Studies relating to an electrochemically assisted coagulation for the removal of chromium from water using zinc anode
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ABSTRACT

In this work, an electrochemically assisted coagulation for the removal of chromium from water has been studied using zinc as anode and galvanized iron as cathode. The effects of pH, current density, concentration of chromium, temperature, adsorption kinetics and isotherms on the removal of chromium were investigated. The results showed that the optimum removal efficiency of 96.5% was achieved at a current density of 0.2 A/dm², at a pH of 7.0. First- and second-order rate equations, Elovich and intraparticle diffusion models were applied to study adsorption kinetics. The adsorption process follows second-order kinetics model with good correlation. An equilibrium isotherm was measured experimentally and the results were analyzed by the Langmuir, Freundlich and Dubinin-Redushkevich model using linearized correlation coefficient. The Langmuir adsorption isotherm was found to fit the equilibrium data for chromium adsorption. Temperature studies showed that the adsorption was endothermic and spontaneous in nature.

Key words | electrocoagulation, zinc, chromium, adsorption, kinetics, isotherm

INTRODUCTION

Excessive release of heavy metals into environment is of major concern worldwide in the last few decades (Aksu & Akpinar 2001). Many industries release large quantities of wastewater containing heavy metals, and it is well known that some metals could have poisonous or otherwise harmful effects on many forms of life (Murathan & Benli 2004; Akar & Malkoc 2004). Among them, chromium (Cr⁶⁺ and Cr³⁺) has become a serious health concern due to its release into environment. Exposure to chromium can cause cancer in the lungs and may cause epigastria pain, vomiting and severe diarrhea (Golder et al. 2007a, b; Thella et al. 2007). Chromium is released into the aquatic environment from the industries such as plating, metal finishing, tannery, chromate preparation, and fertilizer industries and also from industries that employ chromium compounds as corrosion inhibitors (Heidmann & Calmano 2007). Leather industry in particular, generates large quantity of polluting wastewater from tanning of animal skins and hides which contains about 30–35% of initial tanning salt (Golder et al. 2006). These usually contain metal ion concentrations much higher than the permissible levels and do not degrade easily into harmless end-products (Narayanan & Ganeshan 2009). Due to the high toxic effect of chromium on human health, the USEPA had set the maximum contaminant level of 100 (μg/l) for chromium in drinking water (CPCB 2002). The Minimal National Standards (MINAS) of 2.0 mg/l, for safe discharge of effluents containing chromium metal ions in surface waters has been set by The Ministry of Environment and Forests (MOEF), Government of India (Dean et al. 1975). The World Health Organization (WHO) had also recommended the maximum permissible level of 0.05 ppm for chromium in drinking water.

Conventional methods for removing heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, membrane technology and electro-dialysis (Vik et al. 1984; Hazef et al. 2002; Inglezakis et al. 2003; Veglio et al. 2003; Srivastava et al. 2006; Thella et al. 2007). However, these processes have considerable disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring system, high reagent and energy requirements or generation of toxic sludge or other waste products that require disposal. The electrochemical water treatment technologies have undergone rapid growth and development
during the last few decades (Carlos et al. 2006; Christensen et al. 2006; Gabrielli et al. 2006; Miwa et al. 2006; Carlesi Jara et al. 2007; Ikematsu et al. 2007; Onder et al. 2007). One of these technologies is electrochemically assisted coagulation, for in-situ generation of coagulants, which can compete with the conventional chemical coagulation process. Electrochemically generated metallic ions from these electrodes undergo hydrolysis near the anode to produce a series of activate intermediates that are able to destabilize the finely dispersed particles present in the water/waste water to be treated. The advantages of electrocoagulation include high particulate removal efficiency, a compact treatment facility, and the possibility of complete automation (Rajeshwar & Ibanez 1997; Chen et al. 2002; Chen 2004; Adhoum & Monser 2004). This technique does not require addition of chemicals and reduces the volume of produced sludge. This method is characterized by reduced sludge production, a minimum requirement of chemicals, and ease of operation. Although, there are numerous reports related with electrocoagulation as a means of removal of many pollutants from water and wastewater using aluminium as anode material, there are limited work on removal of chromium by electrocoagulation using zinc as anode material and its adsorption and kinetics studies. The main disadvantage of electrocoagulation with respect to aluminium electrode is, the residual aluminium (The USEPA guidelines suggest maximum contamination is 0.05–0.2 mg/L) present in the treated water due to its well known cathodic dissolution. This will lead to severe health problems like cancer. Unlike aluminium electrodes, the zinc electrodes do not have any disadvantage. The USEPA guidelines suggest maximum contamination level of zinc in water is 5 mg/L.

The reactions for zinc electrode is as follows,

At the anode: \[ \text{Zn}^{2+} (aq) + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)_2}^+ \text{+} 2\text{H}^+ (aq) \] (1)

At the cathode: \[ \text{2H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(g) + 2\text{OH}^- \] (2)

This article presents the adsorption characteristics of chromium from aqueous solution onto in-situ generated zinc hydroxide has been studied using zinc as anode and galvanized iron as cathode. In doing so, the equilibrium adsorption behavior is analyzed by fitting models of Langmuir and Freundlich isotherms. The adsorption kinetics of electrocoagulant is analyzed using first and second-order kinetic models. The activation energy has been evaluated for studying the nature of adsorption.

MATERIALS AND METHODS

The electrolytic cell consists of a 1.0 L Plexiglas vessel that was fitted with a polycarbonate cell cover with slots to introduce the anode, cathode, pH sensor, a thermometer and electrolytes. A zinc sheet (commercial grade) with surface area 0.02 m² acted as the anode and the galvanized iron sheets (commercial grade) with the same size as cathode were placed at an inter-electrode 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). The chromium as K2Cr2O7 (Analar Reagent) was dissolved in de-ionized water for the required concentration (5–25 mg/L). The solution of 0.90 L was used for each experiment as the electrolyte. The pH of the electrolyte was adjusted, if required, with 1 M HCl or 1 M NaOH solutions before adsorption experiments.

The concentration of chromium was determined using UV–Visible Spectrophotometer (Merck, Pharo 300, Germany). The SEM and EDAX of zinc hydroxide were analyzed with a Scanning Electron Microscope (SEM) made by Hitachi (model s-3000h).

RESULTS AND DISCUSSION

Effect of current density

Current density is one of the important factors in electrocoagulation processes. To examine the effects of current density, a series of experiments were carried out using 5 mg/L chromium-containing electrolyte, at pH 7.0, with the varied current density from 0.1 to 0.5 A/dm². The removal efficiencies of chromium are 93.1, 96.5, 98.9, 99.3 and 99.4% for current densities 0.1, 0.2, 0.3 and 0.4 and 0.5 A/dm² respectively. From the result, it is found that, beyond 0.2 A/dm² the removal efficiency remains almost constant for higher current densities. Hence, further studies were carried out only at 0.2 A/dm². The results showed that as current density increases, removal of chromium also increases. This can be attributed to the increase in the amount of Zn ions being generated in-situ thereby resulting in rapid removal of chromium. The amount of adsorbent [Zn(OH)2] has been determined from the Faraday law

\[ E_c = \frac{ItM}{ZF} \] (3)

where \( I \) is current in A, \( t \) is the time (s), \( M \) is the molecular
weight, Z is the electron involved, and F is the Faraday constant (96485.3 C/mol). As expected, the amount of chromium adsorption increases with the increase in adsorbent concentration, which indicates that the adsorption depends up on the availability of binding sites for chromium.

Effect of pH

The pH is one of the important parameters affecting the performance of electrochemical process. To study this effect, a series of experiments were carried out using 5 mg/L chromium containing solutions, initially with varying pH in the range of 2 to 12. The removal efficiency of chromium was increased with increasing the pH up to 7. When the pH range is above 7, the removal efficiency increased with increasing the pH up to 7. When the pH decreases, it is found that the maximum removal efficiency was 96.5% at pH 7 and the minimum efficiency was 85.3% at pH 2. According to Zn–H₂O Pourbaix diagram and in thermodynamic point of view, that the precipitation of Zn(OH)₂ would only be significant at pH > 8.6, however, the interfacial pH-increase during the electrocoagulation process favored the zinc hydroxide formation and resulting higher removal efficiency at pH 7.0.

Effect of initial chromium concentration

In order to evaluate the effect of initial chromium concentration, experiments were conducted at varying initial concentration from 5–25 mg/L. Figure 1 shows that the uptake of chromium (mg/g) increased with increase in chromium concentration and remained nearly constant after equilibrium time. The equilibrium time was found to be 60 min for all concentration studied. The amount of chromium adsorbed (qe) increased from 4.56 to 23.14 mg/g as the concentration increased from 5–25 mg/L. The figure also shows that the adsorption is the rapid in the initial stages and gradually decreases with progress of adsorption. The plots are single, smooth and continuous curves leading to saturation, suggesting the possible monolayer coverage to chromium on the surface of the adsorbent. (Malkoc & Nuhoglu 2007).

Adsorption kinetics

First- and second-order kinetic model

A first-order kinetic model is represented by the Lagergren equation as (Sergei Lyubchik et al. 2004).

\[
\frac{dq}{dt} = k_1(q_e - q_t)
\]

where, \(q_t\) is the amount of chromium adsorbed on the adsorbent at time \(t\) (min) and \(k_1\) (1/min) is the rate constant of first-order adsorption. An integrated form of the above equation with the boundary conditions \(t = 0\) to \(>0\) \((q = 0\) to \(>0)\) 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 chromium adsorbed at equilibrium. The \(q_e\) and \(k_1\) were calculated from the slope of the plots of \(\log (q_e - q_t)\) versus time \(t\).

The second-order kinetic model is expressed by (Nadhem Hamadi et al. 2001)

\[
\frac{dq}{dt} = k_2(q_e - q_t)^2
\]

where \(k_2\) is the rate constant of second-order adsorption. The integrated form of Equation (6) with the boundary condition \(t = 0\) to \(>0\) \((q = 0\) to \(>0)\) is

\[
\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t
\]

Equation (7) can be rearranged and linearized as,

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

Figure 2 shows the straight line from the plot between \(t/q_t\) versus time \(t\). 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 $t$. Table 1 depicts the computed results obtained from first and second-order kinetic model.

**Elovich equation**

The Elovich model equation is generally expressed as indicated (Oke et al. 2008)

$$\frac{dq}{dt} = \alpha \exp(-\beta q_t)$$  \hspace{1cm} (9)

the simplified form of Elovich Equation (9) is

$$q_t = \frac{1}{\beta} \log_e(\alpha \cdot \beta) + \frac{1}{\beta} \log_e(t)$$  \hspace{1cm} (10)

where $\alpha$ is the initial adsorption rate (mg h/g) and, $\beta$ is the desorption constant (g/mg). If chromium adsorption fits the Elovich model, a plot of $q_t$ versus $\log_e(t)$ should yield a linear relationship with the slope of $(1/\beta)$ and an intercept of $1/\beta \log_e(\alpha \cdot \beta)$. Lower regression value (0.6097, 0.6547, 0.6824, 0.6751 and 0.7724 for 5, 10, 15, 20 and 25 g/L) shows the inapplicability of this model.

**Intraparticle diffusion**

The intraparticle diffusion model is expressed as (Weber & Morris 1965; Allen et al. 1989)

$$R = k_{id}(t) a$$  \hspace{1cm} (11)

A linearized form the Equation (11) is followed by

$$\log R = \log k_{id} + a \log(t)$$  \hspace{1cm} (12)

in which ‘$a$’ depicts the adsorption mechanism and $k_{id}$ may be taken as the rate factor (percent of chromium adsorbed per unit time). Lower and higher value of $k_{id}$ illustrates an enhancement in the rate of adsorption and better adsorption with improved bonding between pollutant and the adsorbent particles respectively. Table 2 depicts the computed results obtained from Elovich equation and intraparticle diffusion model.

**Table 1** Comparison between the experimental and calculated $q_e$ values for different initial chromium concentration in first- and second-order adsorption kinetics 305 K

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>$q_e$ (exp) (mg/g)</th>
<th>$q_e$ (cal) (mg/g)</th>
<th>$K_1$ (min g/mg)</th>
<th>$R^2$</th>
<th>$q_e$ (cal) (mg/g)</th>
<th>$K_2$ (min g/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4.56</td>
<td>13.26</td>
<td>0.0056</td>
<td>0.8632</td>
<td>4.681</td>
<td>0.0054</td>
<td>0.9999</td>
</tr>
<tr>
<td>10</td>
<td>9.35</td>
<td>15.64</td>
<td>0.0087</td>
<td>0.8965</td>
<td>9.345</td>
<td>0.0065</td>
<td>0.9999</td>
</tr>
<tr>
<td>15</td>
<td>12.99</td>
<td>18.55</td>
<td>0.0091</td>
<td>0.8546</td>
<td>13.041</td>
<td>0.0072</td>
<td>0.9867</td>
</tr>
<tr>
<td>20</td>
<td>18.97</td>
<td>25.67</td>
<td>0.0108</td>
<td>0.8632</td>
<td>19.115</td>
<td>0.0084</td>
<td>0.9978</td>
</tr>
<tr>
<td>25</td>
<td>23.14</td>
<td>30.47</td>
<td>0.0111</td>
<td>0.9001</td>
<td>26.347</td>
<td>0.0093</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

**Table 2** Elovich model and Intra particle diffusion for different initial chromium concentrations at temperature 305 K and pH 7

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Elovich model</th>
<th>Intra particle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$ (mg/h)</td>
<td>$\beta$ (g/mg)</td>
</tr>
<tr>
<td>5</td>
<td>10.53</td>
<td>43.84</td>
</tr>
<tr>
<td>10</td>
<td>5.68</td>
<td>35.34</td>
</tr>
<tr>
<td>15</td>
<td>1.89</td>
<td>18.23</td>
</tr>
<tr>
<td>20</td>
<td>0.99</td>
<td>14.55</td>
</tr>
<tr>
<td>25</td>
<td>0.66</td>
<td>9.88</td>
</tr>
</tbody>
</table>
From Tables 1 and 2 it is found that the values of correlation coefficient decreases from second, first order, intraparticle diffusion to Elovich model. This indicates that the adsorption follows the second order than the other models. The calculated \( q_e \) values also well agree with the experimental \( q_e \) values for second-order kinetics model concluding that the second-order kinetics equation is the best-fitting kinetic model.

**Adsorption isotherm**

**Freundlich isotherm**

The general form of Freundlich adsorption isotherm is represented by (Gasser et al. 2007)

\[
q_e = K C_e^n
\]

Equation (13) can be linearized in logarithmic form and the Freundlich constants can be determined as follows (Uber 1985)

\[
\log q_e = \log k_t + n \log C_e
\]

where, \( k_t \) is the Freundlich constant related to adsorption capacity, \( n \) is the energy or intensity of adsorption and \( C_e \) is the equilibrium concentration of chromium (mg/L). To determine the isotherms, the chromium concentration was used as 5–25 mg/L at an initial pH 7. The Freundlich constants \( k_t \) and \( n \) values are 0.9344 mg/g and 1.122 L/mg respectively. It has been reported that the values of ‘\( n \)’ lying between 0 and 10 indicate favorable adsorption. From the analysis of the results it is found that the Freundlich plots fit satisfactorily with the experimental data obtained in this study.

**Langmuir isotherm**

The linearized form of Langmuir adsorption isotherm model is (Namasivayam & Prathap 2005)

\[
\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o}
\]

where \( C_e \) is the concentration of the chromium solution (mg/L) at equilibrium, \( q_o \) is the adsorption capacity (mg/g) and \( b \) is the energy of adsorption (L/mg). Figure 3 shows the Langmuir plot (1/\( C_e \) versus 1/\( q_e \)) with experimental data. The value of the adsorption capacity \( q_m \) as found to be 676.44 mg/g.

The essential characteristics of the Langmuir isotherm can be expressed as dimensionless constant \( R_L \).

\[
R_L = \frac{1}{1 + b C_o}
\]

where, \( R_L \) is the equilibrium parameter, \( C_o \) is the initial chromium concentration and \( b \) is the Langmuir constant. It is well known that the \( R_L \) values indicate the type of isotherm: irreversible \( (R_L = 0) \), favorable \( (0 < R_L < 1) \), linear \( (R_L = 1) \) or unfavorable \( (R_L > 1) \). In this study, the \( R_L \) values were identified between 0 and 1 for all the concentration of chromium studied (5–25 mg/L).

**Dubinin-Radushkevich (D-R) isotherm**

This isotherm model was chosen to estimate the characteristics porosity of the biomass and apparent energy of adsorption. This model is represented by the

\[
q_e = q_s \exp(-B \varepsilon^2)
\]

where \( \varepsilon \) is Polanyi potential, equal to \( RT \ln(1 + 1/C_e) \), \( B \) is related to the free energy of sorption per mole of the adsorbate as it migrates to the surface of the electrocoagulant \( (\text{Zn(OH)}_2) \) from infinite distance in the solution and \( q_s \) is the Dubinin-Radushkevich (D-R) isotherm constant related to the degree of adsorbate adsorption by the adsorbent surface (Demiral et al. 2008). The linearized form of the Equation (17)

\[
\ln q_e = \ln q_s - 2BRT \ln[1 + 1/C_e]
\]

The isotherm constants of \( q_s \) and \( B \) are obtained from the intercept and slope of the plot of \( \ln q_e \) versus \( \varepsilon^2 \) (Oguz
The mean free energy of adsorption known as the free energy change one mol adsorbate in transferred from infinity in solution to the surface of the adsorbent was obtained from the following relationship given by Hobson

\[ E = -\left(2k\right)^{-0.5} \]

(19)

The magnitude of \( E \) is useful for estimating the type of adsorption process. It was found to be 16.78 kJ/mol, which is bigger than the energy range of adsorption reaction, 8–16 kJ/mol. So the type of adsorption of chromium on zinc anode was defined as chemical adsorption.

The correlation co-efficient values of different isotherm models are listed in Table 3. The Langmuir isotherm model has higher regression co-efficient \((R^2 = 0.999)\) when compared to the other models. The value of \( R_L \) for the Langmuir isotherm was calculated between 0 and 1, indicating the favorable adsorption of chromium.

Studies on effect of temperature

In order to understand the effect of temperature on the adsorption process, thermodynamic parameters should be determined at various temperatures. The amount of chromium adsorbed on the adsorbent increases by increasing the temperature indicating the process to be endothermic.

The diffusion co-efficient \((D)\) for intraparticle transport of chromium species into the adsorbent particles has been calculated at different temperature by,

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

(20)

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 co-efficient in cm²/s. For all chemisorption system the diffusivity co-efficient should be \( 10^{-5} \) to \( 10^{-13} \) cm²/s (Yang & Al-Duri 2001). In the present work, \( D \) is found to be in the range of \( 10^{-10} \) cm²/s. The pore diffusion coefficient \((D)\) values for various temperatures and different initial concentrations of chromium are presented in Table 4 respectively.

To find out the energy of activation for adsorption of chromium, the second-order rate constant is expressed in Arhenius form (Golder et al. 2006).

\[ \ln k_2 = \ln k_0 - \frac{E}{RT} \]

(21)

where \( k_0 \) is the constant of the equation \((g/mg \ min)\), \( E \) is the energy of activation \((J \ mol^{-1})\), \( R \) is the gas constant \((8.314 J/\ mol \ K)\) and \( T \) is the temperature in K. Figure 4 shows that the rate constants vary with temperature according to

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Pore diffusion constant ( D \times 10^{-9} ) (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.447</td>
</tr>
<tr>
<td>10</td>
<td>1.156</td>
</tr>
<tr>
<td>15</td>
<td>0.866</td>
</tr>
<tr>
<td>20</td>
<td>0.745</td>
</tr>
<tr>
<td>25</td>
<td>0.649</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>Pore diffusion constant ( D \times 10^{-9} ) (cm²/s)</td>
</tr>
<tr>
<td>313</td>
<td>1.199</td>
</tr>
<tr>
<td>323</td>
<td>0.998</td>
</tr>
<tr>
<td>333</td>
<td>0.665</td>
</tr>
<tr>
<td>343</td>
<td>0.564</td>
</tr>
</tbody>
</table>

Table 3 | Constant parameters and correlation co-efficient calculated for different adsorption isotherm models at different temperatures for chromium adsorption on zinc hydroxide

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Constants</th>
<th>( q_m ) (mg/g)</th>
<th>( B ) (L/mg)</th>
<th>( R_L )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
<td>676.44</td>
<td>0.912</td>
<td>0.9786</td>
<td>0.9999</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td>0.9344</td>
<td>1.122</td>
<td></td>
<td>0.9658</td>
</tr>
<tr>
<td>D-R</td>
<td>( q_s ) (×10^3 mol/g)</td>
<td>1.654</td>
<td>3.564</td>
<td>16.78</td>
<td>0.9457</td>
</tr>
</tbody>
</table>

Figure 4 | Plot of log \( k_2 \) and 1/T at pH of 7.0, current density of 0.2 A/dm², temperature of 303 K and concentration of 5–25 mg/L.
Equation (21). The activation energy (14.22 kJ/mol) is calculated from slope of the fitted equation. The free energy change is obtained using the following relationship,

$$\Delta G = -RT \ln K_c$$  \hspace{1cm} (22)

where $\Delta G$ is the free energy (kJ/mol), $K_c$ is the equilibrium constant, $R$ is the gas constant and $T$ is the temperature in K. The $K_c$ and $\Delta G$ values are presented in Table 5. From the table it is found that the negative value of $\Delta G$ indicates the spontaneous nature of adsorption. Other thermodynamic parameters such as entropy change ($\Delta S$) and enthalpy change ($\Delta H$) were determined using van’t Hoff equation,

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$  \hspace{1cm} (23)

The enthalpy change ($\Delta H = 12.223$ kJ/mol) and entropy change ($\Delta S = 13.456$ J/mol K) were obtained from the slope and intercept of the van’t Hoff linear plots of $\ln K_c$ versus $1/T$ (Figure 5). 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 ($\Delta G$) show the spontaneous adsorption of chromium on the adsorbent. Positive values of entropy change show the increased randomness of the solution interface during the adsorption of chromium on the adsorbent (Table 5). Enhancement of adsorption capacity of electrocoagulant (Zinc hydroxide) at higher temperatures may be attributed to the enlargement of pore size and or activation of the adsorbent surface.

### Table 5 | Thermodynamic parameters for the adsorption of chromium

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_c$</th>
<th>$\Delta G^o$ (kJ/mol)</th>
<th>$\Delta H^o$ (kJ/mol)</th>
<th>$\Delta S^o$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>0.335</td>
<td>-609.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>0.567</td>
<td>-1256.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>0.701</td>
<td>-2226.45</td>
<td>12.223</td>
<td>13.456</td>
</tr>
<tr>
<td>343</td>
<td>1.115</td>
<td>-2788.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Figure 5](image-url)  
Figure 5 | Plot of $\ln K_c$ and $1/T$ at pH of 7.0, current density of 0.2 A/dm$^2$, temperature of 303 K and concentration of 5–25 mg/L.

![Figure 6](image-url)  
Figure 6 | SEM image of the anode (a) before and (b) after treatment.

**SEM and EDAX studies**

SEM images of zinc anode, before and after, electrocoagulation of chromium electrolyte was obtained to compare the surface texture. Figure 6(a) shows the original zinc plate surface prior to its use in electrocoagulation experiments. The surface of the electrode is uniform. Figure 6(b) shows the SEM of the same electrode after several cycles of use in electrocoagulation experiments. The electrode surface is now found to be rough, with a number of dents. These
dents are formed around the nucleus of the active sites where the electrode dissolution results in the production of zinc 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 chromium-adsorbed zinc hydroxide shown in Figure 7. It shows that the presence of Cr, Zn and O appears in the spectrum. EDAX analysis provides direct evidence that chromium is adsorbed on zinc hydroxide. Other elements detected in the adsorbed zinc hydroxide come from adsorption of the conducting electrolyte, chemicals used in the experiments, alloying and the scrap impurities of the anode and cathode.

CONCLUSIONS

The results of the present investigation illustrates that the optimized removal efficiency of 96.5% was achieved at an optimum current density of 0.2 A dm$^{-2}$ and pH of 7.0 using zinc as anode and galvanized iron as cathode. The zinc hydroxide generated in the cell by in-situ removes the chromium present in the water and making it drinkable. Langmuir adsorption isotherm was found to fit the equilibrium data for chromium adsorption. The adsorption process follows the second-order kinetics. Temperature studies showed that the adsorption was endothermic and spontaneous in nature.

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