Arsenic removal by reverse osmosis

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Abstract

Arsenic is widely distributed in nature in air, water and soil. Acute and chronic arsenic exposure via drinking water has been reported in many countries, especially Argentina, Bangladesh, India, Mexico, Mongolia, Thailand and Taiwan, where a large proportion of ground water is contaminated with arsenic at levels from 100 to over 2,000 micrograms per liter (ppb). Public health standards of maximum of 50 ppb have been adopted by the US and World Health Organization in the 1970s and the 80s. Carcinogenicity and genotoxicity led to the WHO recommendation of 10 ppb maximum level in 1993, followed by the US adoption of the same in 2001, with the US estimate that 5% of all US community water systems will have to take corrective actions to lower the current levels of arsenic in their drinking water. In high arsenic areas of the world, the need for better water treatment and resulting economic impact would be even greater. In this article, we briefly review the geochemistry, natural distribution, regulation, anthropogenic sources and removal mechanisms of arsenic, pointing especially to the promise of reverse osmosis (RO) as a practical means of purification. We conclude that arsenic in the commonly high oxidation states of (V) is very effectively removed by RO. With further attention to the removal of the weakly acidic arsenic (III) species in waters by the operation of RO at sufficiently high pHs made possible by the newer antiscalants, practical processes can be developed with RO to remove all major species of arsenic from water. Further studies are needed in the characterization of the arsenic species being treated and in the design of the RO process to match the demands.

Keywords: Arsenic; Reverse osmosis; Antiscalants, Geochemistry; Natural distribution; Health regulations; Anthropogenic sources; Removal mechanisms; Characterization

1. Introduction

Arsenic is widely distributed in nature in air, water and soil as a metalloid and as chemical compounds both inorganic and organic [1]. This class of compounds was known to the ancient Greeks and Romans both as therapeutic agents as well as poisons. This dual nature as useful substances as well as toxic matter to be controlled has grown over the centuries. While arsenic and arsenials have widened its use in commerce, so have the recognition that their presence in drinking water, largely from natural sources, is a major public health problem around the world.

Acute and chronic arsenic exposure via drinking water has been reported in many countries, especially Argentina, Bangladesh, India, Mexico, Mongolia, Thailand, and Taiwan, where a large proportion of ground (well) water is contaminated with a high concentration of arsenic of 100 to over 2,000 microg/l (ppb) [2]. Studies have linked long-term exposure to arsenic in drinking water to cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate. Non-cancer effects of ingesting arsenic include cardio-vascular, pulmonary, immunological, neurological, and endocrine (e.g. diabetes) disorders [3]. Besides its tumorigenic potential, arsenic has been shown to be genotoxic [4,5]. Given the importance of arsenic as a global environmental toxicant in drinking water, we wish to briefly review the geochemistry, natural distribution, regulation, anthropogenic sources and removal mechanisms, pointing especially to the promise of reverse osmosis as a practical means of purification.

2. Geochemistry

Average concentrations of arsenic in the earth's crust reportedly range from 1.5 to 5 mg/kg. Higher concentrations are found in some igneous and sedimentary rocks, particularly in iron and manganese ores. Common minerals containing arsenic are shown in Table 1. Arsenopyrite, realgar and orpiment are the most important of these minerals, and they are commonly present in the sulfide ores of other metals including copper, lead, silver and gold. Arsenic may be

released from these ores to soil, surface water, ground water, and the atmosphere.

Natural concentrations of arsenic in soil typically range from 0.1 to 40 mg/kg, with an average concentration of 5 to 6 mg/kg. Through erosion, dissolution, and weathering, arsenic can be released to ground or surface water. Geothermal waters can be sources of arsenic in ground water. In Yellowstone National Park in the USA, the arsenic concentrations in geysers and hot springs range from 900 to 3,560 ppb. Waters from these sources cause elevated arsenic levels in rivers downstream. Other natural sources include volcanism and forest fires. Indeed, volcanic activity appears to be the largest natural source of arsenic emissions to the atmosphere, estimated variously between 2,800 to 44,000 metric tons annually. The relative contributions of volcanic sources, other natural sources, and anthropogenic sources to the atmosphere have not been definitively established.

The predominant forms of arsenic in ground and surface water are arsenate(V) and arsenite(III). Examples of inorganic arsenic compounds found in the environment include oxides (i.e. As_2O_3, As_2O_5) and sulfides (As_2S_3, AsS, $HAsS_2$, $HAsS_3^{3-}$). Inorganic arsenic species which are stable in oxygenated waters include arsenic acid (As (V)) species (i.e. H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}). Arsenous acid (As(III)) is also stable as H_3AsO_3 and $H_2AsO_3^-$ under slightly reducing aqueous conditions. Arsenite is generally associated with anarobic conditions. Oxidation state, oxidation-reduction potential, pH, iron concentrations, metal sulfide and sulfide concentrations, temperature, salinity and distribution and composition of biota appear to be the significant factors that determine the fate and transport of arsenic. In surface waters, additional factors include total suspended sediment, seasonal water flow volumes and rates, and time of day.

Sorption of arsenic to suspended sediment may strongly affect the fate and transport of arsenic in surface water systems [6]. Where pH

Table 1
Common minerals of arsenic [3]

Arsenopyrite, FeAsS	Smalite, $CoAs_2$
Lollingite, $FeAs_2$	Cobaltite, CoAsS
Orpiment, As_2S_3	Gersdorffite, NiAsS
Realgar, As_4S_4	Tennantite, $4Cu_2SAs_2S_3$
Chloanthite, $NiAs_2$	Proustite, $3Ag_2SAs_2S_3$
Niciolite, NiAs	Enargite, $3Cu_2SAs_2S_5$

and arsenic concentrations are relatively high and total suspended sediment levels are relatively low, sorption processes may be less important. However, where suspended sediment loads are higher, arsenic concentrations are lower, and pH levels are lower, arsenic is more likely to be present in the suspended particulate phase rather than the dissolved phase. Particulate phase arsenic may settle to bottom sediment in reservoirs and areas with low flow levels. In deeper lakes, remobilization of arsenic from sediment may be minimal, whereas in shallower lakes, arsenic may be remobilized faster from wind induced wave action and high-flow scouring. Diurnal changes of as much as 21% in arsenic concentrations have been observed in rivers, attributable to pH changes due to sunlight and photosynthesis.

3. Natural distribution

Survey of arsenic concentration in natural waters is of importance relative to the desirable maximum limit of 10 ppb or less for human consumption. An attempt has been made to quantify the global element cycle for arsenic, based on published data [1]. Arsenic concentrations in environmental media are presented in Table 2.

In addition to geochemical factors, microbial agents can influence the oxidation state of arsenic in water, and can mediate the methylation of inorganic arsenic to form organic arsenic compounds [8]. Microorganisms can oxidize arsenite to arsenate, reduce arsenate to arsenite or even to arsine (AsH_3). Bacteria and fungi can reduce arsenate to volatile methylarsines. Marine algae transform arsenate into non-volatile methylated arsenic compounds such as methylarsonic acid ($CH_3AsO(OH)_2$) and dimethylarsinic acid ($(CH_3)_2AsO(OH)$) in seawater. Fresh water and marine algae and aquatic plants synthesize complex lipid-soluble arsenic compounds [9]. Organic arsenical compounds were reported to have been detected in surface water more often than in ground water. Surface water samples

Table 2
Arsenic concentrations in environmental media [7]

Environmental media	Arsenic concentration range
Air, ng/m^3	1.5–53
Rain from unpolluted ocean air, ug/L (ppb)	0.019
Rain from terrestrial air, ug/L	0.46
Rivers, ug/L	0.20–264
Lakes, ug/L	0.38–1,000
Ground (well) water, ug/L	<1.0–>1,000
Seawater, ug/L	0.15–6.0
Soil, mg/kg (ppm)	0.1–1,000
Stream/river sediment, mg/kg	5.0–4,000
Lake sediment, mg/kg	2.0–300
Igneous rock, mg/kg	0.3–113
Metamorphic rock, mg/kg	0.0–143
Sedimentary rock, mg/kg	0.1–490
Biota — green algae, mg/kg	0.5–5.0
Biota — brown algae, mg/kg	30

reportedly contain low but detectable concentrations of arsenic species including methylarsonic acid and dimethylarsinic acid. Methylarsenicals have been reported to comprise as much as 59% of total arsenic in lake water. In some lakes, dimethylarsinic acid has been reported as the dominant species, and concentrations appear to vary seasonally as a result of biological activity within waters.

4. Regulations

In the USA, the Safe Drinking Water Act (SDWA) of 1974 called for the establishment of Maximum Contaminant Levels (MCL) as national drinking water standards, and required the Environmental Protection Agency (EPA) to periodically revise the standard. Based on a Public Health Service standard established in 1942, the EPA established a standard of 50 microg/l (50 ppb) as the maximum arsenic level in drinking water in 1975. In 1984, the World

Health Organization (WHO) followed with the same 50 ppb recommendation. Since that time rapidly accumulated toxicity information prompted a revision of the standard and a provisional guideline of 10 ppb was recommended by WHO in 1993. In January 2001, EPA published a revised standard that would require public water supplies to reduce arsenic to 10 ppb by 2006. Perceived hardships in implementation and uncertainty with setting the standard at 3 ppb, 5 ppb, 10 ppb or 20 ppb has led the EPA to announce temporary delays in the effective date for the January, 2001 rule to allow for further cost-benefit analysis and public input. The rule is significant in that it is the second drinking water regulation for which EPA has used the discretionary authority under SDWA to set the MCL higher than the technically feasible level, which is 3 ppb for arsenic-based on the determination that that the costs would not justify the benefits at this level. It appears that a final decision has been made by the EPA to adopt 10 ppb limit for drinking water.

5. Anthropogenic sources

Arsenic is released from a variety of anthropogenic sources, including manufacturing of metals and alloys, petroleum refining, pharmaceutical manufacturing, pesticide manufacturing and application, chemical manufacturing, burning of fossil fuels, and waste incineration. Most agricultural uses of arsenic are banned in the USA. However, sodium salts of methylarsonic acid are used in cotton fields as herbicides. Organic arsenic is also a constituent of feed additives for poultry and swine, and appears to concentrate in the resultant animal wastes. About 90% of arsenic used in the USA is for the production of chromated copper arsenate (CCA), the wood preservative. CCA is used to pressure treat lumber and is classified as a restricted use pesticide by the EPA. A significant industrial use of arsenic is the production of lead-acid batteries, while small amounts of very pure arsenic metal are used to produce gallium arsenide, which is a semiconductor used in computers and other electronic applications. The US Toxics Release Inventory data indicated that 7,947,012 pounds of arsenic and arsenic-containing compounds were released to the environment in 1997, most of which came from metal smelting operations. This data did not include some potentially significant arsenic sources associated with herbicides, fertilizers, other mining facilities and electric utilities.

6. Removal mechanisms

At the regulated maximum arsenic level of 10 ppb, US-EPA estimated that 5% of all US community water systems will have to take corrective action to lower the current levels of arsenic in their drinking water. At high arsenic areas of the world, the need for removal from water supplies is even more acute.

Due to their predominance in natural waters, arsenic(V) acid — H_3AsO_4 and arsenous(III) acid — $HAsO_2$ and their salts can serve as the model for these and alkylated species for the consideration of removal mechanisms. The pK values: arsenic acid = 2.26, 6.76, 11.29 [10] and arsenious acid = 9.29 [10] or 8.85 [11] are of prime importance in determining the degree of ionization at the pHs of the water from which removal strategies are considered. It is readily apparent that at natural pH of 7 to 8, arsenic acid is extensively ionized as divalent ion, while arsenious acid remains largely unionized.

Due to the ionic charge, arsenate(V) is more easily removed from source waters than arsenite(III). In particular, activated alumina, ion exchange and reverse osmosis may achieve relatively high arsenate removal rates, but they show lower treatment efficiencies for arsenite. Elevating the pH such as by caustic injection into reverse osmosis system feed water [12] would be one approach to greater removal of arsenite(III) compounds. Arsenite can also be oxidized to arsenate to improve removal efficiencies. In water that

contains no ammonia or total organic carbon, chlorine rapidly (in less than 5 s at chlorine concentrations of 1.0 mg/L) oxidizes approximately 95% of arsenite to arsenate. Monochloramine at the concentration of 1.0 mg/l oxidized 45% of arsenite to arsenate. Potassium permanganate performs this oxidation rapidly, while oxygen does so slowly unless activated by light and sensitizer.

In contrast to other heavy metals, As(III) and As(V) are not precipitated as hydroxides, only as sulfides. Alkyl and arylarsonic acids are precipitated by quadrivalent metals such as tin, thorium, titanium and zirconium. Tendencies of dissolved arsenic species to adsorb on inorganic particle surfaces such as iron, ferric hydroxide, iron oxide, alumina, sulfur and sulfides allow for removal strategies involving fixed-bed reactors or adsorption/coagulation/filtration schemes. Sulfate, fluoride and phosphate ions are known to be strong competitors of arsenic adsorption in some systems.

7. Reverse osmosis

Reverse osmosis is an effective arsenic removal technology proven through bench and pilot scale studies according to a report prepared for the US-EPA [13]. Various pilot studies reported arsenic removal ranging between 40–99% without specifying the arsenic species removed. One pilot study [14] reported As(V) removal at 96–99%, and As(III) removal at 46–84%. A second pilot study [15] reported As(III) reduction at 73%. Bench-scale studies with RO membranes showed As(V) reductions at 88–96%, and As(III) reductions at 5% [13]. Clearly As(V) rejections reflect the ionized states of the anions, while As(III) rejections are low at neutral pHs.

8. Conclusions

Arsenic in the commonly high oxidation states of (V) is very effectively removed by RO. With further attention to the removal of the weakly acidic arsenic species in waters by the operation of RO at sufficiently high pHs made possible by the newer antiscalants [12], practical processes can be developed with RO to remove all major species of arsenic from water. Further studies are needed in the characterization of the arsenic species being treated and in the design of the RO process to match the demands.

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