Arsenic Removal and Its Chemistry in Batch Electrocoagulation Studies

ANSHUL SHARMA, SRI MALINI ADAPUREDDY AND SUDHA GOEL[+]

The aim of this study was to evaluate the impact of different oxidizing agents like light, aeration (by mixing) and electrocoagulation (EC) on the oxidation of As (III) and its subsequent removal in an EC batch reactor. Arsenic solutions prepared using distilled water and groundwater were evaluated. Optimum pH and the effect of varying initial pH on As removal efficiency were also evaluated. Maximum As (III) removal efficiency with EC, light and aeration was 97% from distilled water and 71% from groundwater. Other results show that EC alone resulted in 90% As removal efficiency in the absence of light and mixing from distilled water and 53.6% from groundwater. Removal with light and mixing but without EC resulted in only 26% As removal from distilled water and 29% from groundwater proving that electro-oxidation and coagulation were more effective in removing arsenic compared to the other oxidizing agents examined. Initial pH was varied from 5 to 10 in distilled water and from 3 to 12 in groundwater for evaluating arsenic removal efficiency by EC. The optimum initial pH for arsenic removal was 7 for distilled water and groundwater. For all initial pHs tested between 5 and 10 in distilled water, the final pH ranged between 7 and 8 indicating that the EC process tends towards near neutral pH under the conditions examined in this study.

Key words : *pH, oxidation, light, mixing, efficiency, batch*

Introduction

Arsenic contamination is a widespread, global problem that affects at least 20 countries. In all these countries, groundwater withdrawals for drinking water and irrigation are steadily increasing and more than 130 million people in Bangladesh and India are at risk due to arsenic contamination. Groundwater from six districts of West Bengal (India) was analyzed and average total arsenic levels ranged from 193 to 737 micro-g/L with a maximum value of 3700 micro-g/L[1]. Nine districts in West Bengal, India and 47 districts in Bangladesh have arsenic levels in groundwater above the WHO guideline value of 10 micro-g/L[2].

Various treatment methods are available for the removal of arsenic from drinking water which include coagulation, filtration, adsorption, and membrane filtration. Cheap, efficient and low maintenance technologies or methods are essential for arsenic removal from ground water to be sustainable in the long-term since the problem affects the poor in rural areas to the greatest extent. Electrocoagulation (EC) is an effective treatment process that is capable of removing a wide-spectrum of contaminants from various drinking waters and is best utilized in decentralized mode. The objective of this study was to evaluate some of the factors influencing arsenic removal efficiency using EC. Distilled water and groundwater solutions of arsenic were evaluated.

Chemistry of Arsenic

Arsenic can be found in solid, liquid and gaseous forms in the environment and in four different oxidation states: -3, 0, +3 and +5. Arsine [AsH_3] gas is the most reduced form of As and can exist in equilibrium with water. Elemental As is insoluble while the most soluble forms of As are arsenite [As(III)] and arsenate [As(V)]. As(III) is the dominant form under reducing or anoxic conditions (groundwaters are often anoxic) and As(V) dominates under oxidizing conditions (in the presence of oxygen as in most surface waters or in the presence of other oxidizing agents like chlorine, ozone, potassium permanganate). The solubilities of arsenic salts are dependent on pH, and the ionic environment. Methylated forms of As are also prevalent but at far lower concentrations compared to the inorganic forms.

Oxidation of As(III) to As(V) : Conversion of As(III) to As(V) is thermodynamically favorable under oxic conditions, but the rate of oxidation may vary from seconds to weeks and

---

Civil Engineering Department, IIT Kharagpur, Kharagpur (India) - 721302

[+] Corresponding author : Associate Professor (Environmental Engineering and Management), Civil Engineering Department, IIT Kharagpur, Kharagpur-721 302. e-mail: sudhagoel@civil.iitkgp.ernet.in , Phone: + 91 3222-283436.

months depending on various factors like pH conditions, light, oxygen, presence of oxyanions, metals, other oxidants, and unknown catalysts[3-5]. Oxidation of As(III) is generally of the order of seconds to days in the presence of light, catalysts, or oxidants[4-6]. In the Bissen et al. [2001] study[4], no oxidation of As(III) was observed in the dark even in one week, while under solar simulated conditions, only 40% of the initial As(III) was oxidized after 25 min. Addition of a catalyst like titanium dioxide increased the oxidation rate to get complete oxidation in 200 seconds. Light wavelength and intensity are factors that were found to influence the oxidation rate of As(III). Atmospheric oxygen can serve as an oxidant, but the reaction order was found to be of the order of weeks[6].

When groundwaters contaminated with arsenic are pumped to the surface, oxidation of arsenite to arsenate begins due to exposure to atmospheric oxygen and light. Removal of arsenic from water is generally due to co-precipitation with Fe (present in water or added as coagulant) or adsorption of the two inorganic species on particles present in water. As(V) has a higher tendency to adsorb on particles including ferric oxides compared to As(III)[3-6]. Therefore, oxidation of As(III) to As(V) is an important factor which needs to be taken into account when evaluating the removal of arsenic from drinking water.

The objective of this study was to determine the optimum operating conditions for the conversion and removal of As(III) and As(V) from distilled water and groundwater solutions of arsenic. Light, mixing conditions and EC were varied in one set of experiments to evaluate the effect of these oxidizing agents on As(III) oxidation and subsequent removal. Initial pH was varied in another set of experiments with As(V) added to distilled water and ground water to determine EC removal efficiency at different pHs.

Materials and methods

Experiments were conducted with distilled water and groundwater solutions of As(III) or As(V). Groundwater was collected as and when required from the Dandakaranya pump house, IIT Kharagpur campus. Since background levels of Arsenic in this groundwater was approximately 1 ppb (based on ICP-MS analysis), the water was spiked with known amounts of As for these experiments.

EC batch reactor and experimental set-up

A 1 L glass beaker was used as the EC batch reactor with two mild steel (MS) electrodes of size 17.5 cm x 2.5 cm x 0.75 cm immersed to a depth of about 12.5 cm in the water. An external DC power supply was used for applying a constant voltage (25 V) across the cell during the course of an experiment. This beaker was supported on a magnetic stirrer to keep its contents mixed. Current was passed through the reactor for 2 hours and the solution was allowed to settle for 1 hour.

Experiments conducted

Oxidation experiments were carried out with As (III) solutions while As (V) solutions were used for experiments with varying initial pH. Four pairs of oxidation experiments (with and without passage of current, i.e., EC) and under different conditions of light and aeration, i.e., mixing were conducted with distilled water and groundwater. An additional six experiments were performed at initial pHs varying from 5 to 10 with distilled water and from 3 to 12 with groundwater.

Sampling protocol

The supernatant was sampled in all experiments at regular time intervals (0, 5, 10, 15, 30, 45, 60, 120, 180 minutes) for pH, conductivity, and arsenic. The supernatant (10 to 15 mL) above the settled floc was removed after 180 minutes and filtered using cellulose nitrate filter paper of 47 mm diameter with a nominal pore size of 0.45 μm (Whatman India).

Arsenic stock solutions

As(III) stock solutions were prepared using As_2O_3 while As(V) stock solutions were prepared using Na_2HAsO_4. Initial concentration of As(III) for the experiments with various oxidizing agents was 1 ppm or mg/L. Initial concentration of As(V) for experiments with varying initial pH was also 1 mg/L.

Analytical methods

As(III) and As(V): Arsenic species were measured in solution following the Silver Diethyl Dithiocarbamate (SDDC) Method 3500-As B, APHA et al., 2005[7].

pH: pH of the aqueous arsenic solutions was adjusted using 0.1M NaOH and 0.1 MHCl and measured using a pH meter.

Turbidity: Turbidity was measured using a turbidity meter.

Results and discussion

Effect of oxidizing agents on arsenic removal

Experiments were conducted under the following conditions with and without electrocoagulation to determine

the impact of light, oxygen availability due to mixing, i.e., aeration, and EC on As(III) oxidation and removal from distilled water and groundwater solutions : Air +Light with mixing; Air + Light without mixing; Air + Dark with mixing; Air + Dark without mixing.

Results of these experiments are summarized in **Table 1** for distilled water and **Table 2** for groundwater. Passage of current through the EC reactors resulted in oxidation of any reduced ions that may be present including As (III). Conversion of As (III) to As (V), and adsorption of both species on precipitates of Fe resulted in arsenic removal by oxidation, coagulation, flocculation and settling in the EC reactor.

Maximum removal efficiency in distilled water solutions under normal conditions of exposure to air and tubelight, without and with EC resulted in removals of 26 and 97%, respectively **(Table 1)**. Similarly for groundwater, maximum removal efficiency obtained without and with EC was 29.4% and 71%, respectively **(Table 2)**. The differences in results between distilled water and groundwater can be attributed to analytical variability and presence of other ions in groundwater that can lower removal efficiency by EC. Minimum removal efficiency was observed in the dark when no mixing or EC were provided (approximately 6% removal in distilled water and 12% removal in groundwater). Electro-oxidation was observed to be extremely powerful as an oxidizing agent for As(III) compared to either light or aeration resulting in 90% removal in the absence of light or mixing in distilled water and

53.6% in groundwater. In all cases with distilled water and groundwater, removal efficiency was dramatically higher with EC demonstrating the efficiency of the process in converting and removing arsenic by oxidation and coagulation (in this paper, coagulation includes the processes of flocculation, settling, co-precipitation and adsorption on floc). These results further prove that of the three oxidizing factors examined, aeration, light and EC, the most effective oxidizing agent was EC, followed by light and then aeration. In general, arsenic conversion or removal from distilled water was much higher than in groundwater and can be attributed to the presence of competing ions in groundwater which lowered EC efficiency.

Reactions during the EC process

Removal of pollutants by EC is attributed to the following reactions at the anode and cathode[8,9].

Anode: oxidation and dissolution of electrode

$$M_{solid} \longrightarrow M_{(aq)}^{n+} + ne^-$$

$$2H_2O \longrightarrow 4H^+ + O_2 (g)\uparrow + 4e^-$$
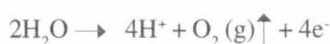
Cathode: deposition of metal oxide layer

$$M_{(aq)}^{n+} + ne^- + (OH^-)_n \longrightarrow M_a(OH)_n$$

$$2H_2O + 2e^- \longrightarrow H_{2(g)}\uparrow + 2OH^-$$

A mechanism for As(III) conversion to As(V) and its removal by EC is proposed : The free energy of the reaction where As (III) is converted to As(V) in the presence of oxygen

Table 1 : Percent removal of As(III) to As(V) in distilled water under different experimental conditions.

Experimental conditions	Removal efficiency without EC (left freely for 2 days)	Removal efficiency with EC
Air + Light, with mixing	25.97	97
Air + Light without mixing	20.95	95
Air + Dark with mixing	17.92	92
Air + Dark without mixing	5.90	90

Table 2 : Percent removal of As(III) to As(V) in groundwater under different experimental conditions.

Experimental conditions	% Removal without EC (left freely for 2 days)	Removal efficiency with EC
Air +Light with mixing	29.4	70.91
Air + Light without mixing	25.8	56.37
Air + Dark with mixing	23.54	59.74
Air + Dark without mixing	12	53.61

can be calculated from the free energies of formation of arsenite and arsenate ($\Delta G_f^{0'}$) as shown below. Based on the "$G_r^{0'}$", this is a spontaneous reaction[10].

$$H_3AsO_3 + \frac{1}{2} O_2 \rightarrow H_3AsO_4$$
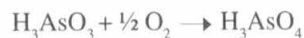
$\Delta G_f^{0'}$: -154.0   0   -184.0

$\Delta G_r^{0'}$: (-184.0) - (-154.0) = -30.0 kcal/mole

It is important to note that oxygen is generated in the EC process and is always available by equilibrium with the atmosphere. Therefore, it cannot be a limiting factor in the proposed reaction mechanism for removal of arsenic under oxic conditions. Further, the conversion of arsenite to arsenate under oxic conditions is known to be a slow reaction[6]. Energy sources like light and electricity as in EC can enhance the kinetics of this reaction and result in faster conversion of arsenite to arsenate.

Effect of initial pH

Experiments were conducted by varying the initial pH of samples ranging from pH 5 to 10 for distilled water and from 3 to 12 for groundwater samples to evaluate the impact of pH on arsenic removal. Experimental results with groundwater are shown in **Fig. 1** Results for distilled water (not shown here) and groundwater were found to be similar where the maximum removal efficiencies were observed at a pH of 7. These results are similar to those of another study with Fe-Fe electrodes and As removal[11]. Based on our knowledge of the solubility domain of Fe oxides and hydroxides, it is expected that at pH <8 -9, cationic polymeric hydroxide species of Fe will dominate in solution. This is likely to lead to charge neutralization of negativelycharged particles or compounds and their removal by coagulation, flocculationand settling. At pH >8 or 9, anionic polymeric hydroxide species of Fe will dominate. The increased concentration of negatively charged hydroxide species will furtherstabilize any negatively charged particles like clay or anionic compounds like As(V) leading to reduced removal efficiencies.

Further, it was observed that irrespective of the initial pH, final pH after electrocoagulation tended to be between 7 and 8 for distilled water solutions(**Fig. 2**). These results highlight one of the major advantages of electrocoagulation versus conventional chemical coagulation (CCC). In CCC, the pH of the solution decreases after addition of coagulant and neutralization is generally required to bring the pH of treated water to an acceptable level. However in electrocoagulation with some contaminants like clay, arsenic and fluoride and low initial concentrations, when the influent pH is acidic, the treated solution pH value rises, and when the influent pH is alkaline, the effluent pH drops resulting in a near neutral final pH. These results are similar to those found when treating distilled water for turbidity removal[12] and restaurant wastewater with EC[13].

It is important to note that despite the results reported in this paper, other studies with different contaminants like nitrate and fluoride show that the final pH is often highly alkaline, irrespective of the initial pH[14]. This suggests that the pH effect in EC is dependent on the nature and concentration
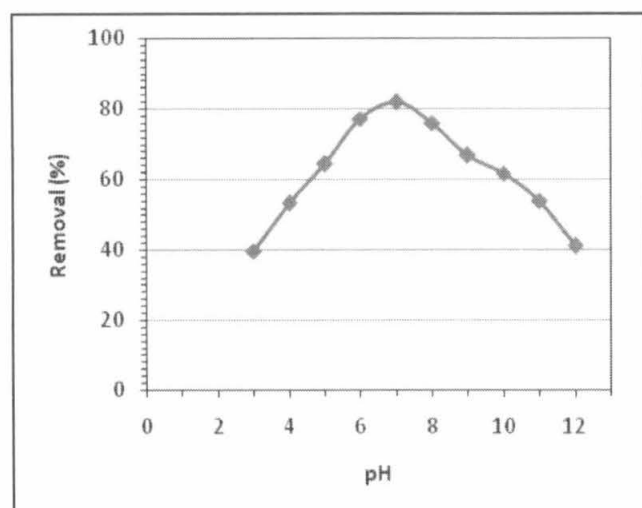

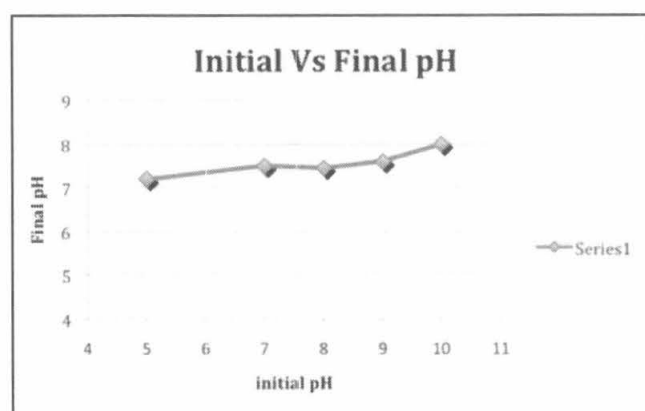Fig. 1 : Arsenic removal efficiency from groundwater as a function of initial pH

Fig. 2 : Change in pH after EC of arsenic solutions in distilled water

of the contaminant and no generalization can be made for the EC process.

Conclusions

Arsenic removal was evaluated in an electrocoagulation (EC) batch reactor where oxidation was followed by coagulation, flocculation, and settling.

Major conclusions from the arsenic studies with EC are:

Oxidizing agents : Electro-oxidation and coagulation in the absence of light and mixing resulted in an arsenic removal efficiency of 90% from distilled water and 53.6% from groundwater. Removal with light and mixing but without EC resulted in only 26% As removal from distilled water and 29.4% removal from groundwater. The highest As removal efficiencies were obtained with all three oxidizing agents: light, mixing and EC, resulting in 97% removal from distilled water and 71% removal from groundwater.

Initial pH: Initial pH was varied from 5 to 10 in distilled water and from 3 to 12 in groundwater for evaluating arsenic removal efficiency by EC. The optimum initial pH for arsenic removal was 7 in both waters. For all initial pHs tested in distilled water between 5 and 10, the final pH ranged between 7 and 8 indicating that the process tends towards neutral pH under the conditions examined, emphasizing the advantage of using EC for As removal.

Acknowledgements

References

1. Chatterjee A, Das D, Mandal BK, Chowdhury T R, Samanta G and Chakraborti D, Arsenic in ground water in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 1. Arsenic species in drinking water and urine of the affected people. *Analyst*, **120**, 643–650 (1995)

2. Das D, Chatterjee A, Samanta G, Chowdhury T R, Mandal B K, Dhar R, Chanda C R, Lodh D, Chowdhury P P, Basu G K, Biswas B K, Chowdhury U K, Rahman M M, Paul K and Chakraborti D, A Simple Household Device to Remove Arsenic from Groundwater and Two Years Performance Report of Arsenic Removal Plant for Treating Groundwater with Community. A Simple Device to Remove Arsenic from Groundwater.www.unu.edu/env/Arsenic/Das.pdf (2000).

3. Edwards M, Chemistry of arsenic removal during coagulation and Fe-Mn oxidation. *Jour Amer Water Works Assoc*, **86(9)**, 64-78 (1994).

4. Bissen M, Vieillard-Baron M-M, Schindelin A J and Frimmel F H, TiO_2-catalyzed photooxidation of arsenite to arsenate in aqueous samples. *Chemosphere*, **44 (4)**,751-757(2001).

5. Dutta P K, Pehkonen S O, Sharma V K, and Ray A K, Photocatalytic oxidation of Arsenic(III): Evidence of hydroxyl radicals. *Environ Sci and Tech*, **39,**1827-1834 (2005).

6. Pierce M L and Morre C B, Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res,***16,** 1247-1253 (1982).

7. APHA, AWWA, WEF, Standard Methods for the examination of water and wastewater(2005).

8. Gomes J G, Daida P, Kesmez M, Weir M, Moreno H, Parga J R and Cocke D L, Arsenic removal by electrocoagulation using combined Al-Fe electrode system and characterization of products. *Jour Haz Mat*, **139(2),** 220–31 (2007)

9. Mollah M Y, Schennach R, Parga J R and Cocke D L, Electrocoagulation (EC) - science and applications. *Jour Haz Mat*, **84(1),** 29–41 (2001).

10. Ferguson J F and Gavis J, A review of the arsenic cycle in natural waters. *Water Res*, **6,** 1259–1274 (2000).

11. Dolo A L,and Goel S,Effect of electrode combinations, pH and current density on Arsenic removal from drinking water using electrocoagulation. *Jour Environ Eng, The Institution of Engineers (India),***90(2),** 21-25 (2010).

12. Adapureddy S M,and Goel S,Electrocoagulation of drinking water for the removal of turbidity, Paper presented in *2012 3rd International Conference on Environment Science and Technology (ICEST 2012)*, Chennai.

13. Chen G,Chen X and Yu P L, Electrocoagulation and electroflotation of restaurant wastewater. *ASCE Jour of Environ Eng,* **126(9),** 858-863 (2000).

14. Babu J M, and Goel S, Defluoridation of drinking water in batch and continuous-flow electrocoagulation systems. *Poll Res,* **32(4),** 29–38 (2013).