Modeling the Crystal Violet Kinetics Removal by Electrocoagulation Process for Wastewater Treatment

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Abstract. A batch reactor is used with an aluminum anode and a stainless steel cathode to decolorize crystal violet solutions by electrocoagulation. Optimization of operating parameters showed that for initial concentrations ranging from 5 to 100 mg/L, initial pH ranging from 6.72 to 5.43, current density of 250 A/m^2, conductivity of 4.27 mS/cm, and inter-electrode distance of 0.5 cm, a yield of 99.75% is achieved on reduction of color and 98.5% for reduction of chemical oxygen demand (COD).

Modeling of crystal violet elimination kinetics were tested. Results showed that homogenous second order kinetics and adsorption kinetics of pseudo second order can be applied. Various isotherms models were investigated. Freundlich isotherm gave better correlation with a coefficient of 0.989.

Variable Order Kinetic (VOK) model has been associated with Freundlich isotherm to take into account production efficiency of adsorbent over the time. Results showed through a statistical analysis that this approach provides a good correlation.

Keywords: Electrocoagulation crystal violet · Optimization · Modeling Adsorption

1 Introduction

Electrocoagulation (EC) is an electro-chemical technique that offers enhanced coagulation in which metal ions are generated on application of potential difference, which forms complex metal hydroxides for removal of impurities. The metal ions generated by anodic oxidation form metal hydroxides due to simultaneous electrolysis of water; these metal hydroxides have higher sorption capacity and thus favor enhanced removal; while generation of cathodic gases assist in electro floatation of impurities [1]. Crystal violet is a cationic dye and widely used as a purple dye for textiles such as cotton and silk. It provides a deep violet color for paints and printing ink. It is also used to dye paper [2].

Different technological approaches like adsorption, coagulation, biological treatment, advanced oxidation process, solar photocatalytic treatment [3], UV and ozone

treatment, membrane separation technologies etc. have been tested for the removal of such dyes. All the above processes have been found to have certain limitations in their applications.

Electrocoagulation offers some distinct advantages over existing processes such as ambient operability conditions, no threat of secondary pollution due to the absence of any extra chemicals. The EC process is attractive due to its simplicity of operation, control and effective removal efficiency [2].

In this study, decolorization of the crystal violet dye solution by electrocoagulation method has been investigated. The performance of electrocoagulation method for removing color from this dye solution has been evaluated. The operating parameters such as current density, pH, conductivity, inter electrode distance has been optimized. An important objective was to obtain a variable order kinetic VOK model that could make reliable prediction of the efficiency of the electrocoagulation process. The VOK model has the advantage of a good description of homogeneous kinetic aspects, adsorption isotherm and variation of the absorbent mass in known time.

So the various phenomena involved in the electrocoagulation process will be modeled by the VOK model associated with the appropriate adsorption isotherm. Interactions between adsorption strength and the initial concentration of crystal violet will be evaluated to predict the optimal conditions in the case of a set industrial use.

2 Materials and Methods

2.1 Characteristics of Crystal Violet

Crystal violet or gentian violet is a triarylmethane dye. When dissolved in water, the dye has a blue-violet color with an absorbance maximum at 592 nm and an extinction coefficient of 87,000 $M^{-1}cm^{-1}$. The color of the dye depends on the acidity of the solution. At a pH of 1.0, the dye is green with absorption maxima at 420 nm and 620 nm, while in a strongly acidic solution (pH = −1), the dye is yellow with an absorption spectrum maximum at 420 nm. Different colors are a result of the different charged states of the dye molecules. In the yellow form, all three nitrogen atoms carry a positive charge, of which two are protonated, while the green color corresponds to a form of the dye with two of the nitrogen atoms positively charged. At neutral pH, both extra protons are lost to the solution, leaving only one of the nitrogen atoms positive charged [4].

2.2 Experimental Device

The experiments were conducted in a cell equipped with an anode of aluminum and a stainless steel cathode. The system operates in batch mode. A VoltaLab PGZ 100 potentiostat type which can provide up to 1 A is used to power the cell.

The operating parameters are optimized by varying respectively: sample volume of 100 mL; the initial concentration from 5 to 100 mg/L; the current density from 100 to 300 A/m² (for an electro-active surface of 14 cm², the current is varied from 0.1 to 0.4 A); the initial pH of 3 to 9 (by addition of NaOH and HCl solutions at 0.1 N); the

initial conductivity of 0.9 to 4.27 (by addition of a mass of NaCl ranging from 0.1 to 1 g/L); the inter-electrode distance (ied) of 0.25 to 1.5 cm.

Dye concentration was spectroscopically determined using the Beer-Lambert law (Absorbance = $\varepsilon \times \ell \times C$) applied at 592 nm, where ε is the molar absorptivity, ℓ is the solution thickness and C the CV concentration. The absorbance are measured by a spectrophotometer SPECORD 250 PLUS.

2.3   Electrode Reactions

Aluminum electrodes are usually used as sacrificial anodes, and their electrochemical dissolution allows generation of the corresponding cations according to the reaction (1).

$$Al \leftrightarrow Al^{3+}_{(aq)} + 3e^- \qquad (1)$$

Stainless steel plates involved as cathode producing gaseous hydrogen (2).

$$2H_2O + 2e^- \leftrightarrow 2OH^-_{aq} + H_{2(g)} \qquad (2)$$
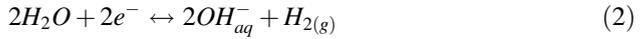
The electrogenerated metallic ions (here Al^{3+}) are hydrolyzed in the electrochemical cell to produce aluminum hydroxide according reactions (3)

$$Al^{3+}_{(aq)} + 3OH^- \leftrightarrow Al(OH)_{3(s)} \qquad (3)$$
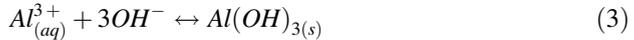
$Al(OH)_{3(s)}$, so called coagulants, can interact with charged (or not charged) species of dye particles in the water and adsorbs them; in fact $Al(OH)_{3(s)}$ neutralizes the electrostatic charges on disperses particles to reduce the electrostatic interparticle repulsion so that the van der Waals attraction predominates, thus enhancing agglomeration; consequence is that flocks appears, which, thanks to the gaseous hydrogen produced at the cathode, float. It is believed that the main pollutant removal mechanism observed during electrocoagulation is adsorption and entrapment onto the amorphous aluminum hydroxide precipitate formed. Except aluminum consumption, the electro-coagulation processes do not require the addition of any chemicals.

2.4   Modeling Experiments

Based on the optimized parameters, we performed treatments on solutions with variable initial concentrations of crystal violet. The absorbance is measured before and after treatment to evaluate the percentage of fading. The equilibrium data such as the concentration and the adsorption capacity is achieved when the estimated discoloration percentage is 98, which corresponds to a quasi-stability of the final concentration. These equilibrium data are used to test the different adsorption isotherms. In determining the adsorption capacity, the samples are filtered when any of the balance is judged reached. After filtering the slurry obtained is dried in an oven and weighed. It is believed that the adsorption capacity is equal to the mass of dye adsorbed on the mass of adsorbent.

The electrodes were weighed before and after each treatment to assess the total mass of consumed aluminum. This allows calculating the Faraday efficiency (φ_c).

To evaluate the efficiency of the formation of aluminum hydroxide (φ_{Al}), the amount of dissolved aluminum in the treated and filtered solution was determined with a multiparameter bench photometer from Hanna Instruments HI83099.

2.5   Model Development

2.5.1   Kinetics and Adsorption Models

First and second order reaction kinetics were used to study the decolorization kinetics of crystal violet.

The contaminants are usually adsorbed at the surface of the metal hydroxides generated during the electrocoagulation process. In order to identify the mechanism of the adsorption process, it is important to establish the most appropriate correlation for the equilibrium curves. Isotherm models with two and three parameters have been considered to establish the relationship between the amounts of crystal violet adsorbed onto the aluminum hydroxides and its equilibrium concentration in the aqueous solution containing crystal violet.

Equilibrium adsorption isotherm data were analyzed according to the Langmuir, Freundlich, Fritz–Schlunder, Radke–Prausnitz and Toth models.

2.5.2   Variable Order Kinetic: Model Development

VOK model is based on a combination of three laws:

- the faraday law;
- the adsorption model static.

A constant courant density fade is proportional to the production of aluminum.

Faraday efficiency describes the efficiency with which charge (electrons) are transferred in a system facilitating an electrochemical reaction.

Faraday's law is defined:

$$m_{theo} = \frac{n \, I_{theo} t}{F} * \frac{M}{z} \tag{4}$$

m_{theo}: Mass of aluminum obtained for a fixed current I_{theo}
t: duration of treatment (min)
F: Faraday constant 96500 C
M: Molar mass of aluminum
z: electrical charge z = 3

Faradic and aluminum yields are given by φ_c and φ_{Al} respectively:

$$\varphi_c = \frac{[Al]_T}{[Al]_{theo}} \tag{5}$$

$$\varphi_{Al} = \frac{[Al]_T - [Al]_{dis}}{[Al]_T} = 1 - \frac{[Al]_{dis}}{[Al]_T} \tag{6}$$

$[Al]_T$: Total concentration of aluminum obtained by weighing the electrodes before and after treatment

$[Al]_{theo}$: Theoretical concentration of aluminum obtained from the faraday law

Mameri et al. [5] show that in the electrocoagulation process producing Al^{3+} is a limiting factor for flock formation. When the current density is 200 A/m^2 the adsorption reaction is instantaneous.

The change in the dye removal rate is proportional to the adsorbent the production rate according to the following relationship:

$$-\frac{d[C]}{dt} = \frac{1}{2} \boldsymbol{\varphi_{Al}} * \varphi_c * \frac{n*I_{theo}}{F} * \frac{M}{zV} * \Gamma \tag{7}$$

Γ represent the adsorption capacity which is depending on the model adopted.

Table 3 gives the expressions of different VOK equations depending on the adsorption isotherm model chosen.

3 Results and Discussion

3.1 Optimization of Operating Parameters

pH of the solution plays an important role in electrochemical and chemical coagulation process [5].

Under certain conditions, various complex and polymer compounds can be formed via hydrolysis and polymerization reaction of electrochemically dissolved aluminum ions. Hence, experiments were conducted to study the effect of pH on the crystal violet removal.

The results obtained are shown graphically in Figs. 1 and 2 for 100 mg/L crystal violet initial concentration.

Figure 1 shows the variation of initial pH observed during experiments. We note that whatever the initial pH of the solution, the pH stabilizes around 8 after 5 min of treatment.

Indeed, as shown in Eq. 5, the reduction of water at the cathode results in a constant production of hydroxides ions which maintains the pH to a basic level. In addition, the electrocoagulation process is characterized by a buffer effect and is observed when the aluminum hydroxide begins to form.

Figure 2 shows that for very acid initial pH (pH = 3) and for the neutral and basic pH (pH = 7 and pH = 9), the removal rate of the crystal violet is quite slow. For initial pH = 5, the speed improves. To an initial solution of 100 mg/L, pH (no change) is 5.43. This value pH gave the best removal rate.

The effects of pH of the initial solution on the electrocoagulation process are related to the solubility of aluminum hydroxide as a function of pH.
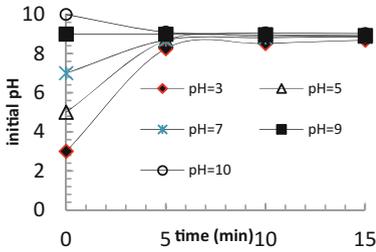
Fig. 1. Evolution of initial pH over time i = 250 A/m^2; ied = 0.5 cm; conductivity = 4.27 mS/cm; initial concentration = 100 mg/L
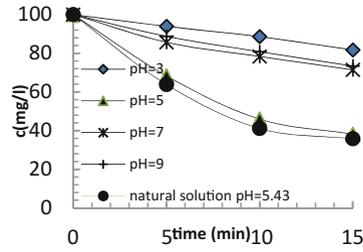
Fig. 2. Evolution of crystal violet concentration over time with different initial pH; i = 250 A/m^2; ied = 0.5 cm; conductivity = 4.27 mS/cm; initial concentration = 100 mg/L

The hydrolysis of aluminum either released from the electrodes in electrocoagulation and the adsorption of the hydrolysis products on the particles are greatly affected by the varying pH of the suspension. Figure 3 shows the solubility diagram for aluminum hydroxide Al(OH)$_{3(s)}$, assuming only monomeric species. Non hydrolyzed Al^{3+} and cationic hydrolysis products, Al(OH)$^{2+}$ and Al(OH)$_2^+$ are the dominant species in solution at pH values less than 5. The cationic hydrolysis products, rather than the non hydrolyzed Al^{3+}, are known to adsorb strongly on negatively charged particles leading to charge neutralization, and also to charge reversal with excess amount of aluminum ions [6]. This explains the low crystal violet removal efficiencies due to electrical repulsion between the particles at pH values less than 5 in the case of electrocoagulation. At pH values 5–8.5, especially with excessive aluminum concentration, amorphous aluminum hydroxide precipitation becomes important. This precipitation may occur either on the surface of quartz particles or the hydroxide precipitates formed in the bulk may attach to the particles. At pH values higher than 8.5, the aluminate ion, Al(OH)$_4^-$, becomes the predominant species which cannot be adsorbed on the negatively charged quartz particles. Hence, the turbidity removal efficiencies deteriorate.

In an electrocoagulation process, when the distance of the electrodes increases, the electrical current is decreased since the potential drop is proportional to the inter-electrode distance. Reducing this distance is of great importance for reducing the electrolysis energy consumption especially when the conductivity is low. For this reason, investigation of this parameter is helpful. When the distance of the electrodes increased from 0.25 to 1.5 cm, the removal rate of the crystal violet progressively decreases when the inter-electrode distance increases. When the inter electrode distance is less than 0.5 cm (ied = 0.25) that speed decreases due to overvoltage phenomena. These results are shown in Fig. 4.

Current density is the one of the important factors in electrochemical processes as it determines the coagulant dosage rate, bubble production rate, size and growth of the flocks, which can affect the efficiency of the electrocoagulation.
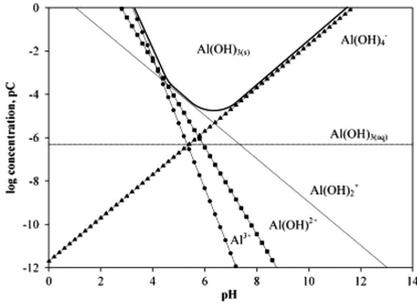
Fig. 3. Solubility diagram of aluminum hydroxide $Al(OH)_{3(s)}$ considering only monomeric aluminum species
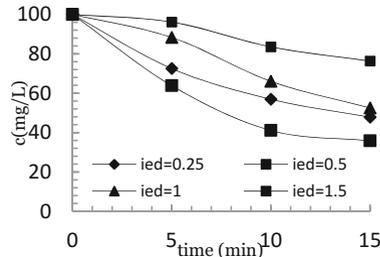
Fig. 4. Evolution of crystal violet concentration over time with different inter electrode distance; i = 250 A/m²; pH = 5.43; conductivity = 4.27 mS/cm; initial concentration = 100 mg/L

Figure 5 shows that the current density between 100 and 200 A/m², the removal rate of the crystal violet is quite low. When a current density of 250 A/m² is imposed, this speed is significantly improved.

NaCl is usually employed to increase the conductivity of the solutions to be treated by electrocoagulation. Increase in salt concentration, increases the ion concentration in the solution and hence reduces the resistance between the electrodes. Increase in salt concentration decreases the cell voltage at constant current density and reduces the power consumption in electrolytic cells.

To see the effect of solutions conductivity on dye removal various experiments were performed using NaCl as the electrolyte in the range of 0.2–1.0 g/L. Figure 6 shows the results.
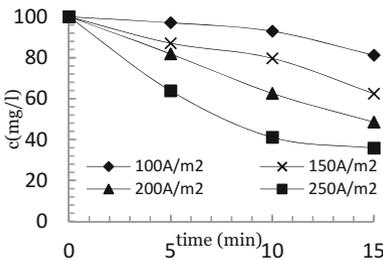
Fig. 5. Evolution of crystal violet concentration over time with different current density; ied = 0.5 cm; conductivity = 4.27 mS/cm; initial concentration = 100 mg/L; pH = 5.43
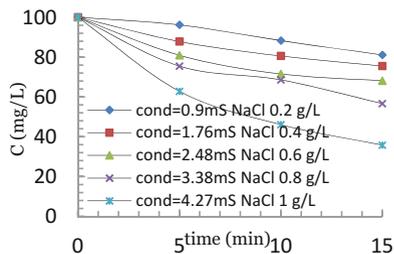
Fig. 6. Evolution of crystal violet concentration over time with different initial conductivity; i = 250 A/m²; ied = 0.5 cm; initial concentration = 100 mg/L; pH = 5.43

When the initial conductivity of the solution increases, the removal rate of the crystal violet increases also. For NaCl mass of 1 g/L (initial conductivity = 4.27 mS/cm) a very significant degradation is observed which does not go beyond.

3.2 Electrocoagulation Kinetics

Kinetics studies of treatment process have important role in determining the hydraulic retention time in any reactor system to achieve desired removal [7]. So, rate constant is very significant in the design of wastewater treatment units. It is very essential to know the type of reaction rates for design a wastewater treatment unit. Rate of reaction describes the rates of change in concentration of reactant per unit time.

The kinetics of first and second order have been studied in comparison with experimental results. Figures 7 and 8 show the results obtained.
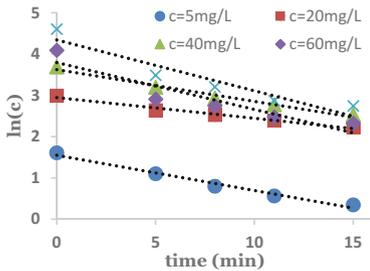
Fig. 7. Linear representation of the first order kinetics with variable initial concentrations: i = 250 A/m^2; ied = 0.5 cm; cond = 4.3 mS/cm y5 = −0,0855x + 1,5505 R^2 = 0,9823; y20 = −0,0502x + 2,9482 R^2 = 0,9796; y40 = −0,077x + 3,6238 R^2 = 0,9812; y60 = −0,1136x + 3,7959 R^2 = 0,8614; y100 = −0,1231x + 4,3433 R^2 = 0,8986
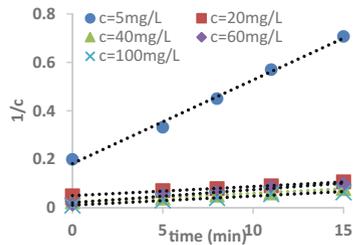
Fig. 8. Linear representation of the second order kinetics with variable initial concentrations: i = 250 A/m^2; ied = 0.5 cm; cond = 4.3 mS/cm; y5 = 0,0345x + 0,1827 R^2 = 0,9935; y20 = 0,0038x + 0,0505 R^2 = 0,997; y40 = 0,0036x + 0,0239 R^2 = 0,9963; y60 = 0,0054x + 0,0216 R^2 = 0,9758; y100 = 0,0037x + 0,0112 R^2 = 0,9844

The results show that for concentrations up to 40 mg/L, the first and second order kinetics are valid. When moving at high concentrations (60 and 100 mg/L), the kinetics of second order is most significant coefficients with higher correlation to 0.97.

The homogeneous kinetic ignores adsorption phenomena involved in the electrocoagulation process. To analyze these effects, the pseudo second-order kinetics was studied.

Considering the results obtained with the second order kinetics and considering that the pollutant is generally adsorbed at the surface of the flocks generated electrochemically, critical analysis of the electrocoagulation of crystal violet dye reveals that there are two separate processes taking place [7]:

– electrochemical process through which the metal flocks are generated;
– physico-chemical process through which the effluents are adsorbed on the surface of the flocks.

The present experimental data have been verified with the pseudo-second order model.

This model supposes that two reactions occurs either in series or in parallel occur; the first one is fast and reaches equilibrium quickly and the second is a slower reaction that can continue for a long period of time [8]. Figure 9 shows the result obtained.

Different regression coefficient obtained with the pseudo second order kinetics are shown in Table 1.

Figure 9 shows the experimental results which confirm the homogeneous kinetics and indicate that crystal violet adsorption follows pseudo second order. Table 1 shows that adsorption coefficients obtained experimentally are of the same order of grader than those obtained with the model.

Fig. 9. Linear representation of the pseudo second order adsorption kinetics with variable initial concentration $i = 250$ A/m^2; ied = 0.5 cm; conductivity = 4.3 mS/cm;   y20 = 0,1108x − 0,6431   R^2 = 0,9979;   y60 = 0,0367x 0,3033 R^2 = 0,9912; y100 = 0,0325x − 0,3281 R^2 = 0,9932
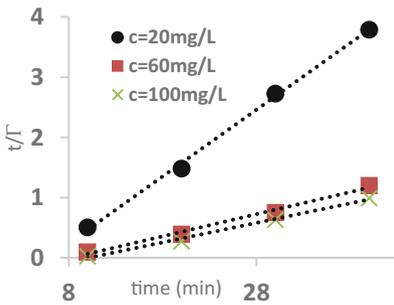
Table 1. Adsorption kinetic model parameters obtained using pseudo second order model

Initial crystal violet concentration (mg/L)	20	60	100
k_3	0.0194	0.0044	0.0032
$\Gamma_{e\text{the}}$	9.025	27.25	30.77
$\Gamma_{e\text{exp}}$	10.98	26.55	30.33
R^2	0.9979	0.9912	0.9932

The effect of the initial concentration on the rate constant shows that the reaction rate constant (k_3) decreased significantly for increasing initial crystal violet concentrations (Table 1). This may be due to the fact that for a given charge, the number of hydroxides flocks generated was insufficient and an increase in the ratio of the initial concentration to the amount of flocks generated resulted in a reduction of the yield of crystal violet removal [9].

3.3 Adsorption Isotherm

Figures 10 and 11 give the results obtained with the representation of the linear model of Langmuir and Freundlich.

$$\frac{\Gamma_e}{\Gamma_{maxL}} = \frac{K_L C_e}{1 + K_L C_e} \tag{8}$$

$$\Gamma_e = K_F C_e^{1/m_F} \tag{9}$$

where Γ_e(mg g^{-1}) is the adsorbed amount at equilibrium, C_e is the equilibrium concentration of the adsorbate (mg.l^{-1}), K_L is Langmuir equilibrium constant and Γ_{maxL} the maximum adsorption capacity (mg g^{-1}).

K_F is Freundlich constant and m_F is the heterogeneity factor. The K_F value is related to the adsorption capacity; while the $1/m_F$ value is related to the adsorption intensity.

The Langmuir model assumes a monolayer deposition on a surface with a finite number of identical sites (Mckay et al. 1982) [10]. It is well known that the Langmuir equation is valid for a homogeneous surface.
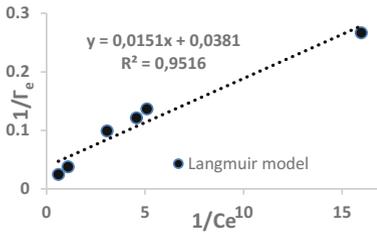
Fig. 10. 1/Γe = f(1/Ce) Langmiuir isotherm   ied = 0.5 cm;   Conductivity = 4.3 mS; i = 250 A/m^2 $\Gamma_{maxL} = 26.24$ and K$_L$ = 2.524
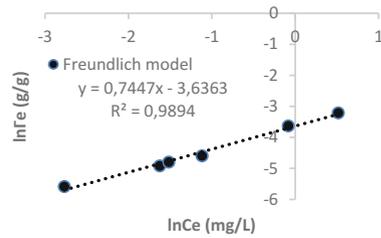
Fig. 11. ln(Γe) = f(lnCe) Freundlich isotherm   ied = 0.5 cm;   Conductivity = 4.3 mS; i = 250 A/m^2 1/m$_F$ = 0. K$_F$ = 0.02635 L/mg

The Freundlich adsorption isotherm typically fits the experimental data over a wide range of concentrations. This empirical model includes considerations of surface heterogeneity and exponential distribution of the active sites and their energies.

The Freundlich constant K$_F$ is a measure of the adsorption capacity. It represent the content of pollutants in the adsorbent at equilibrium. A high K$_F$ reflects a significant adsorption capacity. Constant 1/m$_F$ is an index of affinity crystal violet to aluminum hydroxide. It is noted in the literature that this parameter is very often between 0.70 and 0.95 [10].

The regression lines obtained with the two models will allow to evaluate the constants Γ_{maxL} , K$_{L,}$m$_F$, K$_F$.

Figures 10 and 11 showed that the correlation coefficient R^2 substantially equal to 0.99, the Freundlich constant $K_F = 26.35$ L/mg and the value of the intensity of the adsorption $1/mF = 0.74$ obtained with the Freundlich model indicates that this model is most suitable to describe the phenomena involved in the bleaching solutions crystal violet by the process of electrocoagulation.

The models of Langmuir and Freundlich can be easily linearized to determine the constants (Γ_{maxL}, $K_{L,}m_F$, K_F). This linearization is however not as evident in other models tested. And to assess the parameters of these models, the adsorption capacity of the values obtained experimentally are subject to the tool solver excel. The solver tool allows giving these approximate values to different parameters (A, B, α, β, K_T, K_{RP}, m_{RP}, m_T, Γ_{maxRP}, Γ_{maxT}) to have a resolution models with theoretical adsorption capacities close to those obtained by experiments.

The data obtained in Table 2 are used in the numerical calculation of Matlab software to analyze the different models in combination with a variable order kinetics.

3.4   Variable Order Kinetic Model (VOK)

The variable order kinetic (VOK) gives a description of the electrocoagulation process taking into account the variation of the mass of adsorbent over time. This model has been tested successfully in the case of the removal of fluoride electrocoagulation. Hu et al. [11]. showed that the model successfully describes the fluoride removal reaction, except in a system in which the initial concentration of the acid is less than the initial fluoride concentration.

Table 2. Adsorption isotherm constants for crystal violet

Parameters	Langmuir	Freundlich	Fritz-Schlûnder	Radke-Prausnitz	Toth
Γ_{max} (mg/g)	26.24	–	–	61.1998	0.1256
K (l/mg)	2.524	0.02635	–	0.8221	0.3483
A (l/g)	–	–	0.02927	–	–
B (l/g)	–	–	0.04285	–	–
α	–	–	0.8576	–	–
β	–	–	2.1359	–	–
m	–	1.3428	–	0.5276	0.9054

Essadki et al. [12] indicated that when the evolution of fluoride content was independent of stirring speed, experimental results shows that the kinetics of fluoride removal could be modelled using a variable-order-kinetic (VOK) approach coupled with a Langmuir–Freundlich adsorption model.

These different forms that can take the crystal violet in solution are a model based only on the homogeneous kinetics does not identifies all phenomena involved. On the other hand, the adsorption isotherms do not take into account the variation of the mass of adsorbent which is proportional to the amount of dye removed. VOK. The model appears to be best suited to study complex dyes such as crystal violet.

Figure 12 shows that for low concentrations (c = 5 mg/L) the different models used describe the experimental results but the Freundlich model provides a more accurate superposition of theoretical and experimental data. Indeed is low when the concentration monolayer adsorption is easily verifiable because the amount of adsorbent is produced largely sufficient.

When the crystal violet concentration is relatively high (100 mg/L), Fig. 13 shows that the model Langmuir and Fritz Schlünder are not very suitable. Indeed the solute content of the solution begins to constitute a brake for a monolayer adsorption with energetically equivalent sites.
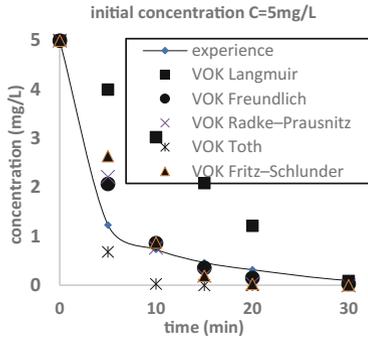
Fig. 12. Matlab resolution for different models with low normalized concentrations ied = 0.5 cm;   Conductivity = 4.3 mS;   i = 250 A/m^2, C_0 = 5 mg/L
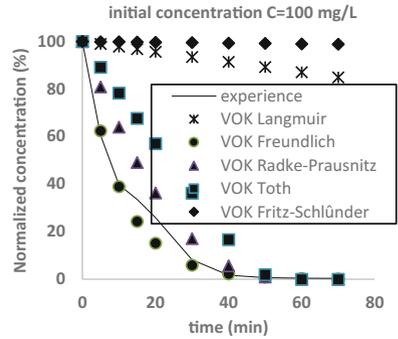
Fig. 13. Matlab resolution for different models with high normalized concentrations ied = 0.5 cm;   Cond = 4.3 mS;   i = 250 A/m^2, C0 = 100 mg/L

3.5   Statistical Analysis

Statistical analysis was performed according to the method called "student test on two samples" [13].

t_{obs} is called the test statistic and is expressed as follows:

$$t_{obs} = \frac{\bar{x} - \bar{y}}{s_{x-y}} \tag{10}$$

$$s_{x-y} = \sqrt{\frac{s_p^2}{n_x} - \frac{s_p^2}{n_y}} \tag{11}$$

$$s_p^2 = \frac{\sum_1^{n_x}(x - \bar{x})^2 + \sum_1^{n_y}(y - \bar{y})^2}{(n_x - 1) + (n_y - 1)} \tag{12}$$

$\bar{x}$ average experimental values for a given initial concentration; $\bar{y}$ averaging the values obtained by modeling for a given initial concentration; $s_{\bar{x}-\bar{y}}$ estimator of the standard deviation of the difference $\bar{x} - \bar{y}$; s_p^2 total variance of the experimental values and model values; n_x number of experimental data; n_y number data obtained by modeling.

Following a risk percentage α, the Student test define a critical value t_α which depends on the number of group data and the total degree of freedom (df). The value t_α is obtained from the student table [14].

So for 2 data groups (experience and model) and a total variance based on the number of samples in each model, Table 3 gives the results obtained. The risk we have chosen is the same for all models its value is $\alpha = 0.05$.

Decision is made as follow: if $|t_{obs}| > t_\alpha$ it is considered that experimental values and the values obtained with the model are considered too different to the model to be upheld.

Table 3 confirms the results seen in Figs. 12 and 13. For low, concentrations the values observed in the different models are less than the values. All the isotherms can be validated in this range of concentrations with a better result for Freundlich isotherm. For higher concentrations, Freundlich isotherms, RadkePrausnitz and Toth verify experimental results with ever better correlation for the Freundlich isotherm.

At the two extremes of concentrations studied, the model Freundlich works best. This shows that the VOK model in association with Freundlich isotherm best describes the electrocoagulation process in the case of crystal violet removal.

The low student has been expanded to different initial concentrations in relation to the Freundlich isotherm and variable order kinetic (VOK). Table 4 gives the results obtained.

Table 3. Statistical analysis with different models

Model	Initial concentration = 5 mg/L				Initial concentration = 100 mg/L			
	ddl	α	t_α	$|t_{obs}|$	ddl	α	t_α	$|t_{obs}|$
Langmuir	14	0.05	1.761	1.157	18	0.05	1.734	6.29
Freundlich	10	0.05	1.812	0.0127	18	0.05	1.734	0.142
RadkePrausnitz	14	0.05	1.761	0.0361	18	0.05	1.734	0.530
Toth	14	0.05	1.761	0.3297	18	0.05	1.734	1.09
Fritz-Schlûnder	14	0.05	1.761	0.1103	18	0.05	1.734	6.941

The results follow a relationship between the intensity of the adsorption and the initial concentration. The parameter 1/mF in which the model Freundlich represents the order of the reaction is variable depending on the initial concentration (Fig. 14).

The obtained correlation coefficient shows a linear relationship between the intensity of adsorption and the initial concentration and assumes that different sites with several adsorption energies are involved. These results show that the VOK model can be used to the kinetic removal adsorption of crystal violet in wastewater by electrocoagulation.

Table 4. Statistical analysis with VOK Freundlich model for different initial concentrations

Initial concentration (mg/L)	5	10	15	20	60	100
Parameters	VOK Freundlich					
ddl	10	8	8	12	14	18
α	0.05	0.05	0.05	0.05	0.05	0.05
t_α	1.812	1.860	1.860	1.782	1.761	1.734
$|t_{obs}|$	0.0127	0.0325	0.0214	0.3306	0.1587	0.142
m_F	1.7818	1.8428	1.9028	1.9928	2.5728	3.3228
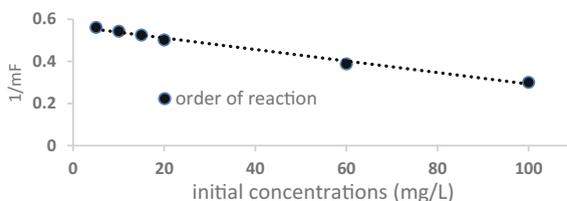
Fig. 14. Linear representation of the Freundlich coefficient as a function of the initial concentrationsied = 0.5 cm;   Conductivity = 4.3 mS;   i = 250 A/m^2 y = −0,0027x + 0,566 R^2 = 0,9918

4   Conclusion

This work was a first step to improve the knowledge regarding the modeling of the kinetic of crystal violet dye removal by electrocoagulation (EC) with aluminum as sacrificial electrodes and stainless steel as cathode. The EC method applied in this study provided a sensitive, rapid and reliable technique for the removal of crystal violet in a synthetic wastewater. By applying linear methods, the mechanism of EC was modeled using second order, and pseudo-second order models and it was shown that the EC kinetic followed pseudo-second order kinetic and that the reaction rate constant was influenced by the initial concentration. The metal hydroxides generated by EC can efficiently remove crystal violet by adsorption, and the EC process was modeled using adsorption isotherm models, showing that the Freundlich model accurately described experimental data. The use of the Variable Order Kinetic (VOK) model which Freundlich equation and the statistical analysis has shown that this model fitted well the experimental data with a correlation coefficient of 0.9894. The elimination kinetics of crystal violet by electrocoagulation is therefore variable order kinetics.

The linear relationship between the initial concentration and the intensity of the adsorption confirms the variability of the order of the reaction and shows efficient adsorption regardless of the initial concentration.

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