Effect of alternating and direct current in an electrocoagulation process on the removal of cadmium from water
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ABSTRACT
The main objective of this study was to investigate the effects of AC and DC on the removal of cadmium from water using iron as anode and cathode. The various operating parameters on the removal efficiency of cadmium were investigated. The results showed that the optimum removal efficiency of 98.1 and 97.3% with the energy consumption of 0.734 and 1.413 kWh/kL was achieved at a current density of 0.2 A/dm², at pH of 7.0 using AC and DC respectively. The adsorption process follows second order kinetics and the temperature studies showed that adsorption was endothermic and spontaneous in nature.

Key words | adsorption kinetics, alternating/direct current, cadmium removal, electrocoagulation

INTRODUCTION
Heavy metal pollution has become one of the most serious environmental problems today. Cadmium is one of the most toxic non-essential heavy metals present in the environment, even at low concentrations. Elevated level of cadmium ions arise from a variety of sources such as wastewater from metal plating industries, nickel–cadmium batteries, phosphate fertilizer, mining, pigments, stabilizers, alloys, petroleum refining, welding and pulp industries (Nrlagu & Pacyna 1988; Tsezos 2001; Bedow et al. 2008). Cadmium poisoning includes kidney damage (Nogawa et al. 2008), lung insufficiency, cancer; it changes the constitution of bone, liver and blood (Schroede 1965). Cadmium accumulated in the rice crops, it developed Itai-Itai disease and renal abnormalities including proteinuria and glucosuria. Cadmium-containing compounds are known as carcinogens (Bui et al. 1975; IARC 1994). The drinking water guideline value is 0.005 mg/L (CPCB).

Conventional methods for removing cadmium from water include ion exchange, reverse osmosis, co-precipitation, coagulation, complexation, solvent extraction, electrochemical treatment and adsorption (Chou & Okamoto 1976; Salpathy & Chaudhuri 1995; Tiwari et al. 1995; Marshall & Johns 1996; Peternele et al. 1999; Cristophi & Axe 2000; Ajmal et al. 2003; Saeed & Iqbal 2003; Gardea-Torresdey et al. 2004; Kocaoba & Ackin 2005; Abbes et al. 2006; Ibrahim et al. 2006; Archana & Sahu 2007; Haider Taqvi et al. 2007; Hanafiah et al. 2007; Rahman & Islam 2010). Physical methods like ion exchange, reverse osmosis and electrodialysis have proven to be either too expensive or inefficient to remove cadmium from water. At present, chemical treatments are not used due to disadvantages like high costs of maintenance, problems of sludge handling and its disposal, and neutralization of the effluent (Vasudevan et al. 2009a, b). The cadmium removal from water by adsorption using different materials has also been explored. The major disadvantages of this studied adsorbent are low efficiency and high cost. Recent research has demonstrated that electrocoagulation offers an attractive alternative to the above-mentioned traditional methods for treating water (Chen et al. 2002). In this process anodic dissolution of metal electrode takes place with the evolution of hydrogen gas at the cathode (Jiang et al. 2002). Electrochemically generated metallic ions from the anode can undergo hydrolysis to produce a series of activated intermediates that are able to destabilize the finely dispersed particles present in the water to be treated. The electrochemical reactions with metal M as anode may be summarized as follows,

\[ \text{At the anode:} \]

\[ M(s) \rightarrow M^{n+}_{(aq)} + ne^- \quad (1) \]
\[ 2\text{H}_2\text{O}(l) \rightarrow 4\text{H}^{+}(aq) + \text{O}_2(g) + 4e^- \]  

(1a)

At the cathode:

\[ \text{M}^{n+}_{(aq)} + ne^- \rightarrow \text{M} \]  

(2)

\[ 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- \]  

(2a)

If Fe- or Al-electrodes are used, the generated \( \text{Fe}^{3+}_{(aq)} \) or \( \text{Al}^{3+}_{(aq)} \) ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. For example, \( \text{Al}^{3+} \) ions on hydrolysis may generate \( \text{Al}(	ext{H}_2\text{O})_6^{3+}, \text{Al}(	ext{H}_2\text{O})_5\text{OH}^{2+}, \text{Al}(	ext{H}_2\text{O})_4\text{OH}^{2+}, \) and the hydrolysis products may form many monomeric and polymeric species such as \( \text{Al}(	ext{OH})^{2+}, \text{Al}_2\text{OH}^{4+}, \text{Al(OH)}_2^{+}, \text{Al(OH)}_3, \) etc., in a wide pH range. Similarly, ferric ions generated by electrochemical oxidation of iron electrodes may form monomeric ions, \( \text{Fe(OH)}_3, \) and hydroxyl complexes, namely \( \text{Fe(H}_2\text{O})_6^{3+}, \text{Fe(H}_2\text{O})_5\text{OH}^{2+} \) etc. These hydroxides/polyhydroxides/polyhydroxy metallic compounds have a strong affinity with dispersed/dissolved ions as well as the counter ions to cause coagulation/adsorption. The advantages of electrocoagulation include high particulate removal efficiency, a compact treatment facility, relatively low cost, and the possibility of complete automation. This method is characterized by reduced sludge production, a minimum requirement of chemicals and ease of operation (Chen 2004; Vasudevan et al. 2008, 2010).

Usually direct current (DC) is used in electrocoagulation processes. In this case, an impermeable oxide layer may form on the cathode as well as corrosion formation on the anode due to oxidation. These prevent the effective current transport between the anode and cathode, so the efficiency of electrocoagulation processes declines. These disadvantages of DC have been overcome by adopting alternating current (AC) in electrocoagulation processes. The main objective of this study is to investigate the effect of direct current (DC) and alternating current (AC) on the removal efficiency of cadmium using iron as anode and cathode. The effect of the initial concentration of cadmium ion, pH, temperature, current density and coexisting ions were investigated. The adsorption kinetics of cadmium ions on iron hydroxide is also studied. The adsorption kinetics of electrocoagulation was analyzed using first and second order kinetic models. Finally, the effects of temperature were studied to determine the nature of adsorption.

**MATERIALS AND METHODS**

**Cell construction and electrolysis**

The electrolytic cell (1.0 – L; Plexiglas vessel) was fitted with a polycarbonate cell cover with slots to introduce the anode, cathode, pH sensor, a thermometer and electrolytes. Iron (Commercial Grade, India) of surface area (0.02 m²) acted as the anode and cathode and placed at an interelectrode distance of 0.005 m. The temperature of the electrolyte has been controlled to the desired value with a variation of ±2 K by adjusting the rate of flow of thermostatically controlled water through an external glass-cooling spiral. A regulated direct current (DC) was supplied from a rectifier (10 A, 0–25 V; Aplab model) and regulated alternating current (AC) was supplied from a source (0–5 A, 0–270 V, 50 Hz; AMETEK Model: EC1000S).

Cadmium nitrate \( \text{Cd(NO}_3)_2.4\text{H}_2\text{O} \) (Analar Reagent, Merck, Germany) was dissolved in water for the required concentration. In all the experiments 20 mg/L of cadmium was used unless or otherwise it is mentioned specifically. The pH of the electrolyte was adjusted, if required, with HCl or NaOH solutions before the electrolysis starts. All the experiments were repeated three times for reproducibility and the accuracy of the results are ±1%.

**Analytical method**

The concentration of cadmium was determined using UV-visible Spectrophotometer with cadmium kits (MERCK, Pharo 300, Germany). The surface morphology of the iron electrode was analyzed by SEM and the constituents present in cadmium adsorbed iron hydroxide were analyzed by EDAX with a Scanning Electron Microscope (SEM) made by Hitachi (model s-3000h).

**RESULTS AND DISCUSSION**

**Effect of current density**

The amount of cadmium removal and removal rate has increased by increasing current density. Further, the amount of cadmium removal depends upon the quantity of adsorbent (Ferric hydroxide) generated, which is related to the time and current density. To investigate the effect of current density on the cadmium removal, a series of experiments was carried out by solutions containing constant cadmium loading of 20 mg/L, at a pH 7.0, with...
current density being varied from 0.1 to 0.5 A/dm² using both AC and DC current source. The results showed that the optimum removal efficiency of 98.1% and 97.3% with the energy consumption of 0.734 and 1.413 kWh/kL was achieved at a current density of 0.2 A/dm², at pH of 7.0 using AC and DC respectively. The results are presented in Table 1. The results show that the removal efficiency of cadmium was higher and energy consumption was lower in the case of AC than DC. This may be due to the uniform dissolution of anode and cathode during electrocoagulation in the case of AC. The removal efficiency was found showing the amount of cadmium adsorption increases with the increase in adsorbent concentration, which indicates that the adsorption depends up on the availability of binding sites for cadmium.

**Effect of pH**

In order to examine the effect of the initial pH for AC and DC source, experiments were carried out in acidic (pH 2.0), slightly acidic (pH 5), neutral (pH 7.0), and alkaline (pH 10.0) media having 20 mg/L of cadmium containing solutions. The percentage of cadmium adsorption was maximum at pH 7, a decreasing trend in adsorption was observed when below and above pH 7 for both AC and DC source. At an initial concentration of 20 mg/L, maximum adsorption of 98.1% and 97.3% at pH 7 for AC and DC source respectively was observed. It can be seen from Figure 1 that cadmium removal efficiencies increased with increasing pH and highest removal efficiencies were obtained at pH 7.0. The high efficiency of cadmium removal at neutral pH might be ascribed to the precipitation of their hydroxides at the cathode. In case of iron anode, when solution pH becomes acidic, the oxidation of ferrous iron (Fe II) to ferric iron (Fe III) diminishes, and therefore cadmium removal efficiency decreases. Neutral and slightly alkaline pH, however, tends to favor Fe (II) to Fe (III) oxidation as well as complex polymerization. Finally, hydroxylated colloidal polymers and an insoluble precipitate of hydrated ferric oxide were formed and the removal efficiency was increased.

**Effect of initial cadmium concentration**

To study the effect of initial concentration, experiments were conducted at varying initial concentrations from 10–50 mg/L using AC and DC. The removal of cadmium increased with time to obtain equilibrium at about 45 min (Figure 2). The amount of cadmium adsorbed ($q_e$) increased from 6.61 to 48.46 mg/g as the concentration was increased from 10 to 50 mg/L for the AC source. The figure also shows

<table>
<thead>
<tr>
<th>Current density (A/dm²)</th>
<th>AC Removal efficiency (%)</th>
<th>Energy consumption (kWh/kL)</th>
<th>DC Removal efficiency (%)</th>
<th>Energy consumption (kWh/kL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>95.2</td>
<td>0.142</td>
<td>94.6</td>
<td>0.962</td>
</tr>
<tr>
<td>0.2</td>
<td>98.1</td>
<td>0.298</td>
<td>97.3</td>
<td>1.214</td>
</tr>
<tr>
<td>0.3</td>
<td>98.3</td>
<td>0.344</td>
<td>97.5</td>
<td>1.366</td>
</tr>
<tr>
<td>0.4</td>
<td>98.4</td>
<td>0.497</td>
<td>97.6</td>
<td>1.381</td>
</tr>
<tr>
<td>0.5</td>
<td>98.6</td>
<td>0.599</td>
<td>97.9</td>
<td>1.476</td>
</tr>
</tbody>
</table>
that the adsorption is the rapid in the initial stages and gradually decreases with progress of adsorption this is because of the great number of sites available for the sorption operation and adsorption equilibrium were then gradually achieved. The plots are single, smooth and continuous curves leading to saturation, suggesting the possible monolayer coverage to cadmium on the surface of the adsorbent (Namashivayam & Ranganathan 1995; Hamadi et al. 2001). In the case of DC the equilibrium time was found to be 55 min for all concentration studied (figure not shown).

Adsorption kinetics and thermodynamic studies

The adsorption of cadmium is analyzed using Lagergren rate equation. The first order Lagergran model is (Uber 1985; Gasser et al. 2007).

\[
dq/dt = k_1(q_e - q_t)
\]

where, \(q_t\) is the amount of cadmium adsorbed on the adsorbent at time \(t\) (min) and \(k_1\) (1/min) is the rate constant of first order adsorption. The integrated form of the above equation with the boundary conditions \(t = 0\) to \(t > 0\) \((q = 0\) to \(q > 0\)) and then rearranged to obtain the following time dependence function,

\[
\log(q_e - q_t) = \log(q_e) - k_1t/2.303
\]

where \(q_e\) is the amount of cadmium adsorbed at equilibrium. The \(q_e\) and rate constant \((k_1)\) were calculated from the slope of the plots of \(\log(q_e - q_t)\) versus time \((t)\) (figure not shown). It was found that the calculated \(q_e\) value do not agrees with the experimental \(q_e\) values. So the adsorption does not obey the first order kinetics adsorption.

The second order kinetic model is expressed as (Namashivayam & Prathap 2005)

\[
dq/dt = k_2(q_e - q_t)^2
\]

where \(k_2\) is the rate constant of second order adsorption. The integrated form of Equation (5) with the boundary condition \(t = 0\) to \(t > 0\) \((q = 0\) to \(q > 0\)) is

\[
1/(q_e - q_t) = 1/q_e + k_2t
\]

Equation (6) can be rearranged and linearized as,

\[
t/q_t = 1/k_2q_e^2 + t/q_e
\]

The second order kinetic values of \(q_e\) and \(k_2\) were calculated from the slope and intercept of the plots \(t/q_t\) versus \(t\) (Figure 3). Table 2 depicts the computed results obtained from first and second order kinetic model for AC and DC source. The calculated \(q_e\) values were found to be quite close to the experimental \(q_e\) values at all the concentrations studied (10–50 mg/L) for AC and DC source. So, it is inferred that the adsorption of cadmium on iron hydroxide followed second order kinetics.

To study the temperature effect, the initial pH was kept at 7 and the concentration of cadmium used was in the range of 10–50 mg/L for both AC and DC (Table 3). The amount of cadmium adsorbed on the adsorbent increases by increasing the temperature indicating the process to be endothermic. The diffusion coefficient (D) for intraparticle transport of cadmium species into the adsorbent particles has been calculated at different temperature by

\[
t_{1/2} = 0.03 \times r_o^2 / D
\]

where \(t_{1/2}\) is the time of half adsorption \((s)\), \(r_o\) is the radius of the adsorbent particle \((cm)\), \(D\) is the diffusion coefficient in \(cm^2/s\). For all chemisorption system the diffusivity coefficient should be \(10^{-5}\) to \(10^{-13} \text{cm}^2/s\) (Yurdakoc et al. 2005). In the present work, \(D\) is found to be in the range of \(10^{-9} \text{cm}^2/s\). The pore diffusion coefficient \((D)\) values for various temperatures and different initial concentrations of cadmium are presented in Table 3 respectively.

To find out the energy of activation for adsorption of cadmium, the second order rate constant is expressed in
ln\(k_2 = \ln k_o - E/RT\) \hspace{1cm} (9)
ln\(k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}\) \hspace{1cm} (11)
The enthalpy change and entropy change were obtained from the slope and intercept of the van’t Hoff linear plots of \( \ln K_c \) versus \( 1/T \) (Figure 4). A positive value of enthalpy change (\( \Delta H \)) indicates that the adsorption process is endothermic in nature, and the negative value of change in internal energy (\( \Delta G \)) shows the spontaneous adsorption of cadmium on the adsorbent. Positive values of entropy change show the increased randomness of the solution interface during the adsorption of cadmium on the adsorbent. Enhancement of adsorption capacity of electrocoagulant (ferric hydroxide) at higher temperatures may be attributed to the enlargement of pore size and or activation of the adsorbent surface. Using Lagergran rate equation, First order rate constants and correlation coefficient were calculated for different temperatures (313–343 K). The calculated \( q_e \) values obtained from the first order kinetics agrees with the experimental \( q_e \) values better than the Second order kinetics model. Table 5 depicts the computed results obtained from first and second order kinetic models. These results indicate that the adsorption follows first order kinetic model at different temperatures used in this study.

From the table, it is found that the rate constant \( k_2 \) increased with increasing the temperature from 305 to 343 K. The increase in adsorption may be due to change in pore size on increase in kinetic energy of the iron species and the enhanced rate of intraparticle diffusion of adsorbate.

### A bench scale study

A bench scale capacity cell was designed, fabricated and operated for the removal of cadmium from water. The system consists of AC/DC power supply, an electrochemical reactor, a water tank, a feed pump, a flow control valve, a flow measuring unit, a circulation pump, settling tank, sludge collection tank, filtration unit provisions for gas outlet and treated water outlet. The reactor is made of PVC with an active volume of 2,000 L. The iron (anode and cathode) each consist of five pieces situated approximately 5 mm apart from each other and submerged in the solution. The total electrode surface area is 1,500 cm\(^2\) for both cathodes and anodes. The cell was operated at a current density of 0.2 A/dm\(^2\) and the electrolyte pH of 7.0. The results showed that the removal efficiency of 97.9 and 96.8% with the energy consumption of 0.799 and 1.665 kWh/kL was achieved at a current density of 0.2 A/dm\(^2\) and pH of 7.0 using iron as electrodes using AC and DC respectively. The results were consistent with the results obtained from the laboratory scale, showing that the process was technologically feasible.

### Surface characterization

#### SEM and EDAX characterization

In order to gain more insight into the effect of alternating current, the morphology of the electrode surface after two kinds of electrolysis (AC and DC) was characterized by SEM as shown in Figure 5(a) and (b). It can be observed that when the AC was fed, less disordered pores formed
and a smooth microstructure of iron emerged, suggesting that the iron electrodes were dissolved uniformly during the electrolysis. For the electrodes fed with DC, the electrode surface was found to be rough, with a number of dents. These dents were formed around the nucleus of the active sites where the electrode dissolution results in the production of ferric hydroxides. The formation of a large number of dents may be attributed to the anode material consumption at active sites due to the generation of oxygen at its surface. Energy-dispersive analysis of X-rays was used to analyze the elemental constituents of cadmium-adsorbed ferric hydroxide (Figure 6). It shows that the presence of cadmium, Fe and O appears in the spectrum. EDAX analysis provides direct evidence that cadmium is adsorbed on ferric hydroxide.

**CONCLUSION**

The results showed that the optimized removal efficiency of 98.1 and 97.3% was achieved for AC and DC sources at a current density of 0.2 A/dm² and pH of 7.0 using iron electrodes. The ferric hydroxide generated in the cell removed the cadmium present in the water and to reduced the cadmium concentration to less than 0.005 mg/L, and made it fit for drinking. The bench scale results showed that the process was technologically feasible. The adsorption process follows second order kinetics. Temperature studies showed that adsorption was endothermic and spontaneous in nature. From the surface characterization studies, it was confirmed that the ferric hydroxide generated in the cell adsorbed cadmium present in the water.

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