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Influence of Some Selected Water Quality Parameters in Removing Trivalent and Pentavalent Arsenic from Groundwater by Activated Alumina

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Abstract: An estimated 35 million people in Bangladesh are now at risk of arsenic toxicity and treatment of arsenic contaminated water is essential. 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. In this research work, the effects of a selected number of water quality parameters such as arsenic concentration, oxidation state of arsenic and pH in removing arsenic by activated alumina were evaluated. Bed Volume (BV), quantity of adsorbed arsenic and removal efficiency up to 50 μg/L arsenic level in the effluent were calculated to evaluate the effectiveness of activated alumina in removing arsenic. The results of the study show that pentavalent arsenic is removed efficiently than trivalent arsenic. The BV of treated water decreases with the increase of arsenic concentration for both of the As(V) and As(III). The study reveals that the removal efficiency of As(V) is better within the pH range of 5.0 to 6.0, whereas As(III) removal increases at higher pH values.

Key words: Activated alumina, trivalent arsenic, pentavalent arsenic, maximum contaminant level (MCL), effectiveness, bed volume (BV).

Introduction

Arsenic contamination in ground water of Bangladesh is currently a widespread phenomenon prevailing in 53 districts out of 64 where the concentration exceeds the Bangladesh Standard (BGS, 2001). The survey results show that 27% shallow tube-wells are arsenic contaminated having concentration beyond the Bangladesh standard (50 ppb) where this figure increased to 46% when WHO standard (10 ppb) is considered. 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 (DPHE, 2000) and a total of 13,333 arsenicosis patients have been identified (EES, 2000). The most important measure needed to combat the arsenic problems is to provide arsenic safe drinking water to the exposed people. 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. Activated alumina adsorption is an effective process for removing pentavalent arsenic from water but trivalent arsenic removal capacity is poor (AWWA, 1990). However, there is still a need to develop design and operating criteria for an effective field deployable household/community level activated alumina adsorptive filter system. Various factors such as arsenic concentration, iron concentration, pH, presence of chloride, sulfate, phosphate, activated alumina size, flow rate, etc. influence the arsenic removal capacity of activated alumina. Quantification of the effects of such 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. Hoque et al. (2004) studied the effect of iron on the activated alumina bed performance in removing arsenic from groundwater and found negative effect in the case of As(V) removal whereas some positive effect was observed during their study for As(III) removal from groundwater. A recent study on the influence of anions in removing arsenic by activated alumina reveals that the phosphate and sulfate has significant negative effect on the performance of activated alumina in removing arsenic from groundwater (Hoque et al., 2005). The major objective of the present research work was to determine the influence of initial arsenic concentration and pH on both the trivalent and pentavalent arsenic removal efficiency from water by activated alumina adsorption process.

Activated Alumina Adsorption

Arsenic contaminated water is allowed to pass through a packed column of activated alumina grains wherein arsenic, as well as, other pollutants in the water are adsorbed on the sorptive surface of the activated alumina 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' (Figure 1). In practice, the column is only operated to a certain breakpoint, e.g. upto 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 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 (AWWA, 1990).

Methods

The study was conducted under different experimental conditions using synthetic groundwater (tap water) to

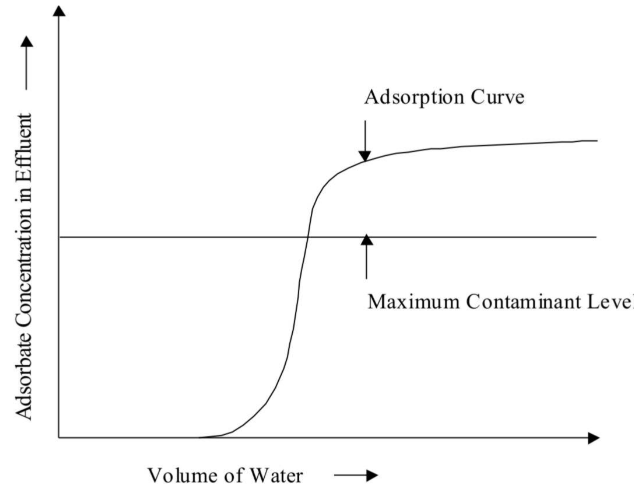

Figure 1: Breakthrough curve for adsorption column.

investigate the effects of selected parameters such as arsenic concentration, oxidation state and pH on arsenic removal efficiency by activated alumina.

Experimental Design

To conduct experimental run, down flow columns were designed to carry out the study. Graduated glass column of 1 cm^2 in cross-sectional area was used as laboratory test column. The experimental setup is shown in Figure 2.

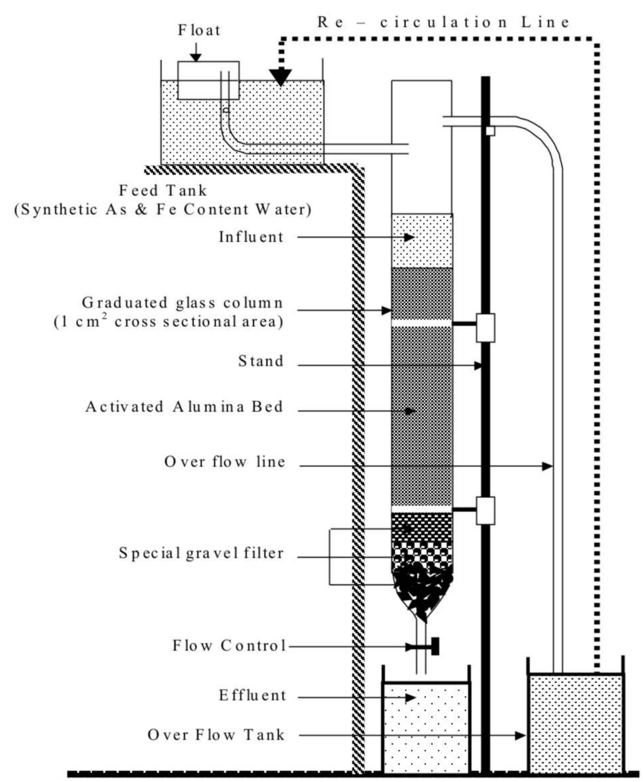

Figure 2: Experimental design for test bed.

Experimental Steps

Laboratory tap water was used for preparing synthetic water. The average composition of tap water sample during the course of the study is presented in Table 1. Stock solutions of As(III), As(V) and Fe(II) were prepared from their salts. The salts were arsenic trioxide (As_2O_3), di-sodium hydrogen arsenate ($Na_2HAsO_4.7H_2O$) and ferrous sulfate ($FeSO_4.7H_2O$). Tables 2 and 3 represent the experimental conditions for As(V) and As(III) removal study.

Table 1: Tap water characteristics

Water quality parameter	*Unit*	*Concentration*
pH	-	6.5
Carbon dioxide	mg/L	45.0
Total alkalinity as $CaCO_3$	mg/L	200.0
Arsenic	µg/L	below 1
Iron	mg/L	0.15
Chloride	mg/L	220.0
Sulfate	mg/L	60.0
Phosphate	mg/L	0.68

Table 2: Experiment for As(V) removal

Major water quality parameters			*Bed height (cm)*	*Activated alumina size*
Arsenic (V) concentration (µg/L)	*pH value*	*Iron content* (mg/L)		
100	6.0	0.15	20	
	5.0	1.0	20	
300	6.0	0.15, 1.0	20	14 × 28
	7.5	1.0	20	
500	6.0	0.15	30	

Table 3: Experiment for As(III) removal

Major water quality parameters			*Bed height (cm)*	*Activated alumina size*
Arsenic (III) concentration (µg/L)	*pH value*	*Iron content* (mg/L)		
100	7.0	1.0	50	
	6.0	1.0	50	
300	7.0	1.0	50	14 × 28
	8.0	1.0	50	
500	7.0	1.0	50	

After the transfer of synthetic raw water from the preparation tank to the feed tank the float system was placed in the tank (Figure 2) and adjusted to obtain a low overflow rate. pH of the feed tank was checked at regular intervals and was adjusted if necessary. The treated water was collected in a plastic bucket placed at the bottom of the column and was acidified immediately after collection for preservation. The experimental run was terminated when 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.

Water Sample Test

Arsenic measurements were done by Graphite Furnace Atomic Absorption Spectrophotometer (GF-AAS, Model AA680, Shimadzu). Thiocyanate method and Mohr method were used to measure the iron and chloride content of water samples respectively. Digital pH meter was used during study and the sulfate as well as phosphate contents were determined by using HACH DR/4000 spectrophotometer. To determine the carbon dioxide concentration and alkalinity of the water samples titration method was employed.

Determination of Effectiveness of Arsenic Removal

Effectiveness of activated alumina in a filter column in removing arsenic was determined in terms of Bed Volume (BV) up to Maximum Contaminant Level (MCL) of arsenic, which is the ratio of the quantity of water treated up to arsenic MCL in the effluent and the volume of activated alumina packed in the column. The result was also expressed through the quantity of adsorbed arsenic by activated alumina (mg/g). In addition, the arsenic removal efficiency (%) by activated alumina bed up to MCL was calculated.

Results and Discussion

Influence of Initial Arsenic Concentration

Removal of Pentavalent Arsenic: Figure 3 depicts that low arsenic concentration in the influent results in lower value of residual arsenic in effluent after the adsorption of arsenic by activated alumina bed, whereas higher values of arsenic concentration in influent result in high residual arsenic as the adsorption sites of activated alumina bed is exhausted at a faster rate. Treated bed volume and quantity of arsenic adsorbed by activated alumina upto 50 µg/L arsenic level for different pentavalent arsenic concentration were determined and presented in Table 4. The bed volume was found to be decreasing with the increase of arsenic concentration in the influent. The quantity of adsorbed arsenic by activated alumina was found higher for higher arsenic concentration in the influent due to higher concentration gradient between activated alumina surface and its

Table 4: Influence of As(V) concentration on treated bed volume and quantity of adsorbed arsenic by activated alumina

Influent iron (mg/L)	*Influent pH value*	*Influent As(V) concentration (μg/L)*	*Bed volume upto 50 μg/L arsenic level*	*Adsorbed As(V) by activated alumina (mg/g)*
		100	2115	0.15
0.15	6.0	300	1383	0.35
		500	375	0.16

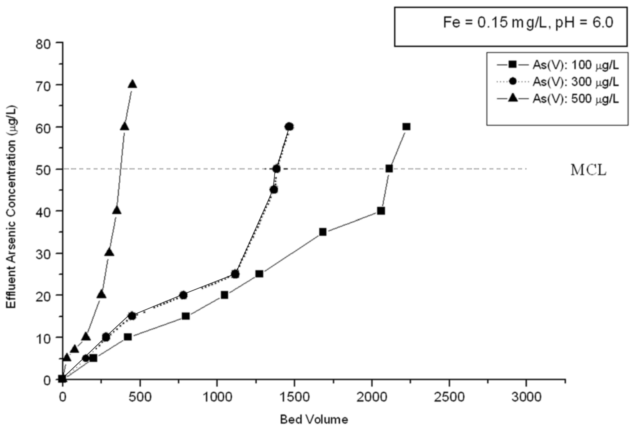

Figure 3: Pentevalent arsenic adsorption curves for synthetic water.

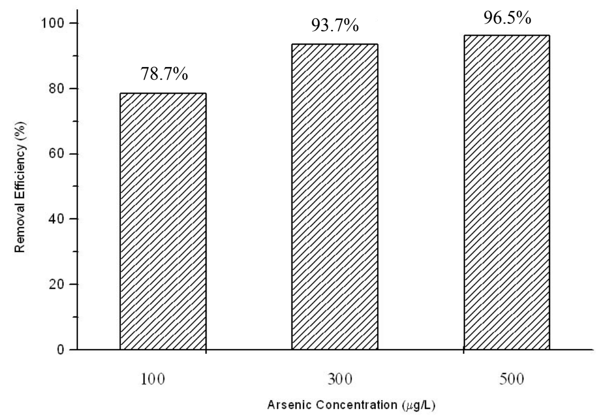

Figure 4: Arsenic removal efficiency with pentavalent arsenic concentration.

surrounding. But the exception was observed for arsenic concentration of 500 μg/L because; the high arsenic concentration in the influent here causes the residual arsenic in the effluent to reach the 50 μg/L level at a very low bed volume.

The bar diagram of arsenic removal efficiency with pentavalent arsenic concentration is illustrated in Figure 4. Arsenic removal efficiency was found to be 78.7%, 93.7% and 96.5% for arsenic concentration of 100 μg/L, 300 μg/L and 500 μg/L, respectively. Arsenic removal efficiency by activated alumina is directly proportional to arsenic concentration gradient between activated alumina surface and the 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.

Removal of Trivalent Arsenic: Since the ground water 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 adsorption curves are shown in Figure 5. The curve for arsenic concentration of 500 μg/L is found to be steeper compared to the 300 μg/L and 100 μg/L curves. In the case of higher arsenic concentration in the influent, adsorption takes place at a faster rate and the mass transfer zone moves faster; thus,

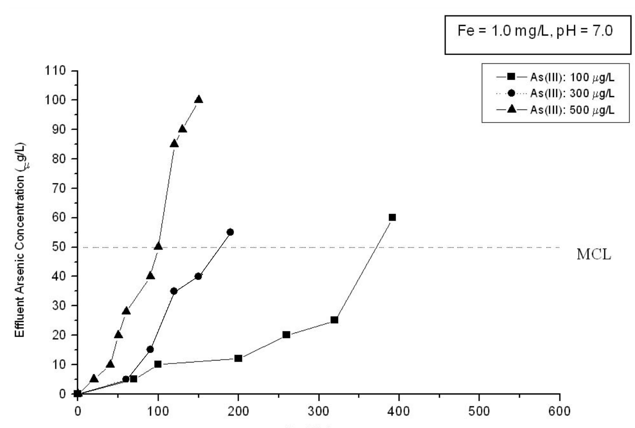

Figure 5: Trivalent arsenic adsorption curves for synthetic water.

the activated alumina bed becomes exhausted by arsenic species more quickly and diminishes the bed capacity that leads the arsenic concentration in the effluent to reach the MCL of 50 ppb at a lower bed volume. Table 5 shows that the bed volume decreases with the increase of influent arsenic concentration whereas the quantity of arsenic adsorbed by activated alumina is found to be slightly increasing with the increase of arsenic concentration as trivalent arsenic shows less affinity to adsorb on alumina surface as compared with pentavalent arsenic in normal pH range (6.0-7.5) due to non-ionization of As(III) species.

Table 5: Influence of As(III) concentration on treated bed volume and quantity of adsorbed arsenic by activated alumina

Influent Iron (mg/L)	*Influent pH value*	*Influent As(III) concentration (μg/L)*	*Bed volume upto 50 μg/L arsenic level*	*Adsorbed As(III) by activated alumina (mg/g)*
1.0	7.0	100	372	0.03
		300	176	0.04
		500	100	0.04

Kartivnen and Martin (1995) run their experiment by using an initial As(III) concentration of 100 μg/L at a pH of 6.0 and able to achieve 300 bed volume. On the other hand, the result from this research shows the bed volume of 372 at a pH value 7.0 instead of 6.0; bed volume increase by 72 in the conducted study may be due to the change of pH as well as the influence of iron content.

Arsenic removal efficiency is found to be 84.5%, 93.4% and 95.9% for 100 μg/L, 300 μg/L and 500 μg/L arsenic concentrations, respectively as shown in Figure 6. Actually higher arsenic concentration gradient between activated alumina surface and it's 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.

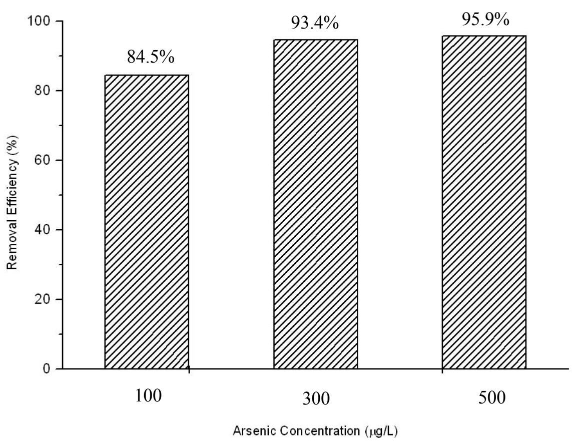

Figure 6: Arsenic removal efficiency with trivalent arsenic concentration.

Influence of pH

Removal of Pentavalent Arsenic: Observation shows that the adsorption curve for pH value 6.0 and 5.0 have more gentle slope as compared with that for pH value 7.5 as plotted in Figure 7. Pentavalent arsenic is dissociated into $H_2AsO_4^-$ 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; the bed volume, as well as, quantity of arsenic adsorbed by activated alumina are also found to be higher at pH value of 5.0 and 6.0 as compared with that at 7.5 as shown in Table 6. Figure 8 reveals the higher arsenic removal efficiency in the level of 92.0% and 93.9% for pH value of 5.0 and 6.0 respectively, optimum pH being 6.0.

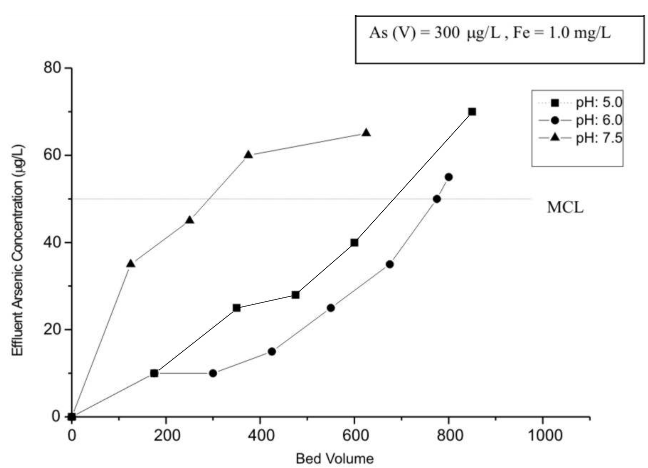

Figure 7: Influence of pH on adsorption characteristics of activated alumina for As(V).

Table 6: Influence of pH on treated bed volume and quantity of adsorbed arsenic by activated alumina for As(V)

Influent As(V) concentration (mg/L)	*Influent iron (mg/L)*	*Influent pH value*	*Bed volume upto 50 μg/L arsenic level*	*Adsorbed As(V) by activated alumina (mg/g)*
300	1.0	5.0	683	0.17
		6.0	775	0.2
		7.5	290	0.07

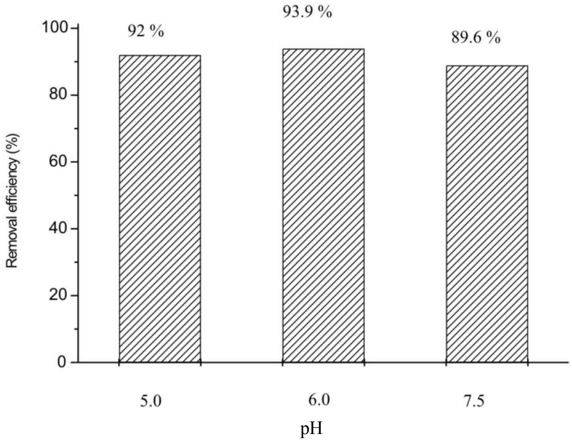

Figure 8: Arsenic removal efficiency with pH value for As(V).

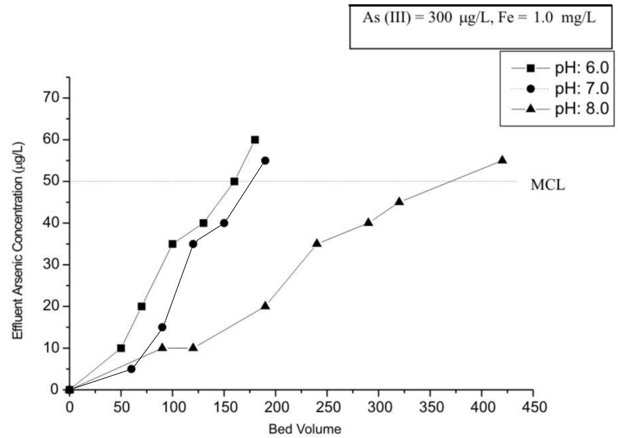

Figure 9: Influence of pH on adsorption characteristics of activated alumina for As(III).

Removal of Trivalent Arsenic: The effluent contains high residual arsenic at a pH less than 8.0 because of the existence of trivalent arsenic in the water in non-ionized form that is shown in Figure 9. The arsenic adsorption rate on activated alumina surface is found to be higher for higher pH value. Observation shows that the iron flocs play a vital role to adsorb arsenic and causes low effluent arsenic concentration. 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). The oxidation rate of ferrous to ferric form for iron flocs formation is found very slow at a pH below 6.5; afterwards the flocs formation rate becomes very fast with the increase of pH value which causes to increase the arsenic adsorption rate on iron flocs and the bed volume, as well as, quantity of adsorbed arsenic as referred in Table 7. The arsenic removal efficiency for different pH can be expressed through the bar diagram, which is shown in Figure 10.

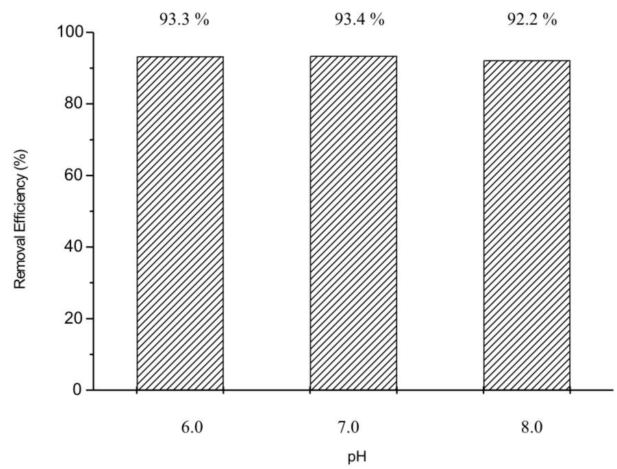

Figure 10: Arsenic removal efficiency with pH value for As(III).

Concluding Remarks

The conducted study reveals that the oxidation state and concentration of arsenic have significant effects on activated alumina adsorption process in removing arsenic from ground water. Bed volume is found decreased significantly with the increase of both As(V) and As(III) concentrations. Pentavalent arsenic is absorbed better in the pH range of 5.0–6.0 with optimum pH of 6.0. Alumina beds adsorb trivalent arsenic better as the pH values increases (pH value of 8.0).

Finally it can be concluded that a pretreatment with iron removal unit as well as pre-oxidation of influent to change trivalent arsenic to pentavalent form will make the activated alumina bed more effective and will give better removal efficiency.

Table 7: Influence of pH on treated bed volume and quantity of adsorbed arsenic by activated alumina for As(III)

Influent As(III) concentration (µg/L)	*Influent iron (mg/L)*	*Influent pH value*	*Bed volume upto 50 µg/L arsenic level*	*Adsorbed As(III) by activated alumina (mg/g)*
		6.0	160	0.04
300	1.0	7.0	176	0.04
		8.0	370	0.09

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