The Dilemma Small Utilities Face in Selecting Processes for Treatment of Arsenic

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Arsenic contamination in drinking water is a serious cause for concern all over the United States and in many other parts of the world. With the U.S. Environmental Protection Agency (EPA) currently lowering the Maximum Contaminant Level (MCL) from 50 parts per billion (ppb) to 10 ppb, many small water utilities are faced with employing efficient, cost-effective methods for arsenic removal. Since nearly 97 percent of the water systems affected by the new standard are small systems that serve less than 10,000 people, it is vital that the treatment technologies developed are effective and affordable.

Arsenic occurs in most natural waters in its inorganic forms. Ingesting inorganic arsenic results in both cancer and non-cancer-related health effects [1].

The EPA has classified arsenic as a Class A carcinogen. Chronic exposure to low arsenic levels (less than 50 µg/L) has been linked to health complications, including cancer of the skin, kidney, lung, and bladder, as well as other diseases of the skin and the neurological and cardiovascular systems [2].

Several design criteria and assumptions need to be established before a treatment process is selected for arsenic removal. These include the maximum flow rate per source, the average flow rate per source, the target finished water arsenic concentration, the method of domestic waste discharge, Technically Based Local Limits (TBLLs) for arsenic and Total Dissolved Solids (TDS), land availability, labor commitment, the acceptable percent water loss, and any state or primary agency requirements that are more stringent than the EPA [3].

This article will review various arsenic treatment technologies, such as coagulation, ion exchange resins, adsorption processes, membranes processes, and natural zeolites, with the purpose of assessing the effectiveness when used by small water utilities to meet the arsenic maximum contaminant level. In almost all the cases mentioned above, the chemical form of arsenic in water must be taken into consideration before a particular treatment process is selected.

Treatment Processes

Inorganic arsenic occurs in two valence states, arsenite (As III) and arsenate (As V). The predominant species for As (III) are $H_3AsO_3^{-1}$ and for As (V) are $H_2AsO_4^-$ and $HAsO_4^{2-}$. This means that arsenate exists as anion at typical pH (5.0 -8.0), while arsenite remains as a neutral molecule in the same pH range.

The oxidation of arsenite to arsenate can be achieved by adding chlorine or permanganate during the pretreatment processes. This is the most important step for optimal performance by any of the five following treatment processes.

Coagulation

Coagulation is the most common technique used for arsenic removal. Coagulation/filtration (C/F) is a treatment process in which the physical or chemical properties of dissolved colloidal or suspended matter are altered so that agglomeration is enhanced to an extent that the resulting particles will settle out of solution by gravity or will be removed by filtration. Major components of a basic C/F facility include chemical feed systems, mixing equipment, basins for rapid mix, flocculation, settling, filter media, sludge handling equipment, and filter backwash facilities [3].

Arsenic removal by the coagulation method is a function of the following factors:

- coagulant type
- pH
- coagulant dosage
- initial concentration of As(III) and As(V)
- co-occurring inorganic solutes
- chemical form of As

Small water systems that are considering this technology should design the process to operate in the optimal pH range (pH 5 to 7 for alum coagulation and pH 5 to 8 for ferric coagulation) in order to achieve a high degree of arsenic removal, per the compliance.

C/F is unlikely to be installed solely for arsenic removal because it is highly uneconomical [4]. The most important design criterion affecting the capital cost in small water systems is the filtration rate, which affects the size of the filter structure and the volume of filter media. Operation and maintenance costs are affected mostly by costs of chemicals (coagulants and polymer dosages) [3].

Disposal of C/F residuals is a function of influent arsenic concentration, coagulant dosage, and suspended solids content. Land application is the most suitable disposal option [2].

The arsenic-contaminated coagulation sludge must be completely dewatered prior to landfill disposal. Disposal of this sludge may be of concern, especially if the nearby landfill is to accept such sludge. All the factors discussed above—extensive infrastructure, significant capital and maintenance costs, and disposal problems—make coagulation a less viable option for small water communities.

Enhanced Coagulation

Enhanced coagulation involves modifications to the typical C/F process, such as increasing the coagulant dosage, reducing the pH, or both [2]. Greater than 90 percent of As (V) is removed under enhanced coagulation conditions using ferric salts [2].

Lowering the pH during enhanced coagulation improves the performance of the alum coagulation process. Enhanced coagulation does ensure that more arsenic is removed, but higher coagulant dosages are involved, producing more sludge. Post pH adjustment is also required for enhanced coagulation (with alum) to control corrosion and to comply with other regulatory requirements [3].

Ion Exchange

Ion exchange (IX) is a physical/chemical process in which ions are swapped between a solution phase and a solid resin phase. The solid resin is typically an elastic, three-dimensional hydrocarbon network containing a large number of ionizable groups electrostatically bound to the resin.

Arsenic is removed (only arsenate in this case) by continuously passing water under pressure through one or more columns packed with strong base anion exchange resin (SBR). Exhaustion occurs when all sites on the resin beads have been filled by contaminant ions.

The EPA expects that ion exchange treatment will soon be a common technology for arsenic removal, either in a central facility or as point-of-use treatment, to meet the new imposed MCL.

Important considerations in the applicability of the ion exchange process include water-quality parameters such as pH, competing ions, the resin type, alkalinity, and the influent arsenic concentration. Ion exchange is generally recommended for use in systems having low sulfates (<120 mg/l) and low TDS [6].

Competing ions, such as sulfates, nitrates, selenium, and fluorides in water, greatly affect the regeneration frequency and control the costs for using this treatment technology. Proper configuration of the ion exchange columns (series operation or countercurrent flow) is important to improve arsenic removal and minimize regeneration capacity.

Removal of As (III) requires pre-oxidation. Suspended solids and precipitated iron can clog the ion exchange bed. Disposal of ion exchange resins and regenerant, which produces arsenic-rich brine, is a major problem associated with ion exchange.

A significant disadvantage of ion exchange is the potential for arsenic peaking, or dumping, when effluent arsenic concentration exceeds influent concentration. For dumping to occur, an ion more preferred than arsenate, such as sulfate, must be present, and the run must be continued beyond arsenic breakthrough. Thus, the EPA does not consider ion exchange for POU/POE compliance to the MCL [7].

Currently, the biggest challenge with the ion exchange process is the quantity of salt required to regenerate the ion exchange column, as well as the disposal of the exhausted salt brine. A few emerging technologies may significantly improve ion exchange treatment for arsenic removal. Most of these technologies are still under investigation. They are:

- advanced ion exchange operation with indefinite brine recycle
- Arsenate, As(V), selective resins
- Continuous counter current ion exchange [8]

Activated Alumina

In the early 1970s, Bellack accidentally discovered that activated alumina (AA) could remove arsenic from water [9]. The mechanism of arsenic removal is similar to that of a weak base ion exchange resin, though ligand exchange and chemisorption are technically more appropriate terms to describe it [10]. Arsenic removal efficiency is excellent (typically > 95 percent), for both arsenite and arsenate, but is controlled primarily by pH, influent arsenic concentration, and speciation [3].

AA is currently the best sorbent for arsenic removal. It is especially useful in high-TDS waters [5]. Arsenic removal by AA is most effective near a pH of 5.5 to 6.0; hence, AA should be put into use in a centralized facility where pH adjustments can be made and pH is better controlled. AA adsorption is considered to be less expensive than membrane separation and is more versatile than the ion exchange process [11].

AA column runs operated under acidic pH conditions (pH 5.5 -6.0) are five to 20 times longer than when operated under natural pH conditions (pH 6.0-9.0) [2]. Small utilities that elect to conduct AA treatment under natural pH conditions should understand that the savings in capital and chemical costs required for pH adjustment and media regeneration offset the costs associated with decreased run length.

Regeneration of the AA media and pH control make it difficult for AA to be used for a point-of-use treatment method. Regeneration is more difficult and less complete (generally 50 to 80 percent) than with ion exchange resins [12]. Also, compared with ion exchange resins, a significantly longer Empty Bed Contact Time (EBCT) is required.

The kinetics of arsenic removal onto the alumina surface is slower than those of ion exchange resins, and some arsenic leakage is often noted in AA systems [4]. AA also requires the storage of dangerous chemicals, such as sulfuric acid and sodium hydroxide, for bed regeneration and pH adjustment, adding costs for advanced training and additional operator responsibilities.

Membrane Processes

Membrane technologies offer a versatile approach for meeting multiple water-quality objectives [13]. In recent years, new nanofiltration and reverse-osmosis membranes have been developed that are capable of both arsenite and arsenate rejection. These membranes operate at low pressures (40-400 psi) and are less expensive than previous versions [14].

In spite of operating at low pressures, these membranes have an improved flux and are capable of almost 95 percent rejection of As (V) in the feed stream. These high arsenic rejection rates producee an extremely low concentration of arsenic in the treated water. Also, with the MCL set low, membrane operations will be more prevalent because blending will not be a feasible option.

Arsenic removal in membranes is a function of source water pH. Typical rejection rates for As (III) and As (V) are 75 percent and 95 percent, respectively [15].

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Factors	**Coagulation**	**Enhanced Coagulation**	**Ion Exchange**	**Activated Alumina**	**Membrane Processes**
EPA BAT	No	Yes	Yes	Yes	Yes
Other Contaminants Treated	Fe^{3+}, Particulates, Pathogens	Fe^{3+}, Mn^{2+}, Particulates, Pathogens, DBP precursors	SO_4^{2-}	F^{-1}	TDS
Pre Oxidation Required	Yes	Yes	Yes	Yes	Possible*
Recommended Water Quality	pH 5.5–8.5	pH 5.5–8.5	pH 6.5–9.0 <5ppm NO_2^- <5ppm NO_3^- <50ppm SO_4^{2-} <500ppm TDS	pH 5.5– 6.0 <250ppmCl^- <2ppm F^{-1}	No particulates
Waste Generated	Backwash water, sludge	Backwash water, sludge	Spent Brine, Spent Resin, Backwash Water	Spent Media, Backwash Water	Reject Water
Other Drawbacks of the Process	None	None	Large volumes of potentially hazardous brine, Nitrate peaking	Feed and Product pH adjustments required	High water loss (15- 75 % of feed water)
Appropriate as treatment for small systems	No	No	Possible	Yes	POU only
Applicable as POU	No	No	Possible	Yes	Yes
POU cost	N/A	N/A	Medium	Medium	Medium
POE cost	Medium	High	High	Medium	High
Operator skills required	High	High	High	High	High

Table1: Arsenic Treatment Technology Summary Comparison [3]

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Arsenic removal is independent of the presence of co-occurring solutes.

Arsenic removal efficiency in membranes is also independent of source water composition. It has been established, however, that arsenic removal is vastly improved at lower temperatures. Arsenic rejection in membranes is mostly attributed to relatively large molecular weights of the arsenite and arsenate ions [4].

Membrane filtration can be used to achieve other objectives apart from arsenic removal. Minimum operational and maintenance costs and no addition of chemicals make membranes a highly favorable option for point-of-use treatment. Membrane operations as a part of a centralized treatment facility for small systems is highly uneconomical because of the high capital and operational costs involved, low water recovery rates (typically 15 to 25 percent), the requirement of high-quality influent water, the need to operate at high pressures, and the risks of membrane fouling. Low water recovery rates are a problem posed by small water utilities located in regions with limited water supplies.

Table 1 summarizes the various arsenic removal technologies and compares the different technologies presently in use. The comparison is based on many factors that will help small water utilities decide the Best Available Technology (BAT) for removal of arsenic from source waters.

Emerging Technologies

In recent years, a tremendous amount of research has been carried out to develop new, cost-effective, easy-to-use systems that can be applied in rural settings. Some of these emerging technologies for arsenic removal, which include the use of porous media (iron oxide-coated sand, granular ferric hydroxide, sulfur modified iron), are considered effective for point-of-use treatment.

The use of low-cost, modified natural zeolites has been shown to be extremely effective in removing As (V) and As (III). Zeolites are naturally occurring minerals with a crystalline structure characterized by large internal pore spaces. Accordingly, they have very large surface areas, and ion exchange capacities.

A chabazite filter was able to remove 1,000 μg/L of arsenate from over 235 bed volumes before arsenic was detected in the effluent [16]. Chabazite and clinoptilolite were effectively modified with ferrous ions to enhance the capacity of zeolite to adsorb arsenic. Adsorption of arsenate onto natural zeolites can be improved by organically modifying the zeolite structure [17].

Most of these technologies rely on oxidation of arsenic, followed by filtration through porous media where arsenic is removed by adsorption and co-precipitation [4]. They have been effective in laboratory studies of industrialized and developed countries, but they need to be evaluated under different environmental settings and in field conditions [5].

Summary & Conclusion

The chemical form of arsenic is the most important criteria in choosing the method for arsenic treatment. Negative charges facilitate removal by adsorption, anion exchange, and co-precipitative processes. Since the net molecular charge of arsenite is neutral at natural pH levels (6-9), this form is not easily removed; however, the net molecular charge of arsenate is negative (-1 or -2) at natural pH levels, enabling it to be removed with greater efficiency. Conversion to arsenate is a critical element of any arsenic treatment process; hence, pre-oxidation is key for the optimal performance of any treatment technology.

Although coagulation is widely used for arsenic removal, it is uneconomical for small communities because of the unaffordable extensive infrastructure required. Enhanced coagulation requires high doses of coagulants and increases sludge production, leading to sludge disposal problems.

Ion exchange can be used either as centralized treatment or as point-of-use treatment technology; however, its applications are limited to areas having low sulfates and TDS. Also, As (III) is not removed and regenerant disposal laden with arsenic rich brine is a problem.

Activated alumina currently offers the best option for arsenic removal; however, pH control is the key to efficient removal of arsenic. Skilled operation of the process is required for optimal, safe performance because the process involves handling dangerous chemicals.

Membranes are best put to use as a point-of-use treatment option. Low water recovery rates and high capital costs are problems facing the implementation of a centralized treatment facility.

Arsenic removal efficiency will vary according to many site-specific chemical, geographic, environmental, and economic conditions, so any technology should be tested under field conditions before being implemented.

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