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Removal of arsenic from aqueous solution using electrocoagulation

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ABSTRACT

Removal of arsenic from aqueous solution was carried out using electrocoagulation. Experiments were conducted using mild steel sacrificial anode covering wide range in operating conditions to assess the removal efficiency. The maximum arsenic removal efficiency was recorded as 94% under optimum condition. The electrocoagulation mechanism of arsenic removal has been developed to understand the effect of applied charge and electrolyte pH on arsenic removal efficiency. Further the experimental data were tested with different adsorption isotherm model to describe the electrocoagulation process.

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1. Introduction

Arsenic in natural water source has been a serious concern worldwide. In many parts of northern India, the underground water is contaminated with arsenic and arsenic contaminated tube-wells are the only viable sources for drinking water even today. In most cases excepting the presence of unacceptable level of arsenic, the groundwater is otherwise quite fit for drinking purpose. Arsenic is a carcinogen and its ingestion may deleteriously affect the gastrointestinal tract, cardiac, vascular system and central nervous system. Due to its high toxic effects on human health, the USEPA has lowered the maximum contaminant level for arsenic in drinking water from 50 to 10 $\mu\text{g l}^{-1}$. Arsenic contamination of the ground water occurs by both natural processes such as weathering of arsenic containing minerals and anthropogenic activities such as uncontrolled industrial discharge from mining and metallurgical industries, and application of organoarsenic pesticides [1–3].

Arsenate [As(V)] and arsenite [As(III)] are primary forms of arsenic in natural waters and the concentration of arsenic species is dependent on redox potentials and pH. It is reported that arsenite is more toxic than arsenate. Arsenate is more prevalent in oxygenated surface water while arsenite is more likely to occur in anaerobic groundwater [4]. Thus finding out a technology for removing both forms of arsenic is a challenge.

Literature survey reveals that there are number of approaches for arsenic removal from drinking water. The most commonly

used treatment techniques for arsenic removal include coagulation with iron and aluminum salts; adsorption onto activated alumina/carbon/activated bauxite/clay minerals; ion-exchange, reverse osmosis and electro-dialysis [5]. The adsorption on activated alumina/carbon is not efficient for arsenic removal. While, though the chemical precipitation with lime/ferric salt is quite effective, it yields large quantities of solid sludge which itself requires further treatment. The other treatment methods such as ion exchange and reverse osmosis have limitations and expensive. This necessitated finding an effective treatment technique which would remove arsenic consistently from drinking water.

In recent years electrocoagulation has been receiving greater attention as this technique offers higher removal efficiency compared to the conventional methods. It is an emerging water purification method adopted successfully for the treatment of various wastewaters: potable water, urban wastewater, smelter effluent, restaurant wastewater and colored water [6–8]. Yilmaz et al. [9] compared the efficiencies of electrocoagulation and chemical coagulation for boron removal and reported more than three times higher removal efficiency for electrocoagulation than chemical coagulation at optimum conditions. Electrocoagulation is essentially an electrolytic process which generates metallic hydroxide flocks in situ by electro-dissolution of soluble anode. The rate of generation of flocks can be controlled by applied charge thus the amount of solid sludge generation is very much minimized resulting in a lucrative technology for water/wastewater treatment. The objective of the present investigation is to evaluate the removal of arsenic from tap water and assess the influence of operating parameters on removal efficiency dosage in order to define the optimum operating conditions for water treatment.

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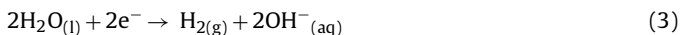
2. Mechanism of electrocoagulation

Electrocoagulation is a complex and interdependent process strongly dependent on the chemistry of the aqueous medium. Conventionally mild steel and aluminum metals are used as sacrificial anodes. When charge is applied through an external power source, the electrolytic dissolution of sacrificial anode produces the cationic monomeric species according to the following equations [10]:

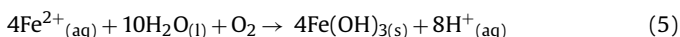
Anodic reaction:



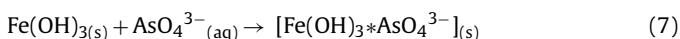
Cathodic reactions:



Bulk reaction:



The formed iron flocks incarcerate the arsenic present in the solution by precipitation and/or adsorption mechanism:



The stable ferric arsenate $\text{Fe}(\text{OH})_3 \cdot \text{AsO}_4^{3-}$ can be separated easily.

3. Experimental

The electrolytic cell consists of a glass beaker of 250 ml capacity with a lid. Mild steel with a submerged area of 4.2 cm² in size were used as sacrifice anode while stainless steel of same size was used as cathode. The electrode distance between anode and cathode was maintained constant of 1.5 cm during electrolysis. A direct current was supplied by a DC-regulated power source (HIL model 3161, 0–5A and 0–30V). Proper agitation was provided to maintain uniform concentration inside the cell. A stock solution As(V) was prepared by dissolving appropriate quantity of sodium arsenate $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in de-ionized water for conducting electrocoagulation. All the experiments were carried out under potentiostatic conditions at room temperature ($28 \pm 2^\circ\text{C}$). The pH of the solution was adjusted by adding either dilute HCl or NaOH. The samples were collected at regular intervals of time and analyzed for arsenic content using atomic absorption spectroscopy (AAS, model Varian A220).

4. Results and discussion

Experiments were carried out covering wide range in operating conditions and the observations are presented in the form of Tables and Figures. Fig. 1 shows the variation of outlet arsenic concentration with electrolysis time. The figure is plotted as ratio of arsenic concentration at time 't' to initial arsenic concentration (i.e., C/C_i) against electrolysis time. It can be ascertained from Fig. 1 that the arsenic outlet concentration decreases with increase in the electrolysis time. The rate of reduction in the arsenic outlet concentration is sharp in the early stages of the process and decreases to gradual reduction in later part of electrolysis. This can be explained based on the fact that the hydroxide flocks are generated in situ once the charge is applied and the generated flocks adsorb the arsenic to form a stable arsenate (Eq. (7)). It can be noticed from the figure that within 30 min of electrolysis more than 50% of arsenic present in the effluent has been reduced. It can be further ascertained from Fig. 1

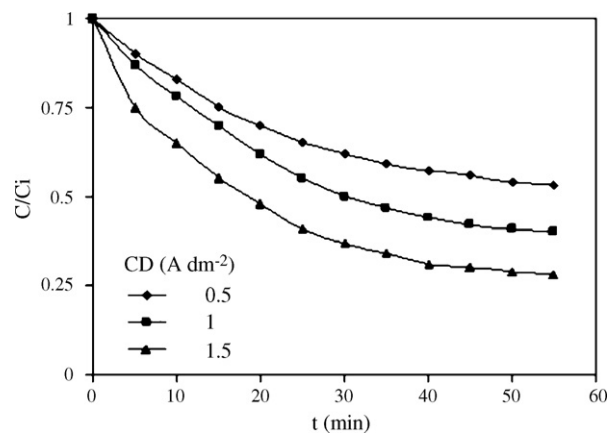


Fig. 1. Variation of arsenic concentration with electrolysis. Influent concentration: 100 ppm; pH 7; supporting electrolyte concentration: 100 ppm; electrode: mild steel.

that the percentage arsenic removal increased with an increase in the applied current density. This can be attributed due to the fact that at high current densities, the extent of anodic dissolution increases which increases the hydroxide cationic complexes resulting in increased arsenic removal.

4.1. Effect of initial pH

It has been reported that the electrolyte pH plays an important role on the electrocoagulation process. To examine the pH effect on arsenic removal, experiments were carried out at various pH covering acidic, neutral and basic conditions and the observations are presented in Fig. 2. It can be ascertained from Fig. 2 that the percentage arsenic removal increased when the electrolyte pH increased from 4 to 7. However, no significant improvement has been observed when the electrolyte pH increased from 7 to 11. This can be attributed to the increased solubility of ferrihydrite at these pH extremes [11].

4.2. Effect of initial effluent concentration

Experiments were carried out at different initial effluent concentration to assess the impact of effluent initial concentration on the efficiency of electrocoagulation. It can be ascertained from Fig. 3 that the percentage arsenic removal decreased significantly with an increase in the initial arsenic concentration. This can be due to

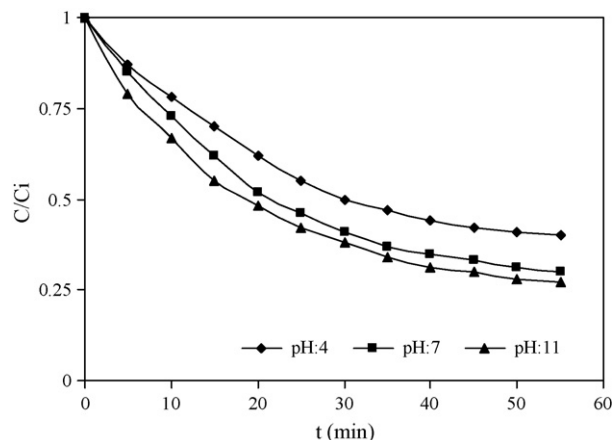


Fig. 2. The influence of solution pH on arsenic removal. Influent concentration: 100 ppm; current density: 1 A dm⁻²; supporting electrolyte concentration: 100 ppm; electrode: mild steel.

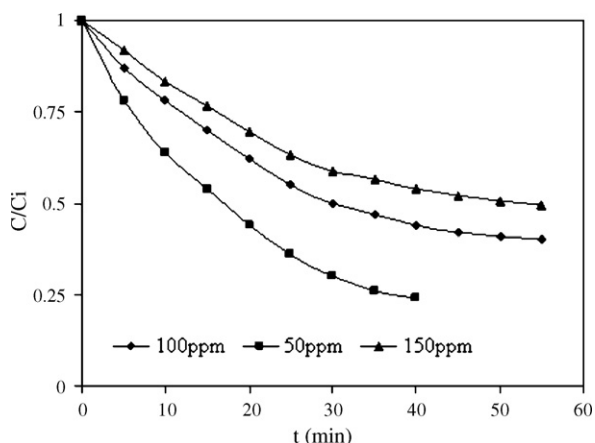


Fig. 3. The influence of arsenic initial concentration on arsenic removal efficiency; current density: 1 A dm⁻²; supporting electrolyte concentration: 100 ppm; solution pH 7; electrode: mild steel.

the fact that the ratio of hydroxo cationic complexes to the initial effluent concentration decreased with influent concentration.

In the electrocoagulation process, the rate of arsenic removal is proportional to the influence concentration and the amount of corresponding hydroxides formed, i.e.

$$\frac{-dC}{dt} = kC_{Ad} \quad (8)$$

where C_{Ad} refers to the concentration of adsorbent present in the system. Since the generation of ferric and aluminum hydroxide can be assumed constant for a given current density, the above equation can be simplified to pseudo first order kinetics as

$$\frac{-dC}{dt} = kC \quad (9)$$

The integration of Eq. (9) yields

$$\log \frac{C}{C_i} = -kt \quad (10)$$

The reaction rate constant 'k', can be estimated from the plot log[C/C_i] versus electrolysis time. Fig. 4 shows the influence of applied current density on reaction rate constant. It can be noticed that the reaction rate constant increases with an increase in the applied current density. It is obvious that the rate of coagulant generation increases with applied current density and in turn the reaction rate constant. Fig. 5 shows a marginal increase in the reaction rate constant when the solution pH increased from 4 to 7 and no significant improvement beyond the pH value of 7. Fig. 6 shows the influence of initial effluent concentration on reaction rate constant.

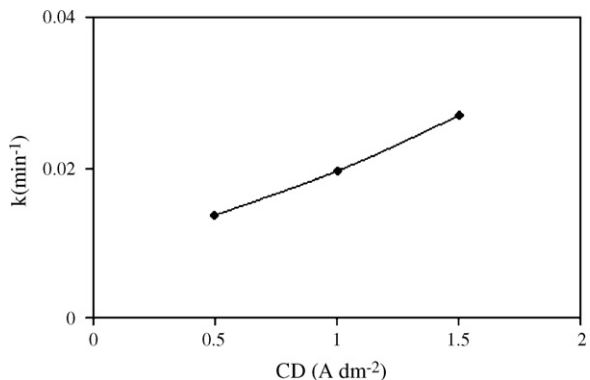


Fig. 4. Variation of reaction rate constant with applied current density. Influent concentration: 100 ppm; pH 7; supporting electrolyte concentration: 100 ppm.

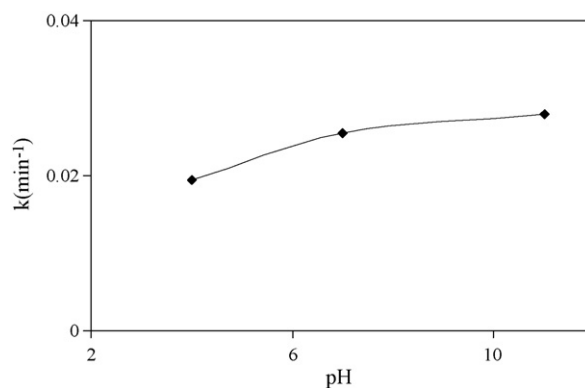


Fig. 5. Influence of solution pH of reaction rate constant. Influent concentration: 100 ppm; current density: 1 A dm⁻²; supporting electrolyte concentration: 100 ppm.

stant. It can be ascertained that the rate constant decreases with an increase in the initial arsenic concentration. This could be due to the decrease in ratio of hydroxo cationic complexes to the initial effluent concentration, which eventually decreases the rate of arsenic removal and in turn the reaction rate constant.

5. Adsorption isotherm

Critical analysis of the electrocoagulation of organic pollutants reveals that there are two separate processes taking place, i.e.

- Electrochemical process through which the metal flocks are generated;
- Physio-chemical process through which the effluents are adsorbed on the surface of the flocks.

The pollutant is adsorbed at the surface of the flocks generated during electrocoagulation. Thus the removal of pollutant is similar to conventional adsorption except the generation of coagulants. The electrode consumption can be estimated according to Faraday's Law and the amount of flocks generated can be estimated stoichiometrically [12]. Since the amount of coagulant can be estimated for a given time, the pollutant removal can be modeled by adsorption phenomenon. It is attempted to test the various adsorption isotherms models for arsenic removal.

5.1. Langmuir isotherm

The Langmuir isotherm assumes monolayer deposition of adsorbate on homogenous adsorbent surface (coagulant). It is well known that the Langmuir equation is intended for a homogeneous

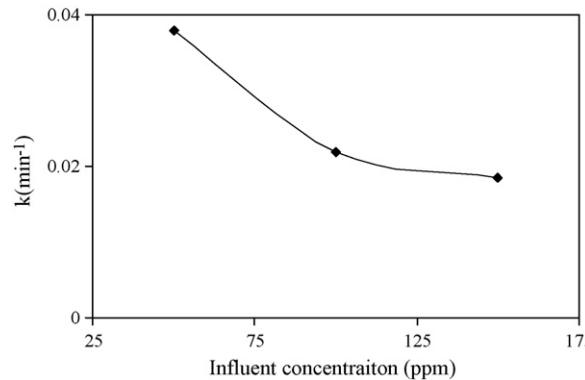


Fig. 6. Influence of arsenic initial concentration on reaction rate constant. Current density: 1 A dm⁻²; supporting electrolyte concentration: 100 ppm, pH 7.

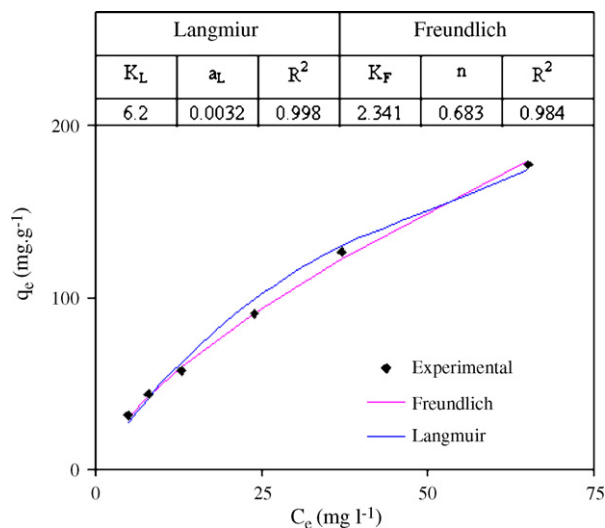


Fig. 7. Adsorption of isotherm of arsenic(V) by charged hydroxo cationic complexes.

surface. The mathematical expression of Langmuir isotherm can be given as

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (11)$$

The linearization of Eq. (11) is given as

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (12)$$

The binding constant (K_L) and the sorbent capacity (a_L) can be estimated by plotting C_e/q_e against C_e . The model simulations along with experimental observations are shown in Fig. 7.

5.2. Freundlich isotherm

The Freundlich isotherm is an empirical model that relates the adsorption intensity of the sorbent towards adsorbent. The isotherm is adopted to describe reversible adsorption and not restricted to monolayer formation. The mathematical expression of the Freundlich model is

$$q_e = K_F C_e^{b_F} \quad (13)$$

where K_F and b_F are the constants which give adsorption capacity and adsorption intensity, respectively. A linear form of the Freundlich model can be written as follows

$$\ln q_e = \ln K_F + b_F \ln C_e \quad (14)$$

Plot of $\ln q_e$ versus $\ln C_e$ gives a straight line with slope K_F and intercept b_F . The model simulation and the constants K_F and b_F values are shown in Fig. 7 along with the experimental values.

Based on the correlation coefficient (R^2), the adsorption isotherm with hydroxo cationic complexes can be better described by the Langmuir isotherm model. The Langmuir isotherm equation represents a better fit with the experimental data than the Freundlich isotherm.

6. Conclusion

Electrocoagulation is a promising remediation tool for the treatment of water containing As(V). Experiments showed the possibility of removing arsenic as adsorbed to or co-precipitate with Iron(III)hydroxide. Increasing the current density from 0.5 to 1.5 A dm⁻² showed significant improvement in the arsenic removal. However, beyond the current density of 1.5 A dm⁻² did not show any significant improvement. More than 98% of arsenic removal has been recorded in the present investigation. The electrocoagulation has been modeled using adsorption isotherm models and observed Langmuir isotherm model match satisfactorily with the experimental observations.

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