A low cost technique of arsenic removal from drinking water by coagulation using ferric chloride salt and alum

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Abstract

A variety of treatment processes have been used for arsenic removal from water. In a laboratory study using natural (tubewell) water, ferric chloride salt and alum were used, which are the most studied and widely used flocculents in water treatment due to their low price, comfortable availability and low risk usability. The solubility of arsenate(III) is much more than arsenite(V). Arsenate(III) was converted into arsenite(V) by proper oxidation using bleaching powder as an oxidizing agent before coagulation. The concentrations of ferric chloride salt and alum dose were varied from 10 mg/l to 200 mg/l, and pH was varied from 4 to 9. After intensive investigation, it was found that at pH 7 and for 100 mg/l to 125 mg/l dose of alum, the removal efficiency of arsenic and iron were around 82 to 86% and 92 to 95% respectively. Again, the optimum removal of arsenic and iron were around 90 to 93% and 97 to 100% respectively at pH 7 for 200 mg/l of ferric chloride salt. This research was carried out not only to observe the removal efficiency of arsenic, but also iron. Because most of the tubewells in Bangladesh, sometimes, contain higher amount of iron.

Keywords Adsorption; alum; arsenic; coagulation; ferric chloride salt; iron

Introduction

Arsenic is the 20th most abundant element in the earth’s crust and the 12th most abundant element in the biosphere, where it is said to be an essential element at least for some animal species, but not for human. Arsenic is a toxic chemical and may pollute air, soil, sediments and water causing health hazards to both human and animal life. Higher arsenic contamination is generally associated with the following environments: (a) basin full deposits of alluvial, lacustrine origin, particularly in semi arid areas, (b) volcanic deposits, (c) geothermal system, and (d) uranium and gold mining areas. Water supply in Bangladesh is primarily based on Ground Water Sources. Ground water based water supply is considered bacteriologically safe, economical and most suitable for scattered population in the rural areas (Ahmed, 1997). However, the groundwater pollution by arsenic in Bangladesh has become a major environmental threat at many places causing health hazard.

Concentration of As in water from tubewells can reach mg l−1 levels (Badal et al., 1996) and frequently exceed both the provisional guideline concentration for drinking water set by the World Health Organization (10 µg l−1 WHO, 1994) and the Bangladesh limit for As in drinking water (50 µg l−1; Department of the Environment, Bangladesh, 1991). The problem seems likely to affect a significant proportion of the 3–4 million tubewells in Bangladesh, which are the main source of drinking water for more than 90% people in Bangladesh that were installed during anti diarrhea campaign to reduce the water borne disease. The distribution of trace inorganic contaminants, such as arsenic, between the dissolved and particulate phase is a critical factor affecting the mobility, reactivity,
bioavailability, and toxicity of contaminants in natural waters and their removal in water treatment. The partitioning of such trace inorganic contaminants to the particulate phase is thus often governed by sorption onto the surfaces of minerals, particulate organic matter, or organisms or by biological uptake (Wilkie and Hering, 1996). Arsenic occurs in several chemical forms in the aquatic environment (Knauer et al., 1999). Arsenic chemistry is quite complex in aqueous systems because arsenic can be stable in four oxidation states when the valence and species are dependent on the oxidation reduction conditions and pH of the water. Arsenate(III) is more likely to be found in anaerobic ground waters and arsenite(V) in aerobic surface waters. Based upon a general review of the literature (Ferguson and Gavis, 1972; Ferguson and Anderson, 1974), in surface water (rivers, lakes, seas), with oxygen from the air providing oxidizing conditions, arsenic occurs in the following states: $\text{H}_3\text{AsO}_4^-$, $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$ and $\text{AsO}_4^{3-}$; in moderately reducing conditions $\text{H}_3\text{AsO}_3^-$, $\text{H}_2\text{AsO}_3^-$, $\text{HAsO}_3^{2-}$ and $\text{AsO}_3^{3-}$ are the dominant forms.

There is a need to develop cost-effective processes for use of small system or home-treatment units in developing areas of the world for removing total arsenic from ground water (Joshi and Chaudhuri, 1996). Therefore, the selection of appropriate process among many utilized technologies should be the most important concern. Precipitation with ferric chloride salt and alum and subsequent filtration of the generated precipitates has proved to be an adequate method for the removal of total arsenic, if arsenate(III) is converted into arsenite(V) before precipitation step to increase binding capacity of iron and alum salts and to minimize treatment by-products and chemical consumption (Jekel and Van Dyck-Jekel, 1989). In the present study, arsenate(III) was converted into arsenite(V) by using bleaching powder, which is usually used as post-chlorination in all treatment plants of Bangladesh. Using the different combinations of coagulant dose, pH, concentration of oxidizing agent, and other conditions, the results give the best removal efficiency keeping the concentration of arsenic below the standard value of Bangladesh. A mathematical calculation was provided in this study for the amount of ferric chloride salt and alum coagulant, if the initial and final concentrations of arsenic, volume of water and adsorption coefficients are known.

**Methods**

Reduction of the arsenic content in water may be achieved by using different technologies. The residual arsenic concentration that can be achieved with each one is different. When we select a technology, it is necessary to consider the final concentration to be reached besides the associated cost and feasibility.

**Sample collection**

On February 12, 15, 18, 24 and March 3, 10, 15, 1998, water samples were collected from 28 shallow tubewells to find out the relationships among arsenic and other elements. Most of the places were sited within 50 to 300 km from Dhaka, the capital city of Bangladesh. The top and base of screen of those tubewells were varied from 20 to 50 m. For jar test (coagulation experiment), the water sample was collected on March 26, 1998 from a shallow tubewell in Sonargao, Narayanganj, which is 35 km from Dhaka and the top and base of its screen were varied from 22 to 45 m. On April 4, 1998, water samples were collected from Manikgonj, which is 55 km from Dhaka, to observe the arsenic removal without any treatment. Each time, during sampling at least 6 to 10 L of water was wasted before the samples were collected. These places were chosen because concentrations of total arsenic were higher and those areas were preferred by many organizations for investigation. Water samples were collected in acid-washed and well rinsed polyethylene containers and before sample collection, the containers were also washed more than three times with the samples.
Chemicals and chemical analyses

All chemicals were reagent grade and were used without further purification. The tests were carried out at different doses of coagulants and their combinations. Oxidation of arsenate(III) to arsenite(V) can be achieved by several oxidants such as chlorine, ozone, UV-activated hydrogen peroxide ($\lambda < 230$ nm), permanganate and solid manganese dioxide (Borho and Wilderer, 1996). Every oxidant has specific advantages and disadvantages. The water samples were treated in a jar test apparatus. Prior to each treatment, different doses of bleaching powder were applied to certain amount of water so that a required concentration of residual chlorine could be available. The water was mixed vigorously at 80 rpm for 10 minutes and then different doses of alum and ferric chloride salt were added. The mix was stirred first vigorously at 50 rpm for 3 minutes and pH was adjusted at required level by concentrated HCl and NaOH. The mix was then again stirred slowly at 25 rpm for 5 minutes. Then it was allowed to settle for 4 hours or more before decanting. Arsenic concentrations in samples were determined by Silver Diethyldithiocarbamate (SDDC) method (Standard Method, 1989). Atomic Absorption Spectrometric (AAS) method (Model AA-680, Shimadzu Corporation) was used to measure the iron concentration and for sulfate, phosphate, chloride, nitrate, and hardness measurement, spectrophotometer (Model DR/4000U, Version 1.07, Hach company) was used. The pH and temperature were measured at the well head.

Results and discussion

Experimental results are divided into three sections. The first section explores the relationship of among arsenic and other elements. The next section summarizes investigations into arsenic and iron removal mechanisms by different coagulants at different conditions. The final section details the adsorption kinetics and mathematical calculation for coagulant dose measurement.

Relationship of arsenic and other elements

In the laboratory experiments, several tests were carried out to investigate the probable relationships among arsenic and other elements, like iron, sulfate, phosphate, chloride, nitrate and hardness. Figure 1 shows the test results. Here the concentration of hardness as CaCO$_3$. It may be observed from this figure that, in general, there is no strong relationship among these elements, even at lower concentration levels. So, it is not possible to predict the presence or absence of arsenic from the presence or absence of other (specially concerned in this regard) elements/compounds in groundwater. At lower concentration levels, it may be possible to establish very weak relationships, but in those cases the values of

Figure 1 Relationship among arsenic and other elements in the groundwater of Bangladesh
correlation coefficient are very poor. Even few elements have the same source, but their presence and absence are totally independent, which shows complex water chemistry. The temperature and pH of these samples were in between 24.8° to 30.2° C and 6.25 to 7.5 respectively. But these data do not give any logical support for any relationship.

**Arsenic and iron removal by coagulation in different conditions**

In the process of coagulation, ferric chloride salt (FeCl₃.6H₂O) and alum ((Al₂(SO₄)₃.24H₂O) were added in different doses and at wide range of pH (from 4 to 9). The stability and dominance of a certain form of arsenic depends directly on the pH value of the solution (Gupta and Chen, 1978; Pakholkov et al., 1980). Bleaching powder was added to oxidize arsenate(III) into arsenite(V) before addition of salt. The doses of bleaching powder were selected to get 0.20 ppm, 0.50 ppm, 0.75 ppm and 1.0 ppm residual chlorine during coagulation. Even from this experiment, it was found that higher residual chlorine had higher arsenic removal efficiency, but those conditions are not acceptable due to the harmful effects of excessive free chlorine. This paper includes only the results for the residual chlorine of 0.20 ppm. The initial iron and arsenic concentration of this sample were 2.0 ppm and 0.184 ppm respectively. The jar tests were carried out by this sample to maintain the equality of the results.

Figure 2 and 3 show that around 91% arsenic was removed at pH 7 to 8 and 100% iron was removed at pH 7 for the dose of 200 ppm ferric chloride salt. Again, Figure 4 and 5 indicate the 81% arsenic and 100% iron removal when 25 to 50 ppm alum was added at pH 8. Under acidic and alkaline conditions both the anionic species (iron and aluminium) have the higher solubility of the solid phase. To enhance the removal efficiency, pH of the system must be kept at this range (Benefield et al., 1982). The experiment was also carried out to observe the iron and arsenic removal without adding any coagulants and oxidizing agent.
Figure 6 illustrates the iron and arsenic removal in natural condition. For the measurement of arsenic and iron, samples were collected on each day from the top of the container without any disturbance. In the sample 1, 2, 3, and 4, arsenic levels were 0.065 ppm, 0.059 ppm, 0.128 ppm and 0.216 ppm respectively and those of iron levels were 38.0 ppm, 20.0 ppm, 7.5 ppm and 1.6 ppm respectively. The temperature and pH of those samples varied from 23° to 28° C and 6.5 to 7.5 respectively. This figure summarizes that with the higher level of iron, the arsenic removal efficiency is also higher. But after 7 days storage of those samples, there were no changes of arsenic removal. Here the dissolved As is often accompanied by dissolved Fe provides an emergency solution to As removal from arseniferous waters (Nickson et al., 2000).

The use of these coagulants shows the stable correlation with the solubility at certain pH level. It is necessary to use any suitable coagulant like ferric chloride salt or alum to get better removal of arsenic and iron. Actually, the removal efficiency also depends on other factors. But in this study only pH, dose of the coagulants and other basic factors were maintained. From the above figures, it was found that these two coagulants have better removal efficiency and they also follow the specific range of pH. Figure 7 reveals the optimum dose for higher arsenic removal at three effective pH levels. It is found from this figure that for ferric chloride salt, pH 7 is the best level for efficient arsenic removal. But in case of alum pH 6 and 8 are most suitable. Depending on the dose of the coagulants, pH can be selected or vice versa.
Adsorption kinetics and mathematical calculation for coagulant dose

In coagulation process, adsorption is the main kinetics of particle removal. Adsorption is a process in which the molecular, atomic or ionic species of one substance get attached to the surface of another, i.e.; the concentration of any particular component is higher at the interface than in the bulk. The solid-solid interfaces become a center of interest in the studies of catalytic promoters and friction. To describe the variation of the amount of solid adsorbed per unit mass of the adsorbent, at constant temperature, Freundlich suggested an empirical equation, which is shown in Eq. (1).

\[ f^* = \frac{x}{m} = kC^\beta \]  \hspace{1cm} (1)

where, \( f^* \) is the surface concentration in mg/g, \( x \) is the mass of solid adsorbed in mg/L, \( m \) is the mass of the adsorbent (dose of coagulant) in g/L, \( C \) is the residual concentration of solid in mg/L, and \( k \) and \( \beta \) are constants which depend on the nature of adsorbate/adsorbent and temperature. The concentration of arsenic in the flocculated iron and alum is calculated according to the equation,

\[ f^* = \frac{A_{\text{initial}} - A_{\text{residual}}}{D} \]  \hspace{1cm} (2)

where, \( A_{\text{initial}} \) and \( A_{\text{residual}} \) are the initial and residual arsenic concentration respectively of the sample in mg/L, \( f^* \) is the equilibrium concentration (surface concentration) of arsenic on coagulants in mg/g and \( D \) represents the dose of coagulants in g/L. The adsorption data shows small deviation from the actual isotherms, which is summarized in Figure 8. A slight deviation of the calculated values of equilibrium concentration from the curves represents the soundness of the analyses. The values of the parameters of Freundlich isotherm during coagulation by ferric chloride salt are \( k = 35.49 \) and \( \beta = 0.553 \) and that of by alum are \( k = 51.52 \) and \( \beta = 0.7082 \).

From the Eq. (2), it is possible to estimate the amount of coagulants, \( A \) in gm, required to treat a volume of water, \( V \) in L, containing an arsenic concentration \( A_{\text{initial}} \) in mg/L, down to a final concentration \( A_{\text{residual}} \) in mg/L, where other conditions (pH and oxidizing condition) are maintained. This equation can be turned into:

\[ D = \frac{A_{\text{initial}} - A_{\text{residual}}}{f^*} \hspace{0.5cm} \text{or} \hspace{0.5cm} A = \frac{A_{\text{initial}} - A_{\text{residual}}}{f^*} \hspace{0.5cm} \text{or} \hspace{0.5cm} A = \frac{(A_{\text{initial}} - A_{\text{residual}})V}{f^*} \]  \hspace{1cm} (3)

**Figure 8** The sorption isotherm of arsenic on flocculated iron and aluminium at pH 7 and the free available chlorine level of 0.20 ppm.
Now simplifying Eq. (1) and (3) we get,

\[ A = \frac{(A_{\text{initial}} - A_{\text{residual}}) V}{k A_{\text{residual}}} \]  

(4)

**Conclusion**

Groundwater at various locations in Bangladesh, which are otherwise safe for human consumption (free of water-borne pathogens), are posing a serious threat to the consumers’ health due to the elevated levels of arsenic in it. Significant variations in total arsenic concentrations were observed in most of the wells serving the cities of Bangladesh, with arsenic concentrations in many wells exceeding the current drinking water standard. Various treatment processes are available for effective removal of arsenic. Correct application of these technologies requires site specific investigations to determine the appropriate chemical doses and operating parameters. Arsenic removal has a better performance using ferric chloride salt than alum as coagulant. The dependence of pH in the efficiency of arsenic removal is greater when alum is used as coagulant. But pre-oxidation may be a critical process in obtaining an effective arsenic removal. Combinations of these oxidation and precipitation agents lead to very low residual arsenic concentrations. Arsenic can be removed successfully by combining several advanced technologies. When the water sources of any underdeveloped or developing country are affected by arsenic, those advanced technologies are not easily affordable. But ferric chloride salt and alum are very cheap, easily available and not hazardous. At the same time, during this process of arsenic and iron removal, we don’t need any expert. The users can easily handle this treatment procedure, if they are taught properly in the beginning. At this sever condition, it is necessary to provide few easily available, cheap, and quick technologies to the people in rural areas.

The values that the World Health Organization recommended are of the greatest interest for those countries where arsenic occurs in their water supplies give the face that, on many occasions, this value is used as referential information to establish the national standard or this value is required by the international organization that gives financial support to the countries that need to remove this contaminant from their water supplies.

**References**


