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Electrochemical Remediation of Arsenic-Contaminated Groundwater — Results of Prototype Field Tests in Bangladesh

Kristin Kowolik, Susan E.A. Addy and Ashok Gadgil

ABSTRACT

According to the World Health Organization (WHO), more than 50 million people in Bangladesh drink arsenic-laden water, making it the largest case of mass poisoning in human history. Many methods of arsenic removal (mostly using chemical adsorbents) have been studied, but most of these are too expensive and impractical to be implemented in poor countries such as Bangladesh. This project investigates ElectroChemical Arsenic Remediation (ECAR) as an affordable means of removing arsenic. Experiments were performed on site in Bangladesh using a prototype termed "sushi". This device consists of carbon steel sheets that serve as electrodes wrapped into a cylinder, separated by plastic mesh and surrounded by a tube-like container that serves as a holding cell in which the water is treated electrochemically. During the electrochemical process, current is applied to both electrodes causing iron to oxidize to various forms of iron (hydr)oxides. These species bind to arsenic(V) with very high affinity. ECAR also has the advantage that As(III), the more toxic form of arsenic, oxidizes to As(V) in situ. Only As(V) is known to complex with iron (hydr)oxides. One of the main objectives of this research is to demonstrate the ability of the new prototype to reduce arsenic concentrations in Bangladesh groundwater from >200 ppb to below the WHO limit of 10 ppb. In addition, varying flow rate and dosage and the effect on arsenic removal was investigated. Experiments showed that ECAR reduced Bangladeshi water with an initial arsenic concentration as high as 250 ppb to below 10 ppb. ECAR proved to be effective at dosages as high as 810 Coulombs/Liter (C/L) and as low as 386 C/L (current 1 A, voltage 12 V). These results are encouraging and provide great promise that ECAR is an efficient method in the remediation of arsenic from contaminated groundwater. A preliminary investigation of arsenic removal trends with varying Coulombic dosage, complexation time and filtration methods is also presented.

Introduction

Arsenic in drinking water is a problem that threatens the lives of close to one hundred million people worldwide. Countries such as Argentina, Chile, Mexico, China and Hungary, as well as some areas of the United States, are severely affected by arsenic-contaminated water. According to the World Health Organization (WHO), in Bangladesh alone, more than 50 million people drink water that is contaminated with arsenic [1].

Prior to 1970, Bangladeshis were using surface water that was highly contaminated with microorganisms; this led to water-borne diseases especially harmful to children. To address this problem, millions of shallow tube wells were drilled into the Ganges aquifer to gain access to the groundwater and to provide the population with clean drinking water. It was unknown at the time that arsenic was being introduced into the drinking water due to the dissolution of minerals and ores caused by erosion from local bedrocks [2]. As a consequence, the concentration of arsenic in water in many areas of Bangladesh is 100 times above the 10 ppb limit recommended by WHO [3]. The Bangladeshi government standard for safe drinking water remains at 50 ppb. According to the British Geological Survey (BGS) study conducted in 1998 on shallow tube wells in 61 of 64 districts in Bangladesh, 51% of the wells were above 10 ppb and 27% were above 50 ppb. The survey estimated that the number of Bangladeshis exposed to arsenic concentrations above 50 ppb is 28 to 35 million and the number exposed to more than 10 ppb is 46 to 57 million[4].

Chronic exposure to arsenic through ingestion of contaminated drinking water leads to serious health problems. These include cancers of the lungs, kidney, bladder, urinary tract and skin and cause neurological disease and failure of the kidneys and liver. The appearance of lesions on the feet and hands are effects of longtime exposure to arsenic [5]. In many parts of southern Bangladesh, one in 10 adults is at risk of dying from arsenic-triggered cancers of internal organs [6].

There are several known methods for water purification using the addition of chemical adsorbents that have been implemented in rural areas. These approaches often apply a point-of-use system leaving the operational cost and maintenance to individual families. Consequently, this method leaves a great time burden on Bangladeshis who live on less than one dollar a day. ElectroChemical Arsenic Remediation (ECAR), implements a community-based system that sells clean water at a price affordable to the rural population. ECAR uses electrochemistry to continuously produce Fe(III) ions in solution which quickly hydrolyze, forming iron oxides, hydroxides and/or oxyhydroxides (collectively referred to as iron (hydr)oxides used to remove arsenic (Figure 1)). ECAR is effective, efficient and inexpensive, requiring only very low maintenance. The electrochemical cell consists of two iron electrodes immersed into simulated Bangladesh groundwater. During the electrochemical process, current is applied to the iron anode to form Fe(III) (hydr)oxides while As(III), the more toxic form of arsenic, is simultaneously oxidized to As(V) at the anode. Fe(III) (hydr)oxides do not bind well to As(III) but have high affinity for As(V) [7]. The iron (hydr)oxides precipitate and coagulate while arsenic adsorbs to the surface, forming insoluble iron-arsenic complexes that can be filtered out using a vacuum filtration system. In the lab, filtration is achieved using a vacuum filter apparatus with a 0.1 micron pore size. Lower cost alternatives are planned for the field, such as simple settling and sedimentation.

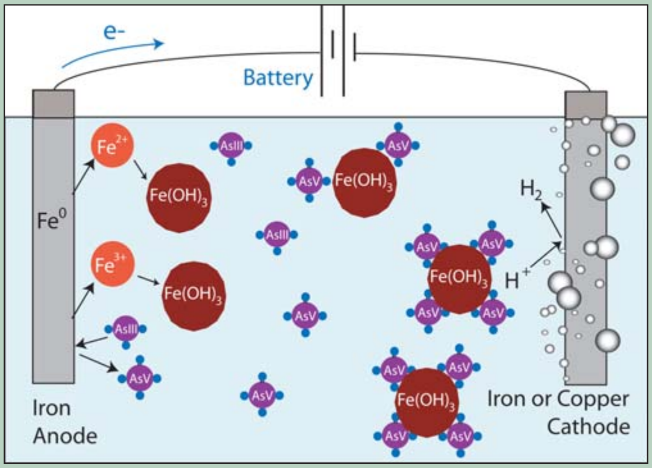

Figure 1. Schematic of using Fe(III) to bind with As(V) for removal from drinking water.

Batch experiments using both simulated and real Bangladeshi groundwater have demonstrated that ECAR is able to reduce arsenic concentration of 600 ppb to less than 10 ppb using current densities between 0.07 and 1.1 mA/cm^2. Prior lab work has also shown that arsenic removal tends to increase with increasing Coulombic dosage (measured in Coulombs per liter or C/L) and increasing complexation time (defined as the total time of contact between generated iron (hydr)oxides and arsenic contaminants).

The benchtop batch process for ECAR was developed into a continuous flow modular prototype by a team of UC Berkeley students. The device is referred to as "sushi" due to the double roll electrode made from flexible carbon steel foil. It was tested in the laboratory using simulated Bangladesh groundwater, but prior to this work, had never been tested using real groundwater in Bangladesh. Testing with real Bangladesh groundwater is important because the chemical composition in a single well may be different from the composite synthetic groundwater based on average chemical composition across Bangladesh. Differences in chemical composition can potentially have a strong effect on arsenic removal using ECAR.

The primary objective of the prototype field experiments was to demonstrate the ability of the "sushi" prototype to reduce arsenic concentrations in real Bangladesh groundwater from >200 ppb to below the WHO limit of 10 ppb. In addition, spot checks at different Coulombic dosages and complexation times were used to compare general arsenic removal trends to trends in the lab. Also, low cost sedimentation was compared to 0.1 micron vacuum filtration as an alternative method for removing ECAR generated iron-arsenic complexes in the filed.

MATERIALS AND METHODS

Arsenic-contaminated water was collected directly at the two wells in the village of Dhingaghanga and stored in 20 L plastic containers that were capped in order to avoid aeration that could lead to oxidation of As(III) to As(V). Prior to water collection, the well was pumped for at least 5 minutes to ensure that the water was coming directly from the aquifer and had not been in contact with the tube well for a long period of time and was free from algae and bacterial contamination. The pH and the dissolved oxygen (DO) of the water was measured and recorded at the field site using a SympHony Ag/AgCl gel-filled combination electrode pH probe and symphony dissolved oxygen probe respectively (VWR International, vwr.com) attached to a portable meter SympHony model SP80PD. To ensure that the collected water contained arsenic, a sample was prepared and tested using a Quick™ Arsenic Test Kit (Industrial Test Systems, Inc, Rock Hill, SC). The test kit contains three reagents that reduce inorganic arsenic to arsine gas. A mercuric bromide test strip is used to measure the arsine gas concentration. It produces a yellow-brown color after exposure to the gas. The test strip is matched to a calibrated color chart in order to obtain a quantitative measure of arsenic in the water sample. Quick™ Arsenic Test Kit works with highest accuracy if the arsenic concentration is below 100 ppb. If arsenic concentrations are >100 ppb, it is recommended to use a dilution factor.

ECAR treatment was conducted within 120 hours of collection. DO and pH measurements were taken and recorded immediately before the experiment. 100 mL of sample water was filtered through Whatman #1 filter paper to remove particulates that could clog the prototype. The total arsenic concentration was tested using Quick™ Test Arsenic Kit. Some initial portion of the sample was stored for more accurate arsenic measurements via atomic absorption spectroscopy (AAS). The collected water was shaken for five minutes before the experiment. This additional step ensures that all the precipitates that had formed and collected on the bottom of the plastic container between collection at the well head and the ECAR treatment became suspended again in the water matrix.

The "sushi" consisted of two sheets of carbon steel separated by plastic mesh and rolled into a spiral surrounded by a Plexiglas® container that serves as a holding cell in which the water is treated electrochemically. The two sheets of carbon steel serve as the anode and cathode and are connected to a constant current source that provides 1 A with a 12 V car battery used as the power supply. The electrodes dissolve with time and will need to be replaced. Exact lifetime depends on Coulombic dosage required for a given area. The prototype device was attached via tubing to a reservoir that was maintained at 5 L of water at a height of 1 m above the prototype to provide a pressurized inflow. Maintaining a constant water level in the reservoir ensured that the flow rate through the Sushi Roll was constant. The flow rate was adjusted via a valve and set during the first 1 L of flow through the prototype device.

Prototype effluent was stirred on a magnetic stir plate with aliquots removed after 60 and 80 minutes followed by filtration using a Milipore (Billerica, MA) hand-pumped metallic vacuum filter with 47 mm diameter and 0.1 micron Milipore filter membrane. The filtrate was tested for arsenic using Quick™ Arsenic Test Kit. 250 mL of treated water was collected and allowed to settle for 2 days without vacuum filtration. At the end of 2 days settling, one sample was filtered in the manner described above and a second sample was drawn from the top of the sample beaker (no additional filtration).

To ensure more accurate results, samples were sent for Atomic Absorption Spectroscopy (AAS) analysis at BUET, Bangladesh University for Engineering and Technology (Dhaka, Bangladesh). All presented results were obtained by using AAS.

Results and Discussion

The water used in the experiments was collected from two different wells and the initial total arsenic concentration at the day of the experiment was 200 ppb for Well 7 and 250 ppb for Well 8. All experiments showed very promising results and confirmed that the prototype is capable of reducing the arsenic concentration in groundwater below the Bangladeshi standard of 50 ppb. ECAR was able to reduce the arsenic concentration to below the WHO standard of 10 ppb for both wells under certain conditions (60 minutes stirring at a Coulombic dosage of 810 and 456 C/L for Well 7 and all tested conditions for Well 8).

Figures 2 and 3 present the residual arsenic concentration after ECAR treatment as a function of charge loading (Coulombic dosage in C/L and flow rate in mL/s). Both figures show the results for stirring for 60 and 80 minutes as well as settling for 2 days after electrochemical treatment. The Coulombic dosage was calculated from the measured flow rate and the applied current using the following formula:

$$q = \frac{I}{f}$$

where q = desired Coulombic dosage (C/L), I = current (Amps) and f = flow rate (L/s).

Using the equation above, a flow rate of 1.23 mL/s yields a Coulombic dosage of 810 C/L. With these experimental parameters, the remaining arsenic concentration for Well 7 (initial arsenic concentration is 200 ppb) is 10 ppb after 60 minutes of stirring and 14 ppb after 80 minutes of stirring (Figure 2). A Coulombic dosage of 456 C/L with a flow rate of 2.19 mL/s applied to the same Well 7 water resulted in a remaining arsenic concentration of 8 ppb after 60 minutes and 9 ppb after 80 minutes of stirring (Figure 2).

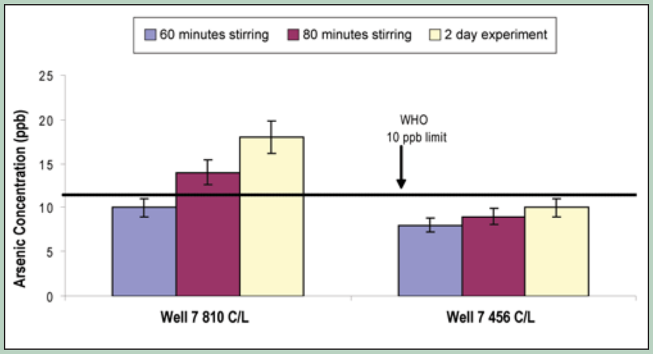

Figure 2. Well 7 water (initial concentration 200 ppb) residual arsenic concentration after electrochemical treatment with a dosage of 810 C/L (flow rate 1.23 mL/s) and 456 C/L (flow rate 2.19 mL/s) after 60 minutes and 80 minutes stirring as well as 2 day settling experiment; error bars indicate error in AAS measurements.

For Well 8 water with an initial concentration of 250 ppb, a Coulombic dosage of 833 C/L and a flow rate of 1.20 mL/s show a residual arsenic concentration of 5 ppb for 60 minutes and 6 ppb for 80 minutes of stirring (Figure 3). A much lower Coulombic dosage of 366 C/L with a flow rate of 2.59 mL/s showed similar results. The remaining arsenic concentration after 60 minutes is 7 ppb and after 80 minutes of stirring it is 8 ppb (Figure 3). In both cases, the trend with decreasing Coulombic dosage was for arsenic removal to stay the same or increase. This trend is different from that seen in the lab (where decreasing Coulombic dosage led to decreasing arsenic removal). More tests are needed to explore the cause of this strange trend.

The 60-minute stirring experiments are most promising. After electrochemical treatment the results showed slightly better residual arsenic concentrations than the 80-minute stirring experiments performed with the same Coulombic dosage and flow rate. Subsequent complexation time during two days of settling showed even less arsenic removal. Possible desorption of arsenic particles during longer stirring time could explain these results. This trend was not observed when similar tests were performed in the laboratory with synthetic water; longer stirring time yielded better results. To better understand these results further experiments are warranted.

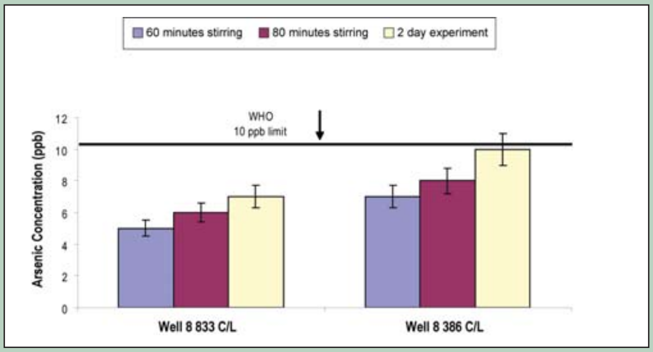

Figure 3. Well 8 water (initial concentration 250 ppb) residual arsenic concentration after electrochemical treatment with a dosage of 833 C/L (flow rate 1.20 mL/s) and 386C/L (flow rate 2.59 mL/s) after 60 minutes and 80 minutes stirring as well as 2 day experiment; error bars indicate error in AAS measurements.

In addition to stirring for 60 and 80 minutes, 250 mL of electrochemically treated water (same Coulombic dosage and flow rate as described above) was set aside for two days and then vacuum filtered and tested for residual arsenic concentration (Figure 2 and 3). A Coulombic dosage of 810 C/L has a residual arsenic concentration of 17 ppb after two days; a Coulombic dosage of 456 C/L has a final arsenic concentration of 9 ppb. Both results are for Well 7 water with an initial arsenic concentration of 200 ppb. The two-day treatment for Well 8 water (initial arsenic concentration is 250 ppb) results in 7 ppb for a Coulombic dosage of 833 C/L and 10 ppb for a Coulombic dosage of 386 C/L. The last result was obtained from Quick™ Arsenic Test Kit (no AAS data was available for this experiment).

Two additional days of complexation time yielded results at or slightly above the WHO standard of 10 ppb. All of the two-day settling experimental results without filtering were below the Bangladeshi standard of 50 ppb, but only the experiments with vacuum filtration had residual arsenic concentrations low enough to be below the WHO standard of 10 ppb. These results suggest that settling and decantation over two days cannot achieve the same arsenic removal as filtration. Some iron-arsenic complexes may still be suspended throughout the water matrix and need to be filtered out in order to ensure a safe final arsenic concentration.

In addition, the two-day settling experiment was also tested for arsenic concentration without a vacuum filter by taking water from the top. These results were then compared to the ones using a vacuum filter (Figure 4). For Well 7 (Coulombic dosage 456 C/L), the residual arsenic concentration is 8 ppb compared to 12 ppb without a vacuum filter. The results for Well 8 (dosage 386 C/L) show 7 ppb with filter versus 16 ppb without vacuum filtering.

The filtered sample of water showed a total arsenic concentration of 281 ppb for Well 7 and 338 ppb for Well 8 whereas the concentrations of the unfiltered water were 200 ppb and 250 ppb, respectively. The above results were measured on the same day. These findings might indicate that arsenic particles bind with the naturally occurring iron ions in the water and are therefore not detected as free arsenic. Filtration may cause the bound arsenic particles to be released from the iron-arsenic complexes and become suspended as free arsenic particles. This behavior is different and has not been observed in the laboratory. Further experimentation is warranted.

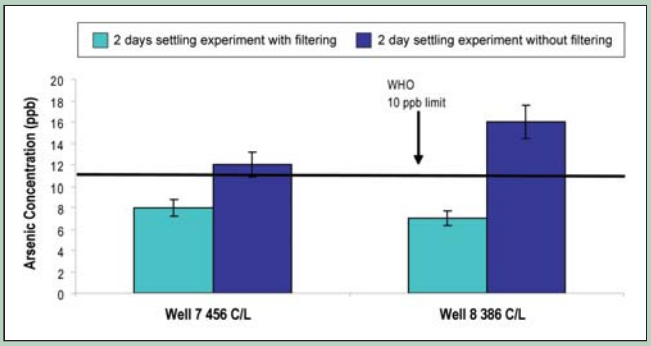

Figure 4. Well 7 (initial concentration 200 ppb) and Well 8 (initial arsenic concentration 250 ppb) residual arsenic concentration after electrochemical treatment with a dosage of 456 C/L (flow rate 2.19 mL/s) and 386 C/L (flow rate 2.59 mL/s) comparing 2 day settling with vacuum filtration and without vacuum filtration; error bars indicate error in AAS measurements.

CONCLUSION

The objective of testing the "sushi" with real Bangladeshi groundwater was to show that the prototype is efficient in removing arsenic below 10 ppb. The data obtained showed that the device is effective at reducing arsenic concentrations to below 10 ppb from real Bangladesh water at an initial arsenic concentration of >200 ppb.

Spot checks at different Coulombic dosages and complexation times showed trends that were different from those observed in the lab. Results showed that smaller dosage and therefore a faster flow rate works equally as well or even better than a larger dosage and slower flow rate. These findings are encouraging since small dosage and fast flow rate are desirable parameters when turning a prototype into an actual device. However, the fact that the trends are inconsistent with lab trends suggests further study is necessary to make conclusions.

The results indicate that filtration is an essential treatment step that will need to be implemented in the design of a complete device. Using precipitation as an alternative to filtration is an option that needs further investigation. The results have shown that a device including a precipitation step will increase the treatment time by at least two full days.

The device was built as a bench style prototype. The experimental flow rates do not reflect flow rates that will be needed in a scaled-up device. The data obtained help to constrain the parameter space for optimization of flow rate and Coulombic dosage.

One future goal is to test the prototype with arsenic water that has a higher initial concentration (preferably higher than 250 ppb) and perform more detailed studies to determine the cause of arsenic removal trends at various ECAR parameters. These experiments are essential in order to ensure that the device is able to remove arsenic robustly in the field.

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