Kinetic and Equilibrium studies of the Removal of Crystal Violet from Aqueous Solution using Modified Carbon

Hala A. Kiwaan*, M.R. Mostafa, Hala El-Ghobashy, Elhossein A. Moawed

Abstract—. The adsorption of crystal violet dye (CVD) from aqueous solution onto modifier carbon with p-aminophenol (AC-COOAP) was studied using batch process. The maximum adsorption of CVD (~100%) was obtained in a pH range of 6–10 with a shaking time of 60 sec. The kinetics were best described by the pseudo-second-order model (R^2 = 0.999). The adsorption capacity of AC-COOAP was 46.9 mg/g for CVD. The isotherms exhibit good correlation (R^2 = 0.999) with a zero intercept (7×10^{-4}). Successful application was achieved for wastewater samples.

Index Terms— Adsorption; Crystal violet; Carbon modifier; Kinetics; Equilibrium.

1. Introduction

Basic dyes were used extensively in the textile, leather, cosmetics, and dyeing industries [1-5]. These dyes are carcinogenic and possess a serious hazard to aquatic living organisms such as severe damage to the kidneys and central nervous system [6-8]. In particular, basic dyes, such as triphenylmethane, are considered to be one of the more problematic classes of dyes. Crystal violet dye (CVD) was used in biological staining and dermatological agent. Also, it was used to prevent the formation of parasites and fungus [9, 10]. CVD was highly soluble in water, therefore, the effluents of this dye have a negative impact on the environment, especially in drinking water and agriculture. Therefore, the removal of dyes from effluents prior to mixing with natural water is very important.

Several methods were used to overcome the removal of dyes from wastewater, e.g. photodegradation, coagulation and ozonation. Adsorption is one of the most efficient methods of removing dyes from wastewater [11-16]. The adsorption processes yield the best results because they can remove different types of coloring materials, especially if inexpensive adsorbents are available. Different sorbents have been used to remove dyes from wastewater [17, 18].

The aim of this study is to develop a new, simple, cheap and rapid removal procedure for crystal violet dye from wastewater using the modified carbon. The carbon modified with p-aminophenol (AC-COOAP) is inexpensive with good stability and a high sorption capacity for the removal of crystal violet from aqueous solutions. In addition, AC-COOAP can be recycled many times for the removal of CVD from wastewater without significantly decreasing its capacities. The removal behavior of AC-COOAP was studied. The optimal conditions for the removal of CVD. Kinetic, thermodynamic and equilibrium data were obtained [19-23].

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2. Experimental

2.1. Reagents

The crystal violet dye was prepared from commercial grade. A 0.5 g/L stock solution of the CVD was prepared by dissolving 0.05 g of CVD in 100 mL of distilled water.

2.2. Apparatus

All spectrophotometric measurements were performed on a JASCO (V-630UV-VIS Spectrophotometer, Japan). The pH measurements were carried out using a Jenway 3510 pH-meter (Beacon Road, Stone, Staffordshire, ST15 OSA, UK). Scanning electron microscope analysis was carried out using the JEOL model JSM-6510LV apparatus, manufactured in the USA. IR spectra were carried out using KBr disc on a JASCO FTIR-410 spectrometer in the 4000–400 cm^{-1} region.

2.3 Recommended procedures

The sorption of CVD onto AC-COOAP was investigated using a batch experiments. 0.1 g of AC-COOAP, was added to 25 mL of the CVD solution, then the solution was shaken, filtered and the remaining dye concentration in solution was analyzed. The effects of pH, contact time, initial CVD concentration were further investigated.

The percentage of CVD removal (%E) and sorption capacity (Q) were calculated from the following equations:

$$\%E = ((C_0 - C_e)/C_0) \times 100 \quad (1)$$

$$Q = C_o\, E\, V/m \quad (2)$$

Where, C_o is the initial CVD concentration, C_e is the concentration of CVD in solution at equilibrium, V is the volume of dye solutions and m is the mass of sorbent.

3. RESULTS AND DISCUSSION

3.2 Optimum conditions for removal of CVD

3.1.1 pH

The effect of the pH on the removal of CVD using AC-COOAP was studied (Fig. 1). The removal rates of CVD onto AC-COOAP increases from 2% to 100% by increasing the pH values from 1 to 6. The maximum adsorption of CVD (~100%) was obtained at a pH range of 6–9. The adsorption percentage was decreased to 80% at pH >12.

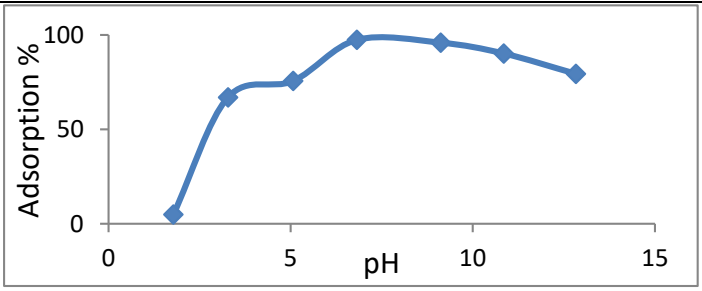


Fig.1 Effect of pH on CVD removal using AC-COOAP

3.1.2 Contact time

The effect of shaking time on the removal of CVD using AC-COOAP was tested (Fig. 2). The removal rate of CVD was initially rapid, where 70% of the total amount CVD were removed within 30 sec. Then the rate became slower with increasing in time until reaching 98%-100% at 60 sec.

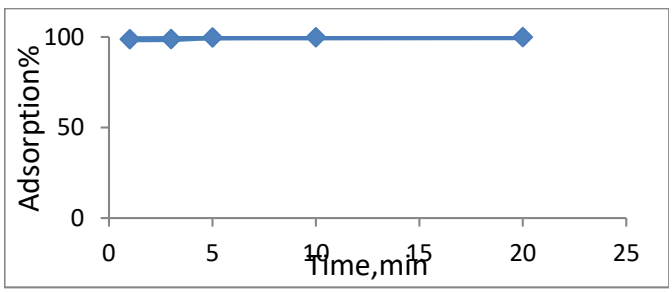


Fig.2 Effect of time on CVD removal using AC-COOAP

3.1.3 Initial dye concentration

The effect of CVD concentration was studied for different CVD concentrations (Fig. 3). The removal rates of CVD using AC-COOAP increased with increase in CVD concentration within a range from 0 to 0.35 mmol/L. The maximum adsorption capacities of AC-COOAP are found 46.9 mgg.

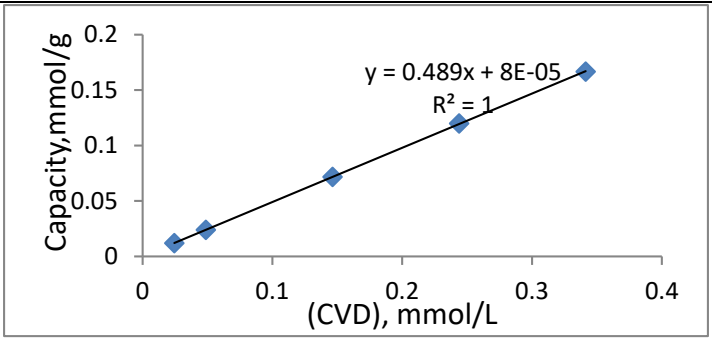


Fig. 3 Effect of CVD concentration on CVD removal using AC-COOAP

3.2 Kinetic studies

. The pseudo first-order (3) and pseudo second-order (4) were used to investigate the mechanism of the adsorption and the rate controlling steps involved in the sorption.

$$\log(Q_e - Q_t) = \log Q_e - (k_1 t/2.303) \quad (3)$$

$$t/Q_t = \left(1/k_2 {Q_e}^2\right) + t/Q_e \quad (4)$$

Where Q_e and Q_t is the adsorption capacity at equilibrium and at time t. k_1 and k_2 is the pseudo first rate constant and the pseudo second order rate constant. The half-life times ($t^{1/2}$) of Pseudo first order are calculated by $t_{1/2} = 0.693/K_1$, while that of second order are calculated by $t^{1/2} = 1/Q_e K_2$.

The data showed that the R^2 of the pseudo second order is higher than that of the first order. Also, higher rate constant and faster half-life time suggests that the sorption is followed pseudo second order which controlled by chemisorption mechanism and depended on both CVD and AC-COOAP.

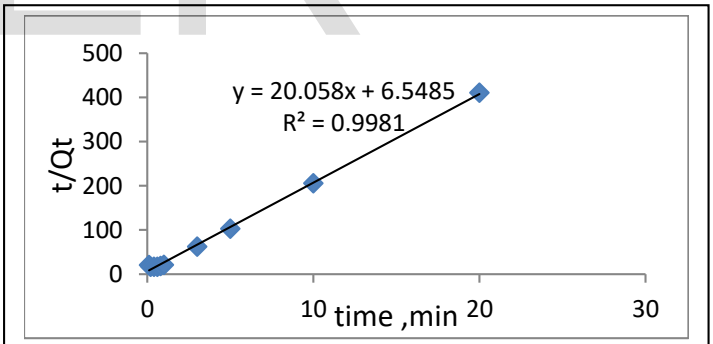


Fig. 4: Pseudo second-order of CVD removal using AC-COOAP

Kinetic modelling of the experimental data allows us to gain insight into the potential rate-controlling steps involved in the sorption process. Two kinetic models (i.e., pseudo-first-order [log(Qe − Qt) = (logQe) − (k1t/2.303)] and pseudo-second-order [t/Qt = (1/k2Q2 e) + (t/Qe)] models) were tested to fit the experimental data for the adsorption of CVD onto AC-COOAP (Fig. 4). Qe is the amount of CVD sorbed at equilibrium, k_1 is the pseudo-first-order rate constant, and k_2 is the pseudo-second-order rate constant.

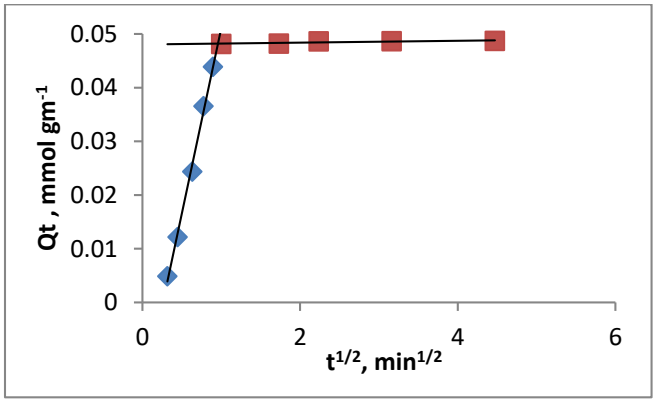
The diffusion mechanism was investigated using the Morris–Weber [Qt = ki √t], Reichenberg [Bt = −0.4977 − ln(1 − F)] and [F = (6/R)(Dit/π) 1/2] equations. Qt is the amount of CVD adsorbed at time t. ki is the intraparticle diffusion rate

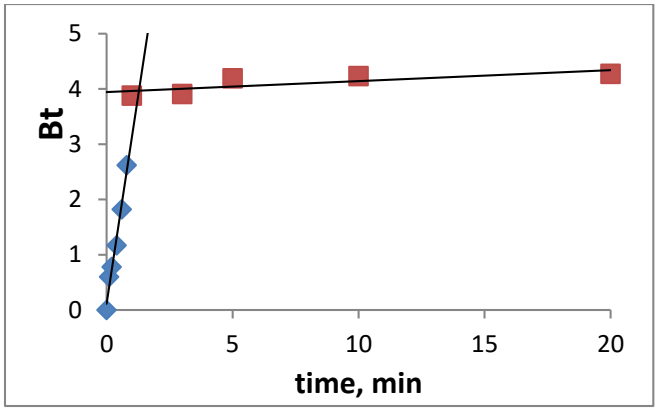
constant (mmol/g $min^{1/2}$). Co is the initial concentration of CVD in the solution. V is the volume of the CVD solution, and m is the mass of AC-COOAP. The Bt value is a mathematical function of F = Qt/Qe. Di is the effective diffusion coefficient, and α and kO are constant.

A plot of Qt as a function of $t^{1/2}$ should be a straight line (R^2 = 0.995) which does not passing through the origin. The diffusion rate of the dyes is rapid in the initial stages and decreases with the passage of time. The average values of ki for CVD adsorption were 0.032 /g $min^{1/2}$. The diffusion rate of the first step was greater than that of the second step (Fig. 5).

The relationship between Bt and t for the adsorption of CVD was investigated, which indicates that a partial film formed along with intraparticle diffusion. The slope of the linear plots of F as a function of $t^{1/2}$ provide the numerical values of the effective diffusion coefficient (Di). The average value of Di for the dye sorption was 2.06×10^{-6} cm^2 /min.The film diffusion rate depended on the size of dyes.

The double logarithmic plots of the Bangham equation as a function of the time gave the perfect linear plots, and the average of the correlation coefficients was 0.972 (Fig. 2). This result indicates that the diffusion of basic dyes into the pores of Iodo-PUP was involved in the rate controlling step. The average value of α was calculated from the slope to be 0.88. The α values was increased as the dye size increased (Table 1). This result is in a good agreement with the results obtained from the Reichenberg model. The regression, correlation coefficient (R2) exceeded 0.94 for the Morris–Weber, Reichenberg and Bangham models, suggesting that both models closely fitted the experimental data. In addition, the regression analysis results indicated that the Reichenberg model (R2 = 0.983) was able to describe the intraparticle diffusion mechanism as film diffusion.





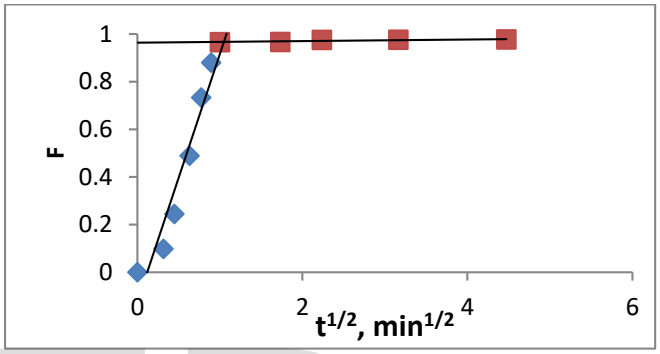


Fig. 5: Diffusion models of CVD removal using AC-COOAP

3.3 Equilibrium studies

The linear plot of ln Qc as a function of ε2 (Dubinin–Radushkevich isotherm, lnQc = lnKD−R − $\beta\varepsilon^2$ and E = 1/ $\sqrt{-2\beta}$, R^2 = 0.900) is shown in figure 6. KD–R is the maximum amount of CVD adsorbed onto AC-COOAP, β is a constant related to the transfer energy of the CVD from the bulk solution to the AC-COOAP, and ε is the Polanyi potential. The β values for the sorption of CVD was −0.002 kJ^2 /mol^2, respectively. The adsorption energy (E) was determined to be 15.8 kJ/ mol for CVD. The E value >8 kJ/mol corresponded to sorption processes controlled by an ion-exchange mechanism. Therefore, this study suggests that the sorption of basic dyes onto AC-COOAP is due to an ion-exchange process. Finally, the sorption of basic dyes onto Iodo-PUP may proceed via ion-association complexes and an ion-exchange mechanism.

Langmuir (5) and Freundlich (6) isotherms were applied to study the removal behavior CVD using AC-COOAP.

$$C_e/Q_c = (1/K_L b) + (C_e/K_L) \quad (5)$$

$$Log\ Q_c = Log\ K_F + 1/n\ Log\ C_e \quad (6)$$

Where Q_c is the amount of CVD adsorbed at equilibrium and C_e is the dye concentration at equilibrium. K_L and b are Langmuir constants, while K_F and n are Freundlich constants.

The results showed that the R^2 of Freundlich is higher than that of Langmuir, whether in the dark or light. Suggesting for multilayer sorption over heterogeneous surfaces. Also, the

values of 1/n are less than 1, referring to a favorable chemisorption process (Fig. 7).

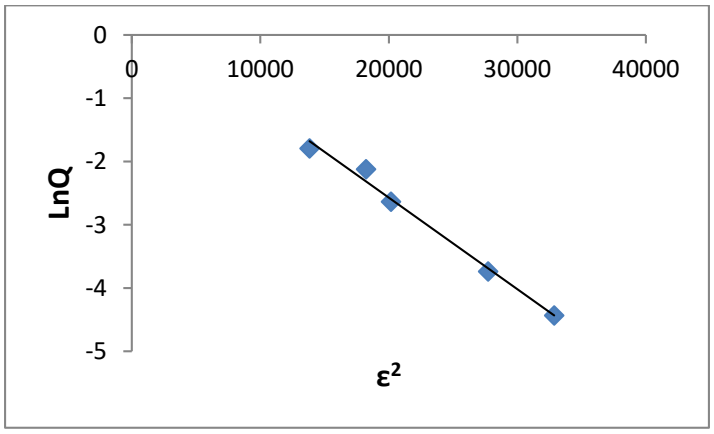


Fig. 6: Dubinin–Radushkevich isotherm of CVD removal using AC-COOAP

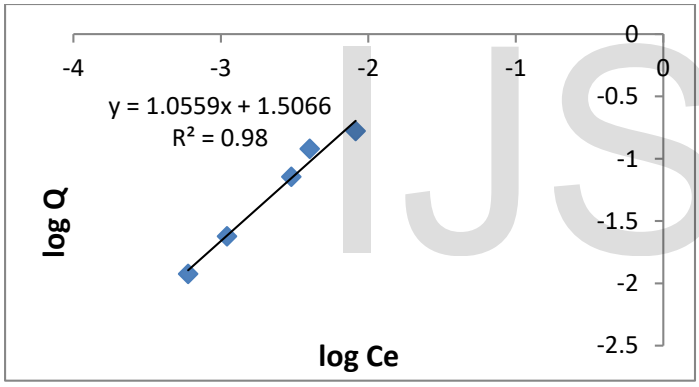


Fig. 7: Freundlich isotherms of CVD removal using AC-COOAP

4. Conclusion

AC-COOAP was tested for the removal of CVD. The maximum adsorption capacity of AC-COOAP was found 46.9 mg/g within 60 sec over a wide pH range (6-10). The kinetic studies were followed by pseudo-second-order model. The equilibrium isotherms showed that Freundlich model were have a good fit to the experimental data. AC-COOAP proved its efficiency in the removal of CVD from wastewater under optimum conditions.

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