Removing arsenic from groundwater for the developing world – a review

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Abstract This paper is principally concerned with summarising the experience to date of treating arsenic containing ground/surface water by oxidation, coagulation/precipitation and adsorption processes. Arsenic (As) has been verified through epidemiological evidence as one of the most carcinogenic and toxic substances in surface and ground water. Oxidation, coagulation/precipitation, and adsorption have been widely used in arsenic removal and the study results demonstrated that these technologies can remove arsenic from ground/surface water efficiently; the residual arsenic concentration in the effluent could be in the range of 5–10 µg/l, against the influent arsenic concentration in the range of 10–500 µg/l. However, these technologies need to be surveyed in order to validate the efficiency, cost and maintenance requirements by considering social and economic situations and the availability of the local resources in the developing world.

Keywords Adsorption; arsenic (As); As chemistry; As removal technologies; developing world; oxidation; precipitation–coagulation

Introduction
Although arsenic is of long legendary toxicity, the presence of trace (micrograms per litre) arsenic levels in public drinking water supplies has not previously cause alarm. Arsenic is both toxic and carcinogenic. Inorganic forms of arsenic dissolved in drinking water are the most significant forms of natural exposure. Organic forms of arsenic that may be present in food are much less toxic to humans. Clinical evidences of arsenic poisoning begin with various forms of skin disease, and proceed via damage to internal organs ultimately to cancer and death. The symptoms of chronic arsenic poisoning may take between five and fifteen years to reveal themselves. Recent studies have indicated that arsenic in drinking water is more dangerous than previously suspected (Smith et al., 1992). The World Health Organisation (WHO, 1996), and the US Environmental Protection Agency (USEPA, 1993) have set up more stringent arsenic regulations to minimise these risks.

International concern has also focused on the problem of arsenic in groundwater in Bangladesh and Bengal, India, because of the large scale of the population who are affected adversely by high arsenic concentrations. In Bangladesh, where drinking water is mainly from groundwater, geochemical conditions favour arsenic dissolution. High concentrations (0.5–5 mg/l) are reported from many districts, and British Geological Survey (BGS) estimates that 25–30 million are now using this water for drinking, cooking and other domestic purposes (BGS, 1999). Similarly, in Bengal, India, nearly 30 million people in the state are exposed to arsenic in the concentration range of 0.2–2.0 mg/l due to the consumption of groundwater for drinking purposes (PHED, 1991). The Bangladesh and India Standard for arsenic in drinking water is 0.05 mg/l, which was based on WHO advice at the time when the regulations were drafted, and the new WHO provisional guideline for As (0.01 mg/l, WHO, 1996) has not been adopted in either Bangladesh or India.

A variety of treatment processes has been used for arsenic removal from water. The most commonly used technologies for the developing world include oxidation, coagulation–precipitation, and adsorption with activated carbon, activated alumina, and
iron-oxide-coated materials (e.g., Song and Logsdon, 1978). These processes are most promising but require validation for efficiency, sustainability, adaptation and adoption using locally available resources. This paper therefore aims to compare the effectiveness and limitations of these arsenic removal technologies and investigates their practicality for the developing world.

**Arsenic chemistry**

In natural waters, the soluble arsenic species are As\(^{3+}\) (arsenite) and As\(^{5+}\) (arsenate). Although both organic and inorganic forms have been detected, organic forms (methylated arsenic) are seldom present at concentration greater than 1 µg/l and are generally considered of less toxicity in comparison with the inorganic species in drinking water treatment.

Thermodynamic predictions provide a useful understanding of the equilibrium chemistry of the inorganic arsenic species in water (Figure 1). In oxygenated waters As\(^{5+}\) is dominant, existing in anionic forms of either \(\text{H}_2\text{AsO}_4^-\), \(\text{HAsO}_4^{2-}\), or \(\text{AsO}_4^{3-}\) over the pH range typically encountered in water treatment.

Under anoxic conditions, As\(^{3+}\) is stable, with arsenous acid (\(\text{H}_3\text{AsO}_3\)) and anionic (\(\text{H}_2\text{AsO}^-\)) species dominant below and above pH 9, respectively. In the presence of sulphides, precipitation of AsS (realgar) or As\(_2\)S\(_3\) (orpiment) may remove soluble As\(^{3+}\) and exert considerable control over trace arsenic concentrations (Ferguson and Garvis, 1972). Although thermodynamics can provide an accurate prediction of possible changes in a given non-equilibrium condition, they give no insight to the rate at which those conditions will occur. In general As\(^{3+}\) and As\(^{5+}\) acid-base reactions can be assumed to occur instantaneously, whereas time periods for the changes between oxidation states are indeterminate in natural waters. For instance, the conversion of As\(^{3+}\) to As\(^{5+}\) in oxygenated water is thermodynamically favoured, yet the rate of the transformation may take days, weeks or months, depending on the specific conditions. Strong acidic or alkaline solutions, the presence of copper salts, carbon, unknown catalysts and higher temperatures can increase the oxidation rate (Johnson and Pilson, 1972). The existence of manganese oxide, chlorine, permanganate and other oxidants can directly transform As\(^{3+}\) to As\(^{5+}\) in the absence of oxygen (e.g., Frank and Clifford, 1986). The reduction of As\(^{5+}\) to As\(^{3+}\) in the absence of oxygen is also chemically slow and may require bacterial mediation.

Arsenic can be immobilized through adsorption-coprecipitation with iron and manganese hydroxides, mobilised when such solids are dissolved under reducing conditions, or released from the precipitate surfaces in the event of competition (for sorptive sur-
face sites) in the presence of orthophosphate and natural organic matter (NOM) (e.g., Peryea, 1991; Xu et al., 1991). The latter factors can explain why arsenic may be correlated to high Mn (II) (dissolved and reduced manganese oxide), Fe (II) (dissolved and reduced Fe(OH)₃), and orthophosphate (competition with arsenic for adsorption sites) in certain waters. (e.g., Peryea, 1991).

The above reactions can occur in both groundwater and surface water sources. For each water source, there are three distinct zones, namely, aerobic, anoxic without sulphide, anoxic with sulphides. Within oxygenated zones, As⁵⁺ is stable and may remain soluble or sorb-coprecipitate with iron and manganese oxides if present. High concentrations of orthophosphate may compete with As⁵⁺ for adsorption sites in the zone, increasing soluble arsenic concentrations and mobility. In anoxic regimes without sulphides, As³⁺ is stable, and dissolved forms of iron and manganese are favoured. Arsenic mobility (or solubility) is highest in this zone because (a) As³⁺ is believed to sorb less strongly onto oxides than As⁵⁺ and (b) coprecipitated-sorbed arsenic is released upon dissolution of arsenic-containing Fe and Mn oxides. In anoxic zones with sulphides, As³⁺ becomes immobilised because of the formation of orpiment (As₂S₃), realgar (As₂S₂), or is coprecipitated with iron pyrite.

**Evaluating arsenic removal technologies**

Arsenic removal technologies generally fall into three major classes: chemical coagulation–precipitation, adsorption and membrane separation. The purpose of the oxidation is to oxidize the As³⁺ to As⁵⁺ and this favours coagulation–precipitation and adsorption. Membrane technologies have been used for arsenic removal in the developed countries (e.g., Song and Logsdam, 1978) but have not been shown to be feasible for the developing world. This section thus compares the technologies of oxidation, coagulation–precipitation and adsorption only for the performance of arsenic removal, and discusses whether these technologies could be adopted in the developing world.

**Oxidation of As³⁺ to As⁵⁺**

Since As⁵⁺ is readily removed by chemical coagulation and adsorption, complete oxidation of As³⁺ to As⁵⁺ is required if these technologies are adapted. There are numerous methods of oxidation available, but important factors such as the residual concentrations, availability and running cost of oxidants and oxidation by-products should be considered when selecting an oxidant. Ozone and UV radiation oxidise As³⁺ normally within about 30–60 seconds. However, it requires a high energy input, which may not be cost effective for small water treatment plants in the developing world. Chlorine is commonly used in the water industry as a disinfectant and is a suitable oxidant. However, the drawback in the use of chlorine is that it will react with natural organic matter to form chlorinated by-products, which are believed to have health concern effects. In addition, it is not so effective for As³⁺ oxidation if the raw water has high turbidity. The most feasible oxidants to date are either potassium permanganate or Fenton’s reagent. These oxidants produce no harmful by-products, and are easily applied.

**Coagulation–precipitation process**

Coagulation with metal coagulants like alum (Al₂(SO₄)₃) and ferric chloride (FeCl₃) has long been recognized as an effective method for removal of arsenic. The efficiency of arsenic removal with FeCl₃ and alum was examined in bench-scale studies (Hering et al., 1996; 1997). As⁵⁺ removal by either FeCl₃ or alum was relatively insensitive to variations in source water composition below pH 8. At pH 8 and 9, the efficiency of As⁵⁺ removal by ferric chloride was decreased in the presence of natural organic matter. The pH range for arsenic removal with alum was more restricted than with FeCl₃. For source waters spiked
with 20 µg/l As$^{5+}$, final dissolved As$^{5+}$ concentrations in the product water of less than 2 µg/l were achieved with both coagulants at neutral pH. Removal of As$^{3+}$ from source waters by FeCl$_3$ was both less efficient and more strongly influenced by source water composition than removal of As$^{5+}$. The effect of coagulation pH on the As removal percentage over wide FeCl$_3$ doses is shown in Figure 2, where the influent As concentration was 0.1 mg/l. Increasing coagulation pH decreased As removal percentage and the optimum coagulation pH for As removal with ferric chloride was 7.

Water samples collected from six sources in West Bengal were studied extensively for arsenic removal with coagulation–flocculation (Pande et al., 1997). The results have shown that a dose of 3.0 mg/l of chlorine (for pre-chlorination) followed by 50 mg/l of FeCl$_3$ was able to remove arsenic from the raw waters. Arsenic removal can also be facilitated by a variety of solids formed during softening including CaCO$_3$, Mg(OH)$_2$, Mn(OH)$_2$, and Fe(OH)$_3$ (e.g., Hering et al., 1997). The extent of As$^{5+}$ removal is decreased in the presence of orthophosphate and carbonate. As$^{3+}$ removal is much lower than As$^{5+}$ removal. At typical solids concentrations, arsenic removal followed a linear isotherm for CaCO$_3$, Mg(OH)$_2$, and Fe(OH)$_3$ with constant percentage arsenic removal regardless of initial arsenic concentrations. However, for Mg(OH)$_2$ solids arsenic removal was sensitive to arsenic concentrations.

The possible use of enhanced coagulation (the term is defined as the optimum coagulation performance could be achieved by modifying the coagulation pH and coagulant dose) for arsenic removal was examined at bench, pilot, and demonstration scales with two source waters (Cheng et al., 1994). Alum and FeCl$_3$, with cationic polymer, were investigated at various influent arsenic concentrations. For the source waters tested, enhanced coagulation could be effective for arsenic removal and that less FeCl$_3$ than alum, on a weight basis, is needed to achieve the same removal percentage.

Arsenic removal efficiencies from the full-scale plants were evaluated (e.g., Scott et al., 1995). Raw water with As$^{3+}$ 0.6–2 mg/l was prechlorinated with 3–5 mg/l of chlorine and coagulated with 3–10 mg/l of FeCl$_3$ or 6–10 mg/l of Al$_2$(SO$_4$)$_3$. Arsenic removal was 81–96% with FeCl$_3$ and 23–71% with Al$_2$(SO$_4$)$_3$. The best results were obtained with 4 mg/l of FeCl$_3$ at a filtration rate 150 m$^3$/m$^2$/day and up to 70 runs. The full-scale study results also suggest that arsenic removal is best achieved by FeCl$_3$ instead of Al$_2$(SO$_4$)$_3$ coagulation. This is consistent with that from the bench-scale results.

![Figure 2](https://iwaponline.com/wst/article-pdf/44/6/89/430485/89.pdf)
**Arsenic removal by adsorption**

Adsorption is a traditional process to separate solutes from solvent or gases, where the solute increases on the surface of the adsorbent and decreases in the solvent. Adsorption equilibrium is achieved when the number of molecules leaving the surface of the adsorbent is equal to the number of molecules being adsorbed on the surface of the adsorbent. Effective adsorbents have a highly porous structure so that their surface area to volume ratio is very large. Adsorbents used for arsenic removal include activated alumina, activated carbon, and iron-oxide-coated sand.

**Activated alumina (AA)**

Granular activated alumina is a commercial porous aluminium oxide with specific surface areas of 200 to 300 m²/g, has high pH of zero-point-of-charge (zpc) (pH \(_{zpc} = 8.2\)) and has the following selectivity sequence:

\[\text{OH}^- > \text{H}_2\text{AsO}_4^- > \text{H}_3\text{SiO}_4^- > \text{F}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^-\]

AA is a promising adsorbent for arsenic removal. It can be used in the fixed bed technique and can be regenerated with diluted NaOH and H\(_2\)SO\(_4\). The sorption equilibria of As\(^{5+}\) on activated alumina were measured by Rosenblum and Clifford (1984). The best pH value for As\(^{5+}\) adsorption was 5.5–6 because the alumina is protonate, but the anions of the acid added (to lower the pH) are not yet competitive in arsenic adsorption. The adsorption capacities were about 5–15 mg/g at equilibrium concentrations of 0.02–0.1 mg/l. The existence of sulphate and chloride ions can reduce the adsorption capacity by up to 50%. As\(^{3+}\) is difficult to be removed by AA, but As\(^{5+}\) is readily to be adsorbed and its breakthrough may occur at 14,000 or 24,000 times the bed volumes (pH 6) against the effluent arsenic concentration of 20 µg/l and 50 µg/l, respectively (Figure 3).

The above findings were confirmed at pilot-scale studies (Rubel and Hathaway, 1987), where the best arsenic removal was achieved at pH 5.5 in the down-flow mode; with up to 15,000 times the bed volumes against the breakthrough concentration of 20 µg/l. Using 4 to 5% NaOH cannot achieve the completed regeneration, and 20% of the arsenic remained in the adsorbed. Operation under non-optimal conditions reduced the run time of the adsorber by about 50%.

The competitive effects of other anions, such as phosphate or fluoride, will reduce the capacity for As\(^{5+}\) adsorption considerably. This may be of particular concern if the competitors are present in the range 0.1–2 mg/l and arsenic has to be removed down to the µg/l range.

**Figure 3** Comparison of breakthrough curves for As\(^{5+}\) and As\(^{3+}\) in filters of activated alumina (reproduced from Rosenblum and Clifford, 1984)
The available study results suggest that AA can be applied successfully for removing arsenic if the influent pH is slightly acidic (e.g., pH 6) and the competing anions are present in small concentrations (e.g., < 0.1 mg/l). The great advantage of AA is its simple operation over one to three months before regeneration is required, making it more feasible for small-scale requirements. However, after regeneration, the run length of AA is only at 75% of the virgin run length (Simms and Azizian, 1997). Another disadvantage of AA adsorption is both sodium hydroxide and sulphuric acid should be used in regeneration process and the spent arsenic contaminated alkaline and acid wastewaters require treatment and disposal of.

Granular activated carbon (GAC)

GAC is very common used for drinking water treatment and wastewater treatment in some cases. GAC has the following characteristics, particle size is 0.5–2 mm, surface area is around 1,000 m²/g and apparent density is 0.4–0.5 g/m³. Factors influencing the GAC performance for arsenic removal could be pH, the type and properties of GAC, and pretreatment of GAC with various metals.

The effect of pH on arsenic adsorption capacities of the activated carbon has been investigated. The maximum As⁵⁺ loading could be achieved at pH values of 5 to 7 (Figure 4), and pH adjustment can control arsenic adsorption and arsenic stripping from GAC (Gupta and Chen, 1978; Lee and Rosehart, 1972). The type of activated carbon also influences the arsenic adsorption capacities. Table 1 shows the arsenic loading of three types of activated carbon, and the contact period with the arsenic solution was 24 hours. Both the peat-based carbon and the coal-based carbon performed better than coconut-shell carbon due to their high ash content. Higher arsenic loading by carbon with high ash content were contributed to interact between the mineral matter (metal oxides and metal ions) and arsenic in the carbon. The results in Table 1 also show that with an increase in the specific surface area of the carbon, there is a decrease in arsenic loading, indicating that surface area of the carbon plays minor role on arsenic adsorption.

The adsorption of arsenic by GAC can also be improved by pre-treating the carbon with metal ions (e.g., Rajakoviv, 1992). This can be performed by contacting the activated carbon with various metal ion solutions. In order to increase metal ion loading on the carbon, the alkalinity of the solution can be raised with the addition of solution hydroxide until the metal hydroxide precipitates onto the carbon surface. A large number of metal ions have been selected for pretreatment. The arsenic adsorption capacities of various pretreated activated carbons are shown in Table 2. The pH values presented are that at which the maximum arsenic adsorption occurred.

**Figure 4** The effect of influent pH on the GAC performance for As removal
From Table 2, it can be seen that pretreatment with copper and ferric salts resulted in greater arsenic loading than that with untreated activated carbon. Arsenic loading following copper pretreatment with and without precipitation of the metal hydroxide was identical (5.79 mg As/g carbon). In the case of Fe(III), arsenic loading dropped from 4.53 mg As/g carbon with precipitation to 4.09 mg As/g carbon without precipitation. The effect of different anions in the copper salts used for the carbon pretreatment was also investigated. Cuprous chloride resulted in the greatest arsenic loading. Arsenic loading by pretreated peat-based carbon was also higher than that of pretreated coconut-shell carbon (7.41 mg/g carbon for the former and 5.79 mg/g carbon for the latter). In addition, arsenic desorption can be achieved using either strong acidic or alkaline solutions. Acidic solutions are more effective and the copper is also eluted.

**Iron-oxide-coated sands (IOCS)**

In recent years, iron-oxide-coated sand (IOCS) (e.g., Joshi and Chuadhuri, 1996) has been prepared and investigated for its performance to remove arsenic. Its characteristics are shown in Table 3. It can be seen that IOCS has high surface area and PZC, and the better adsorption performance is expected in comparison with the plain sand.

Column tests have been undertaken using 75 g of iron-oxide-coated sand in an 11 mm internal diameter glass column (bed depth 525 mm; porosity 0.36) and a flow rate of 1 ml/min to assess the potential of iron-oxide-coated sand as an adsorbent for removing arsenic from ground water. Background batch sorption kinetic tests indicated that the bulk of the arsenic sorption on iron-oxide-coated sand occurred during 30–60 min of contact. A column was run until the effluent arsenic level was well above 0.01 mg/l (the WHO provisional guideline value for arsenic in drinking water). The medium was then regenerated by backwashing with 2 litres of a 0.2N sodium hydroxide solution. This was followed by backwashing with distilled water until the influent and effluent pH was comparable. This constituted one cycle of the column test. The spent regenerant and backwash water were analyzed for the recovered arsenic.

Breakthrough empty-bed volumes at arsenic concentration of 0.01 mg/l were in the range 163–184 and 149–165 per cycle for As$^{3+}$ and As$^{5+}$, respectively. During
regeneration, 94–99% of the removed arsenic was recovered in each cycle. Leaching of iron from the medium was not detected in the effluent. The results indicated promise of IOCS as an adsorbent for use in small systems for removing arsenic from groundwater.

Spent catalysts are generated in various industries (e.g., petrochemical industry). After 2–3 regenerations, they are to be disposed of as solid wastes with significant amount, and have been studied as adsorbents as they consist of porous silica and alumina. The effectiveness of pretreating spent catalysts with iron solutions to improve arsenic removal has been studied (Huang and Liu, 1997). The results indicated that iron-coated spent catalysts could be used as adsorbents for removing As$^{5+}$ from aqueous solutions. The arsenic adsorption capability of spent catalysts was improved by coating iron with 0.01 M Fe(III) solution, and the arsenic adsorption increases with decreasing pH (the optimum pH is at 5). The As$^{5+}$ is proposed to be specifically adsorbed onto the iron-coated spent catalysts and the adsorption capability is comparable to those of other adsorbents.

**Arsenic removal technologies for developing world**

In many developing countries, increase in population, poverty and economic stagnation have left the society with economic problems. In these countries, strategies for development including opening up of new lands, development of new industries and agriculture as means to solve these problems have increased the demand of water resources for agricultural, industrial and drinking water supply. Many countries promoted the use of groundwater, which usually has advantages over surface water in various aspects, however, the quality of groundwater is largely determined by geological conditions and sometimes it turns out to containing various substances harmful to human health. Arsenic (As) in groundwater has become a serious problem in a number of developing countries. A lot of technologies have been developed to remove As from groundwaters. Among which, pre-oxidation,

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<th>Table 3 Characteristics of plain sand and IOCS (Benjamin et al. 1996)</th>
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<td>% Fe by weight</td>
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<td>Surface area by BET ($m^2/g$)</td>
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<td>pH of the PZC</td>
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<th>Table 4 Comparative arsenic removal performance</th>
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<td>Treatment technology</td>
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coagulation–precipitation, and adsorption could be the cost-effective technologies for removing arsenic for the developing world. The comparative As removal performances have been summarised in Table 4, where the arsenic concentration in the effluent could be less than 5–10 µg/l by treatment with pre-oxidation and iron coagulation/precipitation, and adsorption.

A future study should be concerned with a survey of various household technologies for As removal in developing world, in order to validate their efficiency, cost and maintenance requirements by considering social and economy situations and the availability of the local resources. Such household technology would provide a low-cost technology for use, principally by the rural poor; this must therefore be most efficient and robust and require minimal maintenance.

Conclusions
International concern has been focused on the problem of arsenic in groundwater in some developing countries because of the large scale of the population who are adversely affected by high arsenic concentrations.

The inorganic form of arsenic in water is the result of dissolution from the solid phase and is present in stable oxidation states of As\(^{5+}\) (arsenate) and As\(^{3+}\) (arsenite). Arsenate predominates in oxygenated surface waters in three forms: H\(_2\)AsO\(_4\)^–, HAsO\(_4\)^2–, or AsO\(_4\)^3–. Arsenite is favoured under reducing conditions (anaerobic groundwater), and its species is a function of pH and redox potential.

Pre-oxidation, coagulation–precipitation, and adsorption could be the cost-effective technologies for removing arsenic for the developing world. By treatment with pre-oxidation and iron coagulation/precipitation, the arsenic concentration in the effluent could be less than 5 µg/l. Adsorption with AA, GAC and IOCS can also remove arsenic efficiently and the arsenic concentration in the treated water could be less than 10 µg/l. However, using these technologies in groundwater remediation has not been consistently demonstrated. Therefore, a survey to evaluate various household technologies for the arsenic removal and for use by the rural poor is necessary and such technologies should be most efficient with low cost, sustainability, adaptation and adoption using locally available reagents, and requires minimum maintenance.

References


