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Effect of iron on the performance of activated alumina bed in removing arsenic from groundwater

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Abstract

Groundwater is the major source of domestic water supply in Bangladesh. Due to widespread arsenic contamination of groundwater in Bangladesh, immediate measures need to be taken to provide safe drinking water in the arsenic affected areas. In the context of prevalence of high concentration of arsenic in tubewell water, a wide range of technologies has been tried for the removal of arsenic from drinking water. Among the methods available for removing arsenic from water, adsorption onto activated alumina is a promising one for implementing in a small-scale rural community or at household level. Various factors influence the removal efficiency of activated alumina bed and dissolved iron present in groundwater is one of the major influencing factors. Since groundwater in many areas of Bangladesh contains high concentration of iron, it is important to investigate the effect of iron on the performance of activated alumina bed. Laboratory column tests were conducted to determine the effect of iron concentration on the performance of activated alumina bed in removing both trivalent as well as pentavalent arsenic species from groundwater. The efficiency/effectiveness of activated alumina in removing arsenic was determined in terms of Empty Bed Volume (BV) and quantity of arsenic adsorbed onto activated alumina up to 50 ppb arsenic level (allowable limit in Bangladesh) in the effluent. 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 calculated BV for As(V) decreased from 5287 to 160 as the iron concentration increased from 0.0 mg/L to 5.0 mg/l; the corresponding quantities of adsorbed arsenic were 1.4 to 0.04 mg/g, respectively. For As(III) calculated BV increased from 25 to 316 as iron concentration increased from 0.15 mg/L to 5.0 mg/l; the corresponding quantities of adsorbed arsenic were 0.01 to 0.08 mg/g, respectively.

Keywords: Activated alumina, arsenic removal, column tests

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1. Introduction

In Bangladesh, arsenic in groundwater was first detected Chapai Nawabganj in late 1993, following reports of elevated levels of arsenic in groundwater in the adjoining areas of India. According to a survey (DPHE/ DFID/ BGS, 2000), out of 507 upazilas, 268 are arsenic affected. The survey results show that nationwide 27% shallow tubewells have arsenic concentration concentration beyond the Bangladesh standard (50 ppb), this figure increased to 46% when WHO standard (10 ppb) is considered. The population exposed to arsenic concentration exceeding Bangladesh and WHO drinking water standard is estimated to be within 28-35 million and 46-57 million, respectively (DPHE / DFID / BGS, 2000). The most important measure needed to combat the arsenic problems is to provide arsenic safe drinking water to the exposed people. Unless suitable alternative drinking water sources are made available, arsenic removal from hand pump tubewell water through simple and low cost technologies appears to be an immediate and short-term solution of the problem. Among the methods available for removing arsenic from water, adsorption on activated alumina is a promising one for implementing in a small-scale rural community or at household level. Adsorption onto activated alumina is an effective process for removing pentavalent arsenic from water, but removal of trivalent arsenic by this process is relatively poor (AWWA, 1990). If properly designed, activated alumina may be a viable technology for removing arsenic from groundwater. However, there is a need to develop design and operating criteria for an effective field deployable household/community level activated alumina adsorptive filter system. Iron concentration in groundwater influences the arsenic removal capacity of activated alumina significantly and its effect has not been studied in the context of Bangladesh. The objective of this study is to investigate the effect of iron concentration on the performance of activated alumina bed. The groundwater in many areas of Bangladesh contains high concentration of iron. Dissolved iron in shallow tubewell water in about 67% areas of Bangladesh has been found to be in excess of 2 mg/L (Ahmed and Rahman, 2000). This study aims at developing design and operating criteria for an effective arsenic removal system for use at community and household levels.

2. Adsorption by activated alumina

Activated alumina is granular aluminum oxide having sorptive surface. 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 some 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 in the effluent, until the concentration in the effluent equals influent concentration and no removal occurs. This phenomenon is termed ‘breakthrough’. The breakthrough curve is a plot of the adsorbate (arsenic) concentration in the column effluent as a function of either the volume treated, or the number of Empty Bed Volume (BV) treated – i.e., the volume of water treated divided by the volume of adsorbent (activated alumina) in the column. In practice, the column is only operated to a certain break point, e.g., up to the maximum contaminant level (MCL) in the effluent. Then the bed is replaced with fresh activated alumina or the exhausted/spent alumina is regenerated.

The capacity of an adsorption column depends on the surface area, pore size distribution and surface chemistry of the adsorbent, and on the quality of the influent. The mechanism 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 which '≡ Al' represents the alumina surface and over bar denotes the solid phase.

$$\overline{\equiv \mathrm{Al} - \mathrm{OH}} + \mathrm{H}^+ + \mathrm{H_2AsO_4}^- \rightarrow \overline{\equiv \mathrm{Al} - \mathrm{H_2AsO_4}} + \mathrm{HOH}$$

The chemical equation for arsenic desorption (alumina regeneration) may be written as follows:

$$\overline{\equiv \mathrm{Al} - \mathrm{H_2AsO_4}} + \mathrm{OH}^- \rightarrow \overline{\equiv \mathrm{Al} - \mathrm{OH}} + \mathrm{H_2AsO_4}^-$$

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, but the Bed Volume reduced to 300 for 100 ppb As(III) concentration at pH 6.0. Gupta and Chen (1978) reported an arsenic adsorption capacity 4 mg/g of activated alumina for the pH value 6.0; whereas Fox (1989) reported adsorption capacity of 1.0 mg/g for pH ranges between 7.4 to 8.0.

3. Methodology

Activated alumina removes arsenic from water by adsorption. Column study was conducted under different conditions using synthetic groundwater and deionized water to investigate the effects of iron on the arsenic removal efficiency of activated alumina.

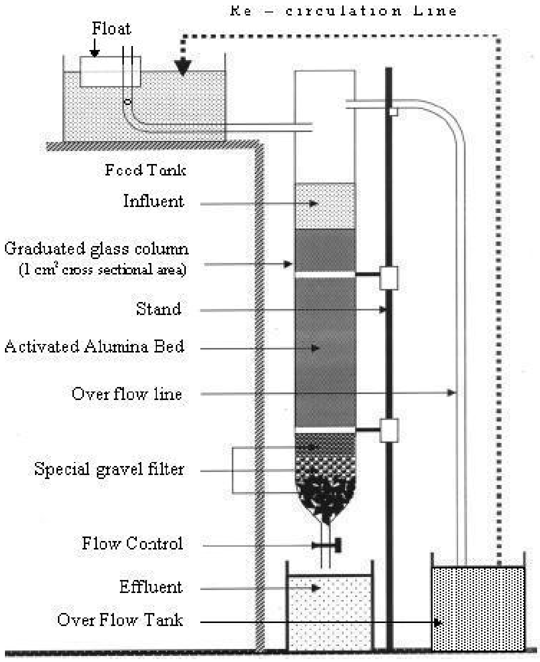

Fig. 1. Laboratory test bed and experimental set up

Down flow columns were set in the environmental engineering laboratory of Civil Engineering Department, BUET to carry out the study. The laboratory test bed and experimental setup is shown in Fig. 1. Graduated glass column of 1cm^2 in cross-sectional area was used as laboratory test column. A special gravel filter was placed at the bottom of the activated alumina bed to avoid flow restriction. Activated alumina was washed using deionized 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 the study, 14x28 mesh size activated alumina was used. 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 elevation than the inflow connection. A float system was used in 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. Experiments were conducted using synthetic raw water under different conditions. The procedures followed are outlined below:

3.1 Preparation of synthetic water

Both deionized water and tap water (groundwater) of the Environmental Engineering laboratory were used to prepare synthetic water for this study. The tap water sample was analyzed several times for detail characterization during the course of the study and the average composition is presented in Table 1. Stock solutions of As(III), As(V), and Fe(II) were prepared from their salts. The salts used were arsenic trioxide (As_2O_3), di-sodium hydrogen arsenate ($Na_2HAsO_4.7H_2O$) and ferrous sulfate ($FeSO_4.7H_2O$).

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 an aeration apparatus to remove excess carbon-dioxide. The stock solutions of As(III), As(V), and Fe(II) were added to the aerated water in required amounts to obtain feed waters of different specific compositions. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used to adjust pH of waters to different fixed values. The experimental conditions are presented in Table 2 and Table 3 for As(V) and As(III) removal studies, respectively.

Table 1
Composition of laboratory tap water

Water quality parameter	Unit	Concentration
pH	--	6.50
Carbon dioxide	mg/L	45.00
Total alkalinity as $CaCO_3$	mg/L	200.00
Arsenic	µg/L	below 1
Iron	mg/L	0.15
Chloride	mg/L	220.00
Sulfate	mg/L	60.00
Phosphate	mg/L	0.68

3.2 *Running of experiments*

Synthetic raw water was transferred from the preparation tank to the feed tank of the experimental set up. 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 from 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 into the glass column and passed through the activated alumina bed. The treated water was collected in a plastic bucket placed at the bottom of the column.

The flow velocity was measured intermittently using measuring cylinder and stopwatch. Cumulative volume of water passing through the alumina bed was measured and effluent samples were collected after specific volume 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 using deionized water during the non-operation period to avoid the drying of the iron flocs contained in the bed. When the run was stopped, the feed tank water was acidified using HCl. On the following day, the experiment was started after proper mixing of water in the feed tank and pH adjustment. All samples collected in plastic bottles 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 μg/L or the flow rate reduced to about 1 mL/cm^2/min.

Table 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		
300	6.0	0.00	20	14x28
		0.15	30	
		1.00	20	
		3.00	20	
		5.00	20	

Table 3
Experimental conditions for As(III) removal study

Major water quality parameters			Bed height (cm)	Activated alumina size
Arsenic (V) concentration, ppb	pH value	Iron content, mg/L		
300	7.0	0.15	30	14x28
		1.00	50	
		3.00	50	
		5.00	50	
		7.00	50	

3.3 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 (Jalil, 1998). 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 a pH meter (Ehamp pH tester, HANA). Mohr's method was used to measure the chloride content of water samples. HACH DR/4000 spectrophotometer was used to determine sulfate (Salfa Ver 4 method) and phosphate (Ascorbic acid method) concentrations.

3.4 Measuring Effectiveness of Arsenic Removal Efficiency

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

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

(ii) Quantity of arsenic adsorbed by activated alumina.

4. Results and discussion

4.1 Removal of Arsenate, As(V)

To study the effect of iron on arsenic removal efficiency of activated alumina, experiments were conducted with synthetic raw water having influent iron concentration of 0.0 mg/l (deionized water), 0.15 mg/l (tap water), 1.0 mg/l, 3.0 mg/l and 5.0 mg/l. pH value was fixed at 6.0 and arsenic concentration was fixed at 300 ppb. Figure 2 shows the relationship between effluent arsenic concentration and flow rate as a function of water passed through the activated alumina column (expressed as bed volume) for different iron concentrations. It is observed that high iron concentration in the influent causes high residual arsenic concentration in the effluent and a sharp drop in the flow rate. Generally, when the iron concentration increases, the deposition of iron flocs on activated alumina surface increases. As a result, available sites for arsenic adsorption on activated alumina decrease. Hence the curve for high iron concentration shows steeper slope, whereas, a better adsorption of arsenic is observed in case of low iron concentration in the influent. Figure 2 also reveals that higher the iron concentration in the influent, the lower the bed volume up to the MCL of 50 ppb. It is to be 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 dissolved arsenic into the inner surfaces of the granules. As the iron concentration increases, the coatings become thicker resulting in progressively lower BV (Table 4). Discontinuities of run and intermittent stirring were responsible for non-smooth nature of the adsorption curves especially for high iron concentration.

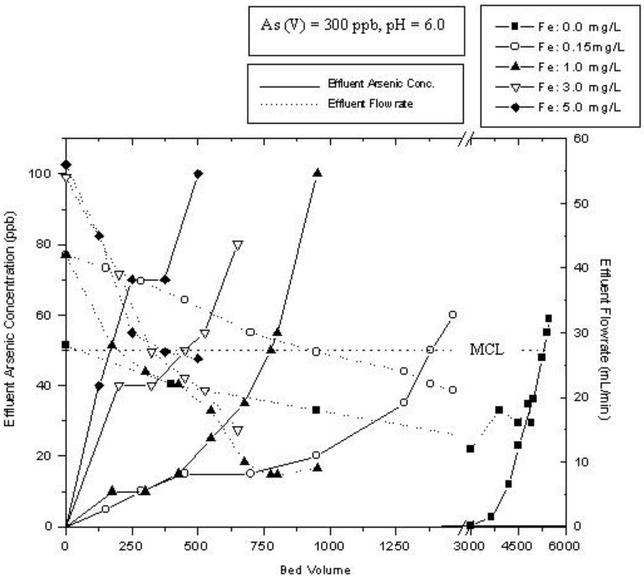

Fig. 2. Effect of iron on adsorption characteristics and flow rate of activated alumina bed for As(V)

Bed volume and quantity of arsenic adsorbed by activated alumina up to 50 ppb of arsenic for different influent iron concentration were determined and presented in Table 4. The quantity of arsenic adsorbed by activated alumina is found to decrease from 1.4 mg/g to 0.04 mg/g as iron concentration increased from of 0.0 mg/L and 5.0 mg/l. Fox (1989) reported arsenic adsorption density of 1.0 mg/g for pH range 7.4 to 8.0. In the presence of iron, as the raw water passes through the bed, the iron flocs adhere to the surface of activated alumina and thus make a barrier for the dissolved arsenic to come in contact with the adsorption sites. The bed flow rate decreases sharply with higher iron concentration in the raw water and enhances flocs deposition rate on the surface as well as into the activated alumina bed. Flocs envelope the alumina particles more quickly with thicker layer around them when the iron concentration is higher and result in higher residual arsenic concentration in the effluent and cause a decrease in the quantity of arsenic adsorbed by activated alumina bed.

Table 4
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 up to 50 ppb As level	As(V) adsorbed (upto 50 ppb As level) by activated alumina (in mg/g)
300	6.0	0.00	5287	1.40
		0.15	1383	0.35
		1.00	775	0.20
		3.00	450	0.11
		5.00	160	0.04

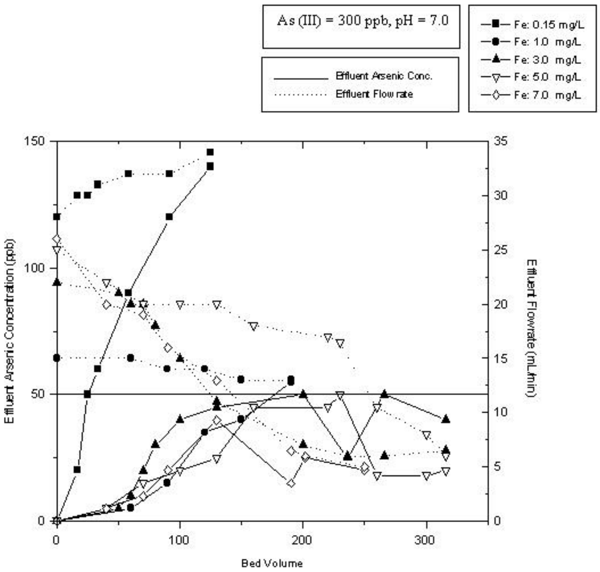

Fig. 3. Effect of iron on adsorption characteristics and flow rate of activated alumina bed for As(III)

Table 5
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 up to 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	-	-

4.2 Removal of Arsenite, As(III)

To observe the effect of iron concentration on removal of As(III), experiments performed with synthetic raw water having 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; pH value was fixed at pH and arsenite concentration was fixed 300 ppb. Figure 3 shows effluent arsenic concentration and flow rate as a function of bed volume of water passed through the column for different iron concentrations. This figure shows that in the presence of iron, As(III) removal efficiency actually improves. Normally arsenite has little affinity for activated alumina surface as compared to arsenate. However, As(III) may get adsorbed onto the iron flocs accumulated in the activated alumina filter bed. In case of low iron concentration, only a small amount of iron flocs is produced and retained by the alumina bed, and little adsorption of arsenic takes place and arsenic in the effluent increases rapidly with passage of water. Higher iron concentrations in the raw water results in higher ion flocs in the feed tank, resulting in adsorption of a significant amount of arsenic before the water 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, oxidation of iron was probably rapid in the feed tank. 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 through the column became progressively slower. Due to longer contact time, higher amount of arsenic was adsorbed onto the iron flocs and arsenic concentration in the effluent increased slowly with increasing BV. Intermittent stirring was mainly responsible for the non-smooth nature 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.

Treated bed volume and quantity of arsenic adsorbed by activated alumina up to 50 ppb arsenic level for different influent iron concentration were determined and presented in Table 5. The quantity of arsenic adsorbed by activated alumina is found to increase from 0.01 mg/g to 0.08 mg/g as iron concentration increased from 0.15 mg/l and 5.0 mg/l. It shows 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 an iron concentration of 7.0 mg/L could not be determined since the run was stopped due to very low flow rate, before effluent arsenic concentration reached 50 ppb. Although presence of iron improved removal of As(III), the treated bed volume up to the MCL of 50 ppb is much lower for As(III) compared to As(V).

5. Conclusions

The present study evaluates the effect of iron on the performance of activated alumina in removing As(III) and As(V) from groundwater. Efficiency of activated alumina in filter columns in removing arsenic was determined in terms of empty Bed Volume (BV) and quantity of arsenic adsorbed onto activated alumina up to 50 ppb arsenic level in the effluent. The following major conclusions could be drawn from this research work:

i. Iron has a very significant effect on the arsenic removal efficiency of an activated alumina bed. The nature of the effect is different for As(III) and As(V).

ii. For As(V), the arsenic removal capacity of activated alumina bed decreases drastically with the increase of iron concentration. The treated bed volumes up to 50 ppb arsenic in the effluent are found to be 5287, 1383, 775, 450 and 160 for iron concentration of 0.0, 0.15, 1.0, 3.0 and 5.0 mg/l, respectively for As(V) concentration of 300 ppb and pH of 6.0.

iii. For As(III), iron appears to have a positive effect on the arsenic removal efficiency of alumina bed, due to the adsorption of iron flocs accumulated on the activated alumina bed. The treated bed volumes up to 50 ppb arsenic in the effluent are 25, 176, 200 and 316 for iron concentration of 0.15, 1.0, 3.0 and 5.0 mg/l, respectively for As(III) concentration of 300 ppb and pH of 7.0.

iv. Pretreatment for oxidation of As(III) to As(V) and iron removal, and providing longer contact time are necessary preconditions for the effective utilization of the arsenic adsorption capacity of activated alumina.

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