Arsenic removal from groundwater using iron electrocoagulation: effect of charge dosage rate

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ABSTRACT

We demonstrate that electrocoagulation (EC) using iron electrodes can reduce arsenic below 10 μg/L in synthetic Bangladesh groundwater and in real groundwater from Bangladesh and Cambodia while investigating the effect of operating parameters that are often overlooked, such as charge dosage rate. We measure arsenic removal performance over a larger range of current density than in any other single previous EC study (5000 fold: 0.02 – 100 mA/cm^2) and over a wide range of charge dosage rates (0.060– 18

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Coulombs/L/min). We find that charge dosage rate has significant effects on both removal capacity (μg-As removed/coulomb) and treatment time and is the appropriate parameter to maintain performance when scaling to different active areas and volumes. We estimate the operating costs of EC treatment in Bangladesh groundwater to be \$0.22/m^3. Waste sludge (~ 80 – 120 mg/L), when tested with the Toxic Characteristic Leachate Protocol (TCLP), is characterized as non-hazardous. While our focus is on developing a practical device, our results suggest that As[III] is mostly oxidized via a chemical pathway and does not rely on processes occurring at the anode.

Keywords: electrocoagulation, arsenic, water treatment, Bangladesh, India, Cambodia, dosage rate

INTRODUCTION

Naturally occurring arsenic contamination in drinking groundwater supplies has been discovered in rural low-infrastructure regions of Argentina, Chile, Mexico, China, Hungary, Vietnam, Cambodia, West Bengal (India), and Bangladesh. [1, 2] In Bangladesh and West Bengal, 63 million people are exposed to arsenic levels that range up to 3200 μg/L, [3] well in excess of the 10 μg/L maximum contaminant level (MCL) recommended by the World Health Organization (WHO). [4] One in five (21.3%) of all deaths in Bangladesh were recently attributed to arsenic in drinking water. [5] Populations at risk of arsenic exposure through groundwater drinking supplies include 0.5 – 1 million people in

Cambodia and South Vietnam. [2] Conventional arsenic treatments are logistically difficult and prohibitively expensive for the local population.

Electrocoagulation (EC) is a method of treating polluted water and wastewater for numerous contaminants, [6-9] including arsenic. [10-14] In EC using iron electrodes, electrolytic oxidation of a sacrificial iron anode produces hydrous ferric oxide (HFO; also called Fe[III] precipitates) in contaminated water. Contaminants form surface complexes on HFO, which then aggregate to form a floc that can be separated from water. For a constant operating current, I [mA], and assuming that iron is the only electrochemically active species, the concentration of iron generated in solution, [Fe] [mg/L], is related to the total charge loading, q [C/L] (i.e. the total charge passed through solution by the current), by Faraday's law, [Fe] = q M/nF where M [mg/mol] is the molecular weight of iron, F [C/mol] is Faraday's constant, and n is the number of moles of electrons/mole of iron (n = 2 assumed here, following [15]). The charge loading q is related to the active electrode area, A [cm^2], solution volume, V [L], electrolysis time, t_e [s] and current density, J= I/A [mA/cm^2] by the relation:

$$q = J\, t_e\, A/V \qquad (1)$$

or equivalently:

$$q = I\, t_e/V \qquad (2)$$

The charge dosage rate (herein called dosage rate) is dq/dt [C/L·min] and is proportional to the rate of iron dissolution into a unit volume of solution during electrolysis. In terms of the operating variables above, dosage rate is:

$$dq/dt = I/V = JA/V \qquad (3)$$

Faraday's law easily converts q to [Fe] and dq/dt to d[Fe]/dt.

EC recently gained attention due to many advantages over chemical coagulation - including pH buffering ability, avoidance of chemical additives, ease of operation, amenability to automation, low maintenance, low sludge production, small system size, and the benefit of electrocatalytic side reactions. [6] EC can also oxidize As[III] to more amenable As[V]. [10] This is a key reaction, as As[III] does not adsorb as strongly as As[V] to mineral surfaces in natural waters, [16] making it difficult to remove without pre-oxidation to As[V], [17, 18] and both As[V] and As[III] are present in appreciable quantities in the groundwater of Bangladesh. [3]

Although much work has been published on Fe(II)/O_2, Fe(II)/H_2O_2, and passive Fe(0) corrosion systems, [19-21] these systems do not take into account adjustable operating parameters unique to EC, such as charge dosage rate. Previous EC research has largely focused on charge loading or current density (due to its affect on charge loading) as the main variable controlling arsenic removal. [10, 13, 15, 22, 23] The effect of dosage rate on either removal or time is rarely mentioned. This omission is despite the effect of dosage rate on the average contact time between arsenic and HFO in solution, in addition to possible effects on the rate of As[III] oxidation, making it critical to understand EC performance and mechanisms.

Earlier studies of EC arsenic removal were performed in Indian domestic municipal tap water, [10] synthetic industrial wastewater, [12] and various salt solutions. [24, 25] Few published studies exist on EC performance in real groundwater [11] and few compare the performance of EC in lab experiments to field treatment of real groundwater of South Asia where the arsenic contamination problem is the most severe. Studies of Fe hydrolysis in the presence of phosphate, silicate, and arsenate report that these ions influence the growth and structure of Fe precipitates [26-28] and can also compete for sorption sites. The growth and aggregation of Fe precipitates is highly relevant to the cost and complexity of separating Fe precipitates from water, as smaller colloidal particles are generally more difficult to remove. The rate and extent of As[III] oxidation may also be affected by groundwater composition. Therefore, to assess the practicality and relevance of EC as a possible technology to address the arsenic crisis, it is critically important to investigate EC performance in real or synthetic South Asian groundwater.

In this study, EC is found to lower arsenic concentrations to levels below the WHO-MCL in synthetic groundwater representative in composition to the contaminated groundwater of Bangladesh, and in real groundwater samples from Bangladesh and Cambodia. Remediation of Cambodian groundwater helped demonstrate the robustness of EC in diverse South Asian aquifers. To investigate an extensive range of practical EC operating conditions, the current density was systematically varied over a larger range than in any other single previous EC study (5000 fold: 0.02 – 100 mA/cm^2) along with the dosage rate from (300 fold; 0.060 – 18 C/L/min; 0.02 – 5.2 mg-Fe/L/min). Other parameters relevant to operating costs were measured, such as the quantity of waste sludge and its disposability as a non-hazardous material according to the US EPA approved Toxic Characteristic Leachate (TCLP) test. We report very attractive and affordable operating costs to reduce initial arsenic concentrations of ~300 μg/L As[III] to below the WHO-MCL in real groundwaters, of about \$0.22/m^3, or about \$0.79/person/year. Our results suggest that As[III] oxidation to As[V] occurs via a chemical pathway and processes occurring at the anode play only a minor role, if any, in the oxidation route.

MATERIALS AND METHODS

Chemical Analysis

Aqueous arsenic concentration was determined by ICP-MS (USEPA method 6020), or in select cases, by GF-AAS (Graphite Furnace - Atomic Absorption Spectroscopy). Reported uncertainty for both techniques was ±10% (minimum ±2 μg/L). Arsenic Quick Test (Industrial Test Systems Inc., SC) was used primarily for field estimates (uncertainty

±33%) but is reported in one case due to the loss of samples in transit. As[III] was determined using filter cartridges containing an arsenate-selective adsorbent. [29]

Electrochemical Reactors

A 3L bench-scale batch reactor contained an iron wire anode (diameter 0.18 cm) positioned above a copper mesh cathode isolated by a polyvinylidene fluoride hydrophilic membrane (SI Fig.SI-I). Copper was chosen as an inexpensive inert cathode material for bench-scale experiments due to the focus on anode reactions and its availability as a mesh, allowing for increased surface area per volume. Initial experiments also tried to take advantage of the electropotential difference between different metals selected for the anode and cathode. In subsequent large-scale experiments, the benefit of current reversal for electrode cleaning outweighed the slight advantage of copper as the cathode material. Fe was used for both anode and cathode in larger field prototypes. Active anode area (A) varied with experiment from 9 to 150 cm^2 (listed in Table 2). Electrode separation (d) was ~1 mm. The cathode was originally isolated in a small beaker with a glass frit to prevent reduction of As[V] to As[III]. However, there was no noticeable effect on performance with and without the frit (results not reported here for brevity), so it was removed. A galvanostatic current (I) was preset at values of 3 to 500 mA using an EG&G model 173 Potentiostat. Reactors were magnetically stirred during electrolysis and for 1 hour after electrolysis (exceptions noted individually in SI Table SI-

1). Aliquots were filtered through 0.1 μm (absolute) pore size membranes or allowed to settle. Electrodes were rinsed in 12.6% HCl solution and washed with DI water before each test.

A bench-scale continuous flow reactor consisted of a plastic cylinder (active volume 1.6 L, active electrode area-to-volume 0.641 cm^{-1}) with water-tight endplates, and with water-tight inlet and outlet hose attachments at either end. A gate valve attached to the outlet hose controlled the flow rate. Two flexible carbon steel sheets (0.05 mm thick) sandwiching a plastic mesh (2.5 mm thick strands making squares 2.54 cm to the side) were rolled into a spiral similar to a sushi roll ($A = 1040\ cm^2$, $d = 2.5$ mm). A galvonostatic current I of 1.1 A was provided with a 12V car battery and a small off-the-shelf circuit (3021/3023 BuckPuck by LuxDrive). Flow rate was 2.2 to 4.4 mL/s based on the desired total charge loading. Aliquots were vacuum filtered using 0.1 μm (absolute) pore size membranes (Bangladesh tests), or gravity filtered using 11 μm pore size filters (Cambodia tests) when no vacuum system was available.

A 100L batch reactor for field trials comprises a cylindrical tank for dosing and mixing connected to a sedimentation tank for coagulant addition and solid/solution separation. The electrode assembly comprises 10 parallel interdigited 30.5cm x 58.4cm (12in x 23in) mild-steel plates (5 anode and 5 cathode) spaced 3cm apart with alternate plates electrically connected. The configuration allows for easy reversal of current, allowing each plate to be alternately deployed as anode and cathode to minimize extensive rust build up and passivation. The electrode assembly rests on a perforated non-conducting base plate. A DC motor attached to a small impeller continuously pushes water under the base plate and through the perforations up between the electrode plates. The voltage across the electrodes was < 3V when operated at I = 4.5 A (dq/dt = 2.7 C/L/min). After dosing the suspension is moved to a settling tank and Aluminum Sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$) is added up to 5 ppm as Al and rapidly mixed for 5 min, slowly mixed for 9 min, and slightly agitated for 16 min before being allowed to settle. Final arsenic concentrations were measured after the supernatant turbidity in the settling tank reached 5 NTU, typically within 2 to 3 hours.

Synthetic Bangladesh Groundwater

Synthetic Bangladesh groundwater (SBGW; Table 1), was prepared using deionized water and stocks of reagent grade $Na_2HAsO_4 \cdot 7H_2O$, $NaAsO_2$, $Na_2HPO_4 \cdot 7H_2O$, $NaHCO_3$, $CaSO_4 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and NaCl. $NaAsO_2$ stock solutions were purged with nitrogen gas and tightly capped for storage. Though present in real groundwater, no Fe salts were added to SBGW due to the large amount of iron added during EC. Appropriate amounts of stock solutions (excluding $NaAsO_2$) were mixed and purged with nitrogen gas to reduce the dissolved oxygen content, leaving a clear solution with pH approximately equal to 8 and 300 μg/L As[V]. The pH was lowered to 5 using carbon dioxide gas followed by addition of freshly prepared stock solution of $Na_2SiO_3 \cdot 5H_20$ was allowed to equilibrate for one hour. Compressed air was then used to raise the pH to 7.0±0.2. Stock solution of $NaAsO_2$ was added within 1 hour of experiments, resulting in a total spiked arsenic concentration of 600 μg/L, half As[III] and half As[V].

Bangladesh and Cambodia Groundwater Samples

Bangladesh groundwater (BGW) samples were obtained from villages in Jhikargachha, Abhaynagar, Sonargaon, and Chandpur Upazilas in the districts of Jessore, Narayanganj, and Chandpur (initial arsenic concentrations 93 – 510 μg/L). Cambodia groundwater (CGW) samples were collected from three communes and villages - Preak Russei, Dei Edth, and Preak Aeng - in the Mekong Delta region of Kandal Province (initial arsenic concentrations 80 – 750 μg/L; average regional water composition in Table 1). Water was collected from each well after approximately 5 minutes of continuous pumping (to avoid bacterial contamination and oxygenated water in the well head) and stored in tightly capped polyethylene bottles filled to the brim. Sample bottles were stored in a cool, dark place (to avoid algae growth and photo-oxidation) for 5 - 32 days before treatment.

Immediate treatment (i.e. without storage) is preferable to avoid precipitation of naturally occurring iron, which can remove some amount of arsenic, phosphate, and other ions through adsorption and settling. As[III] can also oxidize to As[V] during storage. [30]

However, immediate treatment was not possible given logistical constraints. During storage the pH of BGW increased by 0.1 (average), dissolved oxygen increased by 1.1 mg/L (average), and aqueous arsenic decreased by 15 – 72% (40% on average based on the Arsenic Quick Test). For CGW, aqueous arsenic decreased by 30% (average) based on the Arsenic Quick Test. Initial arsenic concentrations reported in this paper are those measured immediately before treatment.

Arsenic Removal Experiments

To examine arsenic removal in SBGW over a variety of operating conditions, batch reactor tests were conducted over a range of initial arsenic concentrations ([As] = 90 – 3000 μg/L), current density (J = 0.02 – 100 mA/cm^2), and dosage rates (dq/dt= 0.060– 18 C/L·min), listed by experiment in Table 2. Given J, I (used to set dosage rate by Equation 3), and A/V, the electrolysis time, t_e, corresponding to a desired q was calculated using Equation 1. Volume changes due to sample removal were taken into account. For low current densities, I and A (controlling J and dq/dt) were adjusted simultaneously to ensure a reasonable experimental time. Experiments were duplicated and results averaged (exceptions noted).

To explore the arsenic removal potential of pre-synthesized HFO adsorbent (ps-HFO; i.e. HFO that was not actively produced in the presence of arsenic), the batch reactor was run in arsenic-free SBGW, matching the conditions of experiment S-5.0 in Table 2. Concentrated As[III] and As[V] stock solutions were added in small volumes (< 0.02% of the active volume) to match SBGW either (a) immediately after electrolysis (fresh ps-HFO), or (b) 60 minutes after electrolysis (aged ps-HFO). Solutions were stirred for an additional 60 min following arsenic contact and filtered before arsenic analysis.

Both the batch and continuous flow reactor were used to remediate BGW and CGW samples at various operating conditions (SI Table SI-1). The total charge loading was varied based on initial arsenic concentration estimated by the Arsenic Quick Test. Experiments could not be repeated due to logistical constraints.

Leachate Experiments

A Toxicity Characteristic Leaching Procedure (TCLP) was performed on spent EC media (EPA Method 1311). As the batch reactor produced negligible amounts of spent media (~80 mg/L) a 25L reactor with parallel steel plates was used to generate 30 grams of spent sludge remediating SBGW to the WHO-MCL or less. The digested leachate was tested for RCRA listed inorganic contaminants (Ag, As, Ba, Cd, Cr, Hg, Pb, Se) using ICP-Atomic Emission Spectroscopy (EPA Method 7470 for mercury, EPA Methods 3010A and 6010B for other metals). Reported error for ICP-AES is ±10%.

RESULTS AND DISCUSSION

Arsenic Removal in Synthetic Bangladesh Groundwater

EC reduced initial arsenic concentrations of 90 – 3000 μg/L to less than the WHO-MCL of 10 μg/L in SBGW containing 50% As[V] and 50% As[III] (Fig.1). Post-treatment pH was 6.7 – 8.1 (0 to 0.8 pH units above the pre-treatment pH). No detectable iron (< 1 μg/L) remained in solution after filtration. This suggests that EC-treated water will be in a potable pH range. The treated water would taste the same as, or possibly better than, the source water because naturally occurring iron, often associated with an objectionable taste, will also be removed.

For all initial arsenic concentrations, the removal efficiency (defined as the mass of arsenic removed per unit charge loading or equivalently, unit Fe[II] mass), was initially high followed by a gradual decrease, consistent with behavior in other water matrices. [10, 24, 31] As arsenic is removed from solution and HFO is continuously added due to anode dissolution, the ratio of As/HFO decreases. As the aqueous concentration drops, so does the maximum loading of arsenic per mg of HFO in equilibrium. Simultaneously, as HFO ages in solution it may aggregate, reducing available surface area and adsorption sites.

This effect is countered by the increase in adsorption sites as HFO is continuously generated. The overall effect, derived from Figure 1, was almost an order of magnitude more arsenic removed per unit Fe[II] mass (or equivalent per coulomb) as initial arsenic concentrations increase. We observe an average removal of 4, 8, 14, and 33 μg-As per mg-Fe[II] for $[As]_{initial}$ = 90, 300, 600, and 3000 μg/L respectively. Thus arsenic removal efficiency (μg-As per mg-Fe[II]) is a very strong function of initial arsenic concentration. We caution the practitioner against normalizing results from experiments conducted at different initial concentrations as a method of comparing removal efficiencies of various arsenic removal technologies independent of concentration.

Ignoring the steep dependence of arsenic removal efficiency on initial arsenic concentration can lead to serious error in estimating the minimum charge loading required to reach the WHO-MCL, q_{min},. For example, q_{min} is 300 C/L for $[As]_{initial}$ of 3000 μg/L (Fig.1). It would be erroneous to assume however that half, i.e. 150 C/L is enough to remediate a sample with half $[As]_{initial}$, of 1500 μg/L. From experiment, 150 C/L was adequate to remediate a sample with 600 μg/L and insufficient to remediate a sample with 1500 μg/L (Fig.1). Arsenic removal efficiency is a poor metric to estimate the required charge loading without prior knowledge of $[As]_{initial}$. Also note the additional non-linearities in data shown in Figure 1. For $[As]_{initial}$ of 90 μg/L, a charge loading increment of 70 C/L is adequate to remediate the water. However, starting with $[As]_{initial}$ of 3000 μg/L, the incremental charge loading to go from 90 μg/L to 10 μg/L is almost double, 150 C/L.

Current Density and Charge Dosage Rate

Figure 2 and 3 show that the WHO-MCL was achievable in SBGW including As[III] and As[V] over a wide range of current densities (J = 0.02 – 100 mA/cm^2) and dosage rates (dq/dt = 0.060 – 18 C/L/min). In some cases (J = 10, 30, and 100 mA/cm^2) final [As] was just above the WHO-MCL (within 5 ppb), however based on the trend shown, the WHO-MCL would likely be reached with an incremental increase in electrolysis time.

The minimum electrolysis time required to reach the WHO-MCL ($t_{e\text{-}min}$, derived from Fig.2) decreased if dosage rate and current density were increased together (t_{e_min}~ 405, 64, 18, 10 min for J = 0.02, 1.1, 5.0, 10 mA/cm^2, dq/dt = 0.060, 2.2, 10, 18 C/L/min respectively) but t_{e_min} remained approximately the same if dosage rate was held constant while current density was increased (t_{e_min} ~ 10 min for J = 10, 30, 100 mA/cm2, dq/dt = 18 C/L/min). The minimum charge loading required to reach the WHO-MCL (q_{min}, derived from Fig.3) follows a similar trend (q_{min} ~ 25, 150, 175, 180 C/L for J = 0.02, 1.1, 5.0,10 mA/cm^2, dq/dt = 0.060, 2.2, 10, 18 C/L/min respectively and q_{min} = 175 C/L for J = 10, 30, 100 mA/cm^2, dq/dt = 18 C/L/min), noting that Δq_{min} for dq/dt = 10 and 18 C/L/min is within experimental error and cannot properly be distinguished (Table 2). These trends suggest dosage rate has more control than current density over both key performance parameters t_{e_min} and q_{min}. For verification, an additional batch test at J = 1.1 mA/cm^2, dq/dt = 0.060 C/L/min was conducted under identical conditions as those above using (1) the same current density but different dosage rate (J = 1.1 mA/cm^2, dq/dt = 2.2 C/L/min) and (2) the same dosage rate but different current density (J = 0.02 mA/cm^2, dq/dt = 0.060 mg/L/min). In both cases, t_{e_min} and q_{min} correlate strongly with dosage rate but not current density (SI Fig.SI-2). We reduced the active electrode area (and hence the ratio of active area to treatment volume, A/V) by a factor of 10 to adjust current density from J = 10 - 100 mA/cm^2 (Table 2) with minimal effect on t_{e_min} or q_{min}, indicating that even large (10x) changes in A/V cannot account for the differences attributed to the dosage rate. This also indicates that A/V has minimal effect of EC performance over a large range.

Dosage rate controls the average contact time between a given HFO particulate (generated some time between t = 0 and t_e) and remaining arsenic in solution. At low dosage rates, a given time increment has a higher average [As]/[HFO] ratio and a given charge loading increment has a longer average contact time with arsenic. Both effects increase arsenic capacity (defined as mg-As removed per mg-HFO) up to some maximum. The dosage rate also controls the ratio of As[III]/Fe[II] at any given time. Roberts et al. [32] has attributed an increased adsorption capacity of Fe[II] salts added in multiple small doses compared to Fe[II] salts added in a single dosage to the increase in As[III]/Fe[II] ratio. In the Robert et al. system, the increased As[III]/Fe[II] ratio increased the competitive advantage of As[III] over Fe[II] for reactive oxidants. If a similar mechanism is responsible for As[III] oxidation in the EC system (this subject is discussed briefly below), then dosage rate could have a similar effect on the rate of As[III] oxidation through the As[III]/Fe[II] ratio. The net effect would be a steady increase in arsenic removal capacity as dosage rate is decreased, resulting in a lower q_{min}. Although it takes less time to reach a smaller charge loading (C/L) at a constant dosage rate, the effect of decreasing dosage rate simultaneously results in a longer net time (i.e. even though q_{min} is lower, it takes longer to reach it). Thus lower dosage rates require a lower q_{min} at the cost of a larger t_{e_min} . Over the tested range of dosage rates, q_{min} can be reduced 6-fold, but only with a corresponding increase in t_{e_min} of 40-fold. This trade-off has important implications in the design of a practical EC reactor, however further discussion is outside the scope of this paper.

The effect of dosage rate on t_{e_min} is contrary to prior published research identifying current density as the key variable controlling minimum treatment time. [10, 33] Current density can easily appear to control treatment time if the active electrode area and volume are held constant across all tests (true of research cited above). In this case a change in current density is equivalent to a change in dosage rate (Equation 3), confounding the effect of the two variables. For practitioners and EC reactor designers who rarely keep a constant electrode area and volume across reactors, dosage rate, and not current density, is the more accurate and applicable scaling parameter.

The observed effect of dosage rate on q_{min} is also contrary to prior published research claiming that q_{min} is independent of EC operating parameters. [8, 10] These conclusions were based on research covering only a small range in dosage rates using only As[V] (i.e. without the need for As[III] oxidation to As[V]).

Arsenic Removal with Pre-Synthesized HFO

Arsenic removal using pre-synthesized HFO, or ps-HFO (i.e. HFO generated in SBGW without arsenic), was highly sensitive to ps-HFO age. Freshly prepared ps-HFO brought into contact with arsenic immediately after generation reduced 600 μg/L arsenic (half As[III], half As[V]) down to 22 μg/L after 120 min of contact. Slightly aged ps-HFO, stirred for 60 min between generation and arsenic contact, achieved only 190 μg/L in the same contact time (Fig.4), well above the WHO-MCL and even above Bangladesh legal arsenic limit.

Neither fresh- nor aged-HFO performed as well as conventional EC, which was capable of achieving the WHO-MCL under the same operating conditions (J = 5.0 mA/cm^2, dq/dt= 10 C/L/min) within 70 minutes (including the 60 min post-electrolysis mixing time). This difference suggests that a practitioner would pay a large penalty for using pre-synthesized HFO from a central EC facility (perhaps to take advantage of an available electricity connection) and supply the adsorbent to dispersed communities or for usein separate household filters.

The decreasing arsenic removal with increasing ps-HFO age can be partially understood by considering the Fe[II]/As[III] ratio in solution when arsenic is added. ps-HFO formed from Fe[II] salts have a higher arsenic removal capacity than ps-HFO formed from Fe[III] salts. [32] This is attributed to (1) oxidation of Fe[II] by dissolved oxygen causing partial oxidation of As[III] to more amenable As[V], demonstrated by Luepin and Hug [34] and (2) a higher As[V] sorption capacity of ps-HFO formed from Fe[II] compared to Fe[III]. [32] Assuming that iron dissolution produces Fe[II] and not Fe[III] (in agreement with [35] and [15]), fresh-ps-HFO may still contain an appreciable amount of Fe[II] when it comes into contact with arsenic, whereas in aged-ps-HFO, most of the Fe[II] will already be oxidized to Fe[III]. In fresh-ps-HFO, more aqueous As[III] can be oxidized with Fe[II], resulting in higher concentrations of As[V] which is more readily removed. In addition, with aged-ps-HFO, arsenic removal plateaus after 20 minutes of contact, with less than 5% total arsenic removal occurring between 20 – 120 min (Fig.4). Fresh-ps-HFO continues to remove arsenic at a decreasing rate (similar to regular EC behavior), with 15% of total removal occurring between 20 – 120 min. This is consistent with the continued oxidation of Fe[II] in fresh-ps-HFO solution, continuing to oxidize and remove As[III] while aged-ps-HFO has already reached a removal equilibrium. Aging of the adsorbent may also reduce available adsorption sites due to aggregation of the HFO particles.

Aqueous As[III] was measured after 60 minutes of arsenic contact in all solutions. In aged-ps-HFO, 43% of the initial As[III] was aqueous (SI Table SI-2) compared to only 12% in fresh-ps-HFO solutions and 4% in EC. This is consistent with increased As[III] oxidation in EC and fresh-ps-HFO, though aqueous As[III] alone cannot be used to determine whether the removed As[III] was oxidized first or directly adsorbed to ps-HFO. However, a recent EXAFS study from our group of EC flocs that had removed both As[III] and A[V] showed no detectable As[III], [36] indicating minimal direct As[III] adsorption.

Implications for As[III] Oxidation Mechanism

While not the focus of this work, it is useful to briefly discuss implications of these results on the As[III] oxidation mechanism in EC. Some oxidation of As[III] during the EC process has been verified by other researchers. [10, 13] However, the mechanism of oxidation has not been settled and various alternative mechanisms have been proposed. The substantial extent of As[III] removal by fresh-ps-HFO (in which no As[III] was exposed to the anode) suggests that the majority of As[III] oxidation occurs through chemical oxidation and not through any processes requiring the active anode, including the anodic generation of chlorine sometimes suggested in the literature. [24] Several researchers have reported As[III] oxidation in parallel to Fe[II] oxidation by dissolved oxygen using a Fenton-type reaction pathway, [19, 37] a mechanism that does not require exposure to an active electrode. This pathway has been shown to oxidize As[III] during natural corrosion of zero-valent iron in groundwater, [19, 34] and a model assuming this pathway as the only mechanism of As[III] oxidation in EC has been shown to agree well with experiment. [38] In our view this is the most likely candidate for As[III] oxidization in EC. Understanding and controlling As[III] oxidation in EC is a subject of ongoing research.

Verification in Real Groundwater

Figure 5 shows the initial and post-treatment arsenic concentrations for EC with groundwater samples from Bangladesh (BGW) and Cambodia (CGW). In every case, EC successfully mitigated initial arsenic concentrations to below the WHO-MCL, using both the batch and continuous flow reactors. In the case of Cambodian water samples, for six out of nine tested wells the mitigation of arsenic was to non-detectable levels (< 1.1 μg/L), even from initial concentrations as high as 760 μg/L. While more tests are required to optimize charge loading and treatment time, it is clear that EC works in real groundwater samples from diverse locations in Bangladesh and Cambodia. It also verifies that EC can remove arsenic concentrations adequately to meet the WHO-recommended MCL in groundwaters known to have phosphate and silicate, [2, 3] which are both known to hinder arsenic removal performance of EC. [39]

Floc Separation

The separation of arsenic-laden HFO flocs from EC-treated water is potentially an expensive, complicated, and time-consuming process. Settling plus decantation is attractive because it is extremely low cost and low maintenance compared to filtration processes, which require frequent replacement and/or frequent cleaning. However, removal of floc from synthetic groundwaters by settling plus decantation required 1 – 2.5 days to reach arsenic levels comparable to membrane filtration across various operating conditions. Floc settling was significantly faster when HFO was generated in 5 mM NaCl solution. Roberts et al. [32] observed a similar speed up in settling during co-precipitation with Fe(II) salts in deionized water compared to synthetic groundwater.

Settling time required for supernatant arsenic concentration to fall below the WHO-MCL significantly decreased by adding a small amount of alum ($Al_2(SO_4)_3 \cdot 18H_2O$) after electrolysis (flash mixed for 2 min followed by 10 min slow mixing). Supernatant arsenic concentrations after treatment with 8.5 mg/L as Al approached results of membrane filtration after 30 min. Additional tests (details not reported here for brevity) showed that only 5 mg/L as Al reduced the settling time in a 100L tank (height 0.76 m) to < 3 hours (further reduction in treatment time is likely with the addition of low cost finishing filters).

Leaching of Toxins from Waste Sludge

All arsenic removal methods produce arsenic-laden sludge or waste that require disposal. Batch tests at $[As]_{initial}$ = 90 – 3000 μg/L produced 80 – 200 mg of dry sludge per liter treated to reach the WHO-MCL. TCLP leachates from waste sludge (average arsenic loading 20 mg-As/g-Fe) were analyzed for RCRA contaminants (SI Table SI-3). Only arsenic was leached in measurable quantities ([As] = 160 μg/L), and this was well below the regulatory limits for wastewater ($[As]_{reg}$ = 5000 μg/L). Thus EC waste sludge is not considered hazardous waste per US EPA regulations and may be disposed of within a US municipal landfill.

Field Test of a 100L Prototype

A 100L 10-electrode Fe-Fe reactor (fully described in methods) was used to remediate water from three arsenic-bearing tubewells in Amirabad village, Murshidabad District, West Bengal, India, operating at dq/dt = 2.7 C/L/min. Initial arsenic concentrations were 140, 84, and 59 μg/L for tubewells 1, 2, and 3 respectively. To create a more challenging scenario, additional As[III] was added such that the initial concentrations were 343±26, 294±5, and 245±2 μg/L respectively. A total of 500L from tubewell 1, and 300L each from tubewells 2, and 3 were remediated with charge loading 150 - 455 C/L to final arsenic concentrations < 12 μg/L, within experimental error of the WHO-MCL (Fig.6). For 350 C/L and above, all final concentrations were below 5 μg/L. Un-spiked tubewell 1 water was also remediated to a final arsenic concentration of 5 μg/L using 150 C/L (not shown in Fig.6). Turbidity reached < 10 NTU after 60 – 120 min settling and < 5 NTU after 70 – 220 min of settling. Current direction was reversed between each batch and no passivation was observed.

Taking experimental error into account, q_{min} cannot be determined from Figure 6 within the range of 150 – 350 C/L, indicating equivalent to poorer performance than the beaker batch tests. This is somewhat surprising when taking into account the lower phosphate levels in the field ([P] = 0.14, 0.15, 0.15 mg/L for tubewells 1, 2, and 3 respectively) compared to SBGW ([P] = 1.3 mg/L), as well as a low dosage rate compared to most of the beaker batch tests and a lower initial total arsenic and As[III] concentration. This indicates the possible presence of other, yet unidentified, competing contaminants in the real water matrix. It also underlines the critical importance of extensive field testing. Silicate concentrations in the field were comparable to SBGW ([Si] = 18.8, 18.8, 22.6 mg/L for tubewells 1, 2, and 3 respectively) and Ca and Mg concentrations were slightly elevated ([Ca] = 104, 101, 118 mg/L and [Mg] = 30, 33, 30 mg/L for tubewells 1, 2, and 3 respectively). Before field trials, the 100L reactor was used to repeatedly remediate SBGW with initial arsenic concentrations of 3000μg/L to levels below to WHO-MCL at a charge loading of 400 C/L, consistent with beaker batch tests (q_{min} was not measured). Some authors have attributed performance variations across EC experiments to variable amounts of remaining unoxidized Fe[II] at the end of dosing. [15] To examine this possibility, water samples were removed from the 100L reactor immediately after dosing and filtered using a 0.45 μm membrane. This procedure was repeated for four separate representative dosing runs. Filterable iron was found to be in the range 0.02 - 0.05 mg/L, indicating negligible unoxidized Fe[II] at the end of dosing. Thus our data does not support the hypothesis attributing performance variations to residual unoxidized Fe[II]. The cause of difference in performance between field and laboratory experiments is the subject of ongoing investigation. All cost estimates in the section below are based on field experiment results, not laboratory experiments.

Estimated Consumable Costs

Consumables for EC comprise (1) the iron consumed in the sacrificial anode, (2) electrical energy supplied for electrolysis and light mixing, and (3) alum added to aid settling. The exact electricity consumption depends on the final device design, including electrode spacing, electrode plate area, resistivity of the source water, and operating current among other factors. [40] These cost estimates use the 100L reactor configuration which was shown to remediate real contaminated groundwater with initial concentrations of ~ 300μg/L As[III] to levels below the WHO-MCL. In both real and SBGW water matrices, the total cell voltage in the 100L prototype did not exceed 3.0V. The mixing system operated at 13W during electrolysis with no optimization for energy consumption, and at 13, 4.5, and 0.7W during alum coagulation for 5, 9, and 16 min respectively. These values were used in estimates.

The required charge loading was taken to be the most conservative q_{min} estimate from field trials, 400 C/L. The input energy cost was assumed to be $0.10/kWh, the standard retail tariff for grid power. For consumable iron in small quantities (< 100 kg) we received a quote from a Mumbai fabricator of $1/kg, consistent with the current cost of hot rolled plate carbon steel in India (worldsteelprices.com). Alum was available in the Mumbai market at 2 rupees per 100g, or ~$0.36/kg.

Using these values, the consumables cost for EC treatment was 0.022 US cents per liter ($0.22/m^3), with energy costs accounting for 31% of the total. Of the total cost, 17% supported alum addition (materials and mixing energy). Assuming per capita consumption of 10L/day, this amounts to $0.79 per capita/year, or $5.56 per family/year, assuming 7 people/family. For comparison, Roy [41] estimated that an average family in West Bengal incurs a cost of $84 per year to consume water with > 50 μg/L arsenic, including the cost of partially-effective preventative measures, medical expenditures, and loss of work due to illness readily attributable to arsenic.

Costs that are not included in this estimate include labor, amortized capital cost of equipment, maintenance and waste sludge disposal. Also not included are costs of appropriate public education and awareness regarding risks of arsenic in drinking water, and preventative measures. Full treatment costs can vary significantly depending on project design, equipment scale, the cost of a civil structure to house the equipment, local labor costs, etc. However, given the low consumables cost and high effectiveness, EC has potential to provide clean water in rural areas at a locally affordable price when taking full costs into account.

CONCLUSIONS

We report several quantitative results for EC using iron electrodes to remediate arsenic-bearing groundwater. Our results are directly relevant to successful implementation and scale-up of the technology for arsenic remediation of drinking water in South Asia. We have verified that EC reduces initial arsenic concentrations of up to 3000μg/L to below the WHO-MCL of 10μg/L in real and synthetic South Asian groundwaters over a large range of current densities (0.02 – 100 mA/cm^2) and charge dosage rates (0.060 – 18 C/L/min). A very important practical finding is that the dosage rate, as opposed to current density, is the appropriate parameter for scaling up EC reactor designs for acceptable arsenic removal performance in realistic systems. We have identified slow settling rates of arsenic bearing sludge as a key challenge of EC operating in realistic groundwater, and also shown that alum at dosages of 5 mg/L (as Al) can drastically reduce the settling time. Our tests show that EC sludge is non-hazardous according to USEPA TCLP standards. We have successfully operated a 100L batch reactor in Amirabad Village (located in the highly arsenic-affected Murshidabad district) showing that EC is effective in realistic conditions. Results from this trial have been used to estimate the consumables cost of EC as \$0.22 per m^3 of remediated water. The high performance and low consumable cost suggest that EC could provide clean water in rural areas at a locally affordable price.

Supporting Information Available

A schematic of the 3L bench scale reactor, details of groundwater samples from Bangladesh and Cambodia, As[III] and Astot concentrations associated with ps-HFO concentrations, full TCLP results and regulatory limits, and a graphical comparison of batch tests at (a) different current density and the same dosage rate and (b) the same current density and different dosage rate, are presented in the Supporting Information.

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LIST OF FIGURE CAPTIONS

Figure 1: Arsenic concentration as a function of charge loading for SBGW with initial total arsenic concentrations of 90 – 3000 μg/L (each comprised half As[III], half As[V]). All tests were run at J = 1.1 mA/cm^2, dq/dt= 2.2 C/L/min, and post-electrolysis mixing time t_m = 60 min. Inset shows the same data on magnified y-axis scale to highlight detail near the WHO-MCL for arsenic (10 μg/L). Dotted and dashed lines indicate for arsenic in drinking water the MCL for Bangladesh (50 μg/L) and WHO (10 μg/L).

Figure 2: Arsenic concentration as a function of electrolysis time in synthetic Bangladesh groundwater for J = 0.02 – 100 mA/cm^2 and dq/dt = 0.060 – 18 C/L/min (corresponding A/V listed in Table 2). Post-electrolysis mixing time was t_m = 60 min for all tests. Dotted and dashed lines indicate the legal Bangladesh limit for arsenic (50 μg/L) and the WHO-MCL for arsenic (10 μg/L).

Figure 3: Arsenic concentration as a function of charge loading in synthetic Bangladesh groundwater (SGWB) for J = 0.02 – 100 mA/cm^2 and dq/dt = 0.060 – 18 C/L/min (corresponding A/V listed in Table 2). Post-electrolysis mixing time was t_m = 60 min for

all tests. Dotted and dashed lines indicate the legal Bangladesh limit for arsenic (50 μg/L) and the WHO-MCL for arsenic (10 μg/L).

Figure 4: Arsenic concentration as a function of contact time with HFO adsorbent generated prior to contact in SBGW (J = 5.0 mA/cm^2, dq/dt= 10 C/L/min) without arsenic. 600 μg/L arsenic (300 μg/L As[III] and 300 μg/L As[V]) was added immediately after electrolysis at time = 0 min). "Aged-HFO" was put in contact with arsenic after electrolysis and 60 minutes of mixing. Dotted and dashed lines indicate the legal Bangladesh limit for arsenic (50 μg/L) and the WHO-MCL for arsenic (10 μg/L) in drinking water.

Figure 5: Initial and post-treatment arsenic concentrations of Bangladesh and Cambodia groundwater samples. Total charge loading was q_{tot} = 85 – 456 C/L (see SI Table SI-1). Error bars represent measurement error. Bars to the left of the dotted line represent samples from Bangladesh and those to the right represent samples from Cambodia.

Figure 6: Final arsenic concentration after EC treatment using a 100L Fe-Fe reactor remediating contaminated groundwater from three tubewells in West Bengal, India. Each contaminated well was spiked with an additional As[III], such that the average initial concentrations were 343 μg/L, 294 μg/L, and 245 μg/L for tubewells 1, 2, and 3 respectively. Data points at charge loading 300 C/L and 400 C/L are staggered slightly along the x-axis so that error bars are visible.

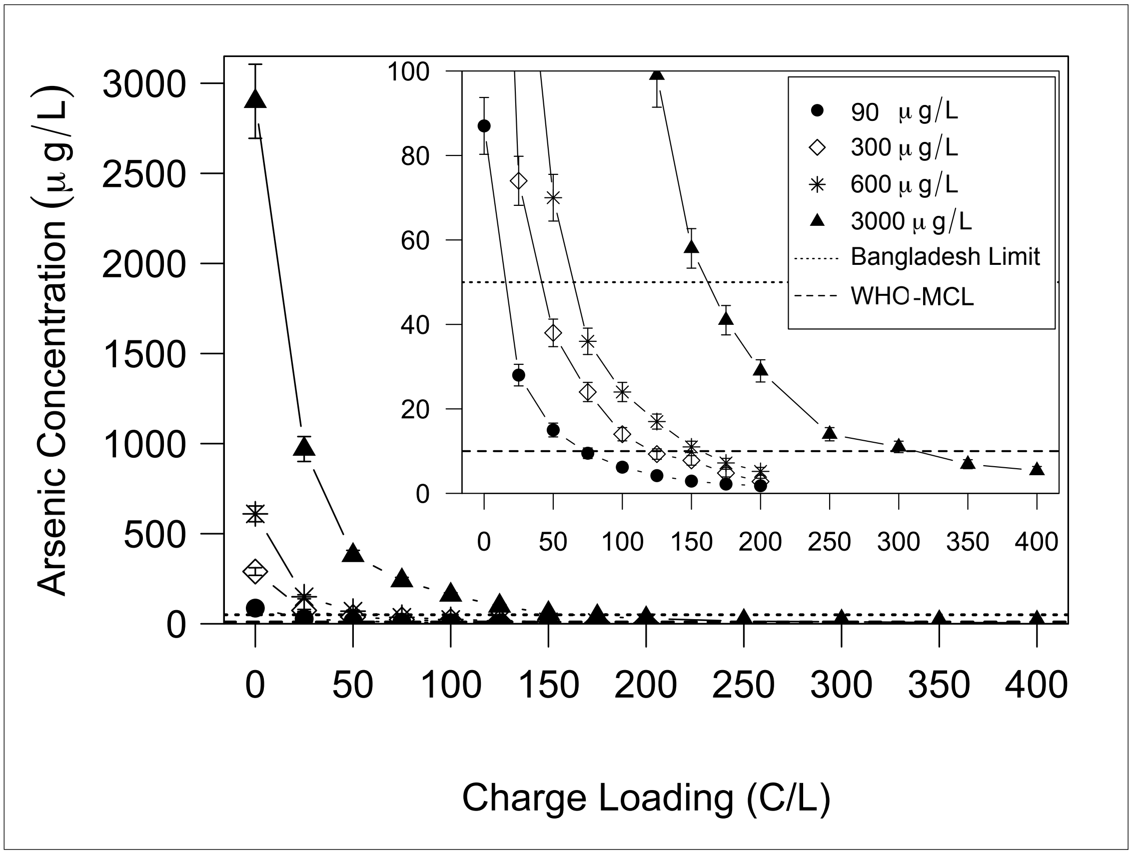

Arsenic Concentration (μ g/L)
3000
2500
2000
1500
1000
500
0
0
50
100
150
200
250
300
350
400
Charge Loading (C/L)
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
● 90 μ g/L
◇ 300 μ g/L
✳ 600 μ g/L
▲ 3000 μ g/L
Bangladesh Limit
WHO-MCL

Fig.1

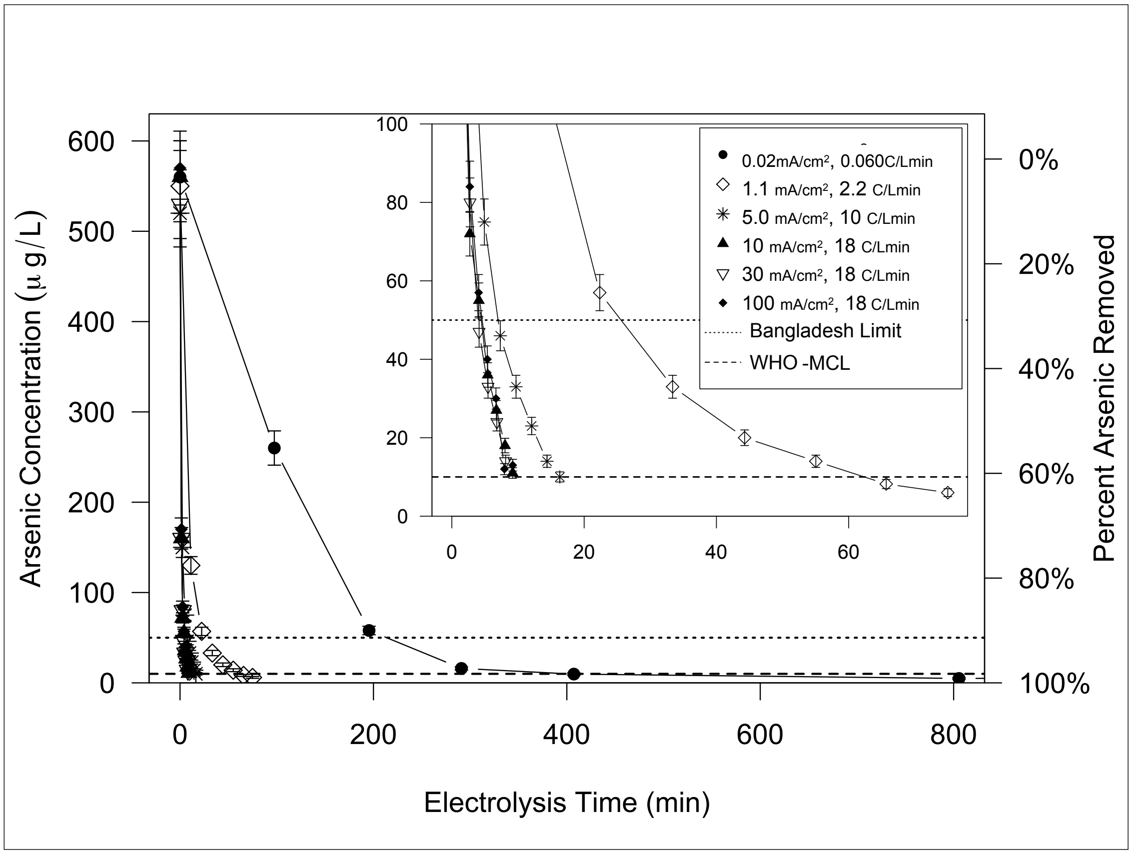

Arsenic Concentration (µ g/L)
600
500
400
300
200
100
0
Electrolysis Time (min)
0
200
400
600
800
Percent Arsenic Removed
0%
20%
40%
60%
80%
100%
100
80
60
40
20
0
0
20
40
60
0.02mA/cm², 0.060C/Lmin
1.1 mA/cm², 2.2 C/Lmin
5.0 mA/cm², 10 C/Lmin
10 mA/cm², 18 C/Lmin
30 mA/cm², 18 C/Lmin
100 mA/cm², 18 C/Lmin
Bangladesh Limit
WHO -MCL

Fig.2

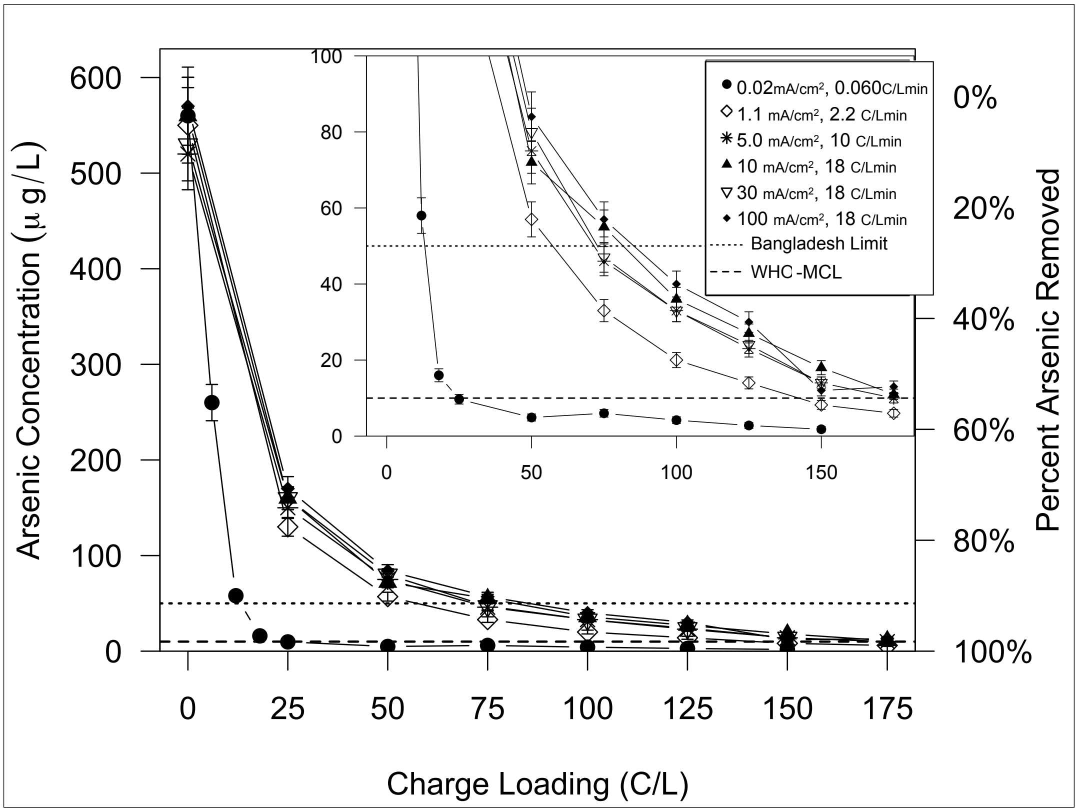
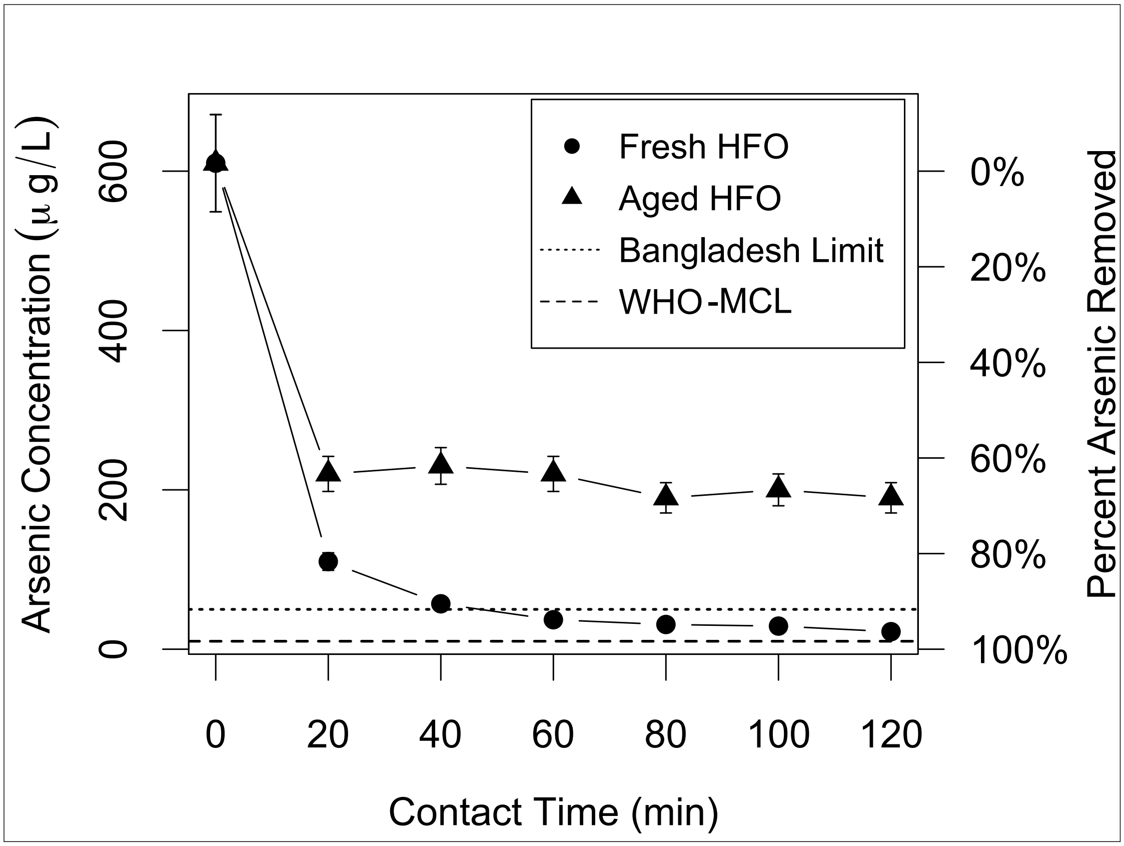
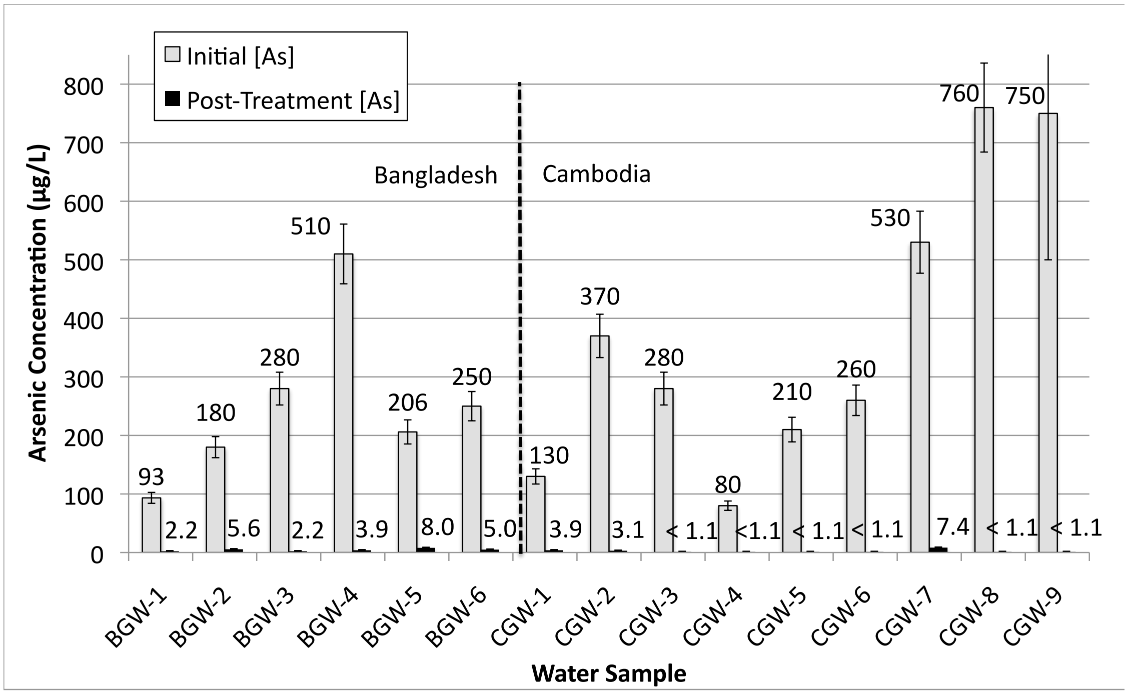

Arsenic Concentration (μ g/L)
Percent Arsenic Removed
Charge Loading (C/L)
0
100
200
300
400
500
600
0%
20%
40%
60%
80%
100%
0
25
50
75
100
125
150
175
● 0.02mA/cm², 0.060C/Lmin
◇ 1.1 mA/cm², 2.2 C/Lmin
✳ 5.0 mA/cm², 10 C/Lmin
▲ 10 mA/cm², 18 C/Lmin
▽ 30 mA/cm², 18 C/Lmin
◆ 100 mA/cm², 18 C/Lmin
Bangladesh Limit
WHC-MCL
0
20
40
60
80
100
0
50
100
150

Fig.3



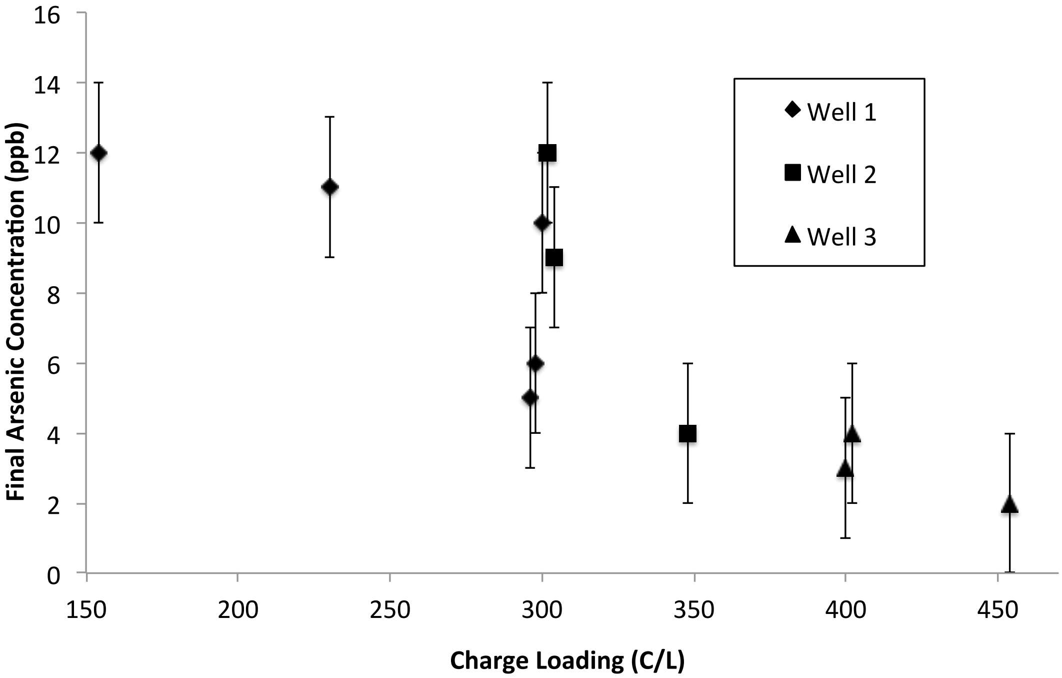
Arsenic Concentration (μg/L)
0
200
400
600
Percent Arsenic Removed
0%
20%
40%
60%
80%
100%
Contact Time (min)
0
20
40
60
80
100
120
● Fresh HFO
▲ Aged HFO
Bangladesh Limit
WHO-MCL

Fig.4



☐ Initial [As]
■ Post-Treatment [As]
Arsenic Concentration (µg/L)
0
100
200
300
400
500
600
700
800
Bangladesh
Cambodia
93
2.2
180
5.6
280
2.2
510
3.9
206
8.0
250
5.0
130
3.9
370
3.1
280
< 1.1
80
<1.1
210
< 1.1
260
< 1.1
530
7.4
760
< 1.1
750
< 1.1
BGW-1
BGW-2
BGW-3
BGW-4
BGW-5
BGW-6
CGW-1
CGW-2
CGW-3
CGW-4
CGW-5
CGW-6
CGW-7
CGW-8
CGW-9
Water Sample

Fig.5



16
14
12
10
8
6
4
2
0
Final Arsenic Concentration (ppb)
150
200
250
300
350
400
450
Charge Loading (C/L)
◆ Well 1
■ Well 2
▲ Well 3

Fig.6

Table 1: Groundwater composition for synthetic Bangladesh groundwater (SBGW) and published/derived values for Bangladesh and the Mekong Delta region of Cambodia.

		SBGW[1]	Bangladesh[3]	Cambodia - Mekong Delta[4]
N Wells		15[2]	1484[3]	90
pH		7.06±0.16	7.05±0.22	7.03
As	(ug/L)	556±29	129±155	233
AsIII	(ug/L)	288±19	91±136	NA
AsIII/ As_{TOT}		0.55±0.02	0.46±0.41	NA
HCO3	(mg/L)	275	501±144	364
PO4 - P	(mg/L)	1.3	1.3±1.5	0.66
SiO3 - Si	(mg/L)	19.5	19.7±5.1	17.2
SO42-	(mg/L)	8	4.6±17.4	21
Ca	(mg/L)	61	66±53	44
Mg	(mg/L)	8	27±21	21
Cl-	(mg/L)	125	81±203	63.4
Na	(mg/L)	138	94±183	79
Fe	(mg/L)	0	5.6±5.9	2.8

(1) Values for pH, As, As[III], As[III]/As_{tot} include measured mean and standard deviation values across all tests, while remaining values are gravimetric. (2) 6 samples were used for As[III] averages. (3) Groundwater parameters in Bangladesh were derived from the BGS. [3] pH, As[III], HCO3 and Cl were from the Special Study areas using 155 wells; all other values taken from the National Survey data using only wells with As > 10 μg/L. (4) Groundwater parameters in Cambodia were derived from Berg et al. [2]

Table 2: Arsenic removal performance and estimated charge loading required to reach the WHO-MCL (10 μg/L) for batch tests in synthetic groundwater.

Exp	Current Density	Charge Dosage Rate	A/V	Initial As[1]	Final As	q_{min}[2]
	(mA/cm^2)	(C/L/min)	(cm^2/L)	(μg/L)	(μg/L)	(C/L)
S4-90	1.1	2.2	33.3	87 ± 23	1.8 ± 1	75
S4-300	1.1	2.2	33.3	290 ± 39	2.8 ± 1	125
S4-600	1.1	2.2	33.3	610 ± 63	5.2±1.3	150
S4-3000	1.1	2.2	33.3	2900±160	5.4 ± 1	300
S2-100	100	18	3.00	570 ± 57	13 ± 1.3	~180[3]
S2-30	30	18	10.0	530 ± 53	14 ± 1.4	~180[3]
S2-10	10	18	30.0	580 ± 58	11 ± 1.1	~180[3]
S2-5.0	5.0	10	33.3	540 ± 54	10 ± 1	175
S2-1.1	1.1	2.2	33.3	590 ± 59	6 ± 1	150
S2-0.02	0.020	0.060	50.0	540 ± 54	1.8 ± 1	25
S3-1.1	1.1	0.060	0.91	570 ± 57	10 ± 1	50

(1) Errors on arsenic concentrations represent the larger of the standard deviation from repeated tests, ± 10% ICPMS measurement errors, and a minimum measurement error of ± 1 μg/L. (2) q_{min} is the minimum charge loading required to reach the WHO-MCL of 10 μg/L. The value is approximated from Figure 3.

(3) Values approximated using data extrapolation from Figure 3. Extrapolation was < 20% of the distance between the last 2 points and each extrapolated value is within 10 C/L of the largest experimental charge loading.