Electrocoagulation using commercial grade aluminium electrode for the removal of crystal violet from aqueous solution

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ABSTRACT

The current research work studies the removal of crystal violet (also known as gentian violet), a kind of dye, from simulated wastewater by electrocoagulation using scrap aluminium roofing sheet as electrode in a batch electrochemical cell. Optimization of different operational parameters – pH, current density, time, initial concentration – was carried out experimentally. The equilibrium was attained at 1 hour and at pH 11. After suitable optimization, a removal of above 90% was achieved at an optimum current density of 20 mA/m². Also, the adsorption behaviour of crystal violet in electrocoagulation was also studied and the isothermal and kinetic models were proposed to be the Dubinin–Radushkevich model and pseudo-first order model. The mechanism involved during the process was suggested as chemisorption. The adsorption thermodynamic studies were a clear indication that the process is spontaneous and endothermic as well as thermodynamically favourable too. Both chemical and physical characterization of the flocs generated during the electrolysis was explained by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) respectively.

Key words | aluminium electrodes, crystal violet, electrocoagulation, FTIR, kinetics, SEM

INTRODUCTION

The major challenge being faced in the present world is for water and energy. Water resources are being contaminated due to both domestic and industrial wastes. Dye is a major constituent in many industries such as textile, paper and pulp, cosmetics, and tannery (Daneshvar et al. 2017; Gaurav et al. 2017; Orietta et al. 2018; Vanitha et al. 2018). The predominant release is from the textile industry due to the low efficiency of the dye fixing on fibres. Effluent releases from this industry are a kind of organic, coloured pollutant (Vanitha et al. 2018). The impact of such activities is to the aquatic environments, which also pose danger when consumed by humans and animals and cause irritation to sense organs and other associated health issues. Therefore it is equally important to look into suitable methods for removal of dyes.

Several biological, chemical and physical methods were chosen for wastewater treatment and in this context for dye removal (Essadki et al. 2008; Wafaa et al. 2010; Hamedreza et al. 2014; Dong et al. 2015; Fernanda et al. 2016). As most dyes are not degradable the first two types of methods are not suitable. Also, chemical oxidation or coagulation can lead to secondary water pollution. Several methods such as reverse osmosis, ultrafiltration, and photodegradation were found suitable for the removal process; still, they were not chosen since they were costly and the effluents did not meet the standards (Abideen & Ramesh 2017; Vanitha et al. 2018). Such issues led to advanced research on electrochemical methods.

Electrocoagulation is a different kind of wastewater treatment method that was found to have high removal efficiency. It is a simple and reliable technique with low sludge produced for disposal (Elazzouzi et al. 2018; Li et al. 2018; Omwene & Kobya 2018). Electrocoagulation has become one of the affordable wastewater treatment processes by reducing electricity consumption and miniaturization of the needed power supplies. In this, electric current is passed through water, and when conditions are favourable,
immediately coagulants are formed which is a result of the dissolution of the sacrificial anode (Ahmed et al. 2015).

The electrodes suitable for the EC process are mainly aluminium and iron as they are cheap, easily available and reactive too. In the case of aluminium, which is used in this study, the major reactions or mechanism is as follows.

Anode: \( \text{Al(s)} \rightarrow \text{Al}^{3+} + 3e^- \)  
(1)

Cathode: \( 3\text{H}_2\text{O} + 3e^- \rightarrow \frac{3}{2}\text{H}_2\text{(g)} + 3\text{OH}^- \)  
(2)

\( \text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \)  
(3)

The newly formed \( \text{Al(OH)}_3 \) flocs (amorphous) have large surface area, which helps in the adsorption of organic compounds which are soluble, and also helps to confine particles which are colloidal in nature. Flocs obtained can finally be removed by sedimentation or hydrogen floatation (Sundram et al. 2008; Subramanyan et al. 2010). Here we focus on the removal of crystal violet (also known as gentian violet) dye. Based on several studies conducted by various organizations it was found that gentian violet is carcinogenic (Jerold et al. 2017). It can cause mutations in rodents. Hence, the present study was aimed at removing crystal violet (CV) dye from synthetic wastewater using a commercial-grade electrode. The removal of the concerned dye by electrocoagulation with the aid of aluminium electrodes was investigated, as well as the impact of operational parameters: pH, the concentration of dye initially, reaction or electrolysis time, and current density.

**MATERIALS AND METHODS**

**Reagents and chemicals**

The process was carried out for the removal of CV dye. This was purchased from Nice Chemicals, India, and was in carbinal form and commercial grade with 70% purity. All other chemicals used in the experiment were purchased locally and were of 98% purity; these were used without further purification. The solution preparation was done using distilled water.

**Dye solution preparation and dye concentration determination**

CV is a basic cationic dye of triphenylmethane group. Preparation of stock solution of the dye was done (1,000 ppm) and diluted to concentrations ranging from 20 to 100 ppm with distilled water. The solution pH was set using 1 mol/L of sodium hydroxide or hydrochloric acid. The absorbance was determined at 580 nm for the various concentrated solutions or the working solutions. With the data obtained, a calibration curve was plotted.

**Design of experimental setup**

The experimental setup used for the electrocoagulation studies is as shown in Figure 1. The electrocoagulation setup consisted of an electrochemical cell, a DC power supply (50 V, 2 A) with connectors and aluminium electrodes. The electrodes were hung and dipped into 700 mL wastewater in a 1,000 mL glass beaker. A good mass transfer was achieved using a magnetic agitator (REMI 2MLH). A suitable choice of electrode material is essential as it affects the cell voltage. The electrode plates of size 7 cm × 5 cm × 0.5 cm were used and a distance of 30 mm between the electrodes was maintained. Since passivation of electrode takes place, it is necessary to wash the electrodes with dilute HCl/NaOH. Except for thermodynamic studies, the experiments were conducted at room temperature.

**Characterization of flocs**

The characterization studies were conducted to obtain the surface morphology by means of scanning electron microscopy (SEM) of the dye-loaded floc, and Fourier transform infrared (FTIR) spectroscopy (Thermo Scientific, Nicolet Avatar 370, India) was used to find out the involvement of functional groups in the dye-loaded floc. Floc spectra were collected at 500–4,000 cm\(^{-1}\).
Electrocoagulation experiment

The experiments were conducted at room temperature using aluminium strips as the electrode material to remove the CV from simulated wastewater. The electrocoagulation experiment was performed in the setup shown in Figure 1. Different operational parameters such as reaction/removal time, the initial concentration of dye, and pH, for the removal of CV were determined. After the process, the flocs formed were separated suitably from the solution by using a table-top centrifuge (Rotek M8E) at 2,000 rpm for 3 min. The supernatant collected was used to find out residual CV present in the solution with the help of a double beam UV-visible spectrophotometer (Perkin Elmer Lambda 650) at 580 nm (wavelength). The dye removal percentage was obtained as follows:

\[
\% \text{ Removal} = \left( \frac{C_0 - C_f}{C_0} \right) \times 100
\]

Here \( C_f \) and \( C_0 \) represent the final and initial concentration of CV (mg/L). Aluminium electrode consumption was estimated based on Faraday's law. The aluminium flocs generated adsorb the pollutant present in the solution. Thus, pollutant removal was represented by adsorption phenomena and the amount of pollutant adsorbed is given by

\[
q_e = \frac{(C_0 - C_e)V}{M}
\]

where \( V \) represents volume of CV solution (L), \( C_e \) and \( C_0 \) stand for equilibrium and initial concentration of CV (mg/L) respectively, \( M \) stands for the quantity of anode dissolved (g).

RESULTs AND DISCUSSION

Optimization

Reaction time impact on removal efficiency

During the process, aluminium hydroxide flocs were formed. The floc formation can be related to time of electrolysis and it was found that with an increase in reaction span the percentage removal also increases, and the concentration of aluminium ions generated increases with time, which is necessary for coagulation and removal of colour (Manisha et al. 2014). Hence, as the time ranges from 15 to 60 minutes the removal efficiency increased from 26.8% to 84% as shown in Figure 2.

Effect of initial concentration of dye on removal efficiency

The quantity of dye in effluent generally varies in concentration. Different dye concentrations over a range of 20 to 100 ppm were chosen. It was clearly seen that an increase in initial dye concentration actually decreased the removal percentage as shown in Figure 3. At 20 ppm the removal efficiency was high compared to other higher concentrations. In this experiment, all parameters except concentration were kept constant. From Figure 3, it is observed that at low concentration (20 ppm) the CV removal percentage was higher. It may be due to the availability of vacant active sites in the aluminium flocs at the initial stage of the electrocoagulation process. However, at higher concentration there is a repulsion of adsorbate due to the lack of binding sites (Sengil & Ozacar 2009; Subramanyan et al. 2010).

Effect of pH on removal efficiency

The pH has an inevitable role in dye removal. This was studied by adjusting the pH in the range of 3 to 11. At pH 11 much higher removal percentage is obtained. It was
found that based on the pH of the solution aluminium can exist in several forms. In the acidic zone up to pH 3, cationic species which are soluble were found to be predominant (Al³⁺ and Al(OH)₂⁺) and hence removal was found to be lower (Kamaraj et al. 2015). When pH is in the range of 4 to 9, monomeric and polymeric species of aluminium are formed. These get converted to Al(OH)₃ by complex polymerization and this is very useful in the removal process. At this stage, the solubility of flocs was also less. A higher removal is obtained at pH 11, as indicated in Figure 4. At this pH, at the cost of Al(OH)₃, there is a tendency to form anionic Al(OH)₄⁻ (Kamaraj et al. 2015). Since the dye is cationic this is favourable as the floc can adsorb the dye easily. Optimum time should be maintained in the process.

Impact of current density on removal efficiency

In an evaluation of the effect of current per unit area or current density, the CV removal was carried out at current densities up to 23 mA/cm². As current density was increased, removal percentage was also found to increase, from 78% to 95.3% as shown in Figure 5. A larger number of aluminium cations were generated as current density increased and the hydroxide formation rate was improved. Beyond 20 mA/cm², no significant removal efficiency was achieved. Hence 20 mA/cm² was found to be optimum in this work. The current density is directly proportional to the formation of Al flocs, which enhances the CV removal (Daneshvar et al. 2004, 2006; Modirshahla et al. 2007).

Support of electrolytes in dye removal

Electrolytes chosen in this study are sodium chloride (NaCl) and sodium carbonate (Na₂CO₃) while keeping a concentration of 0.35 mg/700 mL, maintaining the initial pH 11, 700 mL volume, 30 V voltage, interelectrode distance 3 cm. Higher removal rate was achieved with NaCl compared to Na₂CO₃. This is because Cl⁻ ions can get rid of the passivation layer on the electrode. This can also improve the oxidation reaction, producing more aluminium hydroxide. In the case of carbonate ions, there is a tendency for
these anions to adsorb onto the flocs and hence removal was less.

Characterization studies

The FTIR spectra of CV dye and the dye-loaded flocs (Figure 6) were studied. The similarity in the absorbance trend of both indicates that adsorbance of dye over the floc actually took place during the electrocoagulation (Shon et al. 2010; Subbaiah et al. 2016). The observed variations in the image are a clear-cut indication of the same. The highest peak is found in the 1,500–1,600 cm$^{-1}$ range, which corresponds to C=C=C symmetric stretch. Similarly, C=C=H asymmetric stretch (1,600–1,680 cm$^{-1}$), C=C=C symmetric stretch (3,000–3,100 cm$^{-1}$), and N-H bend (3,180–3,350 cm$^{-1}$), and N-H stretch (3,300–3,500 cm$^{-1}$) were also found (Jerold et al. 2017). The SEM image (Figure 7) is a clear indication of the adsorbance of CV over the flocs (Subbaiah et al. 2016; Naushad et al. 2017). The bright section in the image shows the presence of CV dye (Jerold et al. 2017).

Isotherm and kinetic modelling

Isotherm modelling

The dye in the solution during the electrocoagulation process was adsorbed onto the surface of aluminium hydroxide produced during electrocoagulation (Ramakrishnan & Subramanian 2015). The mechanism of adsorption was studied based on the two-parameter isotherm models of adsorption, viz. Langmuir, Temkin, Freundlich and Dubinin–Radushkevich; various constants as well as correlation coefficients for adsorption of CV onto the flocs were determined to identify the best fit model for the adsorption process (AL-Othman et al. 2012; Yasmine et al. 2014; Jerold & Sivasubramanian 2016).

Langmuir isotherm. The Langmuir adsorption model depicts a unimolecular layer formation of sorbate over the sorbent (Langmuir 1918). The assumption made is that the surface available for adsorption has sites with similar activity, each active site adsors one molecule, molecules which are adsorbed do not interact with each other and only monomolecular adsorption takes place. The mathematical representation of the model equation is as follows:

$$\frac{1}{q_e} = \frac{1}{K_L q_{\text{max}}} \left( \frac{1}{C_e} \right) + \frac{1}{q_{\text{max}}}$$  

(6)

Here $q_e$ indicates the quantity of CV adsorbed at equilibrium dye concentration $C_e$ (mg/g), $q_{\text{max}}$ represents the Langmuir constant, which is an indication of maximum mono-layer adsorption capacity (mg/g), and $K_L$ stands for the constant of binding affinity which is related to affinity towards sorbate (L/mg). The dimensionless constant $R_L$ represents the intensity of adsorption.

$$R_L = \frac{1}{(1 + K_L C_0)}$$  

(7)

$R_L$ value between 0 and 1 is favourable for adsorption. Also if $K_L > 0$, the adsorption system is favourable and here both these conditions were followed. A graph of $1/q_e$ vs $1/C_e$ was plotted to obtain $q_{\text{max}}$ and $K_L$, which are the intercept and slope of the line. Also, values of correlation
Here $n$ and $K_F$ (mg/g) stand for Freundlich constants, which can be related to adsorbent intensity ($n$) and adsorption capacity ($K_F$). They are also called the adjustable parameters ($n > 1$ suggests that adsorption is favourable). This model represents adsorption onto a surface which is energetically non-uniform. Thus heat of adsorption at the available sites are not uniform. Here $n$ value is greater than 1, which suggests that adsorption is favourable.

A graphical representation of $\ln q_e$ vs $\ln C_e$ is helpful in determining the Freundlich constants $K_F$ and $n$, as given in Table 1. The $R^2$ value is a clear indication that the process was not in accordance with this isotherm model.

**Temkin isotherm.** This adsorption isotherm takes into account the interaction between sorbent and sorbate in the sorption process. Unlike the Langmuir and Freundlich models, an assumption made in this adsorption model is that the free energy of adsorption is a function of the surface sites which have already adsorbed the molecules (Temkin & Pyzhev 1940). Mathematically the Temkin isotherm equation in its linearized form is as follows:

$$q_e = B \ln A + B \ln C_e$$

(9)

Here $B = RT/b$: $b$ stands for Temkin isotherm constant (J/mol), $T$ indicates absolute temperature (K), $R$ is known to be the universal gas constant (8.314 J/(mol K)). $B$ and $A$ are binding constants at equilibrium, which correspond to the heat of adsorption and maximum bonding energy respectively. The constants $A$ and $B$ shown in Table 1 were obtained from a plot of $q_e$ vs $\ln C_e$.

**Dubinin–Radushkevich (D-R) isotherm.** The D-R model is an indication of the diversity of surface energies. This model can identify the kind of adsorption process (Dubinin & Radushkevich 1947). It is more specific than the Langmuir model, which was derived based on ideal assumptions like all adsorption sites are equally strong, the absence of steric hindrance between whatever particles are being adsorbed and between the incoming particles, and, at the microscopic level, the surface is homogeneous.

The D-R is represented as follows:

$$\ln q_e = \ln q_s - K_d \varepsilon^2$$

(10)

$$\ln q_e = \ln q_s - 2BD \left( RT \ln \left( 1 + \frac{1}{C_e} \right) \right)$$

(11)

$$E = (BD^{-0.5})$$

(12)
Here $q_e$ represents the quantity of dye adsorbed at a concentration which is at equilibrium $C_e$ (mg/g). $K_{ad}$ is the D-R constant (mol$^2$/kJ$^2$), $q_s$ stands for isotherm saturation capacity theoretically obtained (mg/g), and $\varepsilon$ is the characteristic energy derived from D-R isotherm. When the heat of adsorption is between 20 and 40 kJ/mol, the process corresponds to physisorption, and between 40 and 400 kJ/mol, it corresponds to chemisorption. The energy of sorption, $E$, also offers a better understanding of the process. $E < 8$ kJ/mol and $8 < E < 16$ kJ/mol imply physisorption and chemisorption respectively. The plot of $\ln q_e$ vs $\varepsilon^2$ helped us to conclude that adsorption data were found to fit well with the D-R model, with the highest $R^2$ value as listed in Table 1.

**Kinetic modelling**

The removal of dye can be modelled by the adsorption process. Analysis samples were taken at regular time periods and at initial dye concentrations ranging from 20 to 100 ppm (Figure 8). The mechanism of the process of adsorption was studied using three different kinds of model, namely pseudo-first order, Elovich and pseudo-second order models. Among those models, the suitable fit was chosen based on statistical parameters.

**Pseudo-first order kinetics model.** The Lagergren first order model (Ho & McKay 2007) can be represented as given below

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} (13)

Here $q_e$ (mg/g) represents the CV concentration at equilibrium and $q_t$ (mg/g) is the concentration at time $t$ (min). The rate constant (first order) for adsorption is given by $k_1$ (min$^{-1}$). The rate constants of the reaction $k_1$ at several initial concentrations of dye were found from the linear plot of $\ln(q_e - q_t)$ vs $t$. The graph was found to have good linearity when compared to the other models studied here. Similarly, a better $R^2$ value is obtained. It is a clear indication that this model is suitable for the adsorption of CV over the aluminium hydroxide flocs.

**Pseudo-second order kinetics model.** A kinetic model which considers adsorption process taking place at equilibrium (Ho & McKay 1999) can be represented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (14)

Here $q_e$ is the quantity of CV adsorbed at equilibrium (mg/g), $k_2$ is the second order rate constant (g mg$^{-1}$ min$^{-1}$), second order. A graphical representation of $t/q_t$ vs $t$ at various initial concentrations of CV allows the values of constants $q_e$ and $k_2$ to be determined from the intercept and slope respectively, which are given in Table 2. When comparing the sum of square errors (%SSE) and $R^2$ values of the pseudo-first order and pseudo-second order models, the pseudo-first order is more acceptable.

**Elovich model.** This is a kinetic model which describes the process as being chemisorption, and implies that the adsorption rate decreases exponentially as time increases (Chien & Clayton 1980). It can describe the second order model considering the adsorption sites heterogeneous in a matter of energy. This model was not successful in providing a suitable mechanism for the adsorption process. Mathematical representation is given by:

$$q_t = \frac{1}{\beta} \ln(\alpha \beta * t)$$  \hspace{1cm} (15)

where $\alpha$ is the adsorption rate initially (mg/(g min)), $\beta$ is the desorption constant (g/mg). $1/\beta$ accounts for how many sites are available for adsorption. The $q_t$ vs $\ln t$ plot allows the determination of the $\alpha$ and $\beta$ values, which are the intercept and slope respectively. Better correlation coefficients, when compared to pseudo-second order kinetics, is achieved.
Statistical analysis

The suitable kinetic data fit was obtained by calculating the square of the correlation coefficient $R^2$ and $\%SSE$.

$$\%SSE = \sqrt{\frac{(q_{exp} - q_{cal})^2}{q_{exp}}} \times 100$$  \hspace{1cm} (16)

Here the number of data points is given by $N$. For best data fit the $R^2$ value should be higher and $\%SSE$ should be lower. Also, the theoretical $q_e$ value should be close to the experimental value. In this analysis, the pseudo-first order kinetic model is followed, which was finalized based on various parameters obtained as listed in Table 2.

Thermodynamic modelling

The thermodynamic parameters of enthalpy ($H$), entropy ($S$), and Gibbs free energy ($G$) were estimated using the following reaction.

$$\Delta G^0 = -RT \ln K_d$$  \hspace{1cm} (17)

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$  \hspace{1cm} (18)

where $K_d$ is the equilibrium constant obtained as $K_d = q_e/C_e$ calculated at different temperatures. A linear plot of $\ln K_d$ vs $1/T$ is obtained, from which $\Delta S^0$ and $\Delta H^0$ can be calculated, as listed in Table 3. $\Delta G$ is negative, which implies that the process is spontaneous. A positive value of enthalpy and entropy indicate that the process is endothermic and random respectively.

CONCLUSIONS

In the present study electrocoagulation was used for the removal of CV from wastewater using a commercial-grade scrap aluminium roofing sheet as the electrode. The results showed electrocoagulation is an effective option that can be chosen to treat textile dye effluent. The process was found to depend on factors such as pH, current per unit area or current density, the concentration of dye initially, and contact time. Best removal was achieved at pH 11. The presence of suitable salts and the increase in reaction time and current density helped to make the removal process more efficient, and above 90% removal was achieved. Equilibrium data were in accordance with the D-R isotherm, and the electrocoagulation kinetics went as per the pseudo-first order model. Finally, the obtained thermodynamic parameters were a clear indication of the fact that the process is spontaneous and endothermic. Hence it is suggested that this EC unit with scrap aluminium electrode is an inexpensive way to remove the CV dye from textile dye wastewater.

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