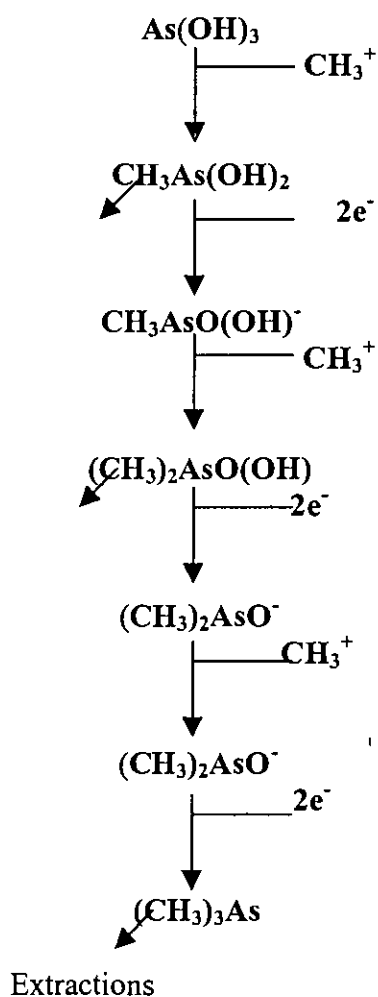


Figure 2.4: Biotransformation in Mammals

Several fungi and bacterial species have been demonstrated to methylate inorganic arsenic by an initial reduction of the arsenate fraction to arsenite, which then is methylated and released to the environment (Kartinen & Martin, 1995). However the concentration of methylated arsenic in the natural waters, whether ground or surface, is normally low, e.g. below 1  $\mu\text{g/l}$ . This is because the methylated arsenic is taken up by the biota where it undergoes metabolic conversion into organic arsenical. Compounds like arsenobetaine and arsenocholine, can thus be found in crustaceans. These compounds are meant not to have any toxicological significance. Upon consumption by many they are directly excreted through urine without any biotransformation (Vahter, 1994).

## 2.7 Toxicology of Arsenic

The toxicology of arsenic compounds depends on the chemical and physical forms of the compound, the route by which it enters the body, the dose and the duration of exposure, dietary levels of interacting elements and the age and sex of the exposed individuals. Figure 2.5 shows a qualitative scale indicating that the toxicity of arsenic compounds

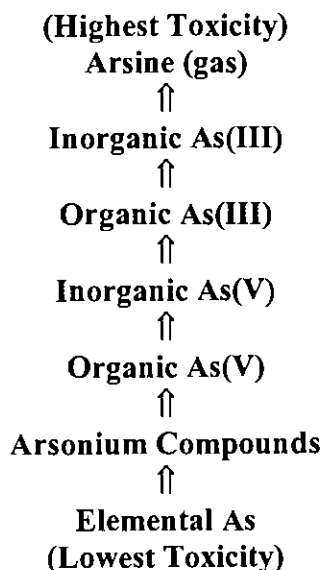


Figure 2.5 : Toxicity Scale of Arsenic

varies to a large extent depending upon their chemical form. The environmental and toxicological importance of arsenic compounds are shown in Table 2.4.

Table 2.4: Arsenic compounds and species and their environmental and toxicological importance in water (Stueart et al. 1996, Kartinen & Martin 1995, WHO 1996).

Compounds	Example	Aquatic Environment	Toxicity
<b>Arsenic</b>	$\text{As}^{3-}$	Major importance	Most toxic As species
<b>Elemental Arsenic</b>	As	Minor importance	Least toxic As species
<b>Trivalent Arsenic</b> Arsenite Inorganic pH	As(III) $\text{H}_3\text{AsO}_3$ $\text{H}_2\text{AsO}_3^-$ $\text{HAsO}_3^{2-}$ $\text{AsO}_3^{3-}$	Anaerobic pH = 0-9 pH = 10-12 pH = 13 pH = 14	10 times more than As(V)
MM As(III) DM As(III) TM As(III)	$\text{CH}_3\text{As(III)O}_2^{2-}$ $(\text{CH}_3)_2\text{As(III)O}^-$ $(\text{CH}_3)_3\text{As(III)}$	Several fungi & bacteria can methylate As(III)	Less than inorganic As(III)
Organo-As(III)		Minor importance	
<b>Pentavalent Arsenic</b> Arsenate	As(V) $\text{H}_3\text{AsO}_4$ $\text{H}_2\text{AsO}_4^-$ $\text{HAsO}_4^{2-}$ $\text{AsO}_4^{3-}$	Aerobic pH = 0-2 pH = 3-6 pH = 7-11 pH = 12-14	10 times less than As(III)
MM As(V) DM As(V) TM As(V)	$\text{CH}_3\text{As(V)O}_3^{2-}$ $(\text{CH}_3)_2\text{As(V)O}_2^-$ $(\text{CH}_3)_3\text{As(V)O}$	Methylation through reduction of As(V) to As(III)	Less than inorganic As(V)
Organo-As(V)		Minor importance	

From practical point of view, it is very easy to identify arsenic affected people, if anybody knows about its symptoms. This is because of the primary effects, like



pigmentation, keratosis and often depigmentation on palm and sole and on abdomen are directly visible and easy distinguishable for a trained health worker. On the other side, there are still no well-established guidelines about how to measure quantitatively the severity of arsenosis in a population. Table 2.5 shows some of the effects of arsenic reported to be due to exposure through drinking water.

Table 2.5: Some of the effects of arsenic reported to be due to exposure through drinking water.

<u>Effect</u>	<u>Symptoms</u>	<u>Remarks</u>
Blackfoot Disease	Dermal lesion, Peripheral neuropathy Keratosis	May necessitate operation
Arsenical dermatosis	Hyperkeratosis, Hyperpigmentation	
None specific	Nausea, Abdominal Pain, Diarrhoea, Vomiting, Conjunctivities, Oedema	Mainly due to acute intoxication
Pregnancy disorders	Spontaneous abortions, Miscarriages	
Heart Disease	Coarctation of aorta, Cardiovascular disturb	Among children
Cancer	Bladder, Kidney, Skin and lungs, Liver and Colon	
Mortality		Mainly due to cancer

## 2.8 Guide line values of Arsenic in Drinking water

Arsenic is toxic in nature and it has significant effect on human health when excess amount of arsenic presents in drinking water. Hence to provide arsenic safe drinking water to the consumer a standard or guide line value for arsenic has been set/proposed by a particular country/organization as shown in Table 2.6.

Table 2.6: Maximum Admissible Concentration for Arsenic in Drinking water (Yamamura, 2001).

<u>Country / Agency</u>	<u>Maximum Admissible Concentration</u>
Australia	: 07 $\mu\text{g/L}$ (0.007 mg/L)
World Health Organization	: 10 $\mu\text{g/L}$ (0.01 mg/L)
Japan	: 10 $\mu\text{g/L}$ (0.01 mg/L)
USA	: 10 $\mu\text{g/L}$ (0.01 mg/L)
European Union	: 10 $\mu\text{g/L}$ (0.01 mg/L)
Canadian Standard	: 25 $\mu\text{g/L}$ (0.025 mg/L)
China	: 50 $\mu\text{g/L}$ (0.05 mg/L)
India	: 50 $\mu\text{g/L}$ (0.05 mg/L)
Srilanka	: 50 $\mu\text{g/L}$ (0.05 mg/L)
Bangladesh Standard	: 50 $\mu\text{g/L}$ (0.05 mg/L)

## 2.9 Treatment Processes

Various treatment technologies exist that are capable of efficient removal of inorganic form of arsenic from water. The following treatment process in various modes of operations can be used for this purpose:

- i. Oxidation
- ii. Coagulation, adsorption and co-precipitation
- iii. Sorption Techniques
- iv. Ion exchange
- v. Membrane Techniques
- vi. Microbial Process

### 2.9.1 Oxidation

Arsenic is present in groundwater in As(III) and As(V) forms in different proportions. Most treatment methods are effective in removing arsenic in pentavalent form and hence include an oxidation step as pretreatment to convert arsenite to arsenate. Arsenite can be oxidized by oxygen, ozone, free chlorine, hypochlorite, permanganate, hydrogen peroxide and fulton's reagent but Atmospheric oxygen, hypochloride and permanganate are commonly used for oxidation in developing countries:



Air oxidation of arsenic is very slow and can take weeks for oxidation (Pierce and Moore, 1982) but chemicals like chlorine and permanganate can rapidly oxidize arsenite to arsenate under wide range of conditions.

### 2.9.2 Coagulation, adsorption and co-precipitation

The most commonly used technology is coagulation and adsorption onto coagulated flocs and subsequent removal through co-precipitation.

In *Alum coagulation* process the dissolved aluminium sulfate reacts with natural alkalinity of water and  $\text{Al}(\text{OH})_3$  macro flocs are produced. During the stirring (flocculation) process all kinds of micro-particles and negatively charged arsenic ions are removed by electrostatic attachment to the flocs. More than 90% arsenic removal can be achieved provided pre-oxidation of As(III) to As(V) and pH adjustment (6.0-7.0) are done.

In coagulation with *Iron salts* freshly precipitated amorphous  $\text{Fe}(\text{OH})_3$  is formed upon addition of the coagulant. Arsenic is primarily removed by adsorption on the surface of

$\text{Fe}(\text{OH})_3$  and subsequently co-precipitated. Iron coagulation seems to perform better than alum coagulants primarily because iron hydroxide is insoluble over a wide pH range (6.0-8.5). Moreover iron coagulants form stronger and better flocs.

In *Lime softening* process precipitated  $\text{Ca}(\text{OH})_2$  acts as sorbing flocculent for arsenic. The highest removals are achieved at pH value 10.6-11.4.

For the same reason described above, up-flow coarse media (gravel) flocculator has been found to be effective in the removal of both arsenic and iron from groundwater through flocculation, sedimentation and adsorption processes while the water containing both arsenic and iron flows through the interstices of coarse media.

The effect of different types of coagulants and their limitations in the removal process is shown in the Table 2.7.

Table 2.7: Effectiveness of Different Types of Coagulants and their limitations in the Arsenic Removal Process.

Type of Arsenic  Coagulants (Advantages & Limitations)	Arsenite, As(III)		Arsenate, As(V)	
	Optimum pH value	Percent Removal capacity	Optimum pH value	Percent removal capacity
<b>Alum Coagulation</b> (Pre-oxidation of As(III) to As(V) required)	6.0 – 7.0	< 20%	6.0 – 7.0	> 90%
<b>Iron Coagulation</b> (More efficient than Alum on weight basis)	6.0 – 8.5	About 50%	6.0 – 8.5	> 90%
<b>Lime Softening</b> (pH adjustment is required & most common chemical)	11.0	About 80%	> 10.5	> 95%

### 2.9.3 Sorption techniques

Arsenic adsorption onto activated alumina, activated carbon, iron coated sand or other adsorption media occurs when arsenic contaminated water is passed through the fixed

bed of these media producing a low arsenic content effluent. The adsorption by activated carbon, iron coated sand and other sorption media are briefly reviewed below. Activated alumina adsorption process is discussed in details separately in the article 2.12.

#### Activated Carbon Adsorption

Activated carbon is manufactured from carbonaceous materials such as wood, coal, petroleum residue, etc. Removal of As(V) by adsorption onto activated carbon is more effective than As(III). Activated carbon is crushed into granules ranging from 0.1 to 2 mm in diameter or is pulverized to a very fine powder. Dissolved materials adsorb to both exterior and interior surfaces of the carbon. When these surfaces become saturated with dissolved substances, the carbon must be regenerated. Design of granular-activated-carbon system is based on flow rates and contact times. Carbon columns can be arranged in parallel to increase the capacity and in series to increase the contact time. A method of pretreatment activated carbon by a ferrous salt to enhance As(V) removal was described by Huang and Vane (1989). They could increase the carbon capacity by a factor of 10, due to primarily adsorption of  $\text{Fe}^{2+}$  arsenate complexes. The carbon could be regenerated with the ferrous salt solution.

Little is known about the adsorption mechanism of arsenic species on activated carbon. The arsenic adsorption mechanism can not be solely explained in terms of molecule-surface interaction, electrostatic interaction, or occlusion. It is apparent that  $\text{H}_2\text{AsO}_4^-$  is the major species removed by activated carbon.

#### Iron Coated Sand Adsorption

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

on iron oxide-coated sand. The medium is regenerated by sodium hydroxide solution. Iron oxide-coated sand is a low cost and simple process for use in small systems or home treatment units in developing areas of the world.

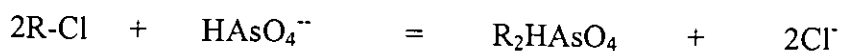
#### Other Sorptive Processes

Several other sorptive media have been reported to remove arsenic from water. These are kaolinite clay, hydrated ferric oxide, activated bauxite, titanium oxide, silicium oxide and many natural and synthetic media. The efficiency of all some sorptive media depend on the use of oxidizing agent as aids to sorption of arsenic. Saturation of media by different contaminants and components of water takes place at different times of operation depending on the specific sorption affinity of the medium to the given component.

#### *2.9.4 Ion Exchange*

Ion exchange is normally used to demineralise, to soften and de-nitrate water. In ion exchange applications, water passes through a column containing ion exchange resins. Pretreatment of these resins using sodium chloride creates an abundance of chloride on the exchange site. When arsenic-containing water passes through this resin bed, the chloride ions are exchanged for the arsenic ions that are present in the water. At exhaustion, the exchange sites are loaded with arsenic which can then be regenerated by passing concentrated sodium chloride solutions through the column (usually applied in the opposite flow direction). The arsenic exchange and regeneration equations with common salt solution as regeneration agent are as follows:

Arsenic exchange (R = Resin)



Regeneration (R = Resin)



If the column is operated beyond exhaustion, peaking may occur. The effectiveness of ion exchange process depends on the relative affinity of the resin for arsenic. Sulfate ions in the influent decrease the effectiveness substantially competing for the adsorption sites. The ion exchange process is less dependent on the pH of water. The efficiency of the ion exchange process is radically improved by pre-oxidation of As(III) to As(V) but the excess oxidants have to be removed before the ion exchange in order to avoid the damage of the resin. Development of an ion-specific resin for the exclusive removal of arsenic can make the process very attractive.

#### *2.9.5 Membrane Techniques*

Membrane techniques like reverse osmosis, nanofiltration and electrodialysis are capable of removing all kinds of dissolved solids including arsenic from water. In this process water is allowed to pass through special filter media which physically retain the impurities present in water. The water, for treatment by membrane techniques, shall be free from suspended solids and the arsenic in water shall be in pentavalent form. Most membranes, however, can not withstand oxidizing agent. These high-tech methods are of no interest in developing countries because of their high costs.

#### *2.9.6 Microbial Processes*

Microbial removal of arsenic is based on two important metal-microbe interactions, one is microbial oxidation of As(III) to As(V) to facilitate its removal by conventional arsenic removal processes and other one is bio-accumulation of arsenic from the surrounding water environment. There are a number of microorganisms capable of oxidizing arsenite at neutral pH. The common iron bacteria, which oxidize ferrous iron to ferric iron, can oxidize as well as absorb arsenic. Arsenic can conventionally be oxidized from As(III) to As(V), adsorbed or assimilated through microbial growth in a simple reactor in nutritionally balanced condition at appropriate temperature and pH, and

subsequently removed by precipitation/filtration. Removal of trace metal from polluted water through accumulation in algae is relatively well known but their application in the treatment of drinking water is yet to be established.

### Comparison of the Treatment Methods

From the overview of different technologies presented in this chapter, it appears that ion exchange and membrane techniques may prove to be too costly for large scale implementation in Bangladesh. Apart from cost, both ion exchange and membrane techniques would require higher levels of technical expertise on the part of the user for operation and maintenance. Presence of high concentrations of iron in the groundwater, which precipitates as ferric hydroxide solids after extraction, would definitely interfere with the efficiency of membranes. Microbial processes for removal of arsenic from drinking water is still at a development stage and does not appear to be a suitable technology for implementation at this stage. A comparison among different treatment methods to remove arsenic from groundwater is presented in Table 2.8.



Table 2.8: Methods advantages and disadvantages.

Method	Advantages	Disadvantages
<u>Oxidation</u> ➤ Air Oxidation ➤ Chemical oxidation	➤ Relatively simple, low-cost but slow process ➤ Relatively simple and rapid process ➤ Oxidizes other impurities and kills microbes	➤ The processes remove only a part of arsenic
<u>Coagulation, adsorption and Co-precipitation</u> ➤ Alum coagulation ➤ Iron coagulation ➤ Lime softening	➤ Relatively low capital cost ➤ Relatively simple operation ➤ Common chemicals available	➤ Produces toxic sludges ➤ Low removal of As(III) ➤ Pre-oxidation may be required ➤ pH adjustment required
<u>Sorption techniques</u> ➤ Activated alumina ➤ Iron coated sand ➤ Other sorbents	➤ Relatively well-known and commercially available ➤ Well-defined technique ➤ Plenty of possibilities and scope for development	➤ Produces toxic solid waste ➤ Replacement/regeneration required ➤ High-tech operation and maintenance ➤ Relatively high cost
<u>Ion Exchange</u>	➤ Well defined medium and hence capacity.	➤ High cost medium. ➤ High tech. operation and maintenance. ➤ Regeneration creates a sludge problem.
<u>Membrane techniques</u> ➤ Reverse osmosis ➤ Electrodialysis	➤ Well-defined and high removal efficiency ➤ No toxic solid wastes produced ➤ Capable of removal of other contaminants	➤ Very high capital and running costs ➤ High-tech operation and maintenance ➤ Toxic wastewater produced
<u>Microbial processes</u> ➤ Microbial oxidation ➤ Microbial removal	➤ Should be less costly	➤ Not yet fully established ➤ Requires extensive research

## 2.10 Arsenic Contamination of Groundwater in Bangladesh

Presence of elevated levels of arsenic in groundwater has become a major concern in Bangladesh. Arsenic pollution of groundwater is particularly challenging in Bangladesh since tubewell water extracted from shallow aquifer is the major source of drinking water for most of its population. A number of studies has been undertaken to know the extent and its effect on human health as well as in food chain. The studies are briefly described below:

### 2.10.1 *Extent of Arsenic Contamination of Groundwater*

Groundwater contaminated by arsenic was first discovered by the Department of Public Health Engineering (DPHE) at Chapai Nawabganj in late 1993 following reports of elevated levels of arsenic in groundwater of the adjoining areas of India. Further testing in 1995 and 1996 showed that contamination extended across a large part of southern and western Bangladesh. As the source of arsenic in groundwater is considered to be geological, the concentration in water varies from place to place within the same district and also differs on zonal basis. The analysis of data on zonal basis indicated that the Khulna and Rajshahi zones were badly affected where the Barisal and Dhaka were less affected. In Chittagong zone, some districts like Chandpur, Laxmipur & Noakhali were badly affected. Some of the large diameter production wells in the districts like Satkhira, Meherpur, Magura, Chuadanga & Chapainawabgonj are also reported to be contaminated with high arsenic (Quadiruzzaman, 1997). A study by BUET and BCSIR first indicated that groundwater in North-Eastern part of Bangladesh is also contaminated with arsenic. Arsenic was also found in deeper aquifers in that zone (Badruzzaman et al., 1997).

In April 1997 a World Bank (WB) Fact-Finding Mission visited Bangladesh to assess the situation and to initiate mitigation program. Part of their recommendations included a broad-ranging Rapid Investigation Program to collate the available data, fill in the

critical gaps in knowledge and undertake surveys of the affected area. This eventually lead to the project entitled '*Groundwater Studies for Arsenic Contamination in Bangladesh*' which was approved by the Government of Bangladesh in late December 1997. The Department for International Development (DFID) of UK agreed to finance the project. Out of 64 districts in Bangladesh, 61 districts have been found arsenic affected. Rangamati, Khagrachari and Bandarban are found to be arsenic contamination free district. According to the survey report of DPHE (1997-2000) published in international workshop report in 2002, 268 upazillas are arsenic affected out of 507 upazillas in Bangladesh. Survey results show that 27% shallow tubewells are arsenic contaminated having concentration beyond the Bangladesh standard (50 ppb) where, this figure increased to 46% when WHO standard (10 ppb) is considered. (DPHE / DFID / BGS, 2000 and [http://www.naisu.info/arsenic\\_2002.htm](http://www.naisu.info/arsenic_2002.htm))

District mean ground water arsenic concentration is shown in Figure 2.6 which shows district mean groundwater arsenic concentration in Bangladesh. Groundwater arsenic contamination in Bangladesh on the basis of arsenic concentration is shown in Figure 2.7.

The population exposed to arsenic from exceeding Bangladesh and WHO drinking water standard is estimated to be within 28-35 million and 46-57 million respectively and a total of 13,333 arsenicosis patients have been identified (DPHE / DFID / BGS, 2000; EES and DCH, 2000). From practical point of view, it is very easy to identify arsenic affected people, if anybody knows about its symptoms. This is because of the primary effects, like pigmentation, keratosis and often depigmentation on palm and sole and on abdomen are directly visible and easy distinguishable for a trained health worker. On the other side, there are still no well-established guidelines about how to measure quantitatively the severity of arsenosis in a population. Thus the correlation between the severity of the disease and the contamination levels of the consumed water are yet to be established. Also a convincing correlation between the concentration of arsenic in the drinking water and the concentrations of arsenic in the urine, hair and nails are yet to be established (Mazumder et al., 1997).



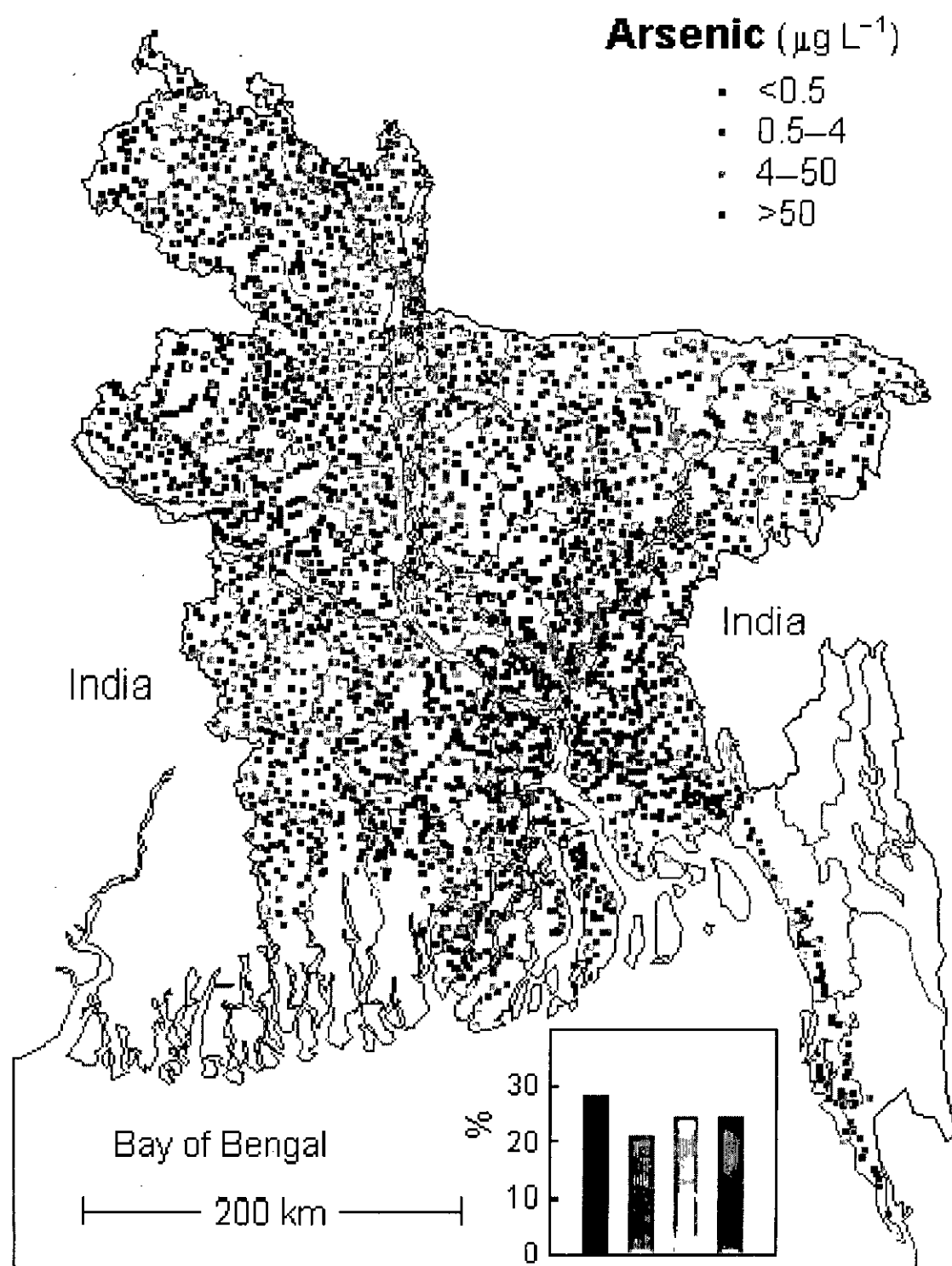


Figure 2.7: Map showing Ground water Arsenic Concentration in Bangladesh (DPHE / DFID / BGS, 2000)

In late 2001 ICDDR,B has started a research project in the Matlab area to study the effects of exposure to arsenic. This project is executed in collaboration with BRAC and supported by WHO, SIDA and USAID. In mid 2002, an annotated overview of all health research on arsenic undertaken in the last few years was published by the Bangladesh Medical Research Council (BMRC).

Many organizations - NGO-Forum, BRAC, DCH, CARE and others are very much involved in arsenic mitigation: awareness raising, patient identification & management and small-scale research. BUET, DU and IDE are also involved in research on mitigation options. In January 2002, the DFID funded (US\$ 49.3 million) Rural Hygiene, Sanitation and Water Supply Project has been started by DPHE with assistance from UNICEF.

DFID also funded a project "Rapid Assessment of Household Level Arsenic Removal Technologies" and it was jointly managed by WaterAid Bangladesh and DFID and implemented by WS Atkins International Ltd. This study (commenced in August 2000 and ended in March 2001) was focused on comparative assessment of the performance and acceptability of nine household level technologies and finally came up with seven. The study also included a comparative evaluation of field test kit also. The report was submitted to the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) Technical Advisory Group (TAG) and TAG reviewed the study and recommended four technologies.

Initial studies have been undertaken to address the concern regarding the contribution to arsenic in the food chain by water contaminated with arsenic and used for irrigation or cooking. Studies undertaken by FAO, CSIRO/Australia & Dhaka University and AIIHPH/Kolkata with WHO, point to substantial contributions to the total arsenic content in green leafy vegetables, when grown with contaminated irrigation water. However a study by Australian National University (ANU) in collaboration with NGO Forum "An Intervention Trial to Assess the Contribution of Food Chain to Total Arsenic

Exposure" in May 2000, which chose exposure based on arsenic content in irrigation water, failed to demonstrate a difference in arsenic content in the small number of raw food samples tested from the high and low contamination areas. Further studies investigating the arsenic content in different types of food from areas with high and low contamination of irrigation water, are recommended. In the backdrop of the widespread arsenic contamination of groundwater in the Bengal Basin, United Nations University (UNU), Tokyo, Japan and Bangladesh University of Engineering and Technology (BUET) undertook a joint research project in the middle of December 2001 to understand the fate of arsenic in the environment. The research was conducted with some crop samples and grain samples. The research revealed that the roots of rice plants accumulated maximum level of arsenic, followed by leaf and stem. Accumulation of arsenic in different parts of the vegetables (potato, tomato, lalshak, datashak, cabbage and cauliflower) was found relatively low (Ali et al., 2003).

It is evident that since 2000 many Government, Non Government and bilateral organizations are working on this issue and much action research has been carried out, however the situation of many communities has not improved greatly. The broad spectrum of institutional arrangement should be such that it ensures sustainable development. The services that are required, be it technological or financial, need to be delivered optimally. The situation now demands to review and reform the institutional arrangement to address sector issues appropriately.

To develop a more coordinated response to the arsenic crisis, Government of Bangladesh (GOB) has taken new initiative to establish Arsenic Policy Support Unit (APSU) in the Local Government Division (LGD) to prepare and implement a National Arsenic Mitigation Programme (NAMP) through a partnership approach. It is an indication that GOB and donors wish to address the arsenic crisis in a more holistic way than has been possible under the BAMWSP. DFID is currently designing a Support to the National Arsenic Mitigation Programme (SNAMP) and would assist APSU in implementing the

recommendations for action that resulted from the International Workshop held in January 2002. ([http://www.naisu.info/arsenic\\_2002.htm](http://www.naisu.info/arsenic_2002.htm))

### *2.10.2 Future Trends in Groundwater Arsenic Concentrations*

#### Influence of pumping and irrigation

There is no long-term water quality monitoring data to definitively establish how arsenic concentrations change over time. The few data that exist, extending over no more than two years, show that some wells have increased in concentration, but cannot yet be taken as proof of general or systematic changes. The Regional Survey showed a strong correlation between the year of construction and the proportion of wells that are contaminated above the Bangladesh Standard. On average, older wells are more likely to be contaminated than recently constructed ones. Only long-term monitoring will determine whether this actually corresponds to increasing concentrations at individual wells.

The possible influence of pumping is a key policy issue for the water sector. There is extensive withdrawal of groundwater for domestic use and irrigation. Although the number of hand pump tubewells is much greater than the number of irrigation wells, they only account for about 10% of groundwater abstraction by volume. The critical question is whether or not pumping of groundwater for irrigation is either creating or exacerbating the problem of arsenic in drinking water. The influence of pumping for irrigation could be expressed as either by the flow of groundwater through the aquifers or by the lowering of the water table. To test these ideas, spatial correlation was attempted between the areas of most intense arsenic contamination and the distribution of groundwater abstraction and also the deepest groundwater levels. No correlation with either heavy abstraction or deep groundwater levels could be found. In fact, the areas of greatest contamination never coincide with either the deepest water levels or the most intensive abstraction.



Possible changes over time were also investigated through the use of numerical groundwater flow and transport models. Modeling the impact of a typical 0.5 cusec irrigation shallow tubewell (STW) with a 6 ha. command area indicates that even under conditions of relatively low arsenic sorption, movement of the arsenic might be of the order of 50 m in 15 years. Therefore while irrigation wells will enhance the movement and dispersion of arsenic, this effect is likely to occur over the times scale of decades.

Although there is evidence that enhanced fluctuation of the water table is not responsible for mobilizing arsenic, this is not to say that irrigation will have no effect on the arsenic problem. In particular, the widespread cultivation of boro rice provides just the conditions that would minimize air entry to the underlying aquifer and would therefore make any ongoing reduction and arsenic release that much more effective. This process would probably take a long time to have an effect, and cannot account for the large-scale problem that currently exists. It nevertheless needs further investigation.

The effect of phosphate fertilizers also needs investigation. Phosphate concentrations are abnormally high frequently more than 0.5 mg/l (as phosphate-P) – and this could make the arsenic more soluble by competing with arsenic for sorption sites on the iron oxides.

The impact of using contaminated irrigation water from shallow tubewells needs investigation from the point of view of possible entry of arsenic into the human food chain, the animal food chain and any effect on soil quality, particularly its microbiological functioning.

#### Effects of floods

Floods are a normal occurrence in Bangladesh, and although the severe flooding in the 1998 monsoon was exceptional, it is unlikely that floods have any long-term effect on the arsenic problem. There may be some increased flow in the uppermost part of the shallow aquifer but this will, if anything, tend to flush out the arsenic that is found there.


## 2.11 Arsenic Removal Technologies in Bangladesh

There are several methods available for removal of arsenic from water in large conventional treatment plants. The most commonly used technologies include oxidation, co-precipitation and adsorption onto coagulated flocs, lime treatment, adsorption onto sorptive media, ion exchange resin and membrane techniques (Cheng et al., 1994; Hering et al., 1996, 1997; Kartinen and Martin, 1995; Shen, 1973; Joshi and Chaudhuri, 1996). A detailed review of arsenic removal technologies is presented by Sorg and Logsdon (1978). Jackel (1994) has documented several advances in arsenic removal technologies. In view of the lowering the drinking water standards by USEPA, a review of arsenic removal technologies was made to consider the economic factors involved in implementing lower drinking water standards for arsenic (Chen et al., 1999).

A comprehensive review of low-cost, well-water treatment technologies for arsenic removal with the list of companies and organizations involved in arsenic removal technologies has been compiled by Murcott (2000) with contact detail. Some of these technologies can be reduced in scale and conveniently be applied at household and community levels for the removal of arsenic from contaminated tubewell water. During the last 2-3 years many small scale arsenic removal technologies have been developed, field tested and used under action research programs in Bangladesh and India. A short review of these technologies is intended to update the technological development in arsenic removal, understand the problems, prospects and limitations of different treatment processes and delineate the areas of further improvement for successful implementation and adaptation of technologies to rural conditions.

### 2.11.1 *Passive Sedimentation*

Passive sedimentation received considerable attention because of rural people's habit of drinking stored water from pitchers. Oxidation of water during collection and subsequent storage in houses may cause a reduction in arsenic concentration in stored water.



Experiments conducted in Bangladesh showed zero to high reduction in arsenic content by passive sedimentation. Arsenic reduction by plain sedimentation appears to be dependent on water quality particularly the presence of precipitating iron in water. Ahmed et. al,(2000) showed that more than 50% reduction in arsenic content is possible by sedimentation of tubewell water containing 380-480 mg/L of alkalinity as  $\text{CaCO}_3$  and 8-12 mg/L of iron but cannot be relied to reduce arsenic to desired level. Most studies showed a reduction of zero to 25% of the initial concentration of arsenic in groundwater. In rapid assessment of technologies passive sedimentation failed to reduce arsenic to the desired level of 50  $\mu\text{g/L}$  in any well (BAMWSP, DFID, WaterAid , 2001).

#### *2.11.2 In-situ Oxidation*

In-situ oxidation of arsenic and iron in the aquifer has been tried under DPHE-Danida. Arsenic Mitigation Pilot Project. The aerated tubewell water is stored in a tank and released back into the aquifers through the tubewell by opening a valve in a pipe connecting the water tank to the tubewell pipe under the pump head. The dissolved oxygen in water oxidizes arsenite to less mobile arsenate and also the ferrous iron in the aquifer to ferric iron, resulting a reduction in arsenic content in tubewell water. Experimental results show that arsenic in the tubewell water following in-situ oxidation is reduced to about half due to underground precipitation and adsorption on ferric iron.

#### *2.11.3 Solar Oxidation*

SORAS (Solar Oxidation and Removal of Arsenic) is a simple method of solar oxidation of arsenic in transparent bottles to reduce arsenic content of drinking water ( Wegelin et al., 2000). Ultraviolet radiation can catalyze the process of oxidation of arsenite in presence of other oxidants like oxygen (Young, 1996). Experiments in Bangladesh show that the process on average can reduce arsenic content of water to about one-third.

#### *2.11.4 Bucket Treatment Unit*

The Bucket Treatment Unit (BTU), developed by DPHE-Danida Project is based on the principles of coagulation, co-precipitation and adsorption processes. It consists of two buckets, each 20 liter capacity, placed one above the other.

Chemicals are mixed manually with arsenic contaminated water in the upper red bucket by vigorous stirring with a wooden stick for 30 to 60 seconds and then flocculated by gentle stirring for about 90 second. The mixed water is then allowed to settle for 1- 2 hours. The water from the top red bucket is then allowed to flow into the lower green bucket via plastic pipe and a sand filter installed in the lower bucket. The flow is initiated by opening a valve fitted slightly above the bottom of the red bucket to avoid inflow of settled sludge in the upper bucket. The lower green bucket is practically a treated water container.

The DPHE-Danida project in Bangladesh distributed several thousands BTU units in rural areas of Bangladesh. These units are based on chemical doses of 200 mg/L aluminum sulfate and 2 mg/L of potassium permanganate supplied in powder form. The units were reported to have very good performance in arsenic removal in both field and laboratory conditions ( Sarkar et al., 2000 and Kohnhorst and Paul, 2000). Extensive study of DPHE-Danida BTU under BAMWSP, DFID, WaterAid (2001) rapid assessment program showed mixed results. In many cases, the units under rural operating conditions fails to remove arsenic to the desired level of 0.05 mg/L in Bangladesh. Poor mixing and variable water quality particularly pH of groundwater in different locations of Bangladesh appeared to be the cause of poor performance in rapid assessment.

Bangladesh University of Engineering and Technology (BUET) modified the BTU and obtained better results by using 100 mg/L of ferric chloride and 1.4 mg/L of potassium permanganate in modified BTU units. The arsenic contents of treated water were mostly below 20 ppb and never exceeded 37 ppb while arsenic concentrations of tubewell water

varied between 375 to 640 ppb. The BTU is a promising technology for arsenic removal at household level at low cost. It can be built by locally available materials and is effective in removing arsenic if operated properly.

#### 2.11.5 Stevens Institute Technology

This technology also uses two buckets, one to mix chemicals ( reported to be iron sulphate and calcium hypochlorite) supplied in packets and the other to separate flocs by the processes of sedimentation and filtration. The second bucket has a second inner bucket with slits on the sides as shown in Figure 2.8 to help sedimentation and keeping the filter sand bed in place. The chemicals form visible large flocs on mixing by stirring with stick. Rapid assessment showed that the technology was effective in reducing arsenic levels to less than 0.05 mg/L in case of 80 to 95% of the samples tested (BAMWSP, DFID, WaterAid , 2001).

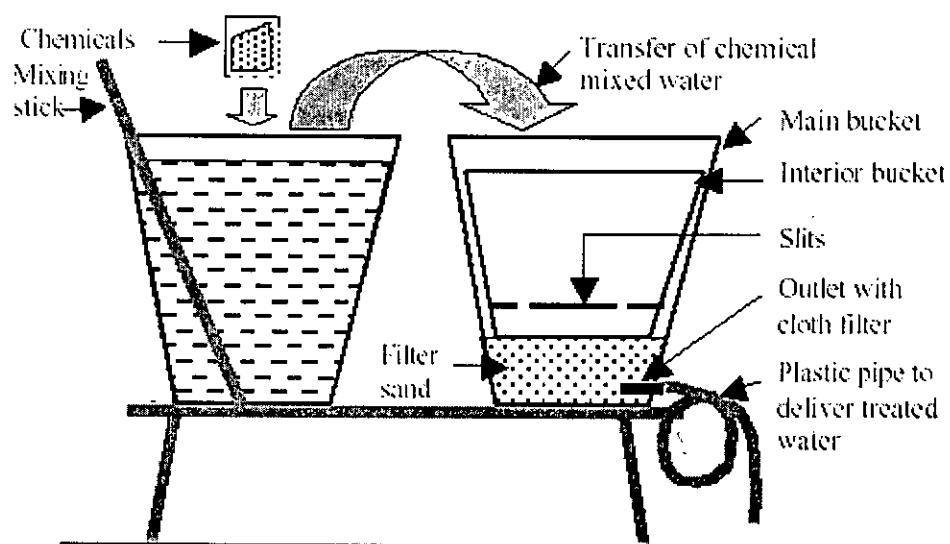


Figure 2.8: Stevens Institute Technology (Ahmed, F., 2001).

The sand bed used for filtration is quickly clogged by flocs and requires washing atleast twice a week.

#### *2.11.6 BCSIR Filter Unit*

Bangladesh Council of Scientific and Industrial Research (BCSIR) has developed an arsenic removal system, which uses the process of coagulation/coprecipitation with an iron based chemical followed by sand filtration. The unit did not take part in a comprehensive evaluation process.

#### *2.11.7 Fill and Draw Units*

It is a community type treatment unit designed and installed under DPHE-Danida Arsenic Mitigation Pilot Project. It is 600 L capacity (effective) tank with slightly tapered bottom for collection and withdrawal of settled sludge. The tank is fitted with a manually operated mixer with flat-blade impellers. The tank is filled with arsenic contaminated water and required quantity of oxidant and coagulant are added to the water. The water is then mixed for 30 seconds by rotating the mixing device at the rate of 60 rpm and left overnight for sedimentation. The water takes some times to become completely still which helps flocculation. The floc formation is caused by the hydraulic gradient of the rotating water in the tank. The settled water is then drawn through a pipe fitted at a level, few inches above the bottom of the tank and passed through a sand bed and finally collected through a tap for drinking purpose as shown in Figure 2.9. The mixing and flocculation processes in this unit are better controlled to effect higher removal of arsenic. The experimental units installed by DPHE-Danida project are serving the clusters of families and educational institutions.

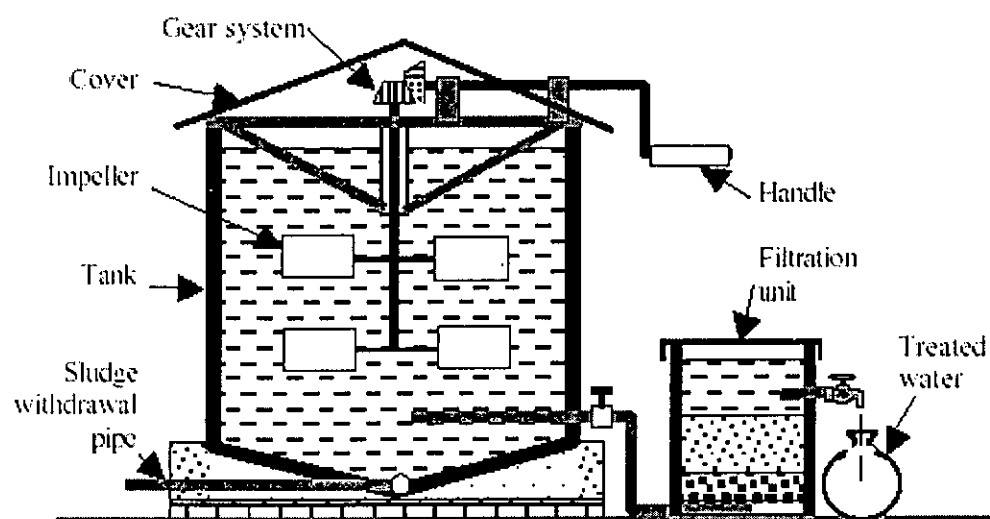


Figure 2.9: DPHE-Danida Fill and Draw Arsenic Removal Unit (Ahmed, F., 2001).

#### 2.11.8 Arsenic Removal Unit Attached to Tubewell

The principles of arsenic removal by alum coagulation, sedimentation and filtration have been employed in a compact unit for water treatment in the village level in West Bengal, India. The arsenic removal plant attached to hand tubewell as shown in Figure 2.10 has been found effective in removing 90 percent arsenic from tubewell water having initial arsenic concentration of  $300\mu\text{g/L}$ . The treatment process involves addition of sodium hypochlorite, and aluminum alum in diluted form, mixing, flocculation, sedimentation and up-flow filtration in a compact unit.

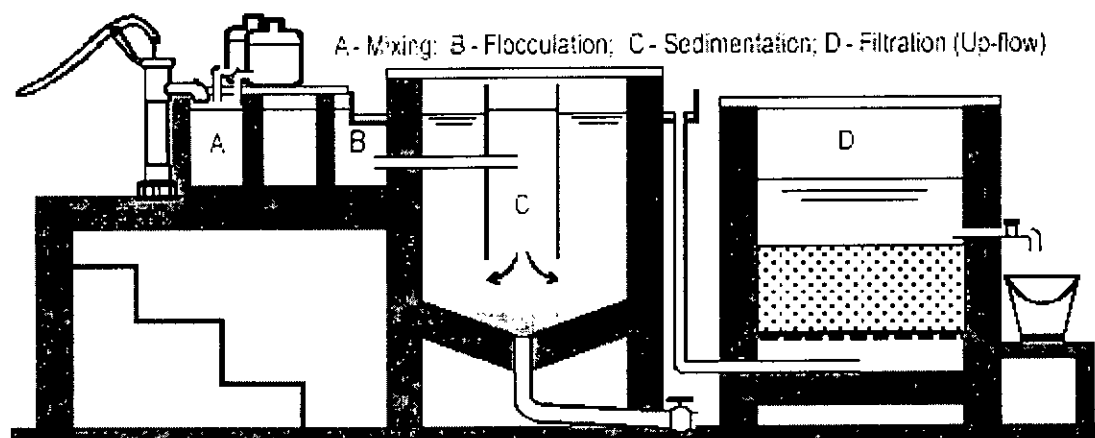


Figure 2.10: Arsenic removal plants attached to tubewell (Ahmed, F., 2001).

#### 2.11.9 Naturally Occurring Iron

The use of naturally occurring iron precipitates in groundwater in Bangladesh is a promising method of removing arsenic by adsorption. It has been found that hand tubewell water in 65% of the area in Bangladesh contains iron in excess of 2 mg/L and in many acute iron problem areas, the concentration of dissolved iron is higher than 15 mg/L. Although no good correlation between concentrations of iron and arsenic has been derived, iron and arsenic have been found to co-exist in ground water. Most of the tubewell water samples satisfying Bangladesh Drinking Water Standard for Iron (1 mg/L) also satisfy the standard for Arsenic (50 µg/L). Only about 50% of the samples having iron content 1 - 5 mg/L satisfy the standard for arsenic while 75% of the samples having iron content > 5 mg/L are unsafe for having high concentration of arsenic.

The iron precipitates  $[\text{Fe}(\text{OH})_3]$  formed by oxidation of dissolved iron  $[\text{Fe}(\text{OH})_2]$  present in groundwater have the affinity for the adsorption of arsenic. Only aeration and sedimentation of tubewell water rich in dissolved iron has been found to remove arsenic. The Iron Removal Plants (IRPs) in Bangladesh constructed on the principles of aeration,



sedimentation and filtration in small units have been found to remove arsenic without any added chemicals. The conventional community type IRPs, depending on the operating principles, more or less work as Arsenic Removal Plants (ARPs) as well. A study suggests that As(III) is oxidized to As(V) in the IRPs to facilitate higher efficiency in arsenic removal in IRPs constructed in Noakhali (Dahi and Liang, 1998). The Fe-As removal relationship with good correlation in some operating IRPs has been plotted in Figure 2.11. Results show that most IRPs can lower arsenic content of tubewell water to half to one-fifth of the original concentrations. The efficiency of these community type Fe-As removal plants can be increased by increasing the contact time between arsenic species and iron flocs. Community participation in operation and maintenance in the local level is absolutely essential for effective use of these plants.

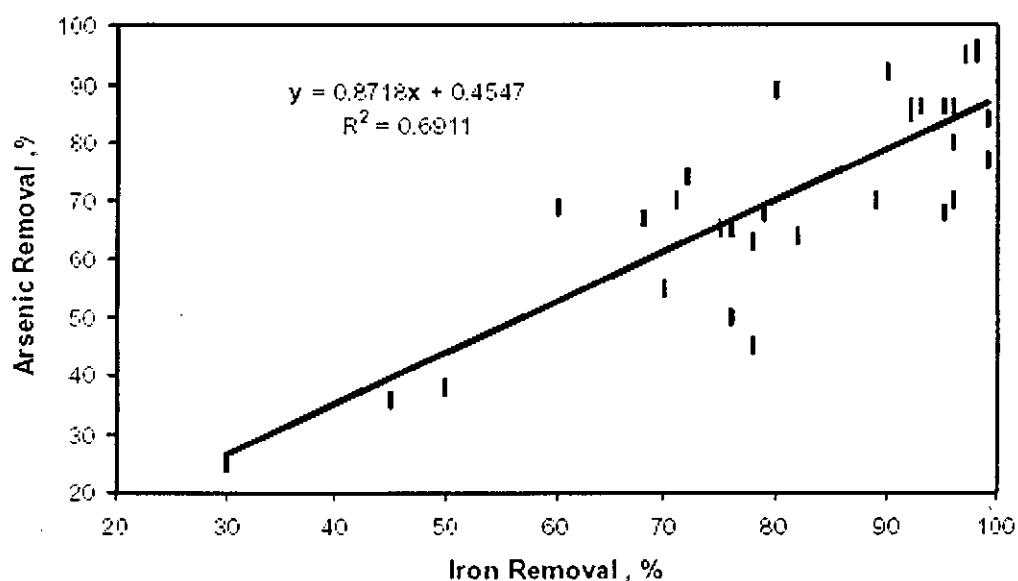


Figure 2.11: Correlation between Fe and As Removal in Treatment Plants (Ahmed, F., 2001).

Some medium scale Fe-As removal plants of capacities 2000-3000 m<sup>3</sup>/d have been constructed for water supplies in district towns based on the same principle. The treatment processes involved in these plants include aeration, sedimentation and rapid sand filtration with provision for addition of chemical, if required.

These plants are working well except that treated water requirement for washing the filter beds is very high. Operations of small and medium size IRP-cum-ARPs in Bangladesh suggest that arsenic removal by co-precipitation and adsorption on natural iron flocs has good potential.

#### *2.11.10 Granular Ferric Hydroxide*

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

#### *2.11.11 Read-F Arsenic Removal Unit*

Read-F is an adsorbent produced and promoted by Shin Nihon Salt Co. Ltd, Japan for arsenic removal in Bangladesh. Read-F displays high selectivity for arsenic ions under a broad range of conditions and effectively adsorbs both arsenite and arsenate without the need for pretreatment. The Read-F is Ethylenevinyl alcohol copolymer(EVOH)-borne hydrous cerium oxide in which hydrous cerium oxide ( $\text{CeO}_2 \cdot n \text{H}_2\text{O}$ ), is the adsorbent. The material contains no organic solvent or other volatile substance and is not classified as hazardous material. Laboratory test at BUET and field testing of the materials at 4 sites under the supervision of BAMWSP showed that the adsorbent is highly efficient in removing arsenic from groundwater (SNSCL, 2000).

#### *2.11.12 Iron Coated Sand*

BUET has constructed and tested iron coated sand based small scale unit for the removal of arsenic from groundwater. Iron coated sand has been prepared following a procedure

similar to that adopted by Joshi and Choudhuri ( 1996). The iron content of the iron coated sand was found to be 25 mg/g of sand. Raw water having 300 µg/L of arsenic when filtered through iron coated sand becomes essentially arsenic-free. It was found that 350 bed volumes could be treated satisfying the Bangladesh drinking water standard of 50 ppb. The saturated medium is regenerated by passing 0.2N sodium hydroxide through the column or soaking the sand in 0.2N sodium hydroxide followed by washing with distilled water. No significant change in bed volume (BV) in arsenic removal was found after 5 regeneration cycles. It was interesting to note that iron coated sand is equally effective in removing both As(III) and As(V). Iron coated brick dust has also been developed in Bangladesh for arsenic removal from drinking water.

#### *2.11.13 Indigenous Filters*

There are several filters available in Bangladesh that use indigenous material as arsenic adsorbent. Red soil rich in oxidized iron, clay minerals, iron ore, iron scrap or fillings and processed cellulose materials are known to have capacity for arsenic adsorption. Some of the filters manufactured using these materials include:

- Sono 3-Kolshi Filter
- Granet Home-made Filter
- Chari Filter
- Adarsha Filter
- Shafi Filter
- Bijoypur Clay/Processed Cellulose Filter

The Sono 3-Kolshi filter uses zero valent iron fillings and coarse sand in the top Kolshi, wood coke and fine sand in the middle Kolshi while the bottom Kolshi is the collector of the filtered water (Khan et. al, 2000). Earlier Nikolaidis and Lackovic (1998) showed that 97 % arsenic can be removed by adsorption on a mixture of zero valent iron fillings and sand and recommended that arsenic species could have been removed through

formation of co-precipitates, mixed precipitates and by adsorption onto the ferric hydroxide solids. The Sono 3- Kolshi unit has been found to be very effective in removing arsenic but the media harbour growth of microorganism (BAMWSP, DFID and WaterAid, 2000). The one-time use unit becomes quickly clogged, if groundwater contains excessive iron.

The Garnet home-made filter contains relatively inert materials like brick chips and sand as filtering media. No chemical is added to the system. Air oxidation and adsorption on iron-rich brick chips and flocs of naturally present iron in groundwater could be the reason for arsenic removal from groundwater. The unit produced inadequate quantity of water and did not show reliable results in different areas of Bangladesh and under different operating conditions. The Chari filter also uses brick chips and inert aggregates in different Charis as filter media. The effectiveness of this filter in arsenic removal is not known.

The Shafi and Adarsha filters use clay material as filter media in the form of candle. The Shafi filter was reported to have good arsenic removal capacity but suffered from clogging of filter media. The Adarsha filter participated in the rapid assessment program but failed to meet the technical criterion of reducing arsenic to acceptable level (BAMWSP, DFID and WaterAid, 2000). Bijoypur clay and treated cellulose were also found to adsorb arsenic from water (Khair, 2000).

## **2.12 Activated Alumina adsorption Process**

### *2.12.1 Introduction*

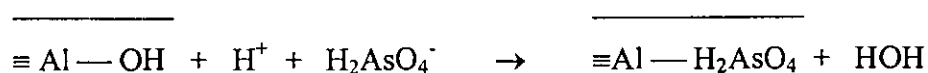
Activated alumina is granular aluminium oxide having sorptive surface. It is an effective process for removing pentavalent arsenic from water (AWWA, 1990). Activated Alumina is an effective medium in a variety of water purification processes including arsenic removal. The typical activated alumina used in water treatment are 28 x 48 mesh (0.3 to

0.6 mm diameter), mixture of amorphous and gamma aluminum oxide ( $\gamma$  -  $\text{Al}_2\text{O}_3$ ) prepared by low temperature ( 300 to 600  $^{\circ}\text{C}$  ) dehydration of  $\text{Al}(\text{OH})_3$ . They have surface areas of 50 to 300  $\text{m}^2/\text{gm}$ .

### 2.12.2 Mechanism of Activated Alumina Adoption

Arsenic contaminated water is passed through packed beds of activated alumina to remove arsenic from water. When the water passes through a packed column of activated alumina grains, arsenic and other pollutants in the water are adsorbed on the surfaces of the grains. For fresh activated alumina, arsenic is readily removed in the region of the bed closest to the influent. Arsenic not removed immediately is adsorbed as it passes through successive levels of the bed in a wavelike manner. Finally as the entire bed becomes exhausted/saturated and the mass transfer zone approaches the end of the bed, increasingly higher concentrations of arsenic are observed until the concentration in the effluent equals influent concentration and no removal occurs. This phenomenon is termed *breakthrough*. In practice, the column is only operated to a certain break point, e.g. up to Maximum Contaminant Level (MCL) in the effluent. Then the bed is to be replaced with fresh activated alumina or the exhausted/spent alumina is to be regenerated.

The mechanism, which is one of exchange contaminant anions for surface hydroxides on the alumina, is generally called adsorption, although ligand exchange and chemisorption are more appropriate terms for highly specific surface reaction involved. By using the model of a hydroxylated alumina surface subject to protonation and deprotonation, the following typical ligand-exchange reaction can be written for arsenic adsorption in acid solution (alumina exhaustion) in which ' $\equiv \text{Al}$ ' represents the alumina surface and over bar denotes the solid phase.



The equation for arsenic desorption by hydroxide (alumina regeneration) is



### 2.12.3 Factors Affecting the Removal of Arsenic by Activated Alumina

Since the removal of arsenic from water with activated alumina is a sorption phenomena, oxidation state of As, pH, presence of ions and anions in the water may influences the capacity in different degrees. A brief description of these factors is given below.

#### a) Oxidation state effect

As(V) has found to be more effectively removed than As(III) (Table 2.9). Because the As(III) usually occurs in non ionized form which is not easily removed by adsorption on the sorption sites of alumina. Oxidation of As(III) to As(V) is thus required as a pre-treatment. This can be achieved by addition of oxidizing agents like chlorine products, or potassium permanganate. As(III) removal, however, can be improved at higher pH value because of the fraction of charged As(III) species ( $\text{H}_2\text{AsO}_3^-$ ) with increasing pH.

The type of arsenic species present in water should be known prior to removal studies, which directly depends on pH and the redox potential Eh. Well aerated surface waters would tend to induces high Eh values, therefore, any arsenic present should be in the arsenate, As(V) form. Mildly reducing conditions, such as can be found in well water, should produce arsenite, As(III). If As(III) is found to be predominate, then oxidation should be considered to convert As(III) to As(V) prior to the treatment. Chlorine or potassium permanganate will easily do this.

Table 2.9: Effect of pH on removal of trivalent and pentavalent arsenic species from water by activated alumina (Kartinen & Martin, 1995; Sueart, RD et al., 1995).

As(III) (mg/L)	As(V) (mg/L)	Total As (mg/L)	pH	Bed Volume treated upto 50 ppb As conc.
100	0	100	6.0	300
0	100	100	5.5	13100
0	100	100	6.0	23000
80	10	90	6.0	700
80	10	90	8.6	800
31	57	88	6.0	9000
0	98	98	6.0	16000
0	98	98	8.8	900

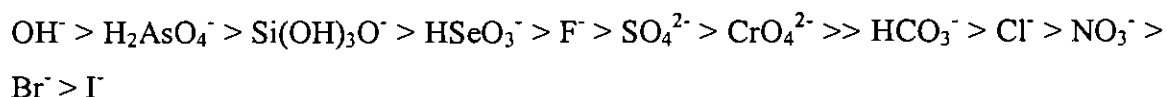
#### b) pH effect

Sorption on activated alumina is sensitive to pH. Anions are best adsorbed below pH 8.2, a typical zero point charge (ZPC) below which the alumina surface has a net positive charge. The optimum pH for arsenic adsorption on to alumina has not been clearly established. Some investigators reported that the removal capacity for As(V) can be maximized at pH values around 6.0. At relatively high pH value (8.6), the adsorption of As(V) on alumina is severely reduced by competition from hydroxide ions. This lead to poor As(V) uptake compared to adsorption at optimum of 6.0. The As(III) uptake at a high pH (8.0) is however, slightly improved compared to that at pH 6.0 because of the increase in the fraction of charged  $H_3AsO_3$ . The effect of pH on removal of trivalent and pentavalent arsenic species from water by activated alumina is shown in Table 2.9(Kartinen & Martin, 1995; Sueart, RD et al., 1995).

#### c) Presence of other Anions

The sorption site on the activated alumina surface are also attractive to a number of anions other than arsenate. The As(V) sorption capacity of alumina may be significantly

reduced in the presence of fluoride ions in influent. Presence of high concentration of other anions such as phosphate, sulfate and chloride in water may reduce the capacity of alumina column to a certain degree through competition for sorption sites. Clifford reports the selectivity sequence of activated alumina in the pH range of 5.5 to 8.5 (Clifford, 1999):



Trussell and others reported a similar selectivity sequence but included phosphate as the second most preferred anion after hydroxyl and placed fluoride above arsenate in the sequence (Trussell et al., 1980)

#### d) Alumina size effect

Alumina is commercially available in four typical size ranges, 8x10, 14x28, 28x48, and 48x100 mesh from largest to smallest. The kinetics of removal are such that the smallest particle sizes provide the most surface area for adsorption/ exchange of arsenic. Some trade off will have to be made because the smaller particle will have a greater tendency to be washed out the bed during backwash and they are more susceptible to rapid dissolution by NaOH.

#### *2.12.4 Regeneration of Activated Alumina*

Spent alumina is regenerated following four sequential steps as described below:

##### Backwash

Upon termination of the treatment run, the bed should be back-washed upto 50 percent bed expansion for 10-15 min. to remove trapped suspended materials, break up the packed bed, and redistribute the media.



### Re-generation

Bench-scale or pilot scale tests should be done to determine the specific design criteria for NaOH elution of the arsenic. It is necessary to choose the NaOH concentration, dosage, and flow rate to regenerate the bed economically for another arsenic removal cycle. A 4% NaOH solution is recommended for the base regeneration of the spent activated alumina either in batch or by down flow through the column. One item to note is that activated alumina is dissolved to some degree by NaOH.

### Neutralization

Once the arsenic has been eluted from the alumina with NaOH, the bed pH must be reduced to the desired level to allow efficient removal of arsenic and to prevent prolonged high pH in the effluent. First excess caustic soda must be rinsed from the bed (raw water can be used for one to two bed volumes at the NaOH flow rate). Then the bed must be rinsed with an acid solution, either  $H_2SO_4$  or HCl. The simplest method for doing this is to pass raw water with its pH adjusted to 2.0 or 2.5 through the bed at the treatment flow rate while monitoring the effluent pH. This effluent should be disposed with the regenerant. When the pH of the effluent drops to the desired level, the water can then be fed into the system again while the influent pH of the water is changed to the desired level.

During the process of regeneration, about 5-10% alumina are lost, and the alumina loses 30-40% of its capacity to remove arsenic. Eventually, the alumina needs to be replaced.

#### *2.12.5 Waste disposal*

Regeneration of the activated alumina columns results in a toxic waste containing high concentration of soluble arsenic. The effluent of acid rinses is mixed with the caustic rinses and this mixed arsenic waste can be disposed on a prepared bed of cow dung in a shallow hole dug in earth. The microorganisms in cow dung transform the arsenic to gaseous arsine (Moore and Ramamoorthy, 1984) and arsenic is thus released into the surrounding air.

## Chapter 3

# METHODOLOGY

### 3.1 Introduction

Activated alumina removes arsenic from water by adsorption. Arsenic contaminated water is passed through a column containing granular activated alumina. The arsenic removal efficiency depends on the oxidation state of arsenic, pH value of water, presence of competing ions, presence of iron, contact time and size of activated alumina. Column study was conducted under different conditions using synthetic groundwater and distilled water to investigate the effects of various parameters on the arsenic removal efficiency of activated alumina. This chapter presents the methodology and laboratory procedure of the column study.

### 3.2 Experimental Setup

Down flow columns were set in the environmental engineering laboratory to carry out the study. The experimental setup is shown in Figure 3.1. Locally available materials were used to construct the experimental setup. Graduated glass column of  $1\text{ cm}^2$  in cross-sectional area was used as laboratory test column. A mechanism was fitted to the bottom of the column to control the outflow in need. A special gravel filter was placed at the bottom to retain activated alumina and to avoid quick clogging of the alumina bed at the bottom of the filter. Activated alumina was washed using distilled water to remove powder from it. The glass column was filled up with the washed activated alumina to a certain bed height keeping sufficient free space for inlet connection. The column was fixed to a stand. In most of the cases, 14x28 mesh size activated alumina was used. Only

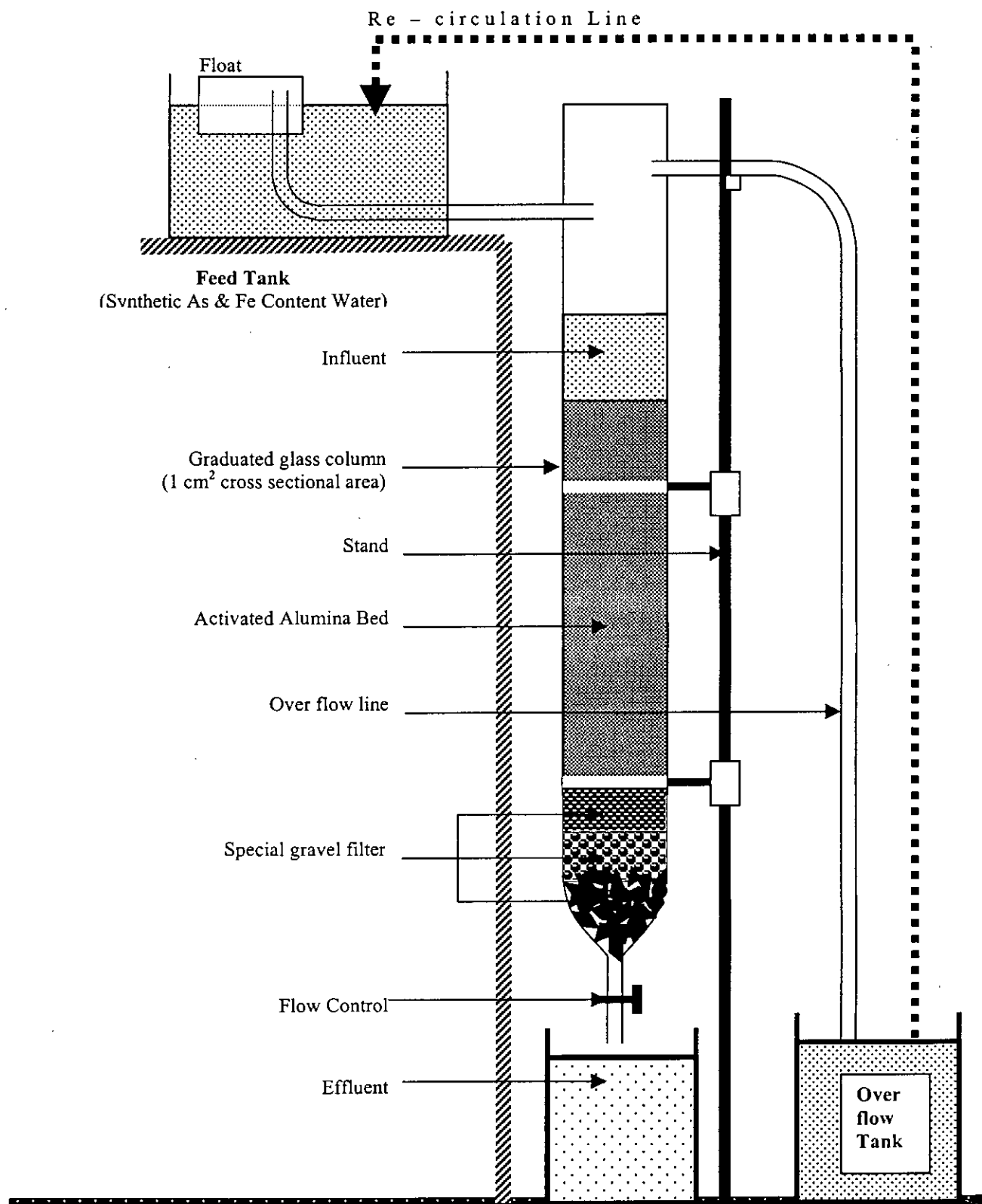


Figure 3.1: Laboratory Test Bed and Experimental Set up

55.0

a few runs were carried out with 28x48 mesh size. The inlet of the alumina column was connected to a feed tank (25L plastic bucket) with a flexible rubber tube. To obtain sufficient head, the feed tank was placed on a high platform. To maintain constant head, an over-flow tube was connected to the column at a higher position than the inflow connection. A float system was introduced into the feed tank to minimize the amount of overflow while maintaining the constant head of flow. The treated water was collected in a plastic bucket placed below the activated alumina column. The overflow was collected in another plastic bucket.

### **3.3 Experimental Procedure**

The activated alumina used for the column study was supplied by UNICEF-Bangladesh. The alumina was manufactured by M/S. Porocell Corporation, Arkansas, USA. Two sizes of alumina namely, size 14x28 and size 28x48 were procured by UNICEF-Bangladesh and the materials were handed over to the Environmental laboratory of Civil Engineering Department, BUET to evaluate its arsenic removal efficiency.

Experiments were conducted using synthetic raw water under different conditions. The procedures followed are outlined in the following sub-sections.

#### *3.3.1 Preparation of synthetic water*

Both distilled water and tap water of the laboratory of BUET were used to prepare synthetic water for this study. A few experiments were conducted with distilled water (as tap water contains some iron) to observe the effect of iron on arsenic removal efficiency of activated alumina bed. In most cases of the study, tap water was used for preparing synthetic water. Groundwater abstracted by deep tubewells at BUET campus is the source of water supply at the Environmental Engineering Laboratory. Water samples

were collected from a tap at the laboratory and were analyzed for arsenic and found to be free from arsenic. The tap water sample was analyzed for detail characterization for a number of times during the course of the study and the average composition is presented in Table 3.1.

Table 3.1: Composition of Laboratory Tap Water

Sl. No.	Water quality Parameter	Unit	Concentration
1	pH	-	6.5
2	Carbon dioxide	mg/L	45.0
3	Total alkalinity as $\text{CaCO}_3$	mg/L	200.0
4	Arsenic	$\mu\text{g/L}$	below 1
5	Iron	mg/L	0.15
6	Chloride	mg/L	220.0
7	Sulfate	mg/L	60.0
8	Phosphate	mg/L	0.68

Stock solutions of As(III), As(V), and Fe(II) were prepared from their salts. The salts were arsenic trioxide ( $\text{As}_2\text{O}_3$ ), di-sodium hydrogen arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) and ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ).

Tap water was taken in a 25 L plastic bucket (preparation tank). As the tap water contained high carbon-dioxide, the water in the preparation tank was aerated vigorously using aeration apparatus to remove the carbon-dioxide. As a result pH of the water did not change significantly due to escape of little remaining carbon-dioxide of the water into the atmosphere during the experiments. The stock solutions of As(III), As(V), and Fe(II) were added to aerated water in required amounts to obtain feed waters of different specific compositions and concentrations. Hydrochloric acid (HCl) and sodium

hydroxide (NaOH) solutions were added to the water to adjust the pH of waters to different fixed values. The experimental conditions are presented in Tables 3.2 and 3.3 for As(V) and As(III) removal study respectively.

Table 3.2: Experimental Conditions for As(V) Removal Study

Major Water Quality Parameters			Bed Height (cm)	Activated Alumina Size
Arsenic (V) Concentration, ppb	pH value	Iron content, mg/L		
100	6.0	0.15	20	14 X 28
300	5.0	1.0	20	
	6.0	0.0	20	
		0.15	20, 30	
		1.0	20	
		3.0	20	
		5.0	20	
	7.5	1.0	20	
500	6.0	0.15	30	

Table 3.3: Experimental Conditions for As(III) Removal Study.

Major Water Quality Parameters			Bed Height (cm)	Activated Alumina Size
Arsenic (III) Concentration, ppb	pH value	Iron content (mg/L)		
100	7.0	1.0	50	14 X 28
300	6.0	1.0	50	
	7.0	0.15	30	
		1.0	50	
		3.0	50	
		5.0	50	
		7.0	50	
	8.0	1.0	50	
500	7.0	1.0	50	

To investigate the effect of chloride, sulfate and phosphate on the arsenic removal efficiency of activated alumina, these anions were added individually to the aerated raw water. Hydrochloric acid was used as the source of chloride ion and sulfuric acid was used as the source of sulfate ion. Potassium di-hydrogen phosphate salt was used to make stock solution of phosphate. The experimental conditions are presented in Table 3.4.

Table 3.4: Experimental Conditions to Study the Effect of Chloride, Sulfate & Phosphate

Water Quality Parameters			Activated Alumina Size	Bed Height (cm)	Added Anion	Added Anion Influent (mg/L)
As(V) (ppb)	Iron (mg/L)	pH				
500	0.15	7.0	14x28	50	Cl	300 700 1100
500	0.15	7.0	14x28	50	SO <sub>4</sub>	60 335 740
300	0.15	7.0	28x48	30	PO <sub>4</sub>	0.68 160 345

### 3.3.2 Column experiments

Synthetic raw water was transferred from the preparation tank to feed tank of the experimental setup. The float system was then placed in the tank and was adjusted by trial and error to obtain a low overflow rate. Dissolved oxygen of the synthetic water oxidized the ferrous iron present in synthetic water to form iron flocs. The water was stirred time to time to break the large iron flocs and to keep all the flocs in suspension. pH of the feed tank was checked at regular interval and was adjusted if necessary. Through the inlet tube, the synthetic raw water entered the test bed and passed through

the activated alumina. The treated water was collected in a plastic bucket placed at the bottom of the activated alumina column. The flow velocity was measured intermittently using measuring cylinder and stopwatch. Cumulative volume of water passing through the activated alumina bed was measured and the effluent samples were collected after specific quantity of flow. Generally samples were collected at an interval of two to three liters when the flow velocity was comparatively high but samples were also collected when a rapid fall of effluent flow rate occurred. The run was stopped at the end of the day and started again in the morning of the next day. The activated alumina bed was kept in submerged condition with distilled water when the experiment was not running. Otherwise, the bed became hard and sticky resulting poor performance of the alumina bed. When the run was stopped, the feed tank water was acidified using HCl acid in order to preserve the influent. On the following day, the experiment was stated after proper mixing of water in the feed tank and pH adjustment. During running of the experiments, in some cases, flow rate reduced to a significantly low level due to the formation of a thin layer of foreign particles on the top of the activated alumina bed. Again, presence of iron in the influent resulted in precipitates of ferric hydroxide and they deposited on the top of the bed. Then clogging of bed with iron took place, not only that, some fine precipitates penetrated into the top portion of the bed. As a result, the top portions of the activated alumina bed became clogged and reduced the flow velocity through the bed. In the cases of heavy clogging the top portions were taken out and the alumina particles were washed to remove the sediment and iron flocs. Then the alumina particles were placed in the columns. In a few cases screening mechanism was placed in the inlet tube to arrest the flow of sediment and iron flocs into the alumina bed. It was found that the screen became clogged within a very short time by the retained iron flocs. Hence the screen was removed. All samples collected in plastic bottle were acidified with hydrochloric acid for preservation. The effluent quality was monitored for arsenic and iron contents. The run was terminated when either the arsenic content of the effluent exceeded the MCL of 50  $\mu\text{g/l}$  or the flow rate reduced to about 1  $\text{mL/cm}^2/\text{min}$ .



### 3.3.3 Regeneration of Spent Alumina

One of the objectives of the study was to develop a suitable regeneration technique of spent alumina and to study the arsenic removal efficiency of the regenerated alumina. Regeneration of spent alumina while keeping it in the column is an expensive method since large amount of acid and alkali solution are to be passed through the column. It was found that by taking the spent alumina out of the column, then regenerating and placing back into the column was more economical and advantageous. It was experienced that simple washing of the spent alumina by water did not remove the iron coatings from the alumina grains satisfactorily. To remove the iron coatings completely, an additional washing with diluted HCl (20%) was given to the spent alumina. The alumina was submerged in the acid solution for 24 hrs. After that the alumina was washed with distilled water prior to base regeneration with sodium hydroxide solution (4%). Then the bed was washed with water to remove excess caustic soda from the granular material. Finally the alumina was treated with dilute hydrochloric acid to neutralize it.

Loss of alumina in the regeneration process was quantified and the regenerated alumina was placed in the column. Table 3.5 presents the laboratory experimental conditions for the regeneration study.

Table 3.5: Laboratory Experimental Conditions for Regeneration Study

Sl. No.	Arsenic, As(V) Concentration (ppb)	Iron, Fe Concentration (mg/L)	Bed Height (cm)	pH Value
1	300	1.0	40	5.0
2	100	1.0	20	6.0

### 3.4 Testing of Water Samples

The water samples collected during the experimental investigation were analyzed for a number of water quality parameters following Standard Methods. Arsenic concentrations were measured by BUET kit. Some of the arsenic measurements were done by Graphite Furnace Atomic Absorption Spectrophotometer (GF-AAS, Model AA680, Shimadzu). Thiocyanate method was used to measure the iron content of water samples. pH was determined using pH meter (Ehamp pH tester, HANA). Mohr method was followed to measure the chloride content of water samples. HACH DR/4000 spectrophotometer was used to determine sulphate (Salfa Ver 4 Method) and phosphate ( Phos ver (Ascorbic Acid) Method) contents of water. Titration method was used to measure the carbon dioxide concentration and alkalinity of the water samples.

### 3.5 Measuring Effectiveness of Arsenic Removal Efficiency

Efficiency/effectiveness of activated alumina in a filter column in removing arsenic was determined in terms of the following parameters:

- Number of Empty Bed Volume (BV) upto arsenic Maximum Contaminant Level (MCL), which is the ratio of the quantity of water treated ( $\Sigma Q$ ) upto arsenic MCL in the effluent and the volume (V) of activated alumina packed in the column i.e.  $BV = \Sigma Q / V$ .

- Quantity of adsorbed arsenic by activated alumina, which is calculated through the equation:

$$\text{Adsorbed arsenic (mg/g)} = \frac{\text{Influent arsenic concentration} - \text{Avg. effluent arsenic concentration upto MCL}}{\text{Weight of activated alumina}} \times \text{Effluent volume upto MCL}$$

- Overall arsenic removal efficiency of the activated alumina bed upto 50 ppb arsenic level in terms of average effluent arsenic concentration, which is calculated by the equation:

$$\text{Efficiency (\%)} = \frac{\text{Influent arsenic concentration} - \text{Avg. effluent arsenic concentration upto MCL}}{\text{Influent arsenic concentration}} \times 100$$

## Chapter 4

# RESULTS AND DISCUSSION

### 4.1 Introduction

The effectiveness of activated alumina in removing arsenic from groundwater was studied under different conditions. Synthetic groundwater spiked with both pentavalent and trivalent arsenic was used as raw water in the experiments. Distilled water was also used during the determination of iron effect on arsenic removal efficiency. Iron, chloride, sulfate and phosphate were added to synthetic groundwater to reveal their effects on arsenic removal efficiency. The effect of pH on arsenic removal efficiency was also experimented in both cases of pentavalent and trivalent arsenic. The experimental data are presented in Appendix-A. Appendix-B contains the analysis to determine the arsenic removal efficiency and bed volume. The results are presented and discussed in the following sections.

### 4.2 Effect of Initial Arsenic Concentration

Both pentavalent and trivalent arsenic were used separately to study the effect of arsenic concentration on the removal efficiency by activated alumina.

#### 4.2.1 *Removal of Pentavalent Arsenic*

To study the effect of pentavalent arsenic concentration on the arsenic removal efficiency of activated alumina experiments were conducted with synthetic groundwater having influent arsenic concentration 100 ppb, 300 ppb and 500 ppb and a fixed pH value of 6.0. Tap water was used to maintain constant iron concentration ( $\text{Fe} = 0.15 \text{ mg/L}$ ). The experimental data are presented in Table-A1, A2 and A3 in Appendix-A. Calculations to determine Bed Volume (the ratio of cumulative volume of effluent and activated alumina bed volume) and arsenic removal efficiency are

presented in tabular form in Appendix- B. Figure 4.1 presents the relationship between effluent arsenic concentration and bed volume. From this Figure it is seen that the adsorption curve for higher arsenic concentration, such as 500 ppb has steeper slope. The adsorption curve for arsenic concentration of 100 ppb is more flat

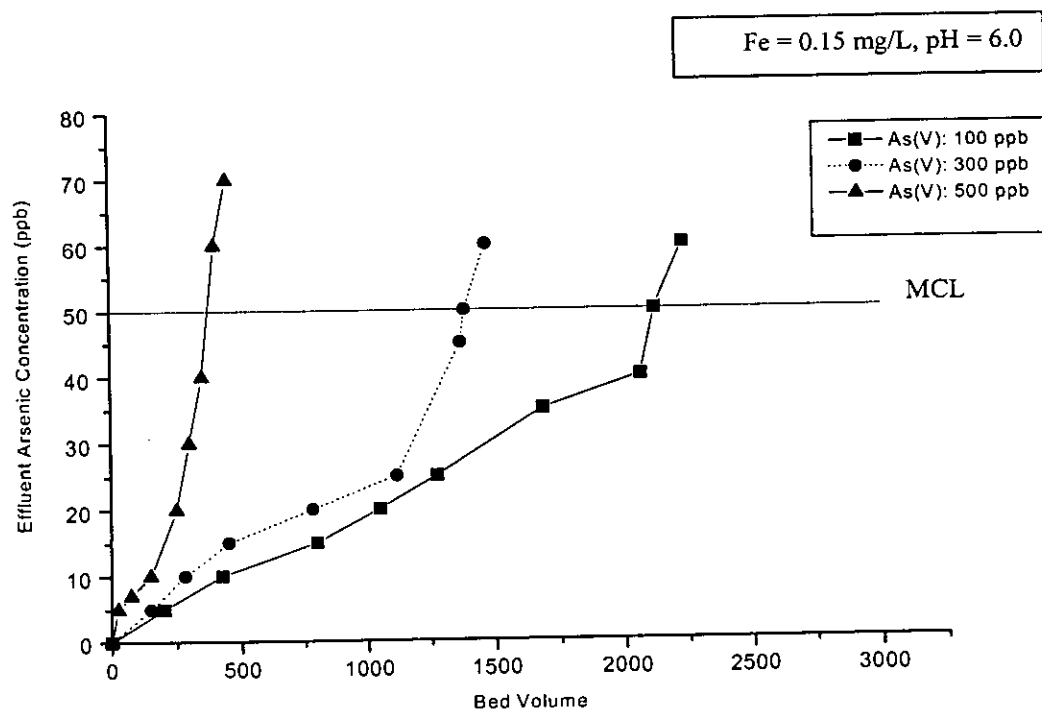


Figure 4.1: Pentavalent Arsenic adsorption curves for synthetic water.

than those of other curves. Low arsenic concentration in the influent causes lower value of residual arsenic in effluent after the adsorption of arsenic by activated alumina bed, whereas, for higher values of arsenic concentration in influent result high residual arsenic. Hence the curve for higher arsenic concentration is steeper in nature as compared to the lower one. Due to the nature of curves explained above, higher arsenic concentration in the influent causes lower bed volume and effluent reaches the Maximum Contaminant Level (MCL) of 50 ppb earlier. The adsorption sites of activated alumina are occupied at a faster rate by arsenic species as the arsenic concentration in the influent increased. This diminishes the bed capacity at a greater rate and the arsenic concentration in the effluent reached the MCL of 50 ppb at a lower bed volume. The adsorption curves are not smooth, especially that for

arsenic concentration of 100 ppb and 300 ppb. This is due to the experimental procedure. In the study it was not possible to run experiments continuously and at the end of the day experiments were stopped and again started next morning. Since tap water contains a little iron concentration ( $\text{Fe} = 0.15 \text{ mg/L}$ ), it is also adsorbed on activated alumina surface and makes a barrier to adsorb arsenic on it. As a result, effluent arsenic concentration raises rapidly and arsenic adsorption rate decreases. In the non-operating period of experiments, arsenic adsorbed on outer surface of activated alumina moves towards the center of alumina particle due to concentration gradient resulting in a decrease of arsenate ions on the outer surfaces. When the run is resumed arsenic is adsorbed at a higher rate initially and hence the effluent concentration does not show smooth variation.

Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level for different influent pentavalent arsenic concentration were determined and presented in Table 4.1. Treated Bed volumes are found to be 2115, 1383 and 375 for 100 ppb, 300 ppb and 500 ppb arsenic concentration, respectively. This data clearly shows that the bed volume decreases with the increase of arsenic concentration in the influent. In a study by Kartinen and Martin (1995), an activated alumina column treating water containing 100 ppb As(V) was able to treat about 23000 Bed volume before the effluent arsenic levels reached the 50 ppb level.

The quantity of adsorbed arsenic by activated alumina is found higher for higher arsenic concentration in the influent due to higher concentration gradient. But the quantity of adsorbed arsenic for 500 ppb arsenic concentration is also found to be low. This is because high arsenic concentration in the influent causes the residual arsenic in the effluent to reach the 50 ppb level at a low bed volume.

Table 4.1: Effect of As(V) concentration on Treated Bed Volume and Quantity of arsenic adsorbed by activated alumina.

Influent Iron (mg/L)	Influent pH Value	Influent As(V) concentration (ppb)	Bed Volume upto 50 ppb As level	As(V) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
0.15	6.0	100	2115	0.15
		300	1383	0.35
		500	375	0.16

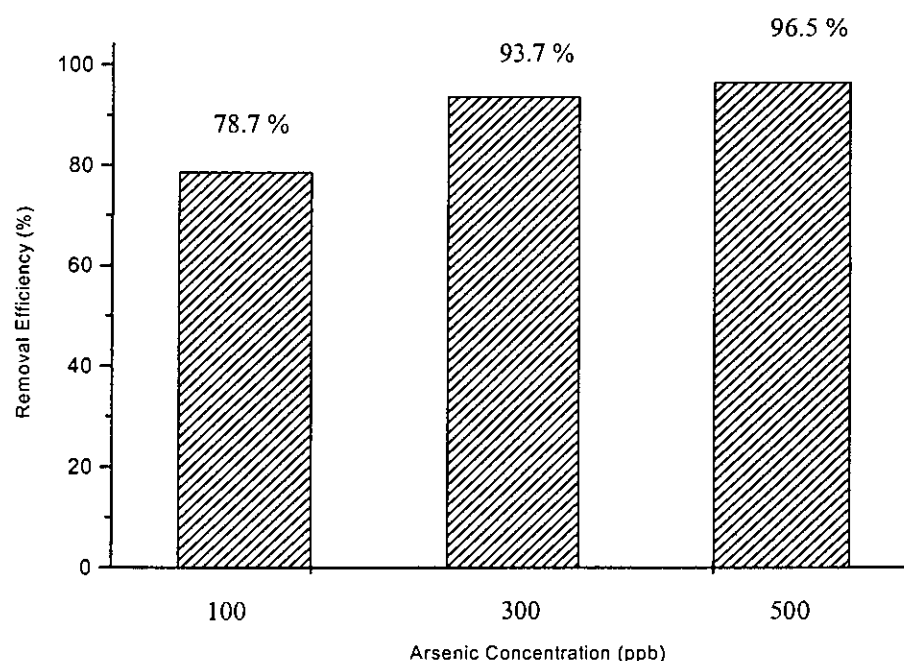


Figure 4.2: Bar diagram of arsenic removal efficiency with pentavalent arsenic concentration

The bar diagram of arsenic removal efficiency with pentavalent arsenic concentration is illustrated in Figure 4.2. Arsenic removal efficiency are found to be 78.7%, 93.7% and 96.5% for arsenic concentration of 100 ppb, 300 ppb and 500 ppb, respectively. Arsenic removal efficiency by activated alumina is directly related with arsenic concentration gradient between activated alumina surface and its surrounding. As the

concentration in the influent increases, arsenic adsorption rate of activated alumina also increases and removal efficiency is found to increase with the increase of arsenic concentration.

#### 4.2.2 Removal of Trivalent Arsenic

To observe the effect of trivalent arsenic concentration, experiment was done with synthetic groundwater having influent arsenic concentration 100 ppb, 300 ppb and 500 ppb and a fixed pH value of 7.0. Since the groundwater in Bangladesh contains iron and maximum acceptable limit according to Bangladesh standard is 1.0 mg/L, the experiments were conducted with a constant iron concentration of 1.0 mg/L. The experimental data are presented in Table-A4, A5 and A6 in Appendix-A and calculations to determine bed volume and arsenic removal efficiency are shown in tabular form in Appendix- B. The adsorption curves are shown in Figure 4.3. The

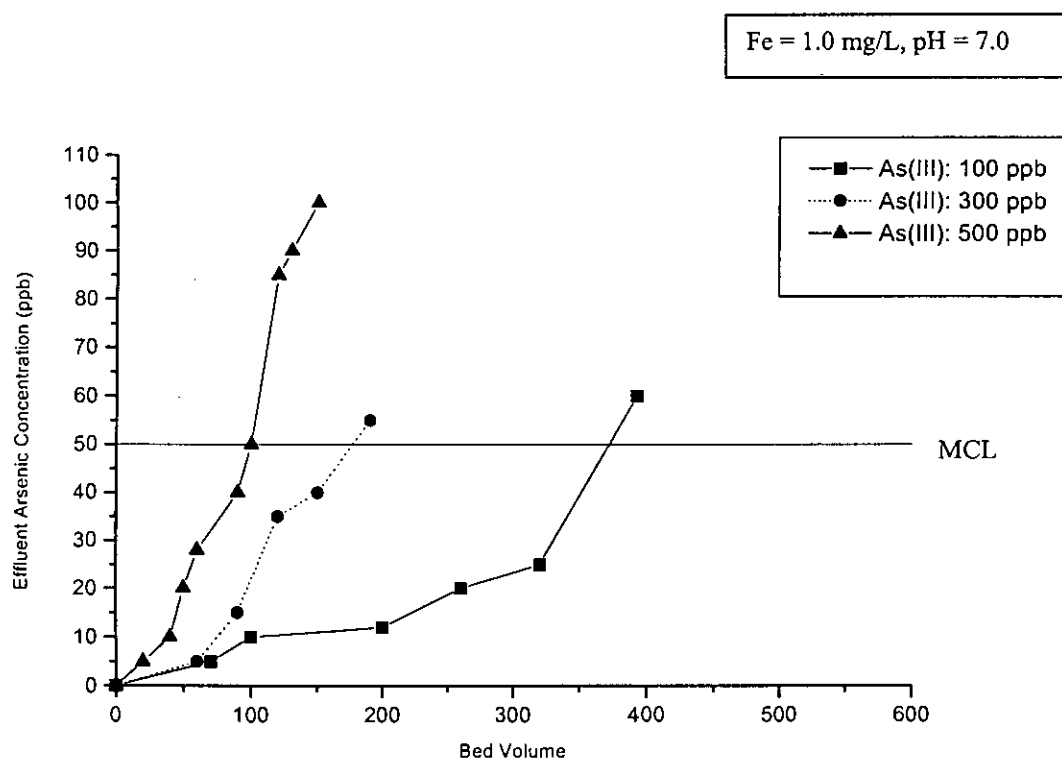


Figure 4.3: Trivalent Arsenic adsorption curves for synthetic water



curve for arsenic concentration of 500 ppb is found to be steeper compared to the 300 ppb curve, whereas, the curve for 100 ppb is less steeper. In the case of high arsenic concentration in the influent, adsorption takes place at a faster rate and the mass transfer zone moves faster. The activated alumina bed becomes exhausted by arsenic species more quickly for high arsenic concentration in the influent. This diminishes the bed capacity at a greater rate and the arsenic concentration in the effluent reaches the MCL of 50 ppb at a lower bed volume. So, the curve, having arsenic concentration 500ppb, reaches the MCL earlier as compared with that for 300 ppb or 100 ppb. Again, the bed volume is too low as compared with corresponding pentavalent arsenic case. It indicates that activated alumina has little affinity for As(III) species. Due to non-ionization of As(III) species within the common pH range (6.0-7.5) of water, As(III) is less adsorbed on activated alumina surface.

Treated Bed Volume and quantity of arsenic adsorbed by the activated alumina bed upto 50 ppb arsenic level for different influent trivalent arsenic concentration were determined using the absorption curves and are presented in Table 4.2. Treated bed volumes are found to be 372, 176 and 100 for 100 ppb, 300 ppb and 500 ppb arsenic concentrations, respectively. The study reveals that bed volume decreases with the

Table 4.2: Effect of As(III) concentration on Treated Bed Volume and Quantity of arsenic adsorbed by activated alumina.

Influent Iron (mg/L)	Influent pH Value	Influent As(III) concentration (ppb)	Bed Volume upto 50 ppb As level	As(III) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
1.0	7.0	100	372	0.03
		300	176	0.04
		500	100	0.04

increase of influent arsenic concentration. In a study by Kartinen and Martin (1995), an activated alumina column treating water with 100 ppb As(III) was able to treat about 300 bed volume at a pH 6.0 before the effluent arsenic levels reached 50 ppb.

This value is some what less than the result obtained from the present study. Presence of iron is mainly responsible for this. Arsenite species are adsorbed on the iron flocs accumulated in the alumina bed resulting in higher bed volume. The quantity of arsenic adsorbed by activated alumina increases with the increase of arsenic concentration. As arsenite is poorly adsorbed on alumina surface, the quantity of arsenic adsorbed does not show any marked variation with influent arsenic concentration. shows high adsorption value.

The bar diagram of arsenic removal efficiency with trivalent arsenic concentration is illustrated in Figure 4.4. Arsenic removal efficiency is found to be 84.5%, 93.4% and 95.9% for 100 ppb, 300 ppb and 500 ppb arsenic concentrations, respectively. Actually high arsenic concentration gradient between activated alumina surface and

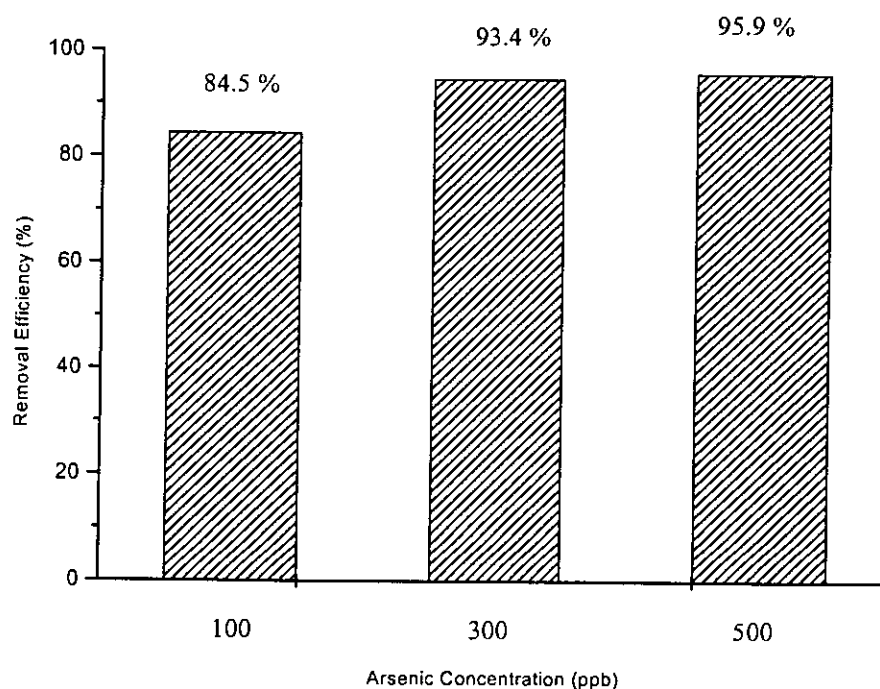


Figure 4.4: Bar diagram of arsenic removal efficiency with trivalent arsenic concentration.

its surrounding cause increase of arsenic adsorption rate on activated alumina surface. As a result, arsenic removal efficiency of activated alumina bed increases when influent arsenic concentration increases.

### 4.3 Effect of Iron Concentration

Iron concentration may have a significant effect on the removal capacity of activated alumina. Both pentavalent and trivalent arsenic were used separately to study this effect.

#### 4.3.1 Removal of Pentavalent Arsenic

To study the effect of iron on arsenic removal efficiency of activated alumina, experiments were conducted with synthetic raw water having influent iron concentration 0.0 mg/L (distilled water), 0.15 mg/L (tap water), 1.0 mg/L, 3.0 mg/L and 5.0 mg/L and a fixed pH value of 6.0 and arsenic concentration of 300 ppb. The experimental data are presented in Table-A7, A8, A9, A10 and A11 in Appendix-A. Calculations to determine bed volume and arsenic removal efficiency are presented in tabular form in Appendix- B. Figure 4.5 shows the relationship between effluent arsenic concentration and bed volume, through which the adsorption capacity of arsenic on the activated alumina bed can be determined. From the Figure it is observed that high iron concentration in the influent causes high residual arsenic concentration in the effluent. Generally when the iron concentration increases the deposition of iron floc on activated alumina surface increases. As a result, available sites for arsenic species adsorption on activated alumina decrease. Hence the curve for high iron concentration shows steeper slope whereas a better adsorption of arsenic species is observed in case of low iron concentration in the influent and the adsorption curve in that case is found less steeper. Figure 4.5 also reveals that higher the iron concentration in the influent, the lower the bed volume is obtained. It is to be

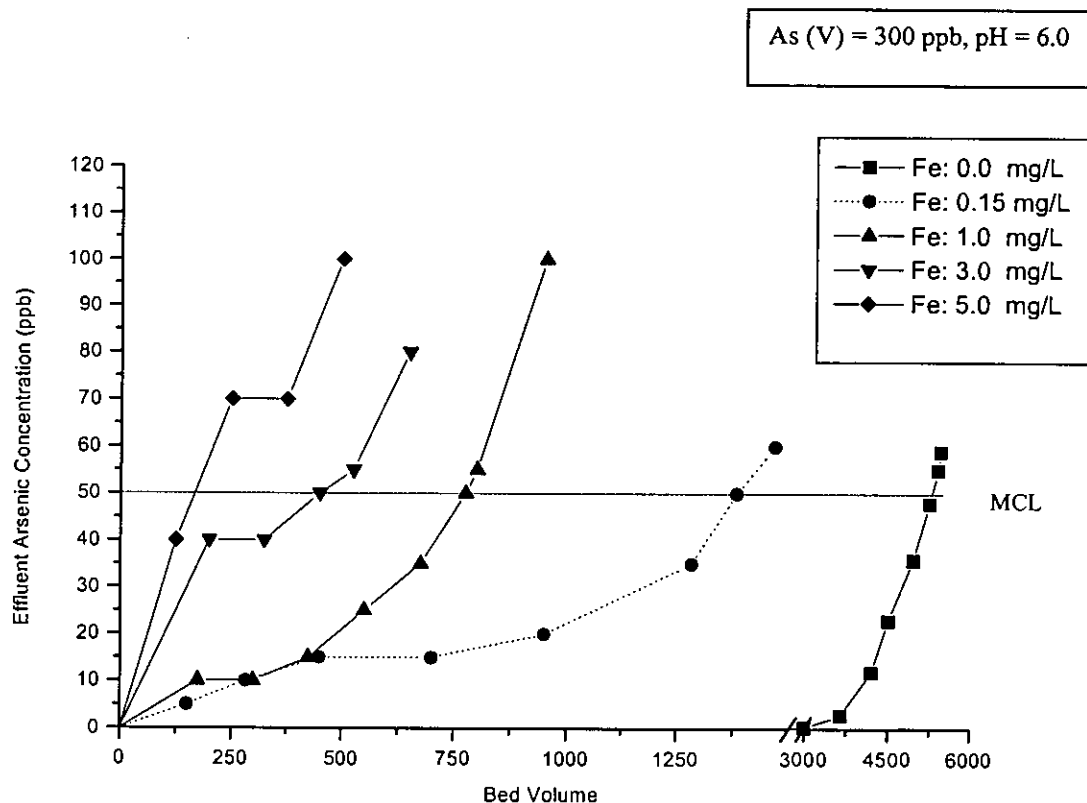


Figure 4.5: Effect of iron on adsorption characteristics of activated alumina for As(V).

noted that, when there is no iron in the influent, a very large BV (5287) is obtained. Presence of a little iron decreases the BV to 1383 by making a coating on the activated alumina granules thereby blocking the diffusion of arsenic species into the inner surfaces of the granules. As the iron concentration increases, the coatings become thicker resulting in progressively lower BV. Discontinuity of run and intermittent stirring were responsible for non-smooth nature of the adsorption curves especially for high iron concentration.

Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level for different influent iron concentration were determined and presented in Table 4.3. Treated bed volumes are found to be 5287, 1383, 775, 450 and 160 for 0.0 mg/L, 0.15 mg/L, 1.0 mg/L, 3.0 mg/L and 5.0 mg/L iron concentrations, respectively. The quantity of arsenic adsorbed by activated alumina is

found decreasing from 1.4 mg/g to 0.04 mg/g for iron concentration of 0.0 mg/L and 5.0 mg/L, respectively. Gupta and Chen reported an arsenic adsorption capacity 4 mg/g of activated alumina for the pH value 6.0 (Gupta and Chen, 1978), whereas, Fox reported 1.0 mg/g for pH ranges between 7.4 to 8.0 (Fox, 1989). The results of the present study support the data obtained by Fox. The bed volume as well as

Table 4.3: Effect of iron on Treated Bed Volume and Quantity of adsorbed arsenic by activated alumina for As(V).

Influent As(V) concentration (ppb)	Influent pH Value	Influent Iron (mg/L)	Bed Volume upto 50 ppb As level	As(V) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
300	6.0	0.0	5287	1.4
		0.15	1383	0.35
		1.0	775	0.20
		3.0	450	0.11
		5.0	160	0.04

quantity of arsenic adsorbed by activated alumina bed is found decreases with the increase of iron concentration. Actually, while influent passes through the bed, the iron flocs adhere to the surface of activated alumina and thus makes a barrier for the arsenic species to come in contact with the adsorption sites. Floc formation rate is more rapid in case of higher iron concentration in the raw water. Hence flocs enveloped the alumina particles more quickly with thicker layer around them when the iron concentration was higher and results in high residual arsenic concentration in the effluent.

The arsenic removal efficiency for different iron concentration is illustrated in Figure 4.6. Arsenic removal efficiency is found to be 97.5%, 94.0%, 93.9%, 89.2% and 91.5% for 0.0 mg/L, 0.15 mg/L, 1.0 mg/L, 3.0 mg/L and 5.0 mg/L iron concentrations, respectively. It is seen that removal efficiency decreases with the increase of iron concentration except that for iron concentration of 5 mg/L. Since iron flocs adhere to the surface of activated alumina and makes a barrier for the arsenic

species to come in contact with the adsorption sites, the adsorption rate of activated alumina decreases as the increases of iron concentration in the influent. But when the iron concentration becomes high such as 5 mg/L, the iron flocs make the alumina ineffective within a short period of time and the efficiency is slightly increased due to adsorption of arsenic on large mass of iron flocs accumulated in the bed.

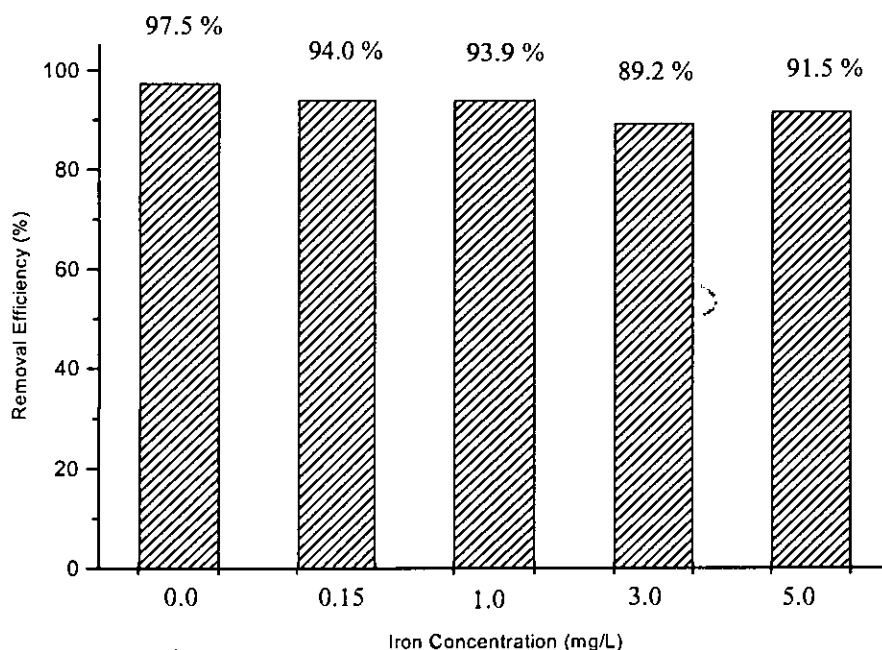


Figure 4.6: Bar diagram of arsenic removal efficiency with iron concentration for As(V).

#### 4.3.2 Removal of Trivalent Arsenic

To observe the effect of iron concentration on trivalent arsenic, test was performed with synthetic raw water having different iron concentrations of 0.15 mg/L (tap water), 1.0 mg/L, 3.0 mg/L, 5.0 mg/L and 7.0 mg/L with a fixed pH value of 7.0 and arsenic concentration of 300 ppb. The experimental data are presented in Table-A12, A13, A14, A15 and A16 in Appendix-A and calculations to determine bed volume and arsenic removal efficiency are presented in tabular form in Appendix- B. Figure

4.5 presents the relationship between adsorption curves. The Figure shows that the presence of iron in raw water at a low concentration produces smooth adsorption curve, whereas, for high iron concentration shows adsorption curves of irregular nature. Normally trivalent arsenic species has little affinity for activated alumina surface as compared with pentavalent one and arsenic is mainly adsorbed onto the iron flocs contained in the activated alumina filter bed. In the case of low iron concentration, a small amount of iron flocs is produced and retained by the alumina bed, little adsorption of the arsenic takes place and the residual arsenic in the effluent increases rapidly resulting in very steeper slope. Higher iron concentrations in the

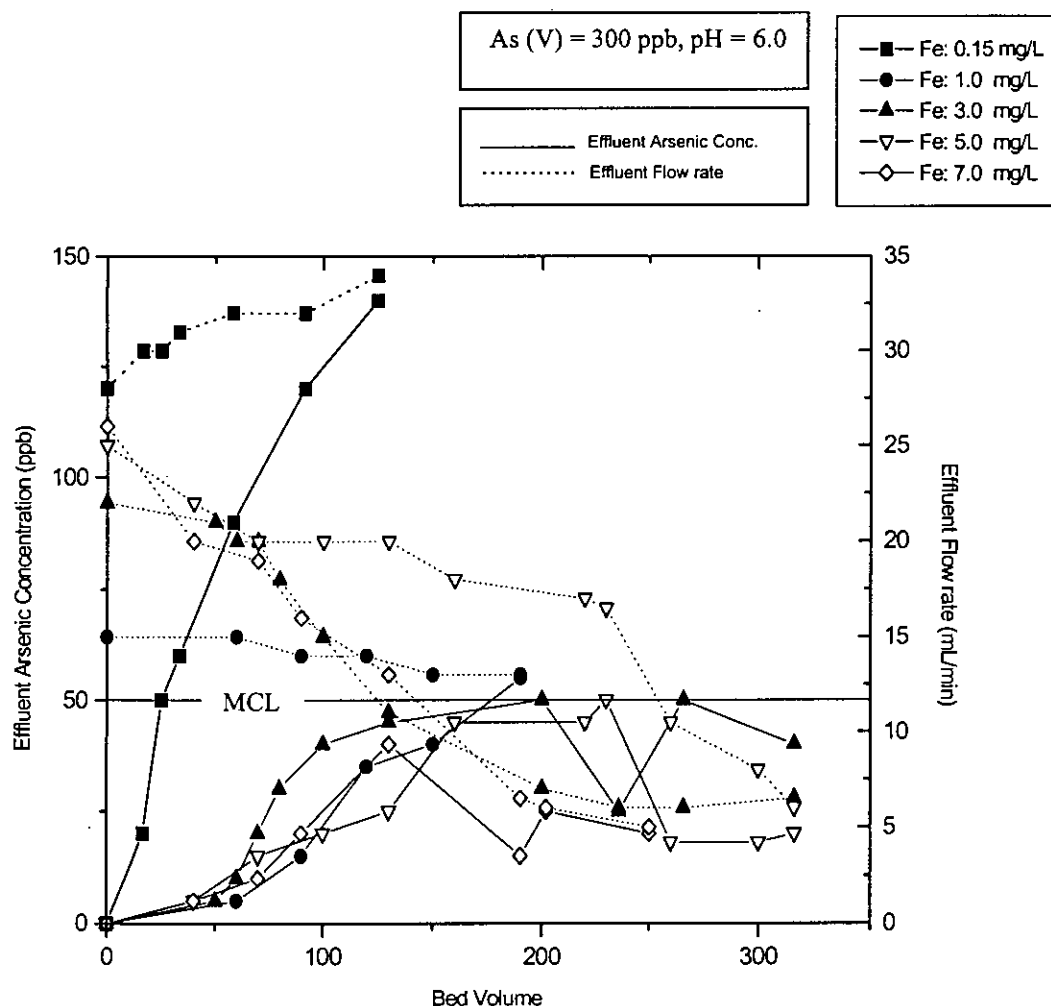


Figure 4.7: Effect of iron on adsorption characteristics of activated alumina for As(III).

influent contribute more adsorbing mass in the feed tank resulting in adsorption of a significant amount of arsenic before the influent flows into the alumina column. The oxidation of ferrous iron to ferric form is faster at pH above 6.5. Since the pH in this experiment was kept at 7.0, the solubility of iron decreased significantly and iron flocs formation rate increased with the increase of iron concentration in the influent. The flocs adhered not only on the surface of the feed tank but also on the activated alumina surface. They were also entrapped within the interstices of activated alumina particles. Due to the entrapping of the flocs, the flow rate of the effluent became progressively lower and resulted in higher empty bed contact time as the cumulative flow volume through the bed increased. Due to longer contact time higher amount of arsenic was adsorbed onto the iron flocs and the concentration of residual arsenic in the effluent increased slowly with increasing BV. Intermittent stirring is mainly responsible for non-smoothness of the adsorption curves for higher iron concentrations. In case of heavy clogging with flocs at high iron concentrations, the bed became inoperative because of very low flow rate and then the effluent arsenic concentration was much lower than the 50 ppb level due to very long contact time. Eventually, the run was stopped.

Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level for different influent iron concentration were determined and presented in Table 4.4. Treated Bed volumes are found to be 25, 176, 200 and 316 for 0.15 mg/L, 1.0 mg/L, 3.0 mg/L and 5.0 mg/L iron concentrations, respectively. The

Table 4.4: Effect of Iron on Treated Bed Volume and Quantity of adsorbed arsenic by activated alumina for As(III).

Influent As(III) concentration (ppb)	Influent pH Value	Influent Iron (mg/L)	Bed Volume upto 50 ppb As level	As(III) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
300	7.0	0.15	25	0.01
		1.0	176	0.04
		3.0	200	0.05
		5.0	316	0.08
		7.0	-	-



quantity of arsenic adsorbed by activated alumina is found increasing from 0.01 mg/L to 0.08 mg/L for iron concentration of 0.15 mg/L and 5.0 mg/L, respectively. It reveals that the bed volume as well as quantity of arsenic adsorbed by activated alumina increases with the increase of iron concentration. Bed volume and quantity of arsenic adsorbed by activated alumina for 7.0 mg/L can not be determined since the adsorption curve failed to reach the 50 ppb level as the run was stopped due to very low flow rate. In general, as As(III) species has little affinity for activated alumina adsorption sites, the presence of iron is responsible for increasing BV with higher iron dosing by supplying higher mass of iron sludge into the bed which adsorbs arsenic and reduces flow velocity enhancing the adsorption.

The increase of iron concentration in the influent causes an increase of arsenic adsorption rate by the accumulated sludge in the activated alumina bed. Increase of iron content virtually causes deep bed penetration of iron flocs along with deposition of iron sludge blanket in thick layer on the activated alumina bed top. In such a case arsenic is removed mainly due to the adsorption on iron flocs retained by the alumina bed.

Figure 4.8 presents bar diagram showing the arsenic removal efficiency for different iron concentrations. Arsenic removal efficiency is found to be 93.9 %, 93.4 %, 90.2 %, 91.7 %,

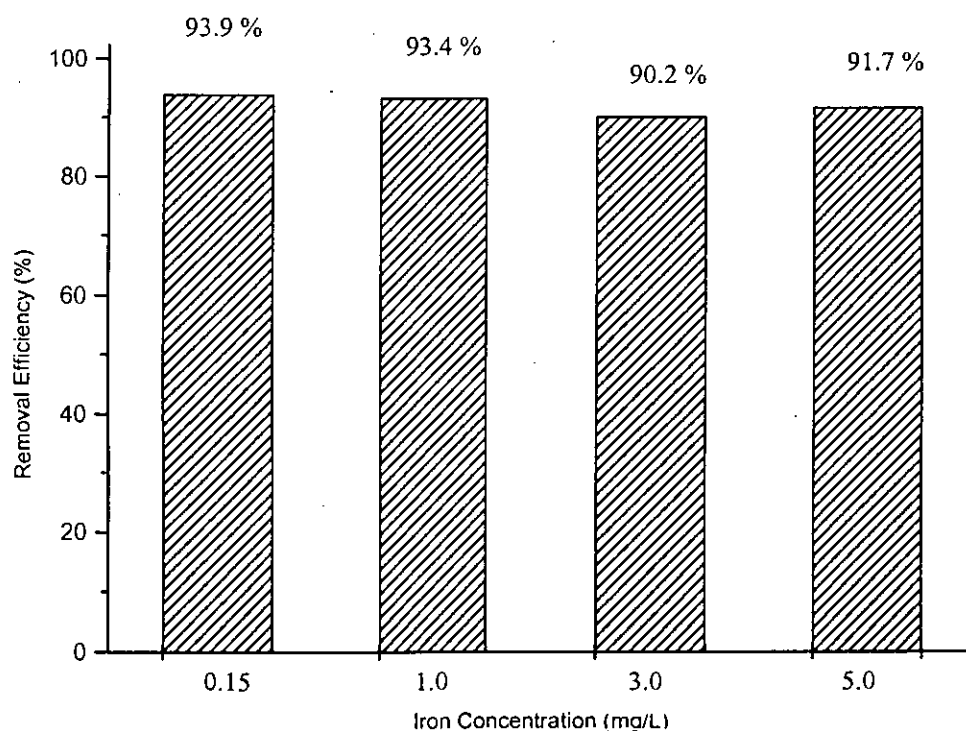


Figure 4.8: Bar diagram of arsenic removal efficiency with iron concentration for As(III).

90.2 % and 91.7 % for 0.15 mg/L, 1.0 mg/L, 3.0 mg/L and 5.0 mg/L iron concentrations, respectively. It is seen that the removal efficiency varies a little with iron concentration.

#### 4.4 Effect of pH

Sorption on activated alumina is sensitive to pH. Both pentavalent and trivalent arsenic were used separately to study the effect of pH on arsenic removal capacity.

##### 4.4.1 Removal of Pentavalent Arsenic

To study the effect of pH on pentavalent arsenic removal efficiency of activated alumina, experiments were conducted with synthetic raw water having influent pH values of 5.0, 6.0 and 7.5 and a constant arsenic concentration of 300 ppb. Since the groundwater in Bangladesh contains iron and maximum acceptable limit according to Bangladesh standard is 1.0 mg/L, the experiments were conducted with a constant iron concentration of 1.0 mg/L. The experimental data are presented in Table-A17, A18 and A19 in Appendix-A and calculations to determine bed volume and arsenic removal efficiency are presented in tabular form in Appendix- B. The relationship between effluent arsenic concentration and bed volume is presented in Figure 4.9. Observation shows that the adsorption curve for pH value 6.0 and 5.0 have more gentle slope as compare with that for pH value 7.5. Pentavalent arsenic is dissociated into  $\text{H}_2\text{AsO}_4^-$  arsenate ion when pH value is less than 7.0 and has relatively higher affinity for activated alumina adsorption sites. Hence the residual arsenic in the effluent has been found relatively lower when pH is 5.0 and 6.0.

Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level for different influent pH value were determined and presented in Table 4.5. Treated bed volumes are found to be 683, 775 and 290 for pH values of

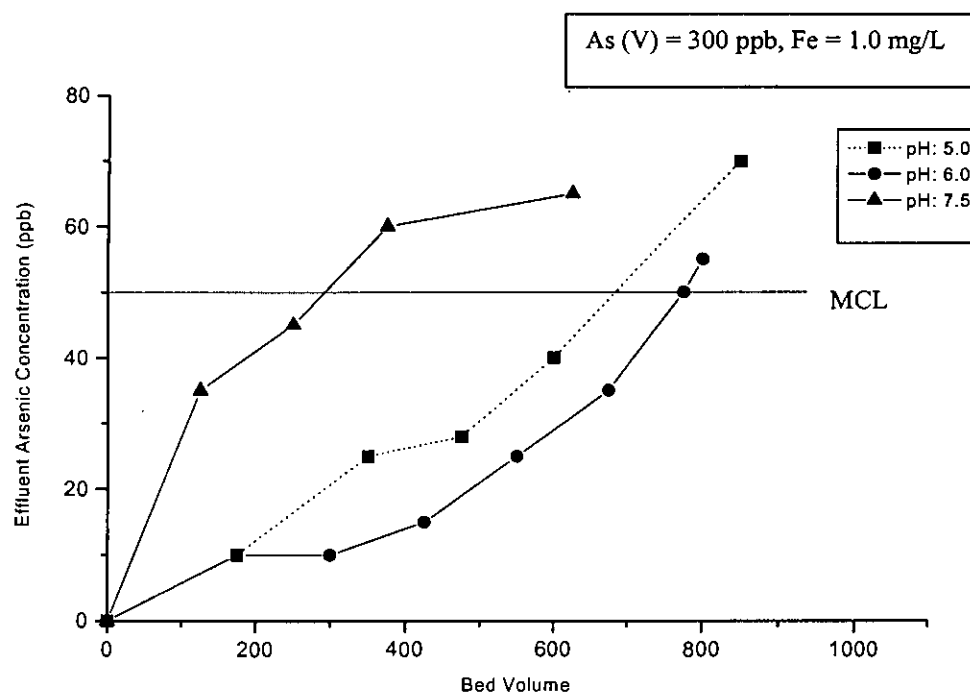


Figure 4.9: Effect of pH on adsorption characteristics of activated alumina for As(V).

5.0, 6.0 and 7.5, respectively. It is revealed that arsenic adsorption rate is enhanced by activated alumina at pH 6.0 as compared with other pH values. Since the degree of adsorption of As(V) species on activated alumina surface is greatly reduced as

Table 4.5: Effect of pH on Treated Bed Volume and quantity of arsenic adsorbed by activated alumina for As(V).

Influent As(V) concentration (ppb)	Influent Iron (mg/L)	Influent pH Value	Bed Volume upto 50 ppb As level	As(V) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
300	1.0	5.0	683	0.17
		6.0	775	0.2
		7.5	290	0.07

the influent water becomes more alkaline, the bed volume as well as quantity of arsenic adsorbed by activated alumina are found low (0.07 mg/L) at pH value of 7.5.

The arsenic removal efficiency for different pH is presented as bar diagram in Figure 4.10. The arsenic removal efficiency is found to be 92.0%, 93.9% and 89.6% for pH value of 5.0, 6.0 and 7.5, respectively. It is observed that arsenic removal efficiency is relatively higher in the pH range of 5.0 – 6.0 and the optimum pH is 6.0.

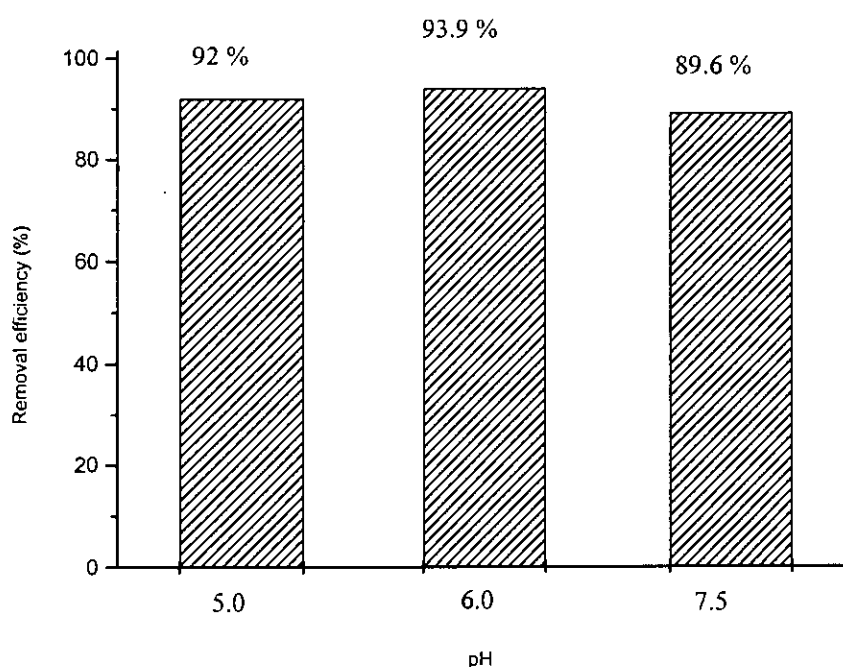


Figure 4.10: Bar diagram of arsenic removal efficiency with pH value for As(V).

#### 4.4.2 Removal of Trivalent Arsenic

To study the effect of pH on trivalent arsenic removal efficiency of activated alumina, experiments were conducted with synthetic raw water having influent pH values of 6.0, 7.0 and 8.0 and a constant arsenic concentration of 300 ppb. Since the groundwater in Bangladesh contains iron and maximum acceptable limit according to Bangladesh standard is 1.0 mg/L, the experiments were conducted with a constant

iron concentration of 1.0 mg/L. The experimental data are presented in Table-A20, A21 and A22 in Appendix-A and calculations to determine bed volume and arsenic removal efficiency are represented in tabular form in Appendix- B. The relationship between effluent arsenic concentration and bed volume is presented in Figure 4.11. From the Figure it is found that the adsorption curve having low pH value (6.0)

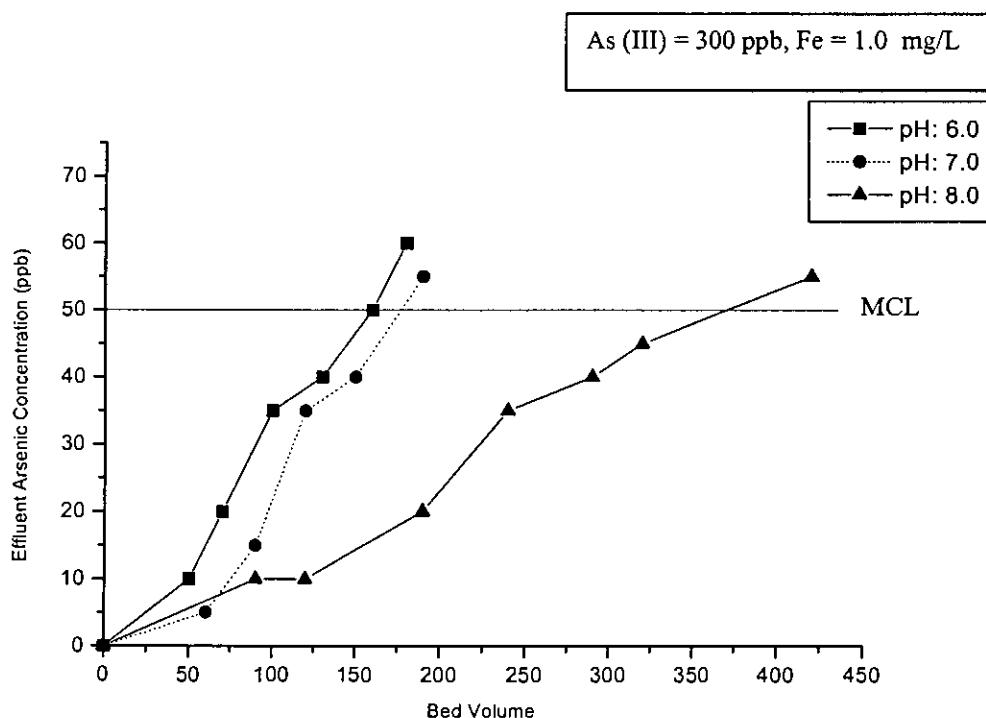


Figure 4.11 Effect of pH on adsorption characteristics of activated alumina for As(III).

shows steeper slope as compared with other pH values. Actually the effluent is found containing high residual arsenic at a low pH because, trivalent arsenic exists in water in non-ionized form when pH value is less than 8.0. As a result the arsenic adsorption rate on activated alumina surface is higher for high pH value. The raw water contained ferrous iron that oxidized to ferric iron by forming iron flocs and caused to adsorb arsenic species at low pH value (less than 8.0). This adsorption rate also increases with the increase of pH value. This is because, the oxidation of ferrous to ferric form is found very slow at a pH below 6.5. The rate of reaction of ferrous iron increases 100-fold with a unit increase in pH. As a result the solubility of iron decreases significantly at a high pH and the large quantity of iron flocs in influent

passes through activated alumina bed. These iron flocs play vital role to adsorb arsenic and results low effluent arsenic concentration.

Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level for different influent pH values were determined and presented in Table 4.6. Treated bed volumes are found to be 160, 176 and 370 for pH values of 6.0, 7.0 and 8.0, respectively. As the activated alumina bed shows better adsorption at a higher pH, the bed volume are found increasing as the pH value increases. Besides, iron oxidation rate as well as iron flocs formation rate increases as the pH value increases and causes to increase the arsenic adsorption rate on iron flocs and the bed volume as well as quantity of adsorbed arsenic is found higher at a high pH value. The quantity of adsorbed arsenic by activated alumina surface is found to be 0.04 mg/g, 0.04 mg/g and 0.09 mg/g for pH value of 6.0, 7.0 and 8.0, respectively.

Table 4.6: Effect of pH on Treated Bed Volume and Quantity of adsorbed arsenic by activated alumina for As(III).

Influent As(III) concentration (ppb)	Influent Iron (mg/L)	Influent pH Value	Bed Volume upto 50 ppb As level	As(III) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
300	1.0	6.0	160	0.04
		7.0	176	0.04
		8.0	370	0.09

The arsenic removal efficiency for different pH can be expressed through the bar diagram, which is shown in Figure 4.12. Arsenic removal efficiency is found to be 93.3 %, 93.4 % and 92.2 % for pH value of 6.0, 7.0 and 8.0, respectively.

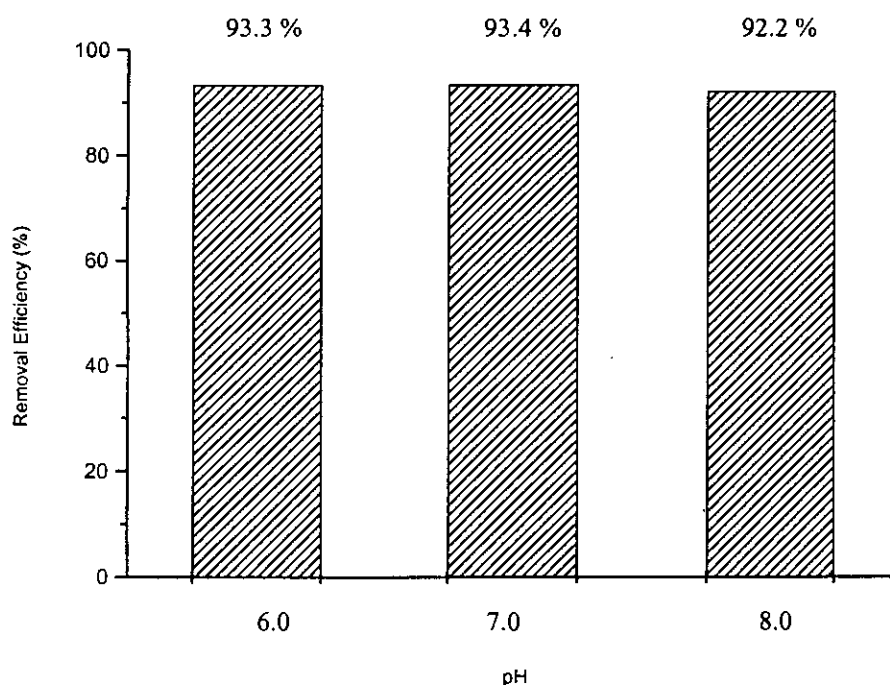


Figure 4.12: Bar diagram of arsenic removal efficiency with pH value for As(III).

#### 4.5 Effect of Chloride

To study the effect of chloride on arsenic removal efficiency of activated alumina, experiments were conducted with synthetic raw water having influent chloride concentrations of 300 mg/L, 700 mg/L and 1100 mg/L and a constant As(V) concentration of 500 ppb and a fixed pH value 7.0. To maintain constant iron concentration tap water was used ( $\text{Fe} = 0.15 \text{ mg/L}$ ) for the experiment. The experimental data are presented in Table-A23, A24 and A25 in Appendix-A and calculations to determine bed volume and arsenic removal efficiency are presented in tabular form in Appendix- B. The relationship between effluent arsenic concentration and bed volume is presented in Figure 4.13. It shows that each of the three adsorption curves for chloride concentrations of 300 mg/L, 700 mg/L and 1100 mg/L in the influent shows low residual arsenic concentration after passing through the activated

alumina bed. Actually the initial flow rate plays a major role and influence the characteristics of these curves. The flow rate for chloride concentration of 300 mg/L was relatively higher as compared with other two observations (both of them had almost same flow rates). As a result the empty bed contact time for that case was found low which causes relatively high residual arsenic concentration in the effluent and the adsorption curve shows higher peak than other two curves. Again, the raw water contained iron and caused iron floc formation during the run. Iron floc deposited on the top of activated alumina bed as well as within the interstices of activated alumina particles. Hence, the flow rates of the runs became too low within a

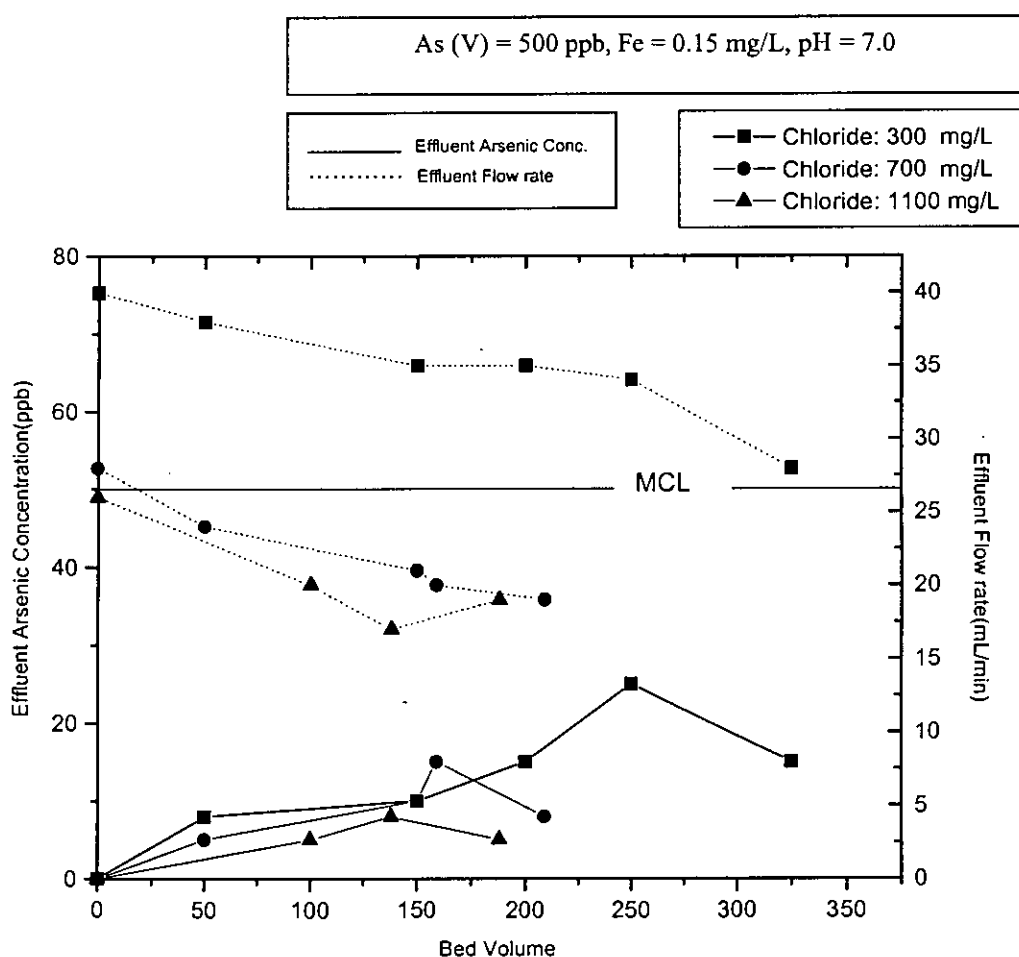


Figure 4.13: Effect of Chloride concentration on adsorption characteristics of activated alumina.



short period of time thus increasing the empty bed contact time. As a result the effluent arsenic concentration did not reach the 50 ppb level. Finally, the runs had to stop due to low flow rate. For that reason it was not possible to determine treated bed volume and quantity of adsorbed arsenic by activated alumina upto 50 ppb arsenic level for different influent chloride concentration. Hence it can be concluded that the presence of chloride in the influent has no effective role on the arsenic removal capacity of activated alumina bed.

#### 4.6 Effect of Sulfate

To study the effect of presence of sulfate on arsenic removal efficiency of activated alumina, experiments were conducted with synthetic raw water having influent sulfate concentration of 60 mg/L, 335 mg/L and 740 mg/L, a constant As(V) concentration of 500 ppb and a fixed pH value 7.0. In this study high sulfate concentrations were used for a clear understanding of its effect on arsenic removal efficiency. To maintain constant iron concentration tap water was used ( $\text{Fe} = 0.15 \text{ mg/L}$ ) for the experiment. The experimental data are presented in Table-A26, A27 and A28 in Appendix-A and calculations to determine bed volume and arsenic removal efficiency are presented in tabular form in Appendix- B. The relationship between effluent arsenic concentration and bed volume is presented in Figure 4.14. It shows that, sulfate changes the arsenic adsorption characteristics of activated alumina. Since sulfate ion has affinity for sorption sites of activated alumina, it competes with arsenic ion for the adsorption sites. Hence, the presence of competing ions (like sulfate) in the influent causes to reduce the adsorption rate of arsenic species on activated alumina surface and results in higher residual arsenic concentration in the effluent. The initial flow rate also influenced the nature of the curves. The flow rate for sulfate concentration of 335 mg/L was relatively low as compared with other two cases which had almost same flow rate. As a result the residual arsenic concentration in the effluent was relatively low for the case of 335 mg/L sulfate concentration.

Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level for different influent pH value were determined and presented in Table 4.7. The bed volumes are found to be 234, 220 and 166 for sulfate concentration of 60 mg/L, 335 mg/L and 740 mg/L, respectively. It reveals that with

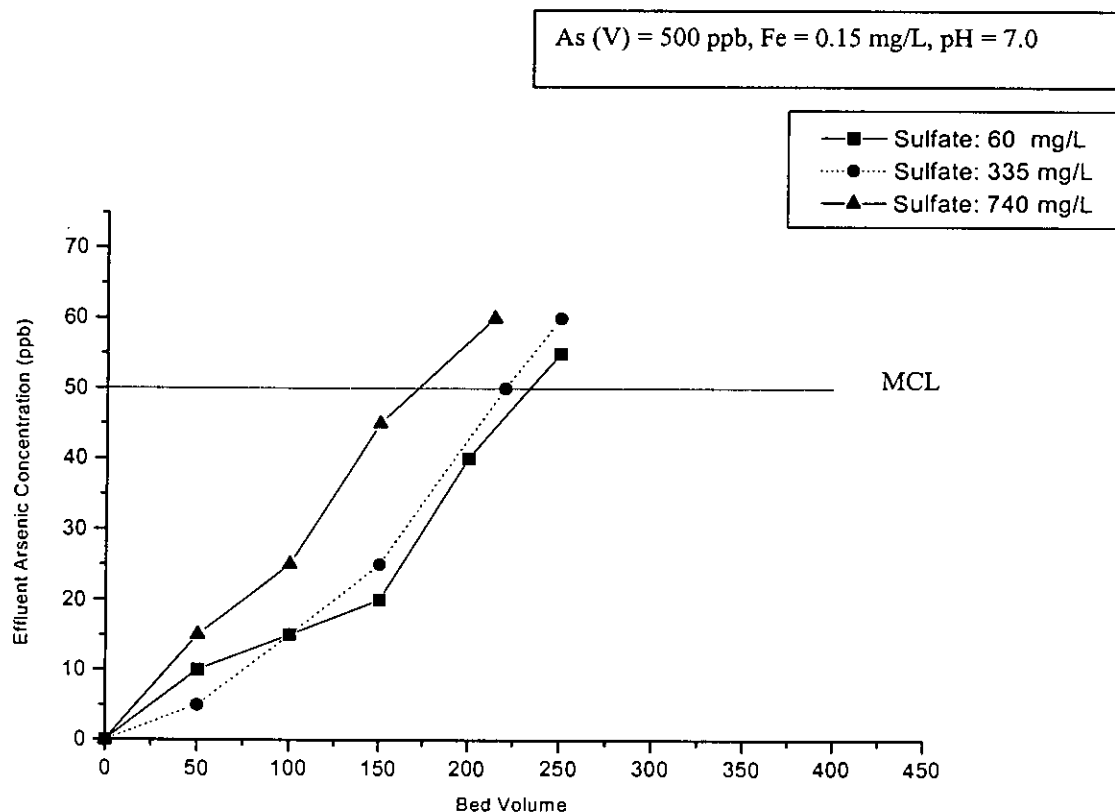


Figure 4.14: Effect of Sulfate concentration on adsorption characteristics of activated alumina.

the increase of sulfate concentration causes to decrease of the effluent bed volume but the reduction in bed volume is significant only at very high sulfate concentrations. The quantity of arsenic adsorbed by activated alumina is also found decrease to a little with the increase of sulfate concentration and the study reveals that the quantity of adsorbed arsenic are 0.1 mg/g, 0.09 mg/g and 0.07 mg/g for sulfate concentration of 60 mg/L, 335 mg/L and 740 mg/L, respectively.

Table 4.7: Effect of Sulfate on Treated Bed Volume and Quantity of adsorbed arsenic by activated alumina for As(V).

Influent As(V) concentration (ppb)	Influent Iron (mg/L)	Influent pH Value	Influent Sulfate (mg/L)	Bed Volume upto 50 ppb As level	As(V) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
500	0.15	7.0	60	234	0.1
			335	220	0.09
			740	166	0.07

The arsenic removal efficiency for different sulfate contents is shown in Figure 4.15. The arsenic removal efficiency is found to be 95.9 %, 96.1 % and 95.3 % for 60 mg/L, 335 mg/L and 740 mg/L sulfate concentrations, respectively.

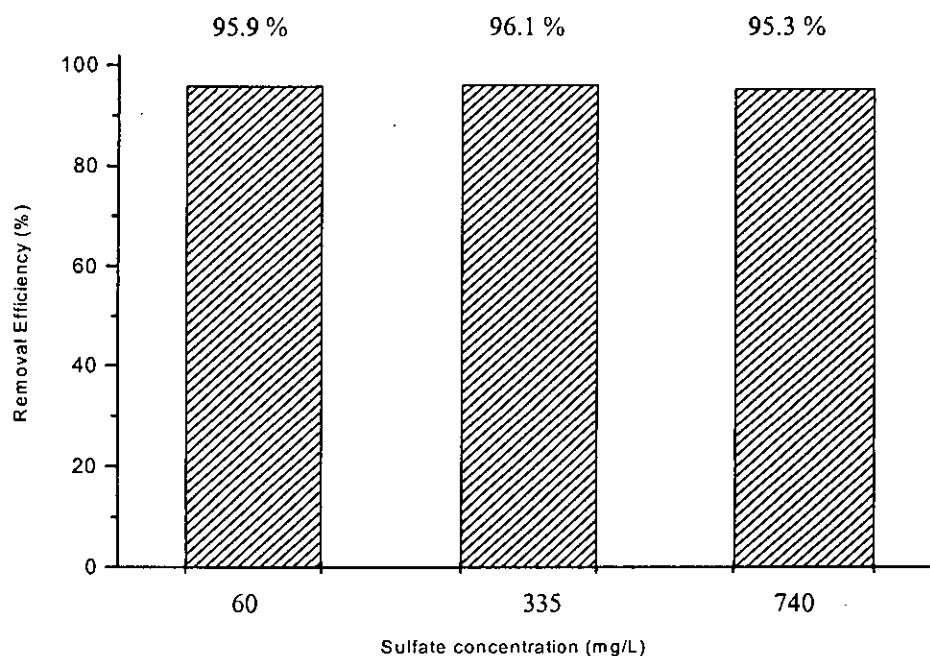


Figure 4.15: Bar diagram of arsenic removal efficiency with Sulfate Concentration.

#### 4.7 Effect of Phosphate

To study the effect of phosphate on arsenic removal efficiency of activated alumina, experiments were conducted with synthetic raw water having influent phosphate concentration of 0.68 mg/L, 160 mg/L and 345 mg/L, a constant As(V) concentration of 300 ppb and a fixed pH value 7.0. In this study high phosphate concentrations were used to highlight its effect on the adsorption phenomenon. To maintain a constant iron concentration tap water was used ( $\text{Fe} = 0.15 \text{ mg/L}$ ) for the experiment. Activated alumina size 28x48 was used in this experiment. The experimental data are presented in Table-A29, A30 and A31 in Appendix-A and calculations to determine bed volume and arsenic removal efficiency are presented in tabular form in Appendix- B.

Effect of phosphate concentration on the adsorption characteristics of activated alumina is shown in Figure 4.16. From the Figure it is seen that the adsorption curve

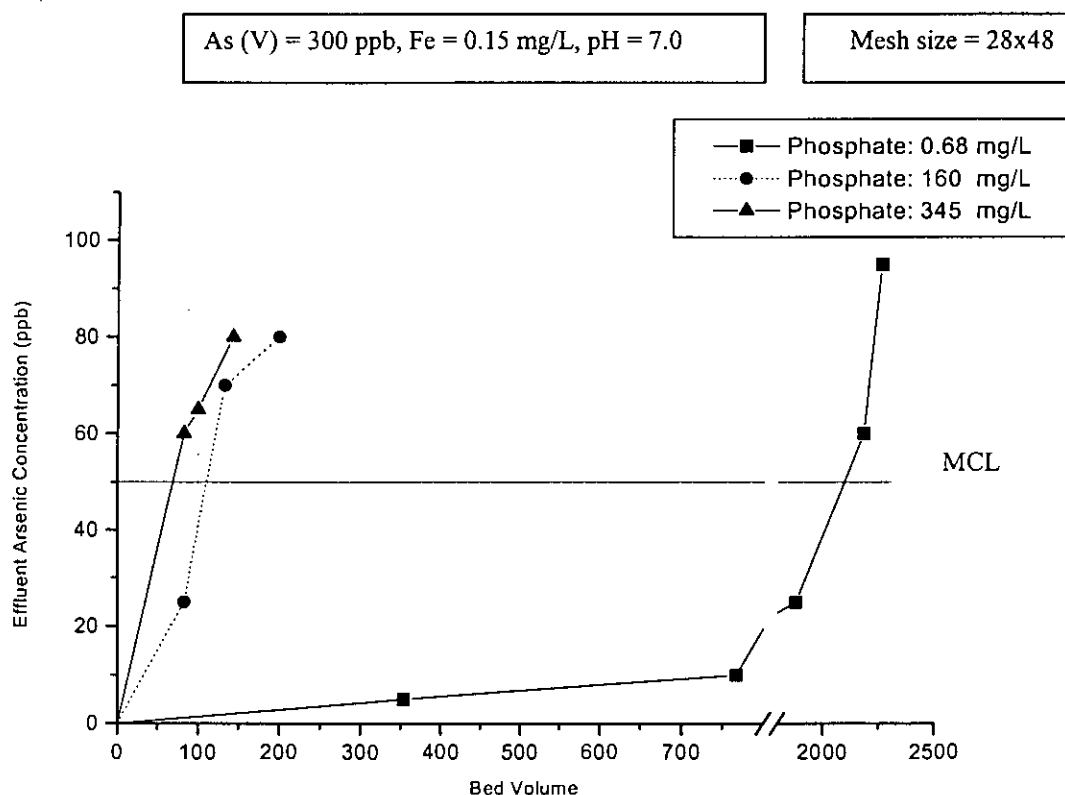


Figure 4.16: Effect of Phosphate concentration on adsorption characteristics of activated alumina.

for a high phosphate concentration (say 345 mg/L) is steeper as compared with that for a relatively lower phosphate concentration and the curve for phosphate concentration of 0.68 mg/L has a mild slope upto a large bed volume. It reveals that phosphate has high affinity for adsorption sites of activated alumina. It competes with the arsenate ion for the adsorption sites resulting in an increase in the effluent arsenic concentration rapidly when the phosphate concentration is high.

Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level for different influent phosphate concentration were determined and presented in Table 4.8. The bed volume are found to be 2100, 110 and 70 for influent phosphate concentration of 0.68 mg/L, 160 mg/L and 345 mg/L, respectively. Table 4.8 also presents the arsenic adsorbed by activated alumina upto 50 ppb arsenic level.

Table 4.8: Effect of Phosphate on Treated Bed Volume and Quantity of adsorbed arsenic by activated alumina for As(V).

Influent As(V) concentration (ppb)	Influent Iron (mg/L)	Influent pH Value	Influent Phosphate (mg/L)	Bed Volume upto 50 ppb As level	As(V) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
300	0.15	7.0	0.68	2100	0.54
			160	110	0.03
			345	70	0.02

The experimental results reveal that high phosphate concentration causes to reach the effluent arsenic concentration to the MCL of 50 ppb early resulting in a relatively low bed volume as well as low quantity of arsenic adsorption by activated alumina. Hence, it can be concluded that the presence of phosphate in water has significant negative effect on the bed volume as well as on the quantity of arsenic adsorbed by activated alumina. The arsenic removal efficiency for different phosphate contents is shown in Figure 4.17 as bar diagram. The arsenic removal efficiency is found to be

94.3 %, 93.8 % and 91.7 % for 0.68 mg/L, 160 mg/L and 345 mg/L phosphate concentrations, respectively. The arsenic removal efficiency upto 50 ppb arsenic level is not affected much with the variation of phosphate in the influent.

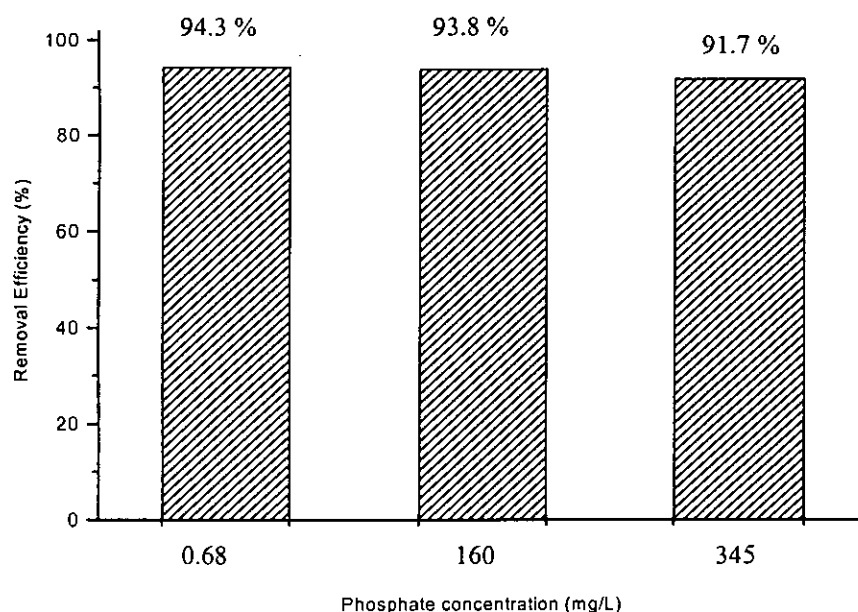


Figure 4.17: Bar diagram of arsenic removal efficiency with Phosphate Concentration.

#### 4.8 Effect of Activated Alumina Size

To observe the effect of activated alumina size experiments were conducted with synthetic raw water having a constant As(V) concentration of 300 ppb. The mesh size of alumina particles were 28x48 and 14x28. The pH values were 7.0 and 6.0 for activated alumina size of 28x48 and 14x28 respectively. Higher pH value (7.0) was chosen during the particular experiment to achieve the break through curve upto 50 ppb arsenic level earlier. To maintain constant iron concentration tap water was used (Fe = 0.15 mg/L) in the run. The experimental data are presented in Table-A32 and A33 in Appendix-A and calculations to determine bed volume and arsenic removal efficiency are presented in tabular form in Appendix- B. Effect of activated alumina size on adsorption characteristics of activated alumina is shown in Figure 4.18. It is

seen that the adsorption curve for activated alumina size of 14x28 has relatively steeper slope as compared with that for 28x48. The alumina having size of 14x28 has relatively low external surface area as compared with that of 28x48 alumina. Due to presence of iron, minute flocs clogs the porous activated alumina resulting in little use of internal surfaces of alumina particles. Hence the external surfaces are mainly responsible for adsorption of arsenic. As a result, the residual arsenic concentration is found increasing at a higher rate for the size of 14x28 and shows a steeper slope whereas the curve for alumina size of 28x48 has a mild slope and the residual arsenic concentration in the later case is found increasing very slowly. Another factor for obtaining higher bed volume for smaller mesh size is the effluent flow rate, which is relatively higher for the activated alumina size of 14x28 than that of 28x48 size. As a

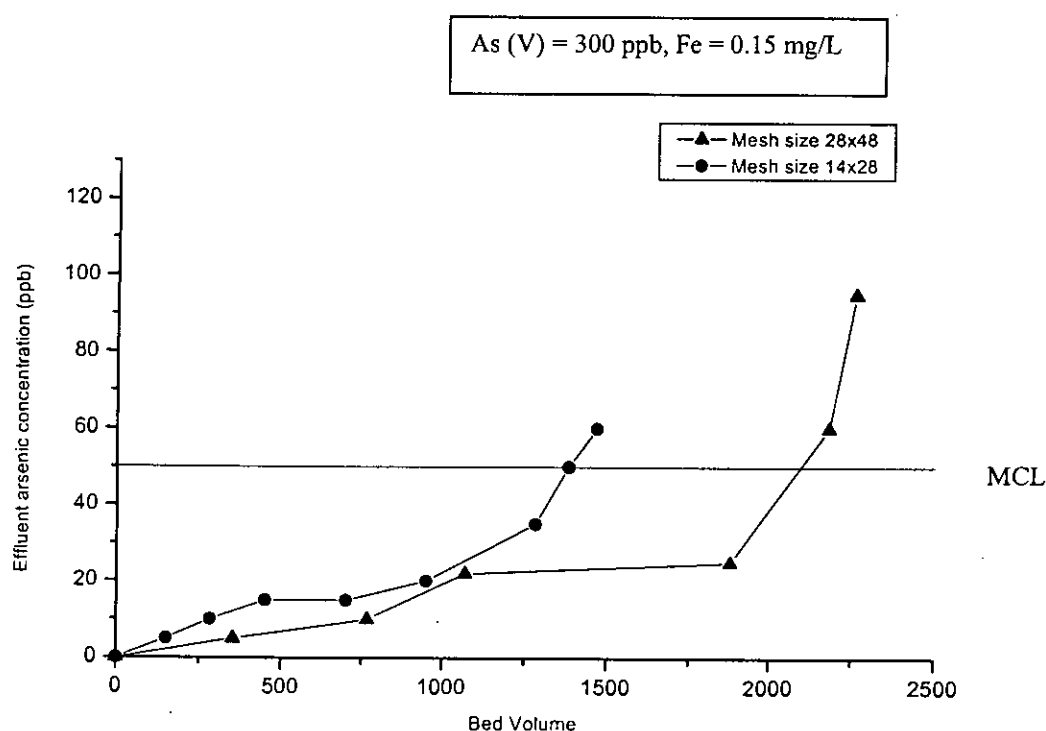


Figure 4.18: Effect of activated alumina size on adsorption characteristics of activated alumina.

result the empty bed contact time for size 28x48 is high and causes to increase the arsenic adsorption rate on activated alumina surface. So the residual arsenic

concentration in that case found to increase very slowly and reaches the 50 ppb arsenic level with a high bed volume.

Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level for the two different activated alumina sizes were determined and are presented in Table 4.9. Here the treated bed volumes are found to be 2100 and 1383 for activated alumina size of 28x48 and 14x28, respectively. Due to the higher external surface area in the case of mesh size 28x48, the bed volume upto 50 ppb arsenic level is found much higher as compared to the mesh size 14x28. It should be mentioned that the bed volume for activated alumina size 28x48 would be higher

Table 4.9: Treated Bed Volume and Quantity of adsorbed arsenic by activated alumina for different activated alumina size.

Influent As(V) concentration (ppb)	Influent Iron (mg/L)	Influent pH Value	Activated alumina size	Bed Volume upto 50 ppb As level	As(V) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
300	0.15	7.0	28x48	2100	0.54
		6.0	14x28	1383	0.35

than 2100 if the pH was maintained at 6.0 instead of 7.0 as As(V) adsorption is optimum at pH value of 6.0. The results also reveal that the adsorbed arsenic by activated alumina is much better for mesh size 28x48 and found to be 0.54 mg/g.

Figure 4.19 presents the bar diagram of arsenic removal efficiency with activated alumina size. The arsenic removal efficiency is found to be 94.3 % and 94.0 % for activated alumina size of 28x48 and 14x28 respectively. It is seen that there is no significant variation in the removal efficiency with the size of alumina particles.



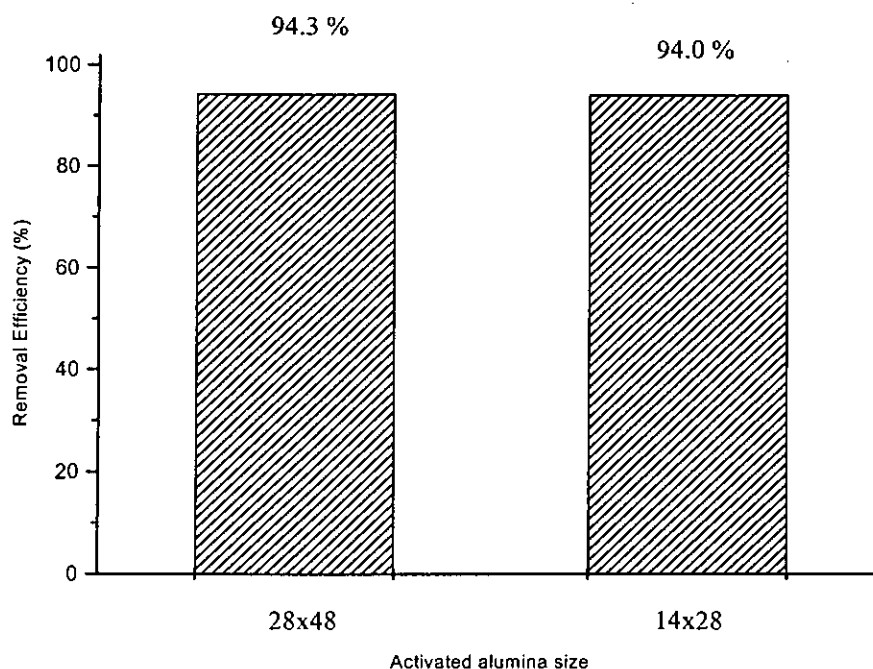


Figure 4.19: Bar diagram of arsenic removal efficiency with activated alumina size.

#### 4.9 Effect of Empty Bed Contact Time

To study the effect of empty bed contact time on arsenic removal efficiency of activated alumina, experiments were conducted with synthetic raw water having influent arsenic concentration of 300 ppb, iron concentration of 0.15 mg/L (tap water) and pH value of 6.0. The experimental data are presented in Table-A34 and A35 in Appendix-A. Calculations to determine bed volume and arsenic removal efficiency are presented in tabular form in Appendix- B. Figure 4.20 shows the relationship between effluent arsenic concentration and bed volume. The Figure shows that the slope of the adsorption curve having longer empty bed contact time has relatively mild slope as compared with the other curve having shorter empty bed contact time. As the bed contact time increases, arsenic species get more time to be adsorbed on activated alumina surface resulting in higher amount of adsorption. Hence the effluent residual arsenic concentration in case of longer empty bed contact time increases very slowly as compared to that for a shorter empty bed contact time.

For that reason the curve for shorter empty bed contact time reaches the 50 ppb arsenic level earlier resulting in lower bed volume.

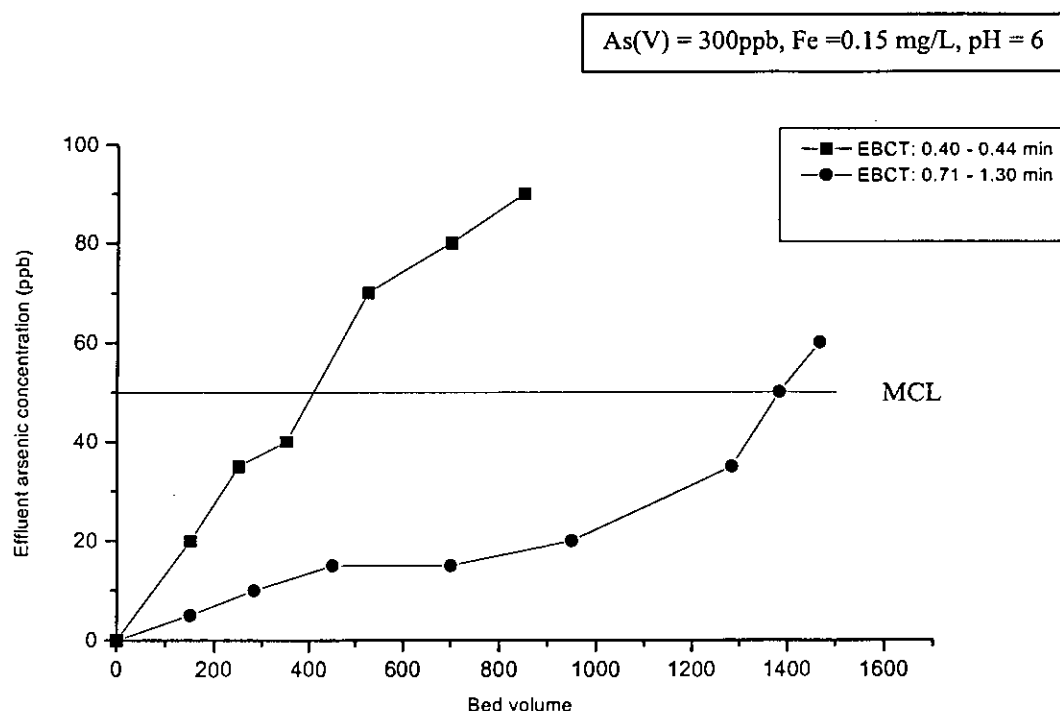


Figure 4.20: Effect of empty bed contact time on adsorption characteristics of activated alumina.

Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level for the two different range of empty bed contact time were determined and are presented in Table 4.10. The treated bed volumes are found to be 400 and 1383 for empty bed contact time ranges of 0.40-0.44 min and 0.71-1.30 min, respectively. The results reveal that the bed volume as well as the quantity of arsenic adsorbed by activated alumina increases significantly as the empty bed contact time increases.

Figure 4.21 shows the bar diagram of arsenic removal efficiency with empty bed contact time. From the Figure it is that the removal efficiency increases from 91.5 % to 94.0 % for the increase of contact time as the surfaces of the activated alumina

Table 4.10: Treated Bed Volume and Quantity of adsorbed arsenic by activated alumina upto 50 ppb arsenic level for empty bed contact time.

Influent As(V) concentration (ppb)	Influent Iron (mg/L)	Influent pH Value	EBCT (min)	Bed Volume upto 50 ppb As level	As(V) adsorbed (upto 50 ppb As level) by Activated Alumina (in mg/g)
300	0.15	6.0	0.40-0.44	400	0.1
			0.71-1.30	1383	0.35

become more effective to adsorb arsenic when contact time increases. As a result the alumina bed shows better arsenic removal efficiency for the longer empty bed contact time as compared with the shorter one.

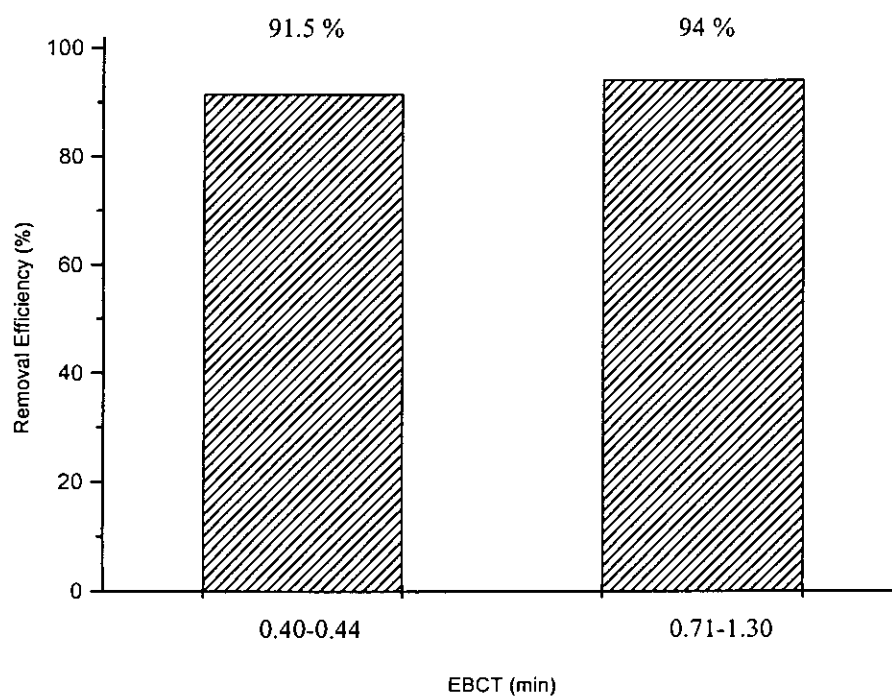


Figure 4.21: Bar diagram of arsenic removal efficiency with empty bed contact time (EBCT).

#### 4.10 Effectiveness of Regenerated Activated Alumina Bed

Two different sets of tests were conducted to observe the effect of regeneration of activated alumina bed. The first set of experiment was conducted with synthetic raw water having influent arsenic concentration of 300 ppb and pH value of 5.0. The arsenic concentration and pH value were 100 ppb and 6.0 respectively for the second set of experiment. Since the groundwater in Bangladesh contains iron and maximum acceptable limit according to Bangladesh standard is 1.0 mg/L, the experiments were conducted in both sets with a constant iron concentration of 1.0 mg/L. In both the cases, the spent activated alumina was regenerated and their performance was compared with the virgin media. The experimental data are presented in Table-A36(a), A36(b), A37(a) and A37(b) in Appendix-A and calculations to determine bed volume and arsenic removal efficiency are presented in tabular form in Appendix- B. The effects of regeneration under different experimental conditions are shown in Figures 4.22(a) and 4.22(b). From both the Figures it is observed that the residual arsenic concentration is low and did not reach the 50 ppb arsenic level. The initial effluent flow rate influenced the nature of the adsorption curves significantly. In both the sets the initial flow rate were lower for regenerated media as compared with that of virgin one. As a result the empty bed contact time for regenerated media was longer and it enhanced the arsenic adsorption rate on the activated alumina surface. Hence, the residual arsenic concentration in the effluent was found lower in case of regeneration media as compared with that of the virgin one. Since the raw water contained iron, formation of iron flocs took place and deposited on the activated alumina surface as well as within the interstices of activated alumina particles. As a result the effluent flow rate was reduced significantly thereby increasing the empty bed contact time. The runs could not be continued upto MCL of 50 ppb of arsenic due to clogging of the bed and experiments were stopped due to very low flow rates. It is seen that the adsorption curves in both the Figures are irregular. The presence of iron in the influent is responsible for this type of behavior, which has been explained earlier.

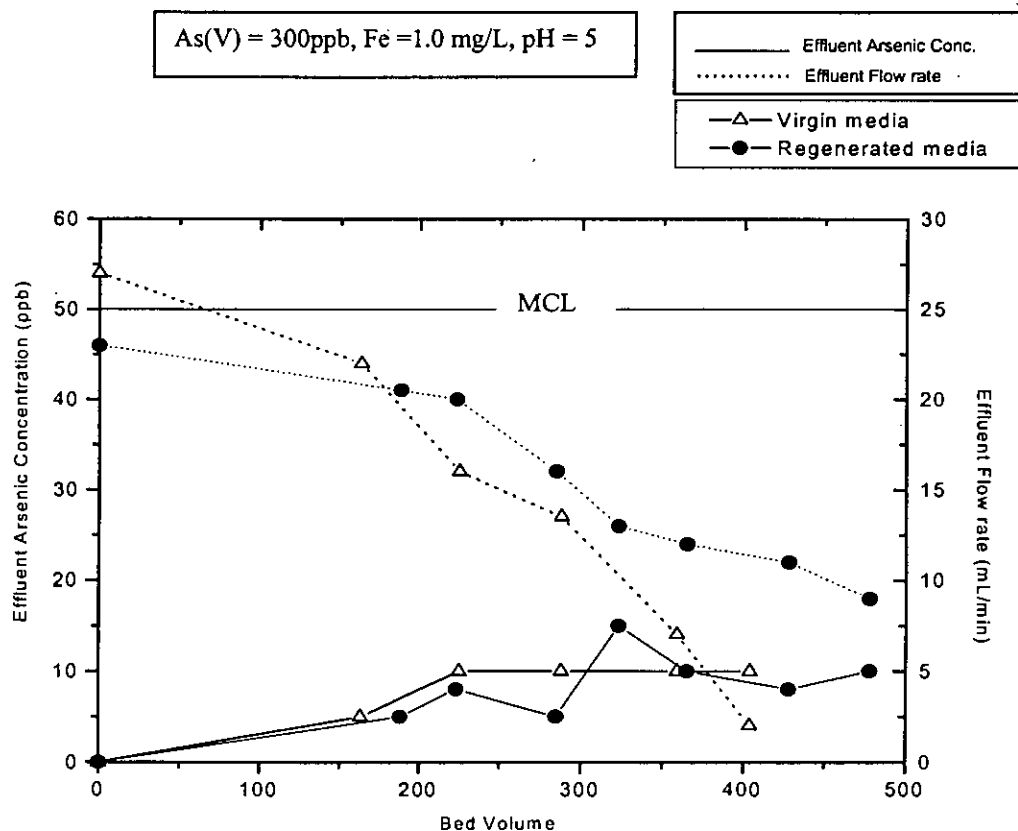


Figure 4.22(a): Effect of Bed Regeneration on adsorption characteristics of activated alumina (Arsenic concentration equal to 300 ppb).

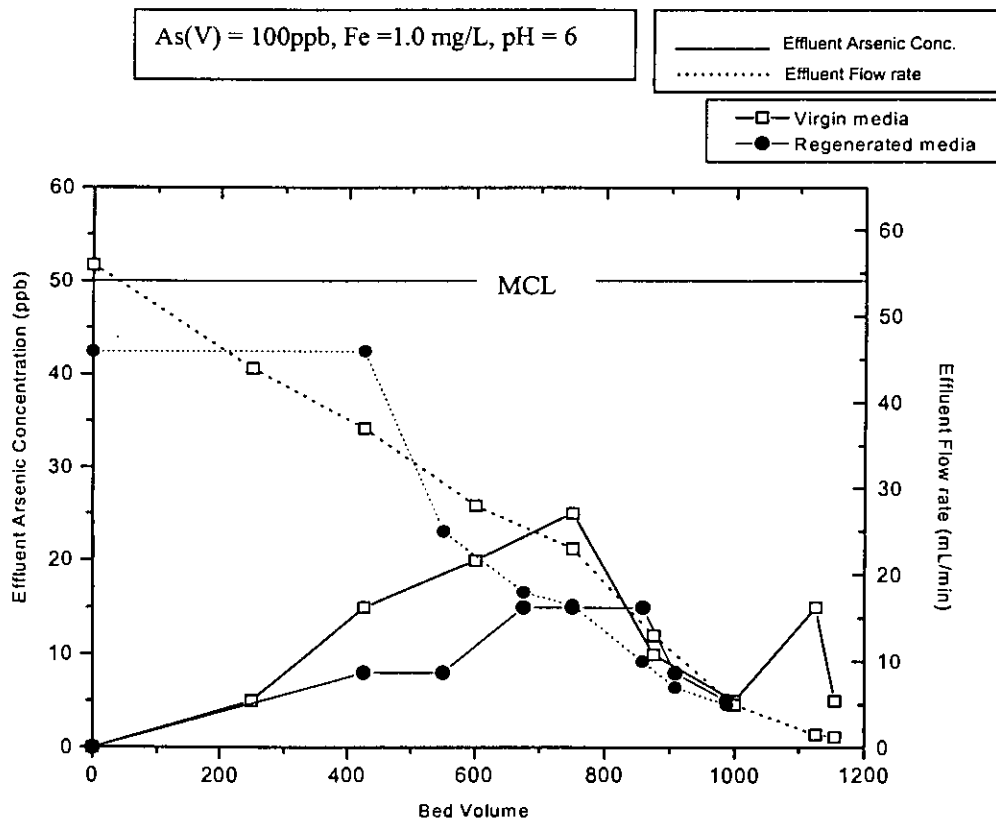


Figure 4.22(b): Effect of Bed Regeneration on adsorption characteristics of activated alumina (Arsenic concentration equal to 100 ppb).

Determination of bed volume and quantity of arsenic adsorbed by activated alumina upto 50 ppb arsenic level were not possible as the runs were stopped due to very low flow rate before reaching the 50 ppb arsenic level. Figure 4.23 shows the bar diagram of arsenic removal efficiency of virgin and regenerated media. In the first set of experiment the arsenic removal efficiency is found to be 88.3 % and 91.9 % for virgin and regenerated media, respectively, whereas, the efficiency is found to be 97.8% and 97.9%, respectively for second set of experiment. Efficiency for the regenerated media are found relatively better due to the initial lower flow rate as compared with the virgin media. The loss of alumina during regeneration was also quantified. It was found that 5 % alumina was lost during the process for both of the set of experiments. Hence it can be concluded that the regeneration process followed was quite effective.

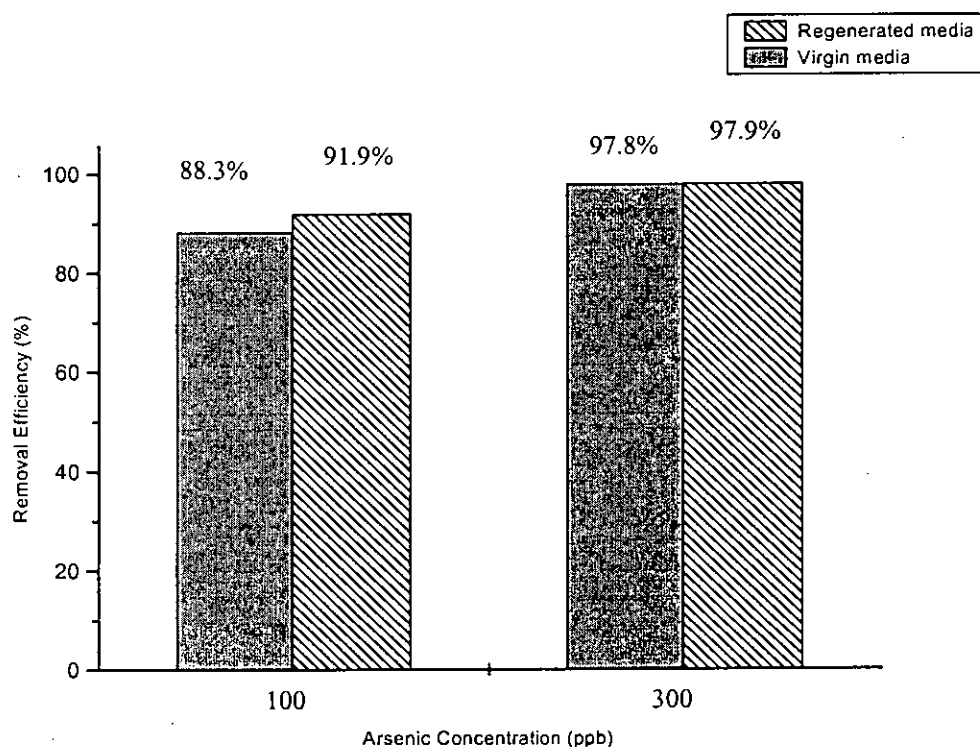


Figure 4.23: Bar diagram of arsenic removal efficiency with Bed Regeneration.

## Chapter 5

# CONCLUSIONS AND RECOMMENDATIONS

### 5.1 General

The present study deals with evaluating the effectiveness of activated alumina in removing arsenic from groundwater. Experiments were carried out using both trivalent and pentavalent arsenic in synthetic raw water. Column studies were conducted to identify the effects of different parameters (arsenic, oxidation state, iron, pH, chloride, sulfate, phosphate, size of activated alumina, empty bed contact time and regeneration of bed media) on arsenic removal efficiency. In majority of the cases, tap water (natural groundwater) was used as the source of the synthetic water. Only one experiment was conducted using distilled water. Efficiency/effectiveness of activated alumina in filter columns in removing arsenic were determined in terms of empty Bed Volume (BV), quantity of adsorbed arsenic and average arsenic removal efficiency upto 50 ppb arsenic level in the effluent.

### 5.2 Conclusions

Based on the results of the present study, the following conclusions can be drawn:

1. Oxidation state and concentration of arsenic have significant effects on arsenic removal efficiency of activated alumina. Bed volume decreases significantly with the increase of both As(V) and As(III) concentrations. For As(V), bed volumes are found to be 2115, 1383 and 375 for 100 ppb, 300 ppb and 500 ppb arsenic concentration respectively at low iron concentration (0.15 mg/L) and pH value of 6.0. The corresponding As(V) adsorption rate ranges from 0.15 to 0.35 mg/g and average arsenic removal efficiency varies from 78.7 % to 96.5 % with the higher values for higher concentrations.

For As(III), bed volumes are 372, 176 and 100 for 100 ppb, 300 ppb and 500 ppb arsenic concentrations, respectively when the raw water contains iron of 1.0 mg/L at pH value of 7.0. As(III) adsorption rate ranges from 0.03 to 0.04 mg/g and the arsenic removal efficiency varies from 84.5% to 95.9 % with the higher values corresponding to the higher concentrations.

2. Iron has a very significant effect on the arsenic removal efficiency of activated alumina bed. For pentavalent arsenic, the arsenic removal capacity of activated alumina bed decreases drastically with the increase of iron concentration. The bed volumes are found to be 5287, 1383, 775, 450 and 160 for iron concentration of 0.0 mg/L, 0.15 mg/L, 1.0 mg/L, 3.0 mg/L and 5.0 mg/L, respectively at As(V) concentration of 300 ppb and pH of 6.0. As(V) adsorption rate ranges from 0.04 to 1.4 mg/g and the removal efficiency varies from 89.2 % to 97.5 % with the higher values corresponding to the lower iron contents and vice versa.

For trivalent arsenic, iron has a positive effect on the arsenic removal efficiency of alumina bed. The bed volumes are 25, 176, 200 and 316 for iron concentration of 0.15 mg/L, 1.0 mg/L, 3.0 mg/L and 5.0 mg/L, respectively at As(III) concentration of 300 ppb and pH of 7.0. The corresponding arsenic adsorption rate varies from 0.01 to 0.08 mg/g and the arsenic removal efficiency ranges from 90.2 % to 93.9 %.

3. The arsenic removal efficiency of an alumina bed is dependent on pH of the influent. Pentavalent arsenic is absorbed better in the pH range of 5.0 – 6.0 with optimum pH of 6.0. The bed volumes are 683, 775 and 290 for pH values of 5.0, 6.0 and 7.5, respectively when the As(V) concentration is 300 ppb and iron concentration is 1.0 mg/L. The arsenic adsorption rate is in the range of 0.07 to 0.2 mg/g, whereas, average arsenic removal efficiency varies from 89.6 % to 93.9 %.

Trivalent arsenic is adsorbed better by alumina beds as the pH values increases. The bed volumes are 160, 176 and 370 for pH values of 6.0, 7.0 and 8.0, respectively if the As(III) concentration is 300 ppb and iron content is 1.0 mg/L.



The adsorption rate varies from 0.04 to 0.09 mg/g and the arsenic removal efficiency lies in the range 92.2 % to 93.4 %.

4. Chloride has no effect on arsenic removal efficiency. Sulfate has little effect on the removal efficiency whereas phosphate has strong negative effect at very high concentration.

The bed volumes are 234, 220 and 166 for sulfate concentrations of 60 mg/L, 335 mg /L and 740 mg/L, respectively when the As(V) concentration is 500 ppb and iron concentration is 0.15 mg/L at a pH of 7.0. The As(V) adsorption rate varies from 0.07 to 0.1 mg/g and the arsenic removal efficiency lies within the range of 95.3 % to 96.1 %.

The treated bed volumes are 2100, 110 and 70 for phosphate concentration of 0.68 mg/L, 160 mg/L and 345 mg/L, respectively at As(V) concentration of 300 ppb and iron content of 0.15 mg/L with pH value of 7.0. The As(V) adsorption rate ranges from 0.02 to 0.54 mg/g and the arsenic removal efficiency varies from 91.7 % to 94.3%.

5. Particular size of activated alumina has significant effect on the arsenic removal efficiency of activated alumina bed. The adsorption efficiency increases as the mesh size of the activated alumina increases. The bed volumes are 2100 at pH of 7.0 and 1383 at pH of 6.0 for activated alumina mesh sizes of 28x48 and 14x28, respectively when As(V) concentration is 300 ppb and iron concentration is 0.15 mg/L. The As(V) adsorption rate varies from 0.35 to 0.54 mg/g and the arsenic removal efficiency is about 94 %.
6. Empty bed contact time has a very significant effect on the amount of arsenic adsorbed by an alumina bed. The treated bed volume increases significantly with the increase of empty bed contact time. The treated bed volumes are 400 and 1383 for empty bed contact time ranges of 0.40-0.44 min and 0.71-1.30 min, respectively when the As(V) concentration is 300 ppb and iron content is 0.15

mg/L at a pH of 6.0. The As(V) adsorption rate varies from 0.1 to 0.35 mg/g and the arsenic removal efficiency ranges from 91.5% to 94 %.

7. Regeneration of spent alumina by taking out the material from filter column, then applying acid wash, sodium hydroxide treatment and pH adjustment is very effective. No reduction in removal efficiency occurs and only 5 % alumina is lost in the process.
8. Pretreatment for oxidation of trivalent arsenic to pentavalent form, iron removal and providing longer contact time are the necessary preconditions for the effective utilization of the arsenic adsorption capacity of activated alumina.

### 5.3 Recommendations for further study

Based on the findings and experiences of the research work presented in this thesis the following recommendations can be forwarded for future study.

1. The removal efficiency of arsenic should be assessed in the laboratory in greater details using iron free influent for better understanding of the phenomena for academic interest.
2. As phosphate concentration of groundwater in Bangladesh may be as high as 18.9 mg/L (as P) (DPHE/ DFID/ BGS, 2001) and it has significant effect on the performance of alumina bed, its effect on the arsenic removal efficiency should be studied elaborately up to this concentration.
3. An appropriate iron removal unit should be attached to an activated alumina column as a pretreatment unit to obtain good performance of the column.
4. A suitable method for oxidation of trivalent arsenic present in natural groundwater to pentavalent form should be established.
5. Synergistic effects of anions on arsenic removal efficiency should be studied.
6. An arsenic iron removal plant based on activated alumina should be developed and tested for different combinations of arsenic, iron and phosphate concentrations in the context of Bangladesh groundwater to determine the design life of the plant.

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## APPENDIX - A

### Performance Study Data of Laboratory Experiment

**Table A1:** Effect of Pentavalent Arsenic Concentration on Activated Alumina Bed (As = 100 ppb)

Arsenic – V Concentration = 100 ppb                      **Removal Efficiency = 78.7 %**  
 Iron Concentration = 0.15 mg/L                      **Bed Volume = 2115**  
 pH = 6.0  
 Activated Alumina Volume = 20 c.c.

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	38	0
4	200	-	5
8.5	425		10
16	800	30	15
21	1050	-	20
25.5	1275	-	25
33.7	1685	19.5	35
41.2	2060	-	40
42.3	2115	20	50
44.5	2225	19	60

**Table A2:** Effect of Pentavalent Arsenic Concentration on Activated Alumina Bed (As = 300 ppb)

Arsenic – V Concentration = 300 ppb                      **Removal Efficiency = 93.7 %**  
 Iron Concentration = 0.15 mg/L                      **Bed Volume = 1383**  
 pH = 6.0  
 Activated Alumina Volume = 30 c.c.

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	42	0
4.5	150	-	5
8.5	283	-	10
13.5	450	35	15
23.5	783	-	20
33.5	1117	37	25
41	1367	15	45
41.5	1383	-	50
44	1467	18	60

**Table A3:** Effect of Pentavalent Arsenic Concentration on Activated Alumina Bed  
(As = 500 ppb)

Arsenic – V Concentration = 500 ppb  
 Iron Concentration = 0.15 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 30 c.c.

**Removal Efficiency = 96.5 %**  
**Bed Volume = 375**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	38	0
0.75	25	-	5
2.25	75	-	7
4.5	150	-	10
7.5	250	33	20
9	300	-	30
10.5	350	-	40
12	400	-	60
13.5	450	24	70

**Table A4:** Effect of Trivalent Arsenic Concentration on Activated Alumina Bed  
(As = 100 ppb)

Arsenic – III Concentration = 100 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.

**Removal Efficiency = 84.5 %**  
**Bed Volume = 372**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	17.5	0
3.5	70	18	5
5	100	18	10
10	200	12	12
13	260	11	20
16	320	11	25
19.6	392	8	60

**Table A5:** Effect of Trivalent Arsenic Concentration on Activated Alumina Bed  
(As = 300 ppb)

Arsenic – III Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.

**Removal Efficiency = 93.4 %**  
**Bed Volume = 176**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	15	0
3	60	-	5
4.5	90	14	15
6	120	-	35
7.5	150	-	40
9.5	190	13	55

**Table A6:** Effect of Trivalent Arsenic Concentration on Activated Alumina Bed  
(As = 500 ppb)

Arsenic – III Concentration = 500 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.

**Removal Efficiency = 95.9 %**  
**Bed Volume = 100**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	21	0
1	20	-	5
2	40	-	10
2.5	50	-	20
3	60	-	28
4.5	90	18	40
5	100	-	50
6	120	-	85
6.5	130	-	90
7.5	150	17	100

**Table A7:** Effect of Iron Concentration in removing Pentavalent Arsenic species (using Distilled water)

Arsenic – V Concentration = 300 ppb

**Removal Efficiency = 97.5 %**

With Distilled Water

**Bed Volume = 5287**

pH = 6.0

Activated Alumina Volume = 20 c.c.

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	28	0
8	400	22	0
19	950	18	0
45	2250	14	0.18
52	2600	15	0.45
60	3000	18	0.31
73	3650	19	2.82
84	4200	20.5	12
90	4500	12	23
99	4950	18	36
105	5250	16	48
108	5400	19	55
109	5450	16	59

**Table A8:** Effect of Iron Concentration in removing Pentavalent Arsenic species (using Tap water)

Arsenic – V Concentration = 300 ppb

**Removal Efficiency = 94.0 %**

Iron Concentration = 0.15 mg/L

**Bed Volume = 1383**

pH = 6.0

Activated Alumina Volume = 30 c.c.

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	42	0
4.5	150	-	5
8.5	283	-	10
13.5	450	35	15
21	700	-	15
28.5	950	27	20
38.5	1283	-	35
41.5	1383	-	50
44	1467	21	60

**Table A9:** Effect of Iron Concentration in removing Pentavalent Arsenic species (Fe = 1.0 mg/L)

Arsenic – V Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 20 c.c.

**Removal Efficiency = 93.9 %**  
**Bed Volume = 775**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	42	0
3.5	175	28	10
6	300	-	10
8.5	425	22	15
11	550	18	25
13.5	675	-	35
15.5	775	8	50
16	800	-	55
18.5	952	9	100

**Table A10:** Effect of Iron Concentration in removing Pentavalent Arsenic species (Fe = 3.0 mg/L)

Arsenic – V Concentration = 300 ppb  
 Iron Concentration = 3.0 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 20 c.c.

**Removal Efficiency = 89.2 %**  
**Bed Volume = 450**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	54	0
4	200	39	40
6.5	325	27	40
9	450	-	50
10.5	525	21	55
13	650	15	80

**Table A11:** Effect of Iron Concentration in removing Pentavalent Arsenic species (Fe = 5.0 mg/L)

Arsenic – V Concentration = 300 ppb  
 Iron Concentration = 5.0 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 20 c.c.

**Removal Efficiency = 91.5 %**  
**Bed Volume = 160**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	56	0
2.5	125	45	40
5	250	30	70
7.5	375	-	70
10	500	26	100

**Table A12:** Effect of Iron Concentration in removing Trivalent Arsenic species (Fe = 0.15 mg/L)

Arsenic – III Concentration = 300 ppb  
 Iron Concentration = 0.15 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 30 c.c.

**Removal Efficiency = 93.9 %**  
**Bed Volume = 25**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	28	0
0.5	16.67	30	20
0.75	25	30	50
1	33.33	31	60
1.75	58.33	32	90
2.75	91.67	32	120
3.75	125	34	140

**Table A13:** Effect of Iron Concentration in removing Trivalent Arsenic species (Fe = 1.0 mg/L)

Arsenic – III Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.

**Removal Efficiency = 93.4 %**  
**Bed Volume = 176**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	15	0
3	60	15	5
4.5	90	14	15
6	120	14	35
7.5	150	13	40
9.5	190	13	55

**Table A14:** Effect of Iron Concentration in removing Trivalent Arsenic species (Fe = 3.0 mg/L)

Arsenic – III Concentration = 300 ppb  
 Iron Concentration = 3.0 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.

**Removal Efficiency = 90.2 %**  
**Bed Volume = 200**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	22	0
2.5	50	21	5
3	60	20	10
3.5	70	20	20
4	80	18	30
5	100	15	40
6.5	130	11	45
10	200	7	50
11.8	236	6	25
13.3	266	6	50
15.8	316	6.5	40

**Table A15:** Effect of Iron Concentration in removing Trivalent Arsenic species (Fe = 5.0 mg/L)

Arsenic – III Concentration = 300 ppb  
 Iron Concentration = 5.0 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.

**Removal Efficiency = 91.7 %**  
**Bed Volume = 316**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	25	0
2	40	22	5
3.5	70	20	15
5	100	20	20
6.5	130	20	25
8	160	18	45
11	220	17	45
11.5	230	16.5	50
13	260	10.5	18
15	300	8	18
15.8	316	6	20

**Table A16:** Effect of Iron Concentration in removing Trivalent Arsenic species (Fe = 7.0 mg/L)

Arsenic – III Concentration = 300 ppb  
 Iron Concentration = 7.0 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	26	0
2	40	20	5
3.5	70	19	10
4.5	90	16	20
6.5	130	13	40
9.5	190	6.5	15
10.1	202	6	25
12.5	250	5	20



**Table A17:** Effect of pH in removing Pentavalent Arsenic species (pH = 5.0)

Arsenic – V Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 5.0  
 Activated Alumina Volume = 20 c.c.

**Removal Efficiency = 92.6 %**  
**Bed Volume = 683**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	64	0
3.5	175	-	10
7	350	45	25
9.5	475	-	28
12	600	32	40
17	850	22	70

**Table A18:** Effect of pH in removing Pentavalent Arsenic species (pH = 6.0)

Arsenic – V Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 20 c.c.

**Removal Efficiency = 93.9 %**  
**Bed Volume = 775**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	42	0
3.5	175	28	10
6	300	-	10
8.5	425	22	15
11	550	-	25
13.5	675	18	35
15.5	775	-	50
16	800	8	55

**Table A19:** Effect of pH in removing Pentavalent Arsenic species (pH = 7.5)

Arsenic – V Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 7.5  
 Activated Alumina Volume = 20 c.c.

**Removal Efficiency = 89.6 %**  
**Bed Volume = 290**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	55	0
2.5	125	-	35
5	250	50	45
7.5	375	-	60
12.5	625	26	65

**Table A20:** Effect of pH in removing Trivalent Arsenic species (pH = 6.0)

Arsenic – III Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 50 c.c.

**Removal Efficiency = 93.3 %**  
**Bed Volume = 160**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	20	0
2.5	50	-	10
3.5	70	-	20
5	100	16	35
6.5	130	-	40
8	160	14.5	50
9	180	12	60

**Table A21:** Effect of pH in removing Trivalent Arsenic species (pH = 7.0)

Arsenic – III Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.

**Removal Efficiency = 93.4 %**  
**Bed Volume = 176**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	15	0
3	60	-	5
4.5	90	14	15
6	120	-	35
7.5	150	-	40
9.5	190	13	55

**Table A22:** Effect of pH in removing Trivalent Arsenic species (pH = 8.0)

Arsenic – III Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 8.0  
 Activated Alumina Volume = 50 c.c.

**Removal Efficiency = 92.2 %**  
**Bed Volume = 370**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	16	0
4.5	90	-	10
6	120	15	10
9.5	190	13	20
12	240	12	35
14.5	290	-	40
16	320	9	45
21.0	420	3.5	55

**Table A23:** Effect of Chloride in removing Arsenic species through Activated Alumina Bed (Chloride = 300 mg/L)

Arsenic – V Concentration = 500 ppb  
 Iron Concentration = 0.15 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.  
 Mesh size = 14x28  
 Chloride (Cl<sup>-</sup>) = 300 mg/L

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	40	0
2.5	50	38	8
7.5	150	35	10
10	200	35	15
12.5	250	34	25
16.25	325	28	15

**Table A24:** Effect of Chloride in removing Arsenic species through Activated Alumina Bed (Chloride = 700 mg/L)

Arsenic – V Concentration = 500 ppb  
 Iron Concentration = 0.15 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.  
 Mesh size = 14x28  
 Chloride (Cl<sup>-</sup>) = 700 mg/L

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	28	0
2.5	50	24	5
7.5	150	21	10
7.95	159	20	15
10.45	209	19	8

**Table A25:** Effect of Chloride in removing Arsenic species through Activated Alumina Bed (Chloride = 1100 mg/L)

Arsenic – V Concentration = 500 ppb  
 Iron Concentration = 0.15 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.  
 Mesh size = 14x28  
 Chloride (Cl<sup>-</sup>) = 1100 mg/L

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	26	0
5	100	20	5
6.9	138	17	8
9.4	188	19	5

**Table A26:** Effect of Sulfate in removing Arsenic species through Activated Alumina Bed (Sulfate = 60 mg/L)

Arsenic – V Concentration = 500 ppb  
 Iron Concentration = 0.15 mg/L  
 pH = 7.0  
 Activated Alumina Volume = 50 c.c.  
 Mesh size = 14x28  
 Sulfate (SO<sub>4</sub><sup>2-</sup>) = 60 mg/L

**Removal Efficiency = 95.9 %**  
**Bed Volume = 234**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	44	0
2.5	50	-	10
5	100	-	15
7.5	150	40	20
10	200	-	40
12.5	250	39	55

**Table A27:** Effect of Sulfate in removing Arsenic species through Activated Alumina Bed (Sulfate = 335 mg/L)

Arsenic – V Concentration	= 500 ppb	<b>Removal Efficiency = 96.1 %</b>
Iron Concentration	= 0.15 mg/L	<b>Bed Volume = 220</b>
pH	= 7.0	
Activated Alumina Volume	= 50 c.c.	
Mesh size	= 14x28	
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	= 335 mg/L	

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	30	0
2.5	50	-	5
5	100	30	15
7.5	150	-	25
11.0	220	-	50
12.5	250	28	60

**Table A28:** Effect of Sulfate in removing Arsenic species through Activated Alumina Bed (Sulfate = 740 mg/L)

Arsenic – V Concentration	= 500 ppb	<b>Removal Efficiency = 95.3 %</b>
Iron Concentration	= 0.15 mg/L	<b>Bed Volume = 166</b>
pH	= 7.0	
Activated Alumina Volume	= 50 c.c.	
Mesh size	= 14x28	
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	= 740 mg/L	

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	48	0
2.5	50	-	15
5	100	25	25
7.5	150	-	45
10.2	214	18	60

**Table A29:** Effect of Phosphate in removing Arsenic species through Activated Alumina Bed (Phosphate = 0.68 mg/L)

Arsenic - V Concentration	= 300 ppb	<b>Removal Efficiency = 94.3 %</b>
Iron Concentration	= 0.15 mg/L	<b>Bed Volume = 2100</b>
pH	= 7.0	
Activated Alumina Volume	= 30 c.c.	
Mesh size	= 28x48	
Phosphate ( $\text{PO}_4^{--}$ )	= 0.68 mg/L	

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	15	0
10.6	353	18	5
23	767	13	10
32.1	1070	13	22
56.4	1880	11	25
65.4	2180	15	60
67.9	2263	18	95

**Table A30:** Effect of Phosphate in removing Arsenic species through Activated Alumina Bed (Phosphate = 160 mg/L)

Arsenic - V Concentration	= 300 ppb	<b>Removal Efficiency = 93.8 %</b>
Iron Concentration	= 0.15 mg/L	<b>Bed Volume = 110</b>
pH	= 7.0	
Activated Alumina Volume	= 30 c.c.	
Mesh size	= 28x48	
Phosphate ( $\text{PO}_4^{--}$ )	= 160 mg/L	

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	18	0
2.5	83	13	25
4	133	11	70
6	200	7	80

**Table A31:** Effect of Phosphate in removing Arsenic species through Activated Alumina Bed (Phosphate = 345 mg/L)

Arsenic – V Concentration	= 300 ppb	<b>Removal Efficiency = 91.7 %</b>
Iron Concentration	= 0.15 mg/L	<b>Bed Volume = 70</b>
pH	= 7.0	
Activated Alumina Volume	= 30 c.c.	
Mesh size	= 28x48	
Phosphate ( $\text{PO}_4^{--}$ )	= 345 mg/L	

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	18	0
2.5	83	11.5	60
3	100	6	65
4.3	143	2	80

**Table A32:** Effect of Activated alumina size in removing Arsenic species through Activated Alumina Bed (Mesh size = 28x48)

Arsenic – V Concentration	= 300 ppb	<b>Removal Efficiency = 94.3 %</b>
Iron Concentration	= 0.15 mg/L	<b>Bed Volume = 2100</b>
pH	= 7.0	
Activated Alumina Volume	= 30 c.c.	
Mesh size	= 28x48	

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	15	0
10.6	353	18	5
23	767	13	10
32.1	1070	13	22
56.4	1880	11	25
65.4	2180	15	60
67.9	2263	18	95



**Table A33:** Effect of Activated alumina size in removing Arsenic species through Activated Alumina Bed (Mesh size = 14x28)

Arsenic – V Concentration = 300 ppb  
 Iron Concentration = 0.15 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 30 c.c.  
 Mesh size = 14x28

**Removal Efficiency = 94.0 %**  
**Bed Volume = 1383**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	42	0
4.5	150	-	5
8.5	283	-	10
13.5	450	35	15
21	700	-	15
28.5	950	27	20
38.5	1283	-	35
41.5	1383	-	50
44	1467	21	60

**Table A34:** Effect of effective bed contact time in removing Arsenic species through Activated Alumina Bed (0.40 min – 0.44 min)

Arsenic – V Concentration = 300 ppb  
 Iron Concentration = 0.15 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 20c.c.

**Removal Efficiency = 91.5 %**  
**Bed Volume = 400**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	50	0
3	150	-	20
5	250	47	35
7	350	-	40
10.5	525	46	70
14	700	-	80
17	850	45	90

**Table A35:** Effect of effective bed contact time in removing Arsenic species through Activated Alumina Bed (0.71 min - 1.3 min)

Arsenic - V Concentration = 300 ppb  
 Iron Concentration = 0.15 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 30 c.c.

**Removal Efficiency = 94.0 %**  
**Bed Volume = 1383**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	42	0
4.5	150	-	5
8.5	283	-	10
13.5	450	35	15
21	700	-	15
28.5	950	27	20
38.5	1283	-	35
41.5	1383	23	50
44	1467	21	60

**Table A36(a):** Effect of Bed Regeneration in removing Arsenic species through Activated Alumina Bed (As = 300 ppb, Virgin media)

Arsenic - V Concentration = 300 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 5.0  
 Activated Alumina Volume = 40 c.c.

**Removal Efficiency = 97.8%**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	27	0
6.5	163	22	5
9	225	16	10
11.5	288	13.5	10
14.35	359	7	10
16.15	404	2	10

**Table A36(b):**Effect of Bed Regeneration in removing Arsenic species through Activated Alumina Bed (As = 300 ppb, Regenerated media)

**Removal Efficiency = 97.9 %**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	23	0
7.5	188	20.5	5
8.9	223	20	8
11.4	285	16	5
12.9	323	13	15
14.6	365	12	10
17.1	428	11	8
19.1	478	9	10

**Table A37(a):**Effect of Bed Regeneration in removing Arsenic species through Activated Alumina Bed (As = 100 ppb, Virgin media)

Arsenic – V Concentration = 100 ppb  
 Iron Concentration = 1.0 mg/L  
 pH = 6.0  
 Activated Alumina Volume = 20 c.c.

**Removal Efficiency = 88.3 %**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	56	0
5	250	44	5
8.5	425	37	15
12	600	28	20
15	750	23	25
17.5	875	13	10
20	1000	5	5
22.5	1125	1.5	15
23.1	1155	1.25	5

**Table A37(b):**Effect of Bed Regeneration in removing Arsenic species through Activated Alumina Bed (As = 100 ppb, Regenerated media)

**Removal Efficiency = 91.9 %**

Cum. Effluent Volume (L)	Bed Volume (BV)	Effluent flow rate (mL/min)	Effluent Arsenic Conc. (ppb)
0	0	46	0
8.5	425	46	8
11	550	25	8
13.5	675	18	15
15	750	16.5	15
17.15	858	10	15
18.15	908	7	8
19.75	988	5	5

## Appendix-B

### Calculation of Results

Table B1: Calculation Data to determine Arsenic removal efficiency and bed volume upto 50 ppb As.

Influent Arsenic Conc.(ppb)	Influent Iron Conc.(mg/L)	AA Bed Volume (cc)	pH	Area under curve(Micro gram)	Effluent Volume upto MCL (Litre)	Avg. Effluent As Conc.(ppb)	Efficiency of the Bed (%)	Bed Volume (BV) upto 50 ppb As	Comments	Observation
100	0.15	20	6	903	42.3	21.3	78.7	2115	As(V)	Effect of As(V) Conc.
300	0.15	30	6	790	41.5	19.0	93.7	1383	As(V)	
500	0.15	30	6	198.75	11.25	17.7	96.5	375	As(V)	
100	1	50	7	288	18.6	15.5	84.5	372	As(III)	Effect of As(III) Conc.
300	1	50	7	174.75	8.8	19.9	93.4	176	As(III)	
500	1	50	7	103	5	20.6	95.9	100	As(III)	
300	0	20	6	801.4	105.74	7.6	97.5	5287	As-V	Iron Effect
300	0.15	30	6	750	41.5	18.1	94.0	1383	As-V	
300	1	20	6	283.75	15.5	18.3	93.9	775	As-V	
300	3	20	6	292.5	9	32.5	89.2	450	As-V	
300	5	20	6	81.5	3.2	25.5	91.5	160	As-V	
300	0.15	30	7	13.75	0.75	18.3	93.9	25	As-III	
300	1	50	7	174.75	8.8	19.9	93.4	176	As-III	
300	3	50	7	295	10	29.5	90.2	200	As-III	
300	5	50	7	393.45	15.8	24.9	91.7	316	As-III	
300	7	50	7	-	-	-	-	-	As-III	
300	1	20	5	304.7	13.66	22.3	92.6	683	As-V	pH Effect
300	1	20	6	283.75	15.5	18.3	93.9	775	As-V	
300	1	20	7.5	181.75	5.8	31.3	89.6	290	As-V	
300	1	50	6	170	8.0	20	93.3	160	As-III	
300	1	50	7	174.75	8.8	19.9	93.4	176	As-III	
300	1	50	8	435	18.5	23.5	92.2	370	As-III	

- \* Area under curve (Micro gram) where effluent arsenic concentration is below MCL is obtained from effluent arsenic volume vs cumulative effluent volume graph.
- \* Effluent volume upto MCL (Litre) is the Cumulative effluent volume at MCL
- \* Average effluent As concentration (ppb) = Area under curve / Effluent volume upto MCL
- \* Efficiency of the Bed (%) = (Influent arsenic conc.- avg. effluent arsenic conc.) X 100 / Influent arsenic conc.
- \* Bed Volume (BV) = Effluent volume upto MCL X 1000 / Activated Alumina (AA) bed volume

Table B1: Calculation Data to determine Arsenic removal efficiency and bed volume upto 50 ppb As level (Contd.)

Influent Arsenic Conc.(ppb)	Influent Iron Conc.(mg/L)	AA Bed Volume (cc)	pH	Area under curve(Micro gram)	Effluent Volume upto MCL (Litre)	Avg. Effluent As Conc.(ppb)	Efficiency of the Bed (%)	Bed Volume (BV)	Comments	Observation
500	0.15	50	7	-	-	-	-	-	Chloride = 300 mg/L	Chloride Effect on As(V)
500	0.15	50	7	-	-	-	-	-	Chloride = 700 mg/L	
500	0.15	50	7	-	-	-	-	-	Chloride = 1100 mg/L	
500	0.15	50	7	239	11.7	20.4	95.9	234	Sulfate = 60 mg/L	Sulfate Effect on As(V)
500	0.15	50	7	212.5	11	19.3	96.1	220	Sulfate = 335 mg/L	
500	0.15	50	7	194.3	8.3	23.4	95.3	166	Sulfate = 740 mg/L	
300	0.15	30	7	1083.65	63	17.2	94.3	2100	Phosphate = 0.68 mg/L	Phosphate Effect on As(V) with Mesh 28x48
300	0.15	30	7	61.25	3.3	18.6	93.8	110	Phosphate = 160 mg/L	
300	0.15	30	7	52.5	2.1	25	91.7	70	Phosphate = 345 mg/L	
300	0.15	30	7	1083.65	63	17.2	94.3	2100	Mesh 28 X 48	Activated alumina size effect on As(V)
300	0.15	30	6	750	41.5	18.1	94.0	1383	Mesh 14 X 28	
300	0.15	20	6	205	8	25.6	91.5	400	0.40 min – 0.44 min	EBCT Effect on As(V)
300	0.15	30	6	750	41.5	18.1	94.0	1383	0.71 min – 1.30 min	
300	1	40	5	106.5	16.15	6.6	97.8	-	Virgin	Regeneration Effect on As(V)
300	1	40	5	120.85	19.1	6.3	97.9	-	Regenerated	
100	1	20	6	269.75	23.1	11.7	88.3	-	Virgin	
100	1	20	6	159.4	19.75	8.1	91.9	-	Regenerated	

- \* Area under curve (Micro gram) where effluent arsenic concentration is below MCL is obtained from effluent arsenic volume vs cumulative effluent volume graph.
- \* Effluent volume upto MCL (Litre) is the cumulative effluent volume at MCL or, the cumulative effluent volume upto close the test (during the observation of regeneration effect on As-V).
- \* Average effluent As concentration (ppb) = Area under curve / Effluent volume upto MCL
- \* Efficiency of the Bed (%) = (Influent arsenic conc.- avg. effluent arsenic conc.) X 100 / Influent arsenic conc.
- \* Bed Volume (BV) = Effluent volume upto MCL X 1000 / Activated Alumina (AA) bed volume

Table B2: Calculation Data to determine the quantity of adsorbed arsenic by activated alumina upto 50 ppb As level

Influent Arsenic Conc. (ppb)	Influent Iron Conc. (mg/L)	AA Bed Volume (cc)	pH	Area under curve (Micro gram)	Effluent Volume upto MCL (Litre)	Avg. Effluent As Conc. (ppb)	Total quantity of Arsenic upto 50 ppb (mg)	Unit weight of activated alumina (g/cc)	Weight of Activated alumina (g)	Adsorbed arsenic by Activated alumina (mg/g)	Comments	Observation
100	0.15	20	6	903	42.3	21.3	3.33	1.1	22	0.15	As-V	As-V Effect
300	0.15	30	6	790	41.5	19	11.66	1.1	33	0.35	As-V	
500	0.15	30	6	198.75	11.25	17.7	5.43	1.1	33	0.16	As-V	
100	1	50	7	288	18.6	15.5	1.57	1.1	55	0.03	As-III	As-III Effect
300	1	50	7	174.75	8.8	19.86	2.47	1.1	55	0.04	As-III	
500	1	50	7	103	5	20.6	2.4	1.1	55	0.04	As-III	
300	0	20	6	801.4	105.74	7.6	30.92	1.1	22	1.4	As-V	Iron Effect
300	0.15	30	6	750	41.5	18.1	11.7	1.1	33	0.35	As-V	
300	1	20	6	283.75	15.5	18.3	4.37	1.1	22	0.20	As-V	
300	3	20	6	292.5	9	32.5	2.41	1.1	22	0.11	As-V	
300	5	20	6	81.5	3.2	25.5	0.88	1.1	22	0.04	As-V	
300	0.15	30	7	13.75	0.75	18.3	0.21	1.1	33	0.01	As-III	
300	1	50	7	174.75	8.8	19.86	2.47	1.1	55	0.04	As-III	
300	3	50	7	295	10	29.5	2.71	1.1	55	0.05	As-III	
300	5	50	7	393.45	15.8	24.9	4.35	1.1	55	0.08	As-III	
300	7	50	7	-	-	-	-	1.1	55	-	As-III	
300	1	20	5	304.7	13.66	22.3	3.79	1.1	22	0.17	As-V	pH Effect
300	1	20	6	283.75	15.5	18.3	4.37	1.1	22	0.20	As-V	
300	1	20	7.5	181.75	5.8	31.3	1.56	1.1	22	0.07	As-V	
300	1	50	6	170	8	21.25	2.23	1.1	55	0.04	As-III	
300	1	50	7	174.75	8.8	19.86	2.47	1.1	55	0.04	As-III	
300	1	50	8	435	18.5	23.51	5.11	1.1	55	0.09	As-III	

- \* Area under curve (Micro gram) where effluent arsenic concentration is below MCL is obtained from effluent arsenic volume vs cumulative effluent volume graph.
- \* Effluent volume upto MCL (Litre) is the Cumulative effluent volume at MCL
- \* Average effluent As concentration (ppb) = Area under curve / Effluent volume upto MCL
- \* Total quantity of arsenic upto MCL (mg) = (Influent arsenic conc.- avg. effluent arsenic conc.) X Effluent volume upto MCL / 1000
- \* Adsorbed arsenic by Activated alumina (mg/g) = Total quantity of arsenic upto 50 ppb (mg) / Weight of activated alumina (g)

Table B2: Calculation Data to determine the quantity of adsorbed arsenic by activated alumina upto 50 ppb As level (Contd.)

Influent Arsenic Conc. (ppb)	Influent Iron Conc. (mg/L)	AA Bed Volume (cc)	pH	Area under curve (Micro gram)	Effluent Volume upto MCL (Litre)	Avg. Effluent As Conc. (ppb)	Total quantity of Arsenic upto 50 ppb (mg)	Unit weight of activated alumina (g/cc)	Weight of Activated alumina (g)	Adsorbed arsenic by Activated alumina (mg/g)	Comments	Observation
500	0.15	50	7	-	-	-	-	1.1	55	-	Chloride = 300 mg/L	Chloride Effect on As(V)
500	0.15	50	7	-	-	-	-	1.1	55	-	Chloride = 700 mg/L	
500	0.15	50	7	-	-	-	-	1.1	55	-	Chloride = 1100 mg/L	
500	0.15	50	7	239	11.7	20.4	5.61	1.1	55	0.10	Sulfate = 60 mg/L	Sulfate Effect on As(V)
500	0.15	50	7	212.5	11	19.3	5.29	1.1	55	0.09	Sulfate = 335 mg/L	
500	0.15	50	7	194.3	8.3	23.4	3.96	1.1	55	0.07	Sulfate = 740 mg/L	
300	0.15	30	7	1083.65	63	17.2	17.82	1.1	33	0.54	Phosphate = 0.68 mg/L	Phosphate Effect on As(V) With Mesh 28x48
300	0.15	30	7	61.25	3.3	18.6	0.93	1.1	33	0.03	Phosphate = 160 mg/L	
300	0.15	30	7	52.5	2.1	25	0.58	1.1	33	0.02	Phosphate = 345 mg/L	
300	0.15	30	7	1083.65	63	17.2	17.82	1.1	33	0.54	Mesh 28 X 48	Activated alumina size effect on As(V)
300	0.15	30	6	750	41.5	18.1	11.7	1.1	33	0.35	Mesh 14 X 28	
300	0.15	20	6	205	8	25.625	2.2	1.1	22	0.10	0.40 min – 0.44 min	EBCT Effect on As(V)
300	0.15	30	6	750	41.5	18.1	11.7	1.1	33	0.35	0.71 min – 1.30 min	
300	1	40	5	106.5	16.15	6.6	-	1.1	44	-	Virgin	Regeneration Effect on As(V)
300	1	40	5	120.85	19.1	6.3	-	1.1	44	-	Regenerated	
100	1	20	6	269.75	23.1	11.7	-	1.1	22	-	Virgin	
100	1	20	6	159.4	19.75	8.1	-	1.1	22	-	Regenerated	

Area under curve (Micro gram) where effluent arsenic concentration is below MCL is obtained from effluent arsenic volume vs cumulative effluent volume graph.

Effluent volume upto MCL (Litre) is the Cumulative effluent volume at MCL

Average effluent As concentration (ppb) = Area under curve / Effluent volume upto MCL

Total quantity of arsenic upto MCL (mg) = (Influent arsenic conc. - avg. effluent arsenic conc.) X Effluent volume upto MCL / 1000

Adsorbed arsenic by Activated alumina (mg/g) = Total quantity of arsenic upto 50 ppb (mg) / Weight of activated alumina (g)

