

Removal of Arsenate from Aqueous Solution by Electro-Coagulation Method Using Al-Fe Electrodes

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Arsenic contamination in ground water is a worldwide problem. In the present work electro-coagulation (EC) has been evaluated as a treatment technology for arsenate [As(V)] contaminated water. EC is carried out using with Aluminum anode and Iron Cathode to assess their efficiency. Experiments were carried out to remove arsenic by the EC covering wide range in operating conditions such as pH(3–9), voltage (2-10 volts) and processing time (0–14 min), initial arsenic conc. (2-30 mgL⁻¹). Arsenate removal obtained was highest at pH 5-8 with 2-5 mgL⁻¹ conc. of arsenate as initial concentration after 12 minutes processing time at 3 volts. The technique was able to bring down arsenate concentration in ground water to less than 10 µgL⁻¹.

Keywords: Arsenate Removal, Electro-Coagulation, Aluminum anode, Iron Cathode, Ground Water.

1. INTRODUCTION

Arsenic, the twentieth most abundant elements in the earth crust, is well-known as deadly poison from the time immemorial [1, 2]. The compounds of arsenic in groundwater are found with both organic and inorganic moiety. The inorganic compounds of arsenic are about 100 times more toxic than the organic ones and are more prevalent in groundwater [3]. The major inorganic compounds of arsenic in natural water are pentavalent arsenate ions [As(V)] like H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻ and AsO₄³⁻ and trivalent arsenite ions [As(III)]: H₃AsO₃, H₂AsO₃⁻ and HAsO₃²⁻ with the latter being more toxic [4]. Under oxygenated condition Arsenate is more common in oxygenated water while arsenite is found in anaerobic or highly reducing conditions [5]. Arsenic is monitored by various Environmental protection agencies due to its carcinogenic nature. Various health problems include stomach pain, nausea, vomiting, diarrhea etc. The long-term exposure of arsenic in drinking

water increases the risk of cancer of skin, kidney, liver, and prostate. Moreover, it also disturbs the functioning of nervous and cardiovascular system and eventually leads to death [6, 7]. Arsenic concentration in various water bodies increases day to day due to several reasons like use of arsenical pesticides, mineral dissolution, mine drainage, disposal of fly ash, and geothermal discharge [8]. Due to its high toxicity, World Health Organization (WHO) has lowered the maximum contaminant level (MCL) for arsenic in drinking water from 50 to 10 μgL^{-1} [9]. Arsenic problem in ground water used for drinking and other house hold purposes are creating havoc in around 70 countries as about 150 million people are drinking arsenic contaminated water globally. 75 % of the total affected people are from South and South-east Asia i.e. Bangladesh, Cambodia, China, India, Laos, Myanmar, Nepal, Pakistan, Taiwan and Vietnam [10]. There are many methods for removal of pollutants and their determination in waters [11- 45]. Therefore, efforts have been made by various workers to develop arsenic removal methods, which include sorption [46-51], ion exchange [52,53], coagulation/flocculation [54-56], nano-filtration [57], and reverse osmosis [58]. A comparison of these methods dictates that electro-coagulation is a simple, efficient and promising technique for the treatment of water/waste water for various types of pollutants such as organic and inorganic contaminants [59-65]. EC has also been used for the removal of arsenic from ground water but these have certain limitations as not capable to work at large scale for providing arsenic free water [66-72]. Therefore, attempts have been made to developed and effective EC method for the removal of arsenate [As (V)] from ground water. The method has been developed by using Al-Fe electrodes. Besides, the optimization was carried out by varying different parameters like initial concentration, contact time, current, pH and temperature.

2. EXPERIMENTAL

2.1 Chemical and Reagent

Sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) was purchased from Merck, Germany. Ammonium molybdate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$], stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and sodium chloride were obtained from Merck, India. The other chemicals such as glycerol and sulfuric acid were supplied by Qualigens, New Delhi, India. All glassware were soaked in 10% HNO_3 for 48 hrs followed by their washing three times with Millipore water and air drying.

2.2 EC procedure and analysis

Arsenate stock solution (100.0 mgL^{-1}) was prepared by dissolving appropriate amount of sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) in Millipore water, and preserves it by adding 2 ml of conc. HCl and stored at 4 °C for longer duration use. The working arsenate solutions were prepared freshly for each experiment. The working solutions were prepared by diluting standard arsenate stock solution with laboratory tap water (New Delhi, India); to achieve the natural ground water conditions. A homemade electro-coagulation unit with cylindrical (7.5 cm \times 1.0 cm) Aluminum and Iron electrodes as anode and cathode respectively was used for the electro-coagulation of the arsenate containing

samples. The space between the vertically positioned anode and cathode of cell was 1.0 cm and dipped in arsenate water. The total submerged surface area of each electrode was 13.36 cm². All the experiments were conducted in batch mode by diluting stock arsenate solution. The EC was carried out in a 100 mL beaker with magnetic stirrer, for constant agitation to reduce the mass transport over potential of the EC cell. Initial pH of the arsenate solution was adjusted by adding either hydrochloric acid or dilute sodium hydroxide. After each experiment, the electrodes were corroded with sand paper to remove scale and then washed with double distill water. The unit was connected to direct power supply for maintaining the current density. The treated water was settled down for 2-3 hours and residue discarded. The solution was then filtered and check for arsenate concentration by using spectrophotometer.

To determine the arsenate in the filtrate solution by using spectrophotometer, a stain was prepared by mixing two reagents i.e. stannous chloride and ammonium molybdate reagents. Stannous chloride reagent (110.8 mM) was prepared in glycerol while the reagent of ammonium molybdate was prepared in Millipore water and was acidified by dilute hydrochloric acid so that overall concentrations of ammonium molybdate and sulfuric acid in solution were 20.23 mM and 5.2 M, respectively. For the development of stain, stannous chloride and ammonium molybdate reagent were mixed together (1:8, v/v), and allowed to stand for five minutes. The stain was prepared fresh before each experiment and was used within 20 min. after preparing the stain. 1.0 ml of stain was mixed with 50.0 ml of the test arsenate solution and kept for 12 hours, which gave the blue color with its intensity depends on the concentration of arsenate. The residual arsenate concentration was determined by using a calibration graph against the blank at 840 nm. Moreover, water quality of laboratory tap water (Jamia Nagar, New Delhi) was also determined as arsenate working solutions were made in these. The parameters analyzed for ground water were conductivity, pH, alkalinity, total dissolved solids (TDS), total hardness (temporary and permanent hardness), chloride, sodium, potassium and calcium.

3. RESULTS AND DISCUSSION

The aliquots sample for the EC was made in natural ground water as distill water have almost zero conductivity and, therefore, EC cannot be done in distilled water. General ground water quality was determined before starting the experiment. Conductivity and pH of the ground water were 1.48 mS/cm and 7.1, respectively. The values of alkalinity, total dissolved solids (TDS), total hardness, sodium, potassium, calcium and magnesium were 280.0, 542.25, 448.0, 2.15, 1.84, 204.0 and 244.0 mgL⁻¹, respectively, while iron was absent. The EC experiment was optimized by varying different parameters like arsenate concentration, pH, voltage, processing time and temperature. The values of different experimental parameters were fixed by considering the amount of arsenic in natural water, other natural water conditions such as pH and temperature and the maximum removal of arsenic during experiments. The effects of these parameters are discussed in the following sub-sections.

3.1. Effect of Initial Arsenate Concentration

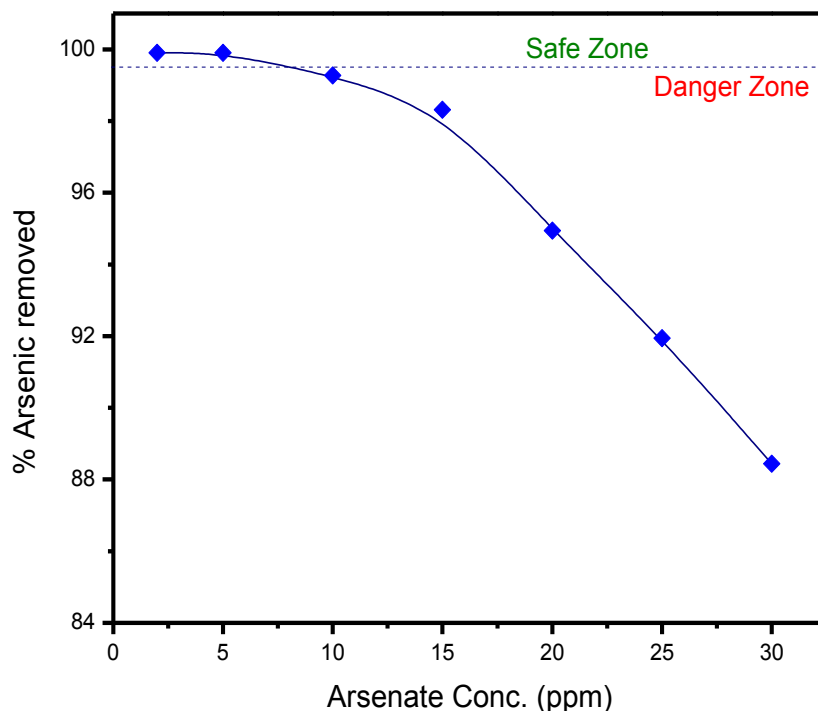


Figure 1. Effect of arsenic initial concentration on percent removal efficiency.

EC was carried out in the concentration range of 2-30 mgL^{-1} to evaluate the efficiency of arsenic removal. Al-Fe electrodes assembly in EC process was found to be very promising for arsenate removal as shown in figure 1. Oxidation of sacrificial aluminum electrode resulted into Al^{3+} ions which on hydrolysis produces $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, $\text{Al}_2(\text{OH})_2^{4+}$, and $\text{Al}(\text{OH})_5^{2-}$, and eventually hydroxyl polymers such as $\text{Al}_{13}(\text{OH})_{32}^{7+}$. All These hydroxides, polyhydroxides, etc. have strong affinity for dispersed particles as well as counter ions like arsenate to cause coagulation [38]. For low arsenate solutions *i.e.* 2 and 5 mgL^{-1} , the arsenic in the treated water was almost absent (removal 99.9 %). In general, the removal efficiency for low arsenate concentration solution was much more as compare to the higher concentration solution. The reason for this trend is quick absorption of low concentration of arsenate on these hydroxides; generated during the electro-coagulation process.

3.2. Effect of pH

The Effect of pH is one of the most important parameter of EC. To examine pH effect on arsenate removal EC were carried out at different pH covering acidic, neutral and basic conditions *i.e.* 3-9 pH range. These observations are presented in Fig. 2.

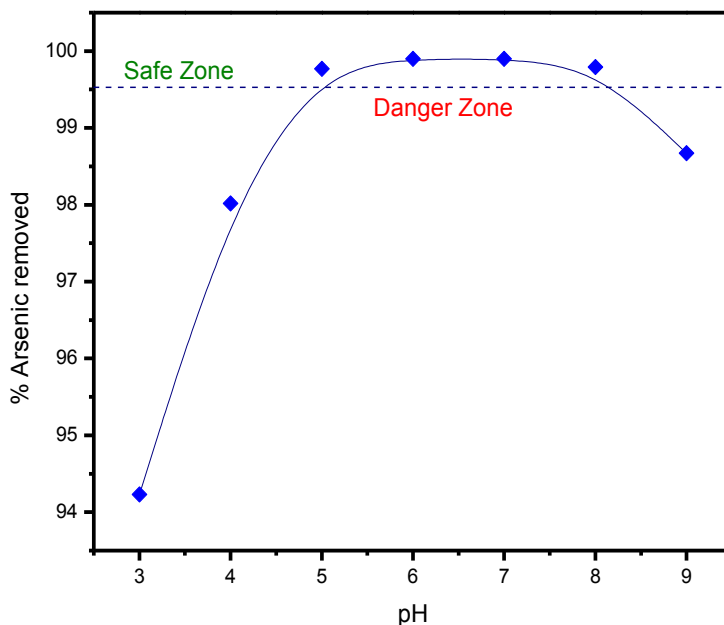


Figure 2. Effect of pH on percent removal efficiency of arsenate.

All of the hydroxides produced during EC as describe above were aqueous species except Al (OH)₃ which is insoluble and most predominant species between pH 5.0-8.8 [73]. Thus, providing the larger surface for the better adsorption of arsenate species on the hydroxide formed and therefore, best removal efficiency was found in the pH range of 5.0 to 8.0.

3.3 Effect of Voltage and Processing Time

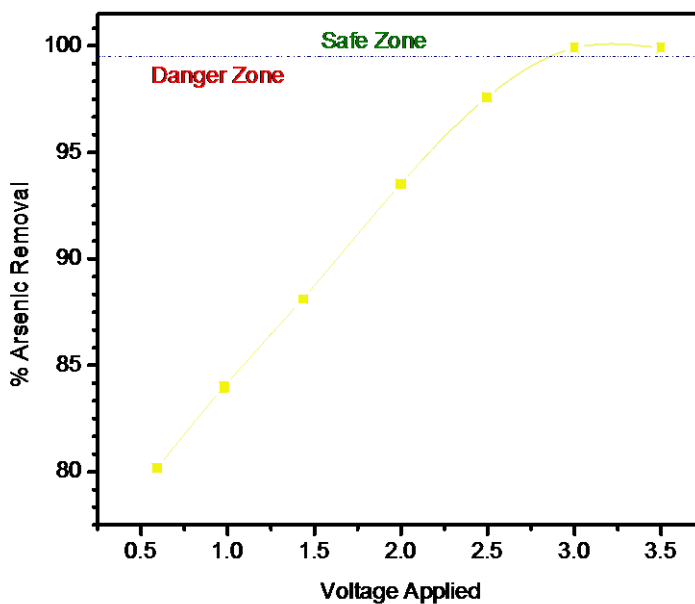


Figure 3. Effect of Applied voltage on percent removal efficiency.

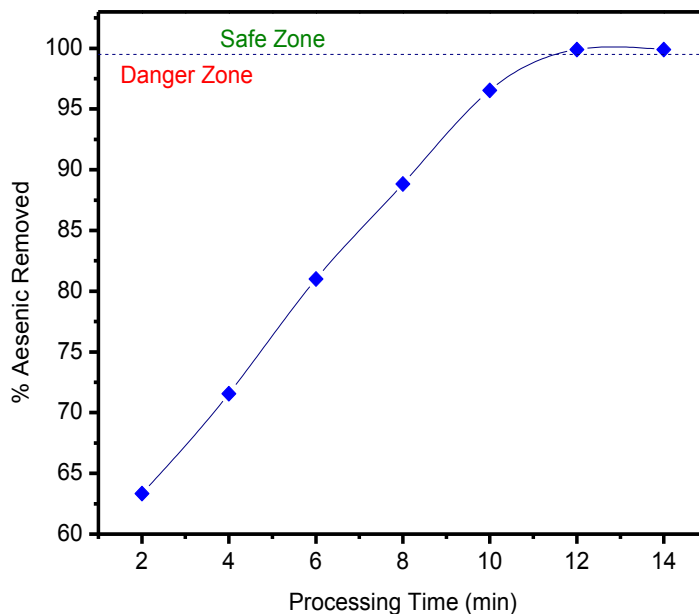


Figure 4. Effect of processing time pH on percent removal efficiency.

The supply of voltage to EC assembly determines the amount of Al^{3+} ions released from the anodic material as the quality of the treated water depends upon the amount of ions produced to from hydroxides and the EC processing time. Thus, the effect of applied potential and processing time on removal efficiency was studied using the initial arsenate concentration of $5mgL^{-1}$ as shown in figures 3 and 4, respectively.

The maximum removal efficiency of 99.9% was achieved when the voltage of 3.0 volts was given to EC unit for 12 min. of processing time. Arsenate ions was more abundant at the beginning of the EC and can easily formed complex with generated aluminum hydroxides, as more than 70% of arsenate removal occurred in first 5 min. of the experiment. EC at 3.0 volts for 12 minutes sufficiently produced so much aluminum hydroxides that could form complex with arsenic present in the water. However, as the experiment preceded the arsenate in the solution reduced while, the concentration of aluminum hydroxide in the solution increased rapidly. As a result of these, the removal became constant after certain time period (12 min).

3.4. Effect of Temperature

The Effect of temperature on EC was studied in the 20-35°C temperature range and the results are plotted in Figure 5. Although the best removal efficiency (99.9%) was found at 30°C but does not change much in the given temperature range (99.48-99.9%). The reason for this type of the graph is that as the temperature increases, the conductivity of water increased leading to increased removal efficiency up to certain temperature (here 30 °C). Further increase of temperature destabilizes the arsenic adsorption on aluminum hydroxide and thus reducing the efficiency.

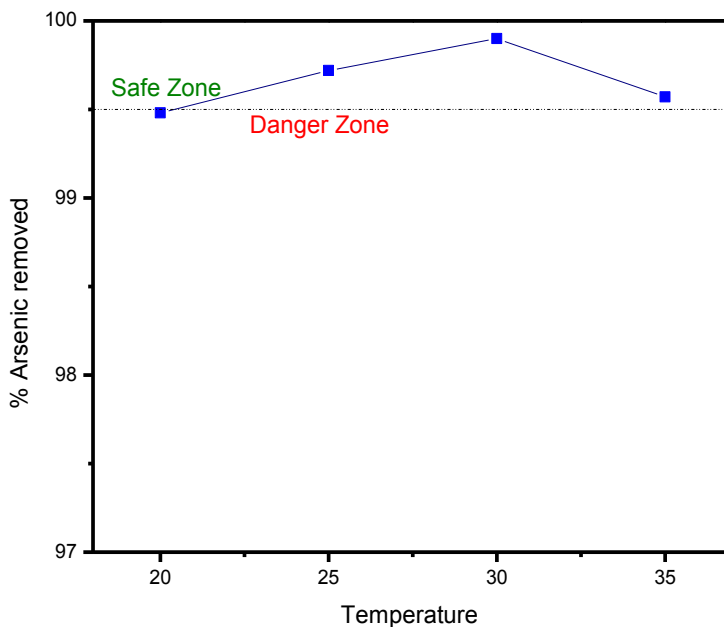


Figure 5. Effect of Temperature on percent removal efficiency of arsenate.

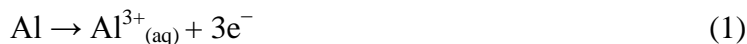
4. SECONDARY CONTAMINATION OF TREATED WATER

The arsenate treated water after EC was investigated for secondary contaminants. Various parameters like alkalinity, hardness (temporary and permanent hardness), pH, conductivity, total dissolved solids (TDS), sodium, chloride, calcium, potassium and magnesium ions were analyzed before and after the EC to observe any change in treated water quality. It was observed that all these values were almost identical before and after the EC with a slight increase in pH; indicating no change in water quality. Moreover, treated water sample was analyzed for aluminum ions and ferrous/ferric ions. It was observed that aluminum and ferrous/ferric ions were absent in the treated water. These results indicate that there was no secondary contamination in treated water after EC process.

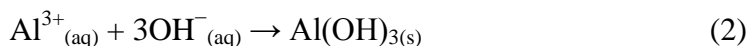
5. MECHANISMS OF ARSENATE REMOVAL

Aluminum gets dissolved from the anode generating corresponding metallic cations *i.e.* Al^{3+} , which almost immediately hydrolyze to aluminum hydroxides, while H_2 production occurs at the cathode. The generated metal hydroxides are excellent coagulating material as they provide active surfaces for the adsorption of the arsenate. Coagulation occurs when these metal hydroxides combine with the negative particles carried towards the anode by electrophoretic motion. They are then removed by sedimentation or filtration. Thus, rather than adding coagulating chemicals as in conventional coagulation process, these coagulating agents are generated in situ. The overall mechanism of arsenate removal is as follows:

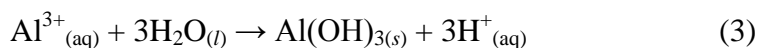
For aluminum anode:



Under alkaline conditions



Under acidic conditions



Reaction at the cathode:



The aluminum hydroxides formed during EC bound the arsenate present in the water by adsorption mechanism:



The treated water is then filtered to get rid off arsenate aluminum hydroxide.

6. CONCLUSION

Electro coagulation was found to be an effective technique for the removal of arsenate from ground water. Experiments were carried to remove arsenic by electro-coagulation covering wide range in operating parameters. The percentage of arsenic removal shows significant influence with applied potential and pH of the initial arsenate solution. More than 99% of arsenic removal capacity was recorded during the investigation. The best removal occurs at pH 5-8 for 2-5 mgL⁻¹ concentration of arsenate at 3 volts of current after 12 min. of EC processing time. Experimental results dictate the possibility of removing arsenate as adsorbed to or co-precipitate with hydrous Aluminum oxide. Due to the high Arsenate removal result by the EC unit, and taking account that it is simple, efficient, easy mode of operation, this EC process signifies a worthy substitute for arsenic treatment in ground water.

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