

Original Research

Removal of Hazardous Metals from Groundwater by Reverse Osmosis

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Abstract

This EPA treatment technology project was designed to collect data on the performance of existing water treatment processes in order to remove arsenic on pilot-scale. Our paper contains verification testing of the reverse osmosis membrane module conducted over a 30-day period at the Spiro Tunnel Bulkhead water (Park City, Utah, USA), which is considered to be a ground water. The total arsenic concentration in the feedwater averaged 60 ppb during the test period and was reduced to an average of 1 ppb in the treated (permeate) water. The work reported here focused on obtaining accurate readings for arsenic valence states (III) and (V), using an anion exchange resin column. The dominant arsenic species in the abandoned silver mine tunnel feedwater was As(V). Results of analysis showed that 70% of the arsenic present in the feedwater was in dissolved form. Arsenic speciation for valence states (III) and (V) showed that arsenic (V) represented 76% of the dissolved arsenic in the source water. The method detection limit (MDL) for arsenic using ICP-MS was determined to be 0.1 ppb. Our matrix spiked recovery, spiked blank samples and reference materials deviated only a few percentage points from the listed true values.

Keywords: arsenic speciation, antimony, reverse osmosis technology, water treatment

Introduction

The pressure technologies of microfiltration, ultrafiltration, nanofiltration and reverse osmosis (RO) are widely used in water treatment applications ranging from grey water quality over potable water to ultrapure water productions. Certain membranes reject more than 99% of all dissolved salts and have molecular weight cut-off in the range from 50 to 100 dalton. A significant advantage of RO over traditional water treatment technologies is that it also reduces the concentration of other ionic contaminants as well as dissolved organic compounds. A rejection of

contaminant removal is a function of membrane type and pore size [1-6].

Groundwater from an abandoned silver mine tunnel in Park City, Utah, is considered stable with respect to quality and quantity, and is known to contain arsenic and antimony. The reverse osmosis membrane module was set up and operated for a month.

Arsenic occurs naturally and can contaminate drinking water through the erosion of rocks and minerals or through human activities such as fossil fuel burning, paper production, cement manufacturing, and mining. Natural contamination of groundwater by arsenic has become a crucial water quality problem in many parts of the world, particularly in Bangladesh, West Bengal, and Vietnam [7-11]. Some water

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systems in the U.S. Western states, parts of Midwest states, and New England have arsenic concentrations in groundwater exceeding 50 ppb. The World Health Organization has a 10 ppb guideline from 1993. It is provisional because of the lack of suitable testing methods, but based on health concerns alone the guideline should be lower from the current maximum level. The current maximum contaminant level (MCL) of arsenic in drinking water is 50 ppb in the United States [12], 10 ppb in the European Union, and 25 ppb in Canada [13].

Epidemiological studies of populations exposed to arsenic in drinking water show that elevated levels can lead to skin, bladder, lung, and prostate cancer, with risk to exposure comparable to that of radon and second-hand tobacco smoke. Non-cancer effects of ingesting arsenic include cardiovascular diseases, diabetes, and anaemia, as well as reproductive and developmental, immunological and neurological abnormalities [14-15].

Inorganic As(III) and As(V) are the major species in groundwater [8,16]. Highly toxic As(III) may also be converted to less toxic forms such as As(V) or methylated forms such as monomethylarsonate (MMA) and dimethylarsinate (DMA) in surface waters. In natural waters, soluble arsenic is virtually always present in the oxidation states of either +3(III) or +5(V) valences. Organic species (methylated) have been reported by the others, but concentrations of the organic compounds rarely exceed 1 ppb and they are considered of little or no significance as drinking water contaminants. In oxygenated waters, the As(V) valence is dominant, existing in the forms of H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} . In waters containing little or no oxygen (anoxic), As(III) exists in the nonionic form (H_3AsO_3) below pH of 9.22 and in the anionic form (H_2AsO_3^-) at pH above 9.22.

A natural source of ground water with high arsenic was used for our studies. Groundwater from the mine in Park City, Utah is considered stable with respect to quality and quantity, and is known to contain arsenic and antimony. The reverse osmosis membrane module was set up and was operated for a month. The feedwater from the Spiro Tunnel Bulkhead in Park City has a total arsenic average level of 60 ppb. Antimony levels in the feedwater averaged 8.7 ppb, where the U.S. maximum contaminates level (MCL) is 6 ppb.

This paper reports the performance of reverse osmosis for removal of arsenic and antimony from drinking water in Park City. Also, it provides results on speciation of arsenic (III and V) removal from drinking water.

Experimental Procedures

Test Site. The verification testing site was the Park City Spiro Tunnel Filtration Plant in Park City. The source of water was Spiro Tunnel Bulkhead water, which is considered a ground water source under the State of Utah Source Protection Program. Water was developed from water-bearing fissures in an abandoned silver mine tunnel.

A two-meter bulkhead, built approximately three km into the tunnel, holds the water back and creates a reservoir. The tunnel is located 300 m or more under remote unoccupied forest in a mountainous region. The water is piped to the treatment plant through a 30.0-cm diameter pipe at a flow rate of 4,400 L per minute and enters the city treatment plant, which was built in 1993. The treatment plant, located 300 m away from the Tunnel portal, is designed to remove iron, manganese, and arsenic from the raw water. For the municipal supply, this water is currently diluted with treatment plant finished water to form a blend containing approximately 35 ppb arsenic that meets the present arsenic standard of 50 ppb. For our test, only the untreated, unblended Spiro Tunnel Bulkhead supply was used. This source is one of the five active sources serving the municipality: 2 tunnels, 2 deep wells, and a spring. None of the other sources contain significant quantities of arsenic and antimony. The water system serves 6,500 residents, and as many as 20,000 people per day during the winter season.

Technology Description

Reverse Osmosis (RO)

In our study two kinds of reverse osmosis membranes, Module 1 and Module 2, were used. The ESPA-2 and TFC-ULP4 reverse osmosis membrane element modules are manufactured by Hydronautic and Koch manufacturers, respectively. The membrane Module 1 is a spiral-wound polyamide membrane with a fiberglass outer wrap. Molecular weight cut-off is approximately 100 daltons. The membrane module 1 is rated for a maximum pressure of 350 psi ($2.4 \cdot 10^5$ Pa) and normal design pressure of 125 psi ($8.6 \cdot 10^5$ Pa). The unit was set to operate at 150 psi ($1 \cdot 10^6$ Pa) inlet pressure, a water recovery of 15%, and a specific flux of 0.26 gallon per day per square foot (10.5 L per day/ m^2) membrane area (25°C) during the first days of operation. The permeate flow averaged 1.01 gallons (3.8 L) per minute. The membrane Model 2 is a hollow membrane made from composite polyamide material with molecular weight cut-off of 300-500 daltons. The membrane module 2 is rated for a maximum pressure of 600 psi ($4.1 \cdot 10^6$ Pa) and normal design pressure of 150 psi ($1 \cdot 10^6$ Pa). The unit was set to operate at 150 psi ($1 \cdot 10^6$ Pa) inlet pressure, a water recovery of 15%, and a specific flux of 0.16 gallon per day per square foot (6.5 L per day/ m^2) of membrane area (25°C). The permeate flow averaged 0.77 gallon (2.9 L) per minute. Performance of reverse osmosis studies is presented in Tables 1 and 2.

The system was operated with a 5 micron cartridge filter in the feedwater line to the system. The filter was initially changed on an every two-day basis for the first 18 days of the test period. Following a high turbidity measurement by filtration plant in-line monitor, the cartridge filter was changed daily for the remaining days of the verification test.

The RO membrane elements were operated for the entire test without shutting down for cleaning. Membrane cleaning was performed at the end of the test cleaning process. The unit was cleaned using 190 L of 2% (wt/wt) citric acid solution. The cleaning solution was circulated through the membrane module for one hour followed by a 100 min soaking time. The units were then rinsed with feedwater for approximately 30 min. and placed back on-line. Operating data collected after the cleaning showed that unit returned to typical operating conditions prior to the cleaning process with permeate flow and a specific flux.

Analytical Procedures

All of the methods used were standard EPA methods. Analyses of As, Sb, and Mn in water samples were accomplished by ICP-MS and ICP (Fe, and Mg only) using EPA Methods 200.8 and 200.7, respectively [17,18]. ICP-MS analyses were conducted on a Perkin-Elmer Sciex model ELAN 6000, equipped with a crossflow pneumatic nebulizer and an automatic sampler. Model Optima 3000, also by Perkin Elmer, was employed for ICP measurements. Yttrium ($^{88.9}\text{Y}$) was added to all samples run by ICP-MS spectrometer as an internal standard to correct for instrument drift. The MDL determined for arsenic was 0.1 ppb. Because arsenic is monoisotopic, all measurements were at a mass/charge ratio

of 75. The chloride isotope (^{35}Cl) appreciably affected the determination of arsenic isotope (^{75}As) by forming molecular species ($^{40}\text{Ar}^{35}\text{Cl}$). To eliminate interference from $^{40}\text{Ar}^{35}\text{Cl}$, all data were corrected using chloride measurements in all samples according to the equation:

$$[^{75}\text{As}(\text{corr})] = [^{75}\text{As}] - 3.127 \cdot \{ [^{40}\text{Ar}^{37}\text{Cl}] - 0.815 \cdot [^{82}\text{Se}] \}$$

Three types of water samples were analyzed in bottles labeled A, B, and C. All the unfiltered water samples (Bottle A) were digested using EPA Method 200.8 prior to analysis [17]. Filtered water samples (Bottles B and C) were analyzed directly without digestion. Field speciation of arsenic technique was developed using an anion exchange resin column (Dowex 1- X8, 100-200 mesh, acetate form) [19-22].

Bottle A (total As) contained 1% HNO_3 (v/v) in a 250 mL of unfiltered water sample, Bottle B (dissolved As III and V) contained 0.05% H_2SO_4 (v/v) in 125 mL of water sample filtered through a 0.45 micrometer disc filter, and Bottle C (dissolved As III only) held 20 mL of the eluate of solution from Bottle B plus 0.5 mL 1:1 HNO_3 . The eluate was obtained by running a portion of the acidified sample from Bottle B through the resin column. Sulfuric acid was used to acidify the sample in container B because nitric acid (an oxidizing agent) could damage the resin or form nitric acid-arsenic redox couples [20, 23, 24]. The resin retained

Table 1. Performance of reverse osmosis systems.

Reverse osmosis systems	Arsenic in feedwater [ppb]	Arsenic in treated water [ppb]	Arsenic rejection [%]
Module no. 1, (Koch TFC-ULP4 [27])	60.0	0.9	98.5
Module no. 2, (Hydronautics ESPA2-4040 [25])	60.0	0.5	99.2

Table 2. Water quality data collection for the feedwater (Feed) and the RO treated water (Treated)

Parameters	pH	As total	As total dissolved	As(V) dissolved	Sb total	Mn total	Fe total	Mg total	Turbidity
Units		[ppb]	[ppb]	[ppb]	[ppb]	[ppb]	[ppm]	[ppm]	[NTU]
Feed	7.33	60.0	42.0	32.0	8.7	15.0	0.170	45.6	1.44
Treated	5.99	0.9	1.3	0.8	< 3.0	< 5.0	< 0.02	< 1.0	< 0.1
Parameters	TDS		TSS	Alkalinity	Silica		SO_4^{2-}	Cl^-	F^-
Units	[ppm]		[ppm]	[ppm]	[ppm]		[ppm]	[ppm]	[ppm]
Feed	540.0		< 4.0	147.0	23.0		274.0	5.5	0.17
Treated	< 10.0		< 4.0	5.0	< 1.0		< 20.0	< 3.0	< 0.05

SRM^{a)} (% recovery) 97-105, CSTD^{b)} (% recovery) 93-103, LSB^{c)} (% recovery) 95-105, LSB^{d)} (% recovery) 95-106, LSM^{e)} (% recovery) 94-107, LSMD^{f)} (% recovery) 94-106

^{a)} Reference standard, ^{b)} Continuing standard, ^{c)} Lab spike blank, ^{d)} Lab spike blank duplicate, ^{e)} Lab spike matrix, ^{f)} Lab spike matrix duplicate. Accuracy (% recovery) is expressed as a ratio of $\text{LSB}_{(\text{found})}$ and $\text{LSD}_{(\text{true})}$ (96 to 104%); the precision (relative% difference) is determined by calculating the difference between the results found for the LSB and LSB^{d)}, and then dividing the difference by the average of the two results (3 to 7%).

As(V), as $H_2AsO_4^-$, and allowed As(III), as H_3AsO_3 , to pass through the column. The dissolved As(V) concentration was calculated by subtracting dissolved As(III) from the total dissolved arsenic concentration of the sample in Bottle B.

Results

Arsenic removal with reverse osmosis technology. The feedwater from Spiro Tunnel Bulkhead had the following average water quality during the verification test period: TDS (total dissolved solids) 540 ppm, pH 7.33, iron 0.170 ppm, sulfate 274 ppm, and alkalinity 147 ppm. Total arsenic concentration in the feedwater averaged 60 ppb over a 34-day test period. Results of analysis showed that 70% of arsenic present in the feedwater was in dissolved form. Arsenic speciation for the valence states (III) and (V) showed that in the feedwater, arsenic (V) represented 76% of the total dissolved element. Reverse osmosis technology was applied for removal of arsenic and other ionic species from the feedwater. In our study two kinds of reverse osmosis membranes, called here Module no. 1 and Module no. 2, have been used. Results of feedwater filtration through membranes showed that concentration of arsenic and antimony were reduced in treated water. These results were comparable for both types of membrane modules. Module no. 1 reduced total arsenic to the average of 0.9 ppb and dissolved arsenic from an average of 42 ppb to less than 1.3 ppb, while Module no. 2 reduced total arsenic to 0.5 ppb and dissolved arsenic to 0.8 ppb. The dominant arsenic species in the Spiro Tunnel water was As(V). Average concentrations of As(V) and As(III) in feedwater were 32 and 8 ppb, respectively, and were reduced in the treated water to an average level of 0.8 and 0.6 ppb, respectively. A summary of the concentrations of arsenic species and other parameters in both, the feedwater and treated water, is presented in Table 2.

In all cases, the permeate concentrations were below the current EPA MCL of 50 ppb and below the promulgated new standard of 10 ppm. Reverse osmosis membrane modules (Module no. 1 and Module no. 2) effectively and consistently rejected all forms of arsenic present in the feedwater. An important parameter of reverse osmosis membrane performance is total dissolved solid (TDS) rejection, which is the ability of the module to reduce TDS concentration in the feedwater stream. Reverse osmosis membrane technology also reduced the total hardness and concentration of allowing meeting recommended or statutory limits. Total arsenic concentrations, using reverse osmosis method, were reduced from an average 60 ppb in the source water to less than 1 ppb in treated water, while chemical coagulation, for example, reduced total arsenic from an average 60 to 4 ppb [25-28].

Conclusions

Results of analysis showed that 70% of the arsenic present in the feedwater was in a dissolved form. Arsenic speciation for valence states (III) and (V) showed that arsenic (V) represented 76% of the dissolved arsenic in the source

water. The groundwater at Spiro Tunnel study of arsenic removal on pilot scale, by two reverse osmosis membrane filtration systems, showed the promise of this technology as a practical means of purification. Total arsenic concentrations by reverse osmosis were reduced from an average 60 ppb in the source water to less than 1 ppb (99%); soluble As(III) and As(V) were reduced 93 and 98%, respectively. Total antimony concentration using reverse osmosis method, was reduced from an average 8.7 ppb in the source water to less than 3 ppb in treated water, while chemical coagulation, for example, reduced total antimony less than 2 percent [25-28]. The speciation of arsenic during treatment process is of great interest to researchers.

Spiro Water Treatment Plant (SWTP) Arsenic Removal Upgrade

After extensive pilot testing of numerous arsenic reduction processes, a cost-effective process was selected in December 2002 that meets the goal of 5 ppb. The SWTP design was completed in September 2003 and construction began in October 2003 to retrofit the current Spiro treatment process to reduce arsenic levels from 3 to 5 ppb. In 2004 the State Division of Drinking Water issued an operating permit for the Spiro Water Treatment plant. The arsenic treatment process is now on-line and meeting Park City's goal of 5 ppb. Park City is well ahead of most water systems, meeting the January 2006 arsenic reduction deadline by almost 2 years. Methods of blending different water sources will also be refined throughout summer 2005 to continue to ensure system concentrations of antimony below the maximum contaminant level of 6 ppb. The goal is to have a process identified and be in the design process by the end of 2005 [29].

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