ABSTRACT

This paper studies the removal of crystal violet (CV) dye by electrocoagulation (EC) process using bipolar iron electrodes. Numerous operating parameters such as initial CV solution concentration, speed of agitation, number of electrodes, type and quantity of supporting electrolyte, temperature and initial pH were investigated. A complete removal of 10 mg/L CV was achieved within 10 min at pH 7, 0.5 g NaCl, 1 LCV, 750 rpm, 9 sheets, 17.36 mA cm$^{-2}$, and 25 °C. The performed energy-dispersive X-ray spectroscopy (EDAX), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) analyses confirmed the adsorption of CV onto the insoluble iron hydroxide flocs. Amongst the studied adsorption isotherms models, Langmuir and Dubinin–Radushkevich were the most applicable. The kinetic of adsorption of CV onto flocs during the EC operation was studied using the pseudo-first-order, pseudo-second-order, and intraparticulate diffusion models, with results affirming that the adsorption process proceeded according to the pseudo-second-order model. The study of thermodynamic parameters ($\Delta G^0$, $\Delta H^0$, and $\Delta S^0$) of the CV removal at different temperatures reflected the feasibility of the spontaneous randomness of endothermic adsorption, especially at lower temperatures. The multiple regression equation of the removal of CV by EC technique under the different studied conditions was predicted.

INTRODUCTION

About ten thousand dyes and pigments are currently in use in the textile industry (Daneshvar et al. 2006). During textile industry procedures, large amounts of unfixed dyes on fibers (60–90%) are produced (O’Neill et al. 1999). The discharging of untreated textile wastewater into water bodies causes many problems to the ecosystem. Furthermore, the discharged industrial effluent into sewage networks also produces disturbance in biological treatment processes. Textile wastewater is characterized by strong colors, high chemical oxygen demand total organic carbon, low biodegradability, and high-salt content (Koby et al. 2016). Many processes were used to remove dyes from colored effluents such as biochemical photodegradation, adsorption, precipitation, membrane filtration and chemical coagulation (Singh & Arora 2011). However, these processes are quite expensive and involve several operational problems. For these reasons, there has been an increasing interest in the use of electrocoagulation (EC) technique (Brillas & Martinez-Huitle 2015; Koby et al. 2016). EC is an effective primary treatment for highly polluted industrial wastewater. It has been used successfully for the treatment of various industrial effluents including effluents from food industries (Inan et al. 2004), tanneries (Golder et al. 2007), heavy metals (Merzouk et al. 2009), mechanical workshops (soluble oil) (Cañizares et al. 2007), polymerization manufactures, and textile industries (Zongo et al. 2009; Merzouk et al. 2011). EC technique has many advantages: the process can proceed without need for chemical additives during the treatment, production of less sludge, requirement of small area, and low cost (Koby et al. 2016). The EC process involves many chemical and physical
mechanisms (Mollah et al. 2004). In the EC process, iron anodic electrode dissolves and forms different coagulant species and hydroxides that destabilize and coagulate the suspended particles or precipitate and adsorb dissolved contaminants. Generally, the EC process involves three successive stages (Heidmann & Calmano 2008).

The first stage implies the formation of coagulants by electrolytic oxidation that leads to the anodic dissolution and the water electrolysis that occurs at both cathode and anode as follows (Equations (1)–(3); Durango-Usuga et al. 2010; Koby et al. 2016):

$$\text{Fe(s)} \rightarrow \text{Fe}^{2+} (aq) + 3e^- \quad (1)$$

$$2\text{H}_2\text{O}(aq) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- \text{ (cathodic reaction)} \quad (2)$$

$$2\text{H}_2\text{O}(aq) \rightarrow 4\text{H}^+ (aq) + \text{O}_2(g) + 4e^- \text{ (anodic reaction)} \quad (3)$$

where, subscripts (s), (aq) and (g) refer to solid, aqueous and gas phases, respectively.

The second stage refers to destabilization of the contaminants, particulate suspension, breaking of emulsions, and the direct electrochemical reduction of iron cations (Fe$^{n+}$) which may occur at the cathode surface. Furthermore, the hydroxide ions formed at the cathode increase the pH of the wastewater thereby inducing precipitation of iron ions as corresponding hydroxides, and co-precipitation with iron hydroxides as given (Equations (4) and (5); Durango-Usuga et al. 2010; Koby et al. 2016):

$$\text{Fe}^{n+} + ne^- \rightarrow n\text{FeO}^0 \quad (4)$$

$$\text{Fe}^{n+} + n\text{OH}^- \rightarrow \text{Fe(OH)}_n^{(a)} \quad (5)$$

The third stage expresses the coagulation of the destabilized phases and the formation of flocs in addition to the reaction of anodic iron ions and hydroxide ions in the bulk wastewater to form various hydroxides and build up big particles as shown (Equations (6) and (7); Durango-Usuga et al. 2010; Koby et al. 2016):

$$\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3^{(s)} \quad (6)$$

$$n\text{Fe(OH)}_3^{(s)} \rightarrow \text{Fe}_n\text{(OH)}_{3n(s)} \quad (7)$$

It was recorded that the pH of the aqueous medium affects the presence of other ionic species, such as dissolved Fe(OH)$^{2+}$, Fe$_2$(OH)$_5^{4+}$, and Fe(OH)$_4^{-}$ hydroxo complexes in the bulk. The suspended iron hydroxides can remove pollutants from the solution by sorption, co-precipitation, or electrostatic attraction, followed by coagulation (Mollah et al. 2004).

Triphenylmethane dye compounds, such as crystal violet (CV), are largely used in the paper, leather, cosmetic, and food industries. The textile industry consumes large amounts of these substances for dyeing nylon, wool, cotton, and silk, as well as for coloring oil, fats, waxes, varnish, and plastics (Gessner & Mayer 2001). Moreover, some of the triphenylmethane dyes are used as medicine and biological stains (Azmi et al. 1998). These compounds not only cause coloration of water, but also pose a serious risk to aquatic life and a possible human health hazard (Nassar & Magdy 1997; Palma-Goyes et al. 2010).

Most of the previous studies on the removal of CV using EC technique implemented aluminium sheets as scarifying electrodes (Kuleyin & Balcoğlu 2009; Mbacké et al. 2013); they reached maximum removal of only 95%. On the other hand, Durango-Usuga et al. 2010 compared both aluminium and iron as scarifying electrodes and concluded that iron anodes were shown to have the highest efficiency in removing the dye in about 5 minutes. In the literature there is little work done regarding the removal of CV by EC, especially using iron electrodes (Durango-Usuga et al. 2010).

Because of the few studies on the usage of iron electrodes, we preferred to study the removal of CV by EC technique using iron electrodes and the CV adsorption mechanism in different conditions. This work aims to investigate the capacity of CV removal from aqueous solutions by EC technique using iron electrodes at different conditions of initial CV concentration, speed of agitation, number of electrodes, type and quantity of supporting electrolyte, temperature- and initial pH. The removal features can be identified by Fourier transform infrared spectroscopy (FTIR), energy-dispersive X-ray spectroscopy (EDAX) and scanning electron microscopy (SEM). Also, different models of adsorption isotherms, kinetic equations, and thermodynamics can be used to assess the removal procedure.

**MATERIALS AND METHODS**

**Materials**

CV was purchased from SDFCL S D Fine-Chem Limited (C$_{25}$H$_{30}$N$_3$Cl; 75% purity). Anhydrous sodium sulphate, hydrochloric acid, sodium carbonate, and sodium hydroxide were provided from Merck.
Analytical measurements

Stock solution of CV was prepared by dissolving 1 g of CV in 1,000 mL of double distilled water. The stock solution was then appropriately diluted to get the desired dye concentrations. The CV concentration was determined using Unico UV-2000 spectrophotometer. The Beer–Lambert law (\( A = \varepsilon \times \ell \times C \)) was applied at 590 nm, where \( \varepsilon \) was the molar absorptivity, \( \ell \) was the cell thickness, and \( C \) was the CV concentration. Different standard concentrations of CV were analyzed spectrophotometrically to draw the calibration curve. The data of different conditions were obtained and the % removal of CV (\% Re) was computed according to the following equation:

\[
\% Re = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]  

(8)

where, \( C_0 \) and \( C_t \) were the initial and time (t) concentrations of CV, respectively.

Adsorption isotherms, kinetics, and thermodynamics studies on the removal of CV by EC technique

Three adsorption isotherms models Langmuir (1918), Freundlich (1906), and Dubinin–Radushkevich (D–R) (Dubinin & Radushkevich 1947) were applied to study the adsorption procedure. However, the acceptability and suitability of the isotherm equation to the equilibrium data were based on the values of the correlation coefficients \( R^2 \) estimated from the linear regression of the least square fit statistic on the Micro Math Scientist software.

The amount of CV coagulated at equilibrium, \( Q_e \) mg/g was calculated in the different variable removal conditions using the equation below:

\[
Q_e = \frac{(C_0 - C_e)V}{W}
\]  

(9)

where \( C_0 \) and \( C_e \) (mg/L) were the initial and equilibrium CV concentrations in the liquid phase, \( V \) is the volume of the solution (L), while \( W \) is the mass of the iron coagulant (g) which can be estimated from Faraday’s Law according to the following equation:

\[
W = \frac{Mt}{nF}
\]  

(10)

Experimental setup

The characteristics of EC reactor are given in Table 1. In a typical experiment, the specified volume of CV was
poured into the cell, an initial sample was taken, and the current was then applied under regular magnetic stirring. To attain uniform mixing, stirring was achieved using a magnetic stirrer. A drain tube with a fitted sampling valve was installed at the bottom of the cell for pouring out CV samples at different intervals time. The anode and cathode were connected to a DC power supply to provide a DC current. Two ammeters (Sunwa, China) were used, of which one functioned as a voltmeter while the other functioned as an ammeter.

**Procedure**

Before each experiment, the electrodes were abraded with sandpaper, then dipped in hydrochloric acid solution, cleaned with distilled water, and finally dried in an oven at 110 °C for 30 min. The cell was cleaned by washing twice with tap water then with distilled water. Each prepared CV standard solution was added to the cell after fixing the electrodes in their trenches. The CV standard solution (bulk solution) was stirred magnetically at the required speed. A 5 mL sample from the bulk CV solution in the cell was drawn at 10 min intervals. The samples were filtered by 12.5 cm filter paper (Whatman) before analysis, and then the unknown concentration of CV in the filtrated samples was evaluated from the calibration curve.

The effect of different variables of initial CV concentration, speed of agitation, number of electrodes, quantity and type of supporting electrolyte (sodium chloride, sodium carbonate, and sodium sulphate), temperature, and initial pH were assigned on the removal operation. The pH values were measured before and after the removal by the pH meter (model 607). The function groups of the flocs was estimated by PLATINUM Diamond ATR accessory and VERTEX 70 FTIR Bruker spectrometer. The surface characteristics and the elemental composition of the surface of electrodes and flocs before and after the CV removal were estimated by SEM and EDAX techniques using Quanta 250 SEM FEI-Orbit Scientific, respectively. The instrument was operated under low vacuum at an accelerating voltage to get the sharp image of the sample.

**RESULTS AND DISCUSSION**

**Effect of initial pH**

Many studies examined the effect of pH on the treatment of wastewaters by EC technique (Koparal *et al.* 2008; Un & Aytaç 2013). In the present study, the effect of different initial pH values on % removal of CV (% Re) using 0.1 M sodium hydroxide or 0.1 M hydrochloric acid is studied (Figure 1).

![Figure 1](https://iwaponline.com/wst/article-pdf/77/2/323/242658/wst077020323.pdf)

**Figure 1** The % Re of CV in different initial pH values; $C_i = 150$ mg/L, 0.5 g NaCl as supporting electrolyte, volume of CV solution = 1 L, speed of stirring = 750 rpm, 9 iron sheets, current density = 17.36 mAc㎡, and $T = 25^\circ$C.

The % Re in the initial pH values of 2–5, 7, and 8–11 are investigated. The best performance of CV removal by EC reactor is observed at pH 11, whereas, the lowest CV removal is obtained at pH 4. The removal efficiency of CV ranges from 94.90 to 99.88% during 60 min. Thus, in the
present work there is no need to add any chemical compounds to buffer the bulk solution to obtain a constant pH during EC process; however, the initial pH has insignificant effect on the removal efficiency of CV. The observed removal is consistent with the work by Durango-Usuga et al. (2010). The previous results concluded that the usage of iron anodes in the treatment of CV by EC was more effective than the aluminum anodes due to the poor solubility of iron species in the different pH values (Kin et al. 2006; Durango-Usuga et al. 2010). The change in the % Re may be attributed to the concentration of Fe ions, which is strongly dependent on the pH variation in the bulk solution due to the buffering capacity in the EC system, i.e. the OH− generation or the H⁺ consumption (Durango-Usuga et al. 2010).

**Effect of initial concentration**

The effect of different initial concentrations (10, 20, 40, 80, 100, 120 and 150 mg/L) on % Re of CV by EC technique was studied (Figure 2). The lowest CV concentration (10 mg/L) shows a complete removal within 10 min, whereas, the complete removal of both 40 and 80 mg/L concentrations occurs after 20 min of the experiment procedure. Furthermore, the higher concentrations of 100, 120 and 150 mg/L reach the complete removal after 30 min. In contrast, the initial concentration of 20 mg/L is completely removed after 1 hour. This may be related to the cathode passivation which originated from CV deposits on the cathode material. However, the cathode passivation prevents the electron transfer between anode and cathode and hinders the iron hydroxide formation which negatively impacts the performance of the process. This observation does not appear in higher concentrations due to the formation of the iron hydroxides flocs with CV molecules that show up as a nucleus of greater flocs which permits complete removal with time. It was stated that the removal processes with EC using iron electrodes are mostly affected by the generated iron species in the medium (Ghernaout et al. 2008). However, at the beginning of the EC process, the electrochemical dosing of iron into solution results in a relatively limited removal rate and Fe(OH)2(s) (dark green flocs) is mostly produced in the bulk solution. As time progressed to >10 min, the pH value had already changed from 6.8 to 9.4 due to the increase of Fe (OH)3 formation in the presence of hydroxyl ions and the color spontaneously changed from dark green to yellow brown.

**Effect of number of electrodes**

Figure 3 illustrates the relation between the % Re of CV with the number of electrodes (1–7 electrodes). The presented results indicate that the increase in the electrode number from 1 to 7 electrodes gives a complete CV removal within lower operating time of 50, 20, and 10 min,

![Figure 2](https://iwaponline.com/wst/article-pdf/77/2/323/242658/wst077020323.pdf)
respectively. However, the increase in the iron electrode number leads to the increase in the surface area that generates more coagulants in EC process. Also, the increase in the electrode number generates greater amounts of iron polymers with slower movements that tend to aggregate in the sludge and adsorb the CV molecules rather than be attracted to the electrode surface (Modirshahla et al. 2013).

**Effect of supporting electrolyte**

The % Re of CV in presence of different weights of NaCl electrolyte (0.5, 1.5, 2.0, 2.5 g) is investigated (Figure 4). The lowest % Re is observed in the presence of the minimum NaCl weight (0.5 g), whereas, the other NaCl weights (1.5, 2.0, 2.5 g) give similar removal efficiencies. On the other hand, the usage of the same weight (1.5 g) of three different supporting electrolytes NaCl, Na₂SO₄, and Na₂CO₃ gives approximately similar % Re values of 99.71, 99.97, and 99.92, respectively. The presence of electrolytes increases the conductivity, diminishes the resistance, and lessens the energy cost of the process (Chiang et al. 2000; Lei et al. 2007). Generally, the effect of supporting electrolyte on the electricity consumption in EC technique depends on the type of anode (Fe or Al) and the kind of pollutant (Yildiz et al. 2007; Chang et al. 2010). Izquierdo et al. (2010) discovered relatively similar treatments of the wastewater that incorporated soluble oil using either NaCl or Na₂SO₄ in the presence of either Al or Fe electrodes.

**Effect of speed of agitation**

The relatively similar % Re of 99.94, 99.97, and 99.96 for 1 L of 300 mg/L CV in the presence of 1.5 g Na₂SO₄ and at room temperature for 250, 750, 1,000 rpm, respectively, indicate that the speed of agitation does not affect the CV removal by EC process by using iron electrodes.

**Characterization of the electrode surface and formed flocs**

The possibility of direct deposition of CV and iron hydroxides onto the electrode surface and the CV adsorption onto hydroxide flocs are studied with the EDAX analyses before and after the removal process (Figures 5(a), 5(b), and 6). The EDAX results for iron electrode before and after the removal procedure indicate that there is no CV deposition on its surface and ensure the presence of the iron hydroxide species due to the evolution of the gases.
from the aqueous solution (Figure 5(a) and 5(b); Shafaei et al. 2011). Consequently, the direct iron hydroxides deposition onto the iron electrode has insignificant effect on the removal of CV from its aqueous solution. In contrast, the insoluble iron hydroxides that form flocs by surface complexation or electrostatic attraction can remove CV molecules (Figure 6). However, it was assumed that in surface complexation, the pollutant can act as a ligand to bind a hydrous iron moiety (monomeric and polymeric iron) with precipitation and adsorption mechanisms (Daneshvar et al. 2006). The FTIR data for the pure iron hydroxide, pure CV and the formed flocs after CV removal confirms the adsorption of CV onto the insoluble iron hydroxides of the flocs (Figure 7). By inspecting Figure 7, it is found that the FTIR of Fe(OH)₃ appears at absorption bands at 3,331.58, 1,586.41, 1,356.74, and 816.33 cm⁻¹ are relatively similar to the spectrum of a pure Fe(OH)₃ (3,400, 1,640, 1,380 and 886 cm⁻¹; Mustafa et al. 2015). Also, it seems that the adsorption bands of CV spectrum shift from their original positions for the pure composition due to the overlap of bands of ferric hydroxides of the flocs (Figure 6; Al-Kadhemy et al. 2015). However, N–H stretching vibrations are assigned by two bands at 3,331 and 2,883 cm⁻¹. The benzene rings found at peaks at 1,517.00 cm⁻¹ for the C=C stretching, peak at 2,800.04 cm⁻¹ for C–H stretching with asymmetric CH₃ group. The peak at 1,064.97 cm⁻¹ refers to C–H bending vibrations and a peak at 1,171.15 cm⁻¹ corresponds to the C–N stretching vibrations. There has been more than one peak obtained in the region of the C–H bending vibrations (940.95–562.4 cm⁻¹) that can support the presence of an aromatic structure.

On the other hand, the SEM micrograph of the electrodes’ surface that was performed before and after the CV removal process by EC shows the change in the morphology due to the deposition of the insoluble hydroxides of iron (Fe(OH)ₙ) after the removal procedure (Figure 8).

**Applied adsorption isotherms for EC process of CV removal**

The equilibrium data from this study are described with three adsorption isotherms models: Langmuir (1918), Freundlich (1906), and Dubinin–Radushkevich (D–R) (Dubinin & Radushkevich 1947).

The Langmuir isotherm equation is based on the following assumptions: (1) that the entire surface for the adsorption has the same activity for adsorption, (2) that there is no interaction between adsorbed molecules, and (3) that all the adsorption occurs by the same mechanism and the extent of adsorption is less than one complete monomolecular layer on the surface (Langmuir 1918; Adeogun & Balakrishnan 2017). Linear Langmuir’s isotherm model can be evaluated as follows (Langmuir 1918):

\[
\frac{1}{q_e} = \frac{1}{K_qQ_m} \frac{1}{C_e} + \frac{1}{Q_m}
\]  

(12)
where $Q_m$ (mg/g) and $K_a$ (L/mg) are the isotherms’ constants assigned to the saturation and capacity of adsorption, respectively.

The essential characteristics of the Langmuir isotherm can be expressed as the dimensionless constant $R_L$ (Shirani et al. 2014; Salehi et al. 2016):

$$R_L = \frac{1}{1 + \frac{K_L C_0}{C}}$$

where, $C_0$ is the initial concentration (mg/L) and $K_L$ is the Langmuir equilibrium constant (L/mg). The value of
Figure 6 | EDAX of the formed flocs after CV removal by EC technique.

Figure 7 | FTIR of the pure ferric hydroxide, pure CV, and the formed flocs of the CV removal by EC technique.
separation parameter $R_L$ provides important information about the nature of adsorption. The value of the $R_L$ indicates the type of Langmuir isotherm; however, it can be irreversible when $R_L = 0$, favorable when $0 < R_L < 1$, linear when $R_L = 1$, and unfavorable when $R_L > 1$. Also, the values of $R_L > 0$ confirm the favorability of the adsorption process (Salehi et al. 2016). The presented data of CV removal indicate the feasibility of adsorption ($R_L = 0.679$; Table 2).

The Freundlich isotherm describes non-ideal and reversible adsorption. It is not restricted to the formation of a monolayer (Foo & Hameed 2010) and can be applied to multilayer adsorption in heterogeneous systems. Linear Freundlich’s model is shown as follows (Freundlich 1906):

$$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e$$

(14)

$K_f$ is the Freundlich constant related to the adsorbent capacity, and $n$ is the constant indicative of the intensity of the adsorption process. The values of the constants, $n$ and $K_f$, were calculated from the slope and the intercept of the equation. It has been reported that values of $n$ lying between 0 and 1 indicate favorable adsorption, whereas, the values of $n_f < 1$, reflect the unfavorable adsorption conditions (Table 2).

Langmuir and Freundlich isotherms do not give any information about adsorption mechanism (Tharcila et al. 2013). On the other hand, D–R isotherm generally expresses the adsorption mechanism (physical or chemical) with a Gaussian energy distribution onto the heterogeneous surfaces (Dubinin & Radushkevich 1947; Tharcila et al. 2013). Accordingly, D–R isotherm is more applied for heterogeneous adsorbents’ surfaces with porous structure than Langmuir’s. The linear form of D–R isotherm equation is represented as:

$$\ln q_e = \ln q_m - Be^2$$

(15)

where $q_m$ is the theoretical saturation capacity (mol/g), $B$ is a constant related to the mean free energy of adsorption per

![Figure 8](#)  
SEM of electrodes’ surface: (a) before and (b) after CV removal by EC technique.

Table 2 | The parameters of the used adsorption isotherm models for the CV removal by EC technique

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Dubinin–Radushkevich</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_m$ (mg/g)</td>
<td>1.140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_a$ (L/mg)</td>
<td>1.580</td>
<td>$n_f$</td>
<td>0.956</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.679</td>
<td>$R^2$</td>
<td>0.891</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.990</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_f$ (mg/g)(L/mg)$^{1/n}$</td>
<td>0.001</td>
<td></td>
<td>284.918</td>
</tr>
<tr>
<td>$q_m$ (mol/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E$ (KJ/mol)</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.911</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
mole of the adsorbate (mol²/j²), and ε is Polanyi potential which is mathematically expressed by the following equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$$ (16)

where $C_e$ is the equilibrium concentration of adsorbate in solution (mol/L), $R$ is the gas constant (8.314 J/molK) and $T$ is the absolute temperature (K). The D–R model constants can be determined from the intercept and slope of the linear plot of ln$q_e$ versus $\varepsilon^2$, respectively. Additionally, the other D–R isotherm’s value ($B$) can give an idea about the mean free energy of adsorption ($E$) and can be computed from the given relationship (Soliman et al. 2013):

$$E = \frac{1}{\sqrt{2B}}$$ (17)

The values of the mean free energy of adsorption ($E$) express the type of adsorption, whether it is a chemical ion exchange ($E$ = 8–16 kJ mol⁻¹) or a physical adsorption ($E$ < 8 kJ mol⁻¹) (Chakraborty et al. 2011). The calculated ($E$) value obtained from the D–R isotherm calculations ($E$ < 8 kJ mol⁻¹) implies the physical adsorption of CV onto the formed flocs.

**EC kinetics studies**

In order to investigate the mechanism of the adsorption process pseudo-first-order, pseudo-second-order, and intraparticulate diffusion models are applied to describe the kinetics of adsorption of CV onto the generated iron hydroxides (flocs) during the EC process.

The application of the pseudo-first-order kinetic model for CV adsorption process is achieved by following the equation below (Lin et al. 2011; Adeogun & Balakrishnan 2017):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1t}{2.303}$$ (18)

where $q_t$ is the amount of CV adsorbed on the flocs at time $t$ (min), $k_1$ (1/min) is the rate constant of first-order adsorption, and $k_1$ and $q_e$ are calculated from slope and intercept of the plot of log$(q_e - q_t)$ versus $t$, respectively (Table 3).

<table>
<thead>
<tr>
<th>Table 3</th>
<th>The parameters of the used kinetic models for the CV removal by EC technique</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kinetics model</strong></td>
<td><strong>Parameters and regression coefficient</strong></td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td>$K_1$ (1/min)</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>$K_2$ (g/mg min)</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>Intraparticle diffusion model</td>
<td>$K_{dif}$ (mg/g min¹/²)</td>
</tr>
<tr>
<td></td>
<td>$C$ (mg/g)</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
</tbody>
</table>

On the other hand, the pseudo-second-order kinetic model can be examined as follows (Adeogun et al. 2010, 2011):

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e}$$ (19)

where $k_2$ (g/mg min) is the rates constant of pseudo-second-order adsorption. The plot of $t/q_t$ versus $t$ gives the values $k_2$, and $q_e$ (mg/g). The best fit straight line ($R^2 = 0.990$) for the pseudo-second-order kinetics model indicates that the removal of CV by EC process follows this model and depends on the CV and iron hydroxides concentrations (Table 3).

Also, the definite mechanism of the adsorption of CV can be tested by the intraparticle diffusion model according to Weber & Morris (1965). The intraparticle diffusion coefficient $k_{dif}$ is defined by the following equation:

$$q_t = k_{dif}t^{1/2} + C$$ (20)

where $k_{dif}$ is the intraparticle diffusion rate constant (mg/g min¹/²), and $C$ is the intraparticle diffusion constant (mg/g). The constants $k_{dif}$ and $C$ can be obtained from the slope and intercept of the plot of $q_t$ versus $t^{1/2}$, respectively, (Table 3). The relative value of $C$ gives an idea about the boundary layer thickness, i.e. the larger the intercept value, the greater...
the boundary layer effect (Lin et al. 2011; Adeogun & Balakrishnan 2017).

Thermodynamic parameters

Thermodynamic parameters including $\Delta G^0$, $\Delta H^0$, and $\Delta S^0$ are estimated according to the following relations:

$$\Delta G^0 = -RT \ln K_d$$  
(21)

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$  
(22)

The equilibrium constant, $K_d$, is obtained from the value of $q_e/C_e$ at the equilibrium conditions in various temperatures. Van ’t Hoff plot of $\ln K_d$ versus $1/T$ gives a straight line with an intercept of $\Delta S^0/R$ and a slope of $\Delta H^0/R$ (Chakraborty et al. 2011; Aljeboree et al. 2015). The thermodynamic parameters for the removal of CV by EC technique are calculated (Table 4). The computed negative standard Gibbs free energies ($\Delta G^0$) values at different temperatures (30, 35, 40, 45, 50, and 55 ºC) reflect the spontaneous feasibility of the CV adsorption process. Also, the increase of $\Delta G^0$ value with the increase of temperature suggests the easier adsorption at lower temperatures. The positive value of entropy change ($\Delta S^0 = 0.41$ kJ/molK) shows the randomness of the adsorption system. Furthermore, the positive value of enthalpy change ($\Delta H^0 = 0.027$ kJ/mol) indicates the endothermic nature of CV adsorption process (Zehra et al. 2016).

The correlation matrix and multiple regression analyses

The correlation matrix and multiple regression analyses for different variables including contact time, pH, the mass of Fe coagulant, $\%$ Re, initial ($C_0$), and interval concentrations ($C_i$) are assigned using STATISTICA 6.0 (Table 5). The high correlation coefficients of correlation matrix confirms the dependence of $C_i$ on the contact time ($r = -0.5698; p = 0.000$), mass of Fe coagulant ($r = -0.5698; p = 0.000$), and pH value ($r = -0.5867; p = 0.000$). Also, the removal of CV is affected by contact ($r = 0.688; p = 0.000$) and interval times ($r = -0.7741; p = 0.000$) as well as the pH value ($r = 0.7546; p = 0.000$). Additionally, the mass of Fe coagulant is affected by the pH value ($r = 0.4791; p = 0.000$).

The multiple regression of the previously mentioned variables gives the following highly significant equation that represents the CV removal by EC:

$$\% \text{ Re} = -57.42 + 0.50 \ C_i + 0.44 \text{ pH} + 0.32 \ C_0 + 0.18 \ \text{contact time} \ (R = 0.93657; p<0.000)$$

CONCLUSIONS

The removal of CV by EC technique using bipolar iron electrodes under different variables (initial CV concentration, speed of agitation, number of electrodes, type and quantity of supporting electrolyte, temperature, and initial pH of solution) were studied. The results indicated that the best removal performance of the EC reactor was at pH 11 and the increase in the CV initial concentration elevated the required removal time. In contrast, the data indicated that the increase in iron electrode number reduced the removal time. The quantity of 0.5 g of NaCl supporting electrolyte was the most optimal
quantity that provides an excellent conductivity. Interestingly, relatively similar removal of CV was obtained during the usage of different supporting electrolytes (NaCl, Na₂CO₃, and Na₂SO₄). Relatively similar removals were achieved during the performance of the variable studied agitation speeds (250, 750, and 1,000 rpm). The possibility of the deposition of iron hydroxides on the electrode surface and the adsorption of CV on flocs during EC procedure were studied by different instrumental analyses (EDAX, SEM, and FTIR) and by kinetics and thermodynamic models as well as statistical calculations. EDAX, SEM, and FTIR analyses significantly improved the removal of CV from the bulk solution in a short time by its adsorption on the insoluble iron hydroxides of the flocs. The equilibrium data were described by three adsorption isotherms models: Langmuir, Freundlich, and Dubinin–Radushkevich (D–R). Furthermore, the calculations of D–R model reflected that the adsorption of CV on the flocs can be considered as a physical adsorption process. The mechanism of the adsorption CV was investigated by pseudo-first-order, pseudo-second-order, and intraparticulate diffusion models. The removal of CV by EC process followed the pseudo-second-order kinetics model, i.e. it depends on the CV and iron hydroxides concentrations. The thermodynamic parameters (ΔG°, ΔH°, and ΔS°) of the CV adsorption on the flocs at different temperatures (30, 35, 40, 45, 50, and 55 °C) referred to its spontaneous randomness endothermic nature. The correlation matrix and multiple regression analyses for different variables including contact time, initial pH, mass of Fe coagulant, % Re, initial and interval concentrations were performed by STATISTICA 6.0.

REFERENCES


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