

Modelling of Equilibrium Data for the Adsorption of Crystal Violet onto Activated Carbon by Non-Linear Regression Method

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ABSTRACT: The feasibility of preparing activated carbon from *Eichornia Crassipes* by chemical activation was investigated. Batch experiments were carried out for the sorption of Crystal violet onto the prepared activated carbons. Equilibrium data for the adsorption of the dyes onto activated carbon were obtained from batch adsorption experiments. Two parameter isotherm models including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich were employed for fitting equilibrium data. Three parameter isotherm models including Redlich-Peterson, Toth, and Koble-Corrigan models were also employed for fitting the equilibrium data. Non-linear regression method was used to determine the best fit model to the equilibrium data. The results were interpreted using correlation coefficient, coefficient of determination, MPSD and HYBRID functions for calculating error and determining goodness of fit of the various isotherms.

KEYWORDS: crystal violet, activated carbon, non-linear regression

I. INTRODUCTION

Dyes are toxic due to their complex structure and synthetic origin. Over 10,000 dyes are commercially available having different structure, solubility and impact on ecosystems. Wastewater containing dyes is difficult to treat because dyes are resistant to aerobic digestion, stable to light, heat and oxidizing agents due to their structure and molecular size [1]. Crystal violet is the deepest blue of all the methyl violets. It is not used as a textile dye, but is used to dye paper, leather and as a component of navy blue and black inks for printing, ball-point pens and ink-jet printers [2]. It is also used to give colour to various products such as fertilizers, anti-freezes and detergents. The dye is also used as a histological stain, antibacterial, antifungal and antihelminthic. It has serious toxic side effects and is persistent in water.

Crystal violet has dose-related carcinogenic potential. The Food and Drug Administration in the US [3] banned its use in animal feed and in farm raised seafood where it is used as an antimicrobial. It is poorly degraded by microbial enzymes, and persists in a variety of environments. It is mutagenic and mitotic poison [4], therefore concerns exist regarding the ecological impact of the release of crystal violet into the environment in wastewater.

Numerous methods have been developed to treat crystal violet pollution such as electrochemical degradation, ion exchange [5], biodegradation [2] and photodegradation [6]. In recent years, there is a growing interest in using low cost materials for the adsorption of dyes. *Eichornia crassipes* is an aquatic weed that grows profusely in places where untreated organic waste is discharged into water bodies. *Eichornia crassipes* can be used to prepare activated carbon and its potential for the removal of pollutants has been investigated earlier [7]. The use of *Eichornia crassipes* as a bioprecursor for the removal of crystal violet (CV) with NiCl₂ and Co(NO₃)₂ as the initial dopants is being investigated in this paper. This study was conducted to investigate the adsorption capacities of activated carbon prepared from *Eichornia crassipes* by chemical activation at comparatively lower temperature.

Equilibrium data was analysed to find the best fitting equilibrium sorption isotherm that describes the relationship between adsorbent and adsorbate. The equilibrium parameters calculated for the adsorption isotherms predict how the adsorbate interacts with the adsorbent.

II. MATERIALS AND METHODS

1. Biosorbent Preparation

The activated carbons AC-Ni and AC-Co were prepared from *Eichornia Crassipes* as described in [8], by taking NiCl₂ and Co(NO₃)₂ as the initial doping material.

2. Preparation of Dye Solution

The dye CV was used without any further purification. A stock solution of 1 g L⁻¹ was prepared using distilled water. Synthetic dye solutions of different concentrations were prepared by diluting appropriate amount of stock solution. All the adsorption experiments were carried out at room temperature (30 ± 2°C).

3. Sorption equilibrium

The sorption process involves a solid phase and a liquid phase containing the dissolved dye. The uptake of dye by the adsorbent, is measured in terms of adsorption capacity.

The adsorption capacity of the adsorbent phase at time t and at equilibrium was calculated according as

$$q_t = (C_o - C_t) \frac{V}{W} \quad - 1$$

$$q_e = (C_o - C_e) \frac{V}{W} \quad - 2$$

where C_o and C_e are the initial and equilibrium concentrations (mg L⁻¹) respectively of the dye in solution, V is the volume (L) and W is the weight (g) of adsorbent.

4. Adsorption Experiments

The experiment was done by agitating a mixture of 0.1 g of the sorbent, AC-Ni / AC-Co and 25 mL of adsorbate CV. The dye solutions of different concentrations were agitated with activated carbon for the required time intervals. The adsorbent and adsorbate were separated using qualitative filter paper and the first 5 ml of the filtrate was discarded. The concentration of the dye remaining in solution was estimated colorimetrically (Deep Vision Model 313) at the maximum wavelength of 618 nm.

5. Validity of adsorption isotherms

The applicability of the isotherms to the adsorption process is determined using various error functions. Apart from the correlation coefficient (r²) and coefficient of determination (R²), Marquard's percent standard deviation (MSPD) and Hybrid error function (HYBRID) were used to determine goodness of fit. MSPD and HYBRID can be defined as

$$\text{MSPD} = 100 \sqrt{\frac{1}{N-P} \sum_{i=1}^N \frac{(q_e^{\text{exp}} - q_e^{\text{cal}})^2}{q_e^{\text{exp}}}} \quad - 3$$

$$\text{HYBRID} = \frac{100}{N-P} \sum_{i=1}^N \left[\frac{(q_e^{\text{exp}} - q_e^{\text{cal}})^2}{q_e^{\text{exp}}} \right] \quad - 4$$

where q_e^{exp} is the equilibrium adsorption capacity from the batch experiment ($mg.g^{-1}$), q_e^{cal} is the equilibrium capacity obtained by calculation from the isotherm models ($mg.g^{-1}$), N is the number of observations in the experimental isotherm and P is the number of parameters in the regression model. The smaller values of MPSD and HYBRID indicate a better fit between experimental data and the equilibrium capacity obtained by calculation from the isotherm models. MPSD and HYBRID functions were chosen as the number of parameters in the isotherm are also accounted for in calculating error.

III. RESULTS AND DISCUSSIONS

Isotherm modelling

The biosorption equilibrium describes the distribution of the dye CV between the liquid phases and solid phases after the sorption reaction reached equilibrium. Equilibrium data were fitted into seven isotherms namely Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Redlich-Peterson, Toth and Koble-Corrigan models.

The Langmuir [9] adsorption model describes monolayer adsorption of adsorbate onto a homogeneous adsorbent surface. There is negligible interaction between the adsorbed molecules and the adsorption sites have uniform energies. The empirical Freundlich model [10] is based on the assumption of multilayer adsorption of the adsorbate on the heterogeneous solid surface. Freundlich's model also assumes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. K_F is defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. K_F is a constant for the system related to bonding energy. $1/n$ indicates the adsorption intensity of dye onto adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value of $1/n$ below 1 indicates cooperative adsorption.

The Temkin model [11] assumes that the fall in heat of adsorption is linear rather than logarithmic as implied by Freundlich. The Dubinin-Radushkevich [12] equation is based on the assumption that the amount of adsorbate adsorbed for any concentration of the adsorbate is a Gaussian function of the Polanyi potential.

The three-parameter Redlich-Peterson equation [13] combines the features of both Langmuir and Freundlich isotherm models. The Toth [14] and Koble-Corrigan isotherm [15] models are two three parameter isotherms which have terms with exponential dependence on concentration in the numerator and denominator and usually used to describe heterogeneous adsorption surfaces.

Non-linear optimisation provides a better method for determining isotherm parameter values. The ability of the widely used isotherms to model the equilibrium data was examined by using solver add-in with Microsoft's spreadsheet, Microsoft Excel. The coefficient of determination value is used to minimize the error distribution between the experimental equilibrium data and the predicted isotherms.

The applicability of the isotherm equation to describe the adsorption process was judged based on the correlation coefficients, coefficient of determination, MPSD and HYBRID values. The equations for each isotherm and their expressions are listed in Table 1.

Table 1 - Isotherms and their expressions

Isotherm	Equations	Isotherm	Equations
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	Redlich-Peterson	$q_e = \frac{A_{RP} C_e}{1 + B_{RP} C_e^s}$
Freundlich	$q_e = K_F C_e^{1/n}$	Toth	$q_e = \frac{K_T C_e}{(a_T + (C_e)^d)^{1/d}}$
Temkin	$q_e = q_m \ln(K_T C_e)$	Koble-Corrigan	$q_e = \frac{A_{KC} C_e^P}{1 + B_{KC} C_e^P}$
Dubinin-Radushkevich	$q_e = q_m e^{-\beta \varepsilon^2}$		

The values of the parameters, and the correlation coefficients, coefficient of determination, MPSD and HYBRID obtained by applying non-linear regression to the equilibrium data for the adsorption of CV on AC-Ni and AC-Co are listed in Table 2.

The results of non-linear regression method reveal that among the two parameter isotherm models, Langmuir's model fits better to the equilibrium data for the adsorption of CV. In the Langmuir adsorption model [9], adsorption of CV takes place at specific homogeneous sites within the adsorbent and is dominated by the formation of a monolayer.

In the Freundlich model [10], the adsorption of CV occurs on a heterogeneous surface by multilayer sorption and the adsorption capacity increases with an increase in adsorbate concentration. The Freundlich isotherm constant, n, gives an idea for the favourability of the adsorption process. The value of n should be less than 10 and higher than unity for favourable adsorption conditions. Value of n above 1 indicates a normal Freundlich/Langmuir isotherm.

The value of n for the adsorption of CV on AC-Ni is between 1 and 10 indicating cooperative adsorption. The smaller value of n means that adsorption is good at high concentration but is much poorer at lower concentrations. The value of n for the adsorption of CV on AC-Co, is greater than 10, confirming the high degree of heterogeneity of the prepared carbon and favouring adsorption over large ranges in concentration of CV. But, the coefficient of determination, MPSD and HYBRID values clearly show that both these models cannot describe the adsorption process completely over wide concentration ranges.

The Koble Corrigan model [15] gave the best fit for the adsorption of CV as seen in non linear regression data. These facts clearly indicate the existence of a great degree of heterogeneity in the surface of AC-Ni and AC-Co. The Langmuir adsorption capacity values for the adsorption of CV are 59.69 and 92.06 mg.g⁻¹ for AC-Ni and AC-Co respectively.

The constant β from Dubinin Radushevich isotherm [12] gives an idea about the mean free energy E (kJ mol⁻¹) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution. If the magnitude of E is between 8 and 16 kJ mol⁻¹, the adsorption process proceeds via ion-exchange or chemisorption, while for the values of E which are less than 8 kJmol⁻¹, the adsorption process is physical in nature. Since the energy of adsorption is less than 8 kJ mol⁻¹ for both the adsorbents, it may be concluded that the adsorption of CV takes place through physical adsorption. The major factors which affect physical adsorption include the surface area of the adsorbent, pore structure of the adsorbent, surface chemistry of the adsorbent, nature of the adsorbate, pH of the solution, and the presence of competing adsorbates.

The value of g for Redlich Peterson [13] isotherm model lies between 0 and 1 indicating favourable adsorption showing greater tendency to form a monolayer, conforming to Langmuir model. The adsorption capacity of activated carbon prepared by using $\text{Co}(\text{NO}_3)_2$ as the initial dopant is greater than when NiCl_2 is used.

Table 2 : Isotherm parameters by non linear method for the sorption of CV by AC-Ni and AC-Co.

Isotherm		Parameters	AC-Ni	AC-Co	
Langmuir	R^2		0.7095	0.6556	
	MPSD		170	65.58	
	HYBRID		288	43	
	Parameters	q_m (mg g ⁻¹)		59.69	92.06
		K_L (L mg ⁻¹)		0.02058	0.2144
Freundlich	R^2		0.3122	0.9414	
	MPSD		154	155	
	HYBRID		238	240	
	Parameters	K_F (mg g ⁻¹)(Lmg ⁻¹)		23.3	93.48
		N		6.907	445
Temkin	R^2		0.7519	0.7397	
	MPSD		136	44.75	
	HYBRID		186	20.03	
	Parameters	q_m (J mol ⁻¹)		11.77	5.942
		K_T (L mg ⁻¹)		0.3080	21475
Dubinin-Radushkevich	R^2		0.6643	0.5323	
	MPSD		426	720	
	HYBRID		1819	5186	
	Parameters	q_m (mg g ⁻¹)		93.7	148.2

		β ($\text{mol}^2 \text{KJ}^{-2}$)	0.003468	0.000907	
		E (J mol^{-1})	-12.01	-23.48	
Redlich-Peterson	R^2		0.7803	0.7488	
	MPSD		180	61.96	
	HYBRID		163	19.2	
	Parameters	g		0.6685	0.9289
		$A_{RP}(\text{mg g}^{-1})(\text{L mg}^{-1})$		1590	4652
$B_{RP} (\text{L mg}^{-1})^g$			189.1	74.57	
Toth	R^2		0.7709	0.7453	
	MPSD		188	62.08	
	HYBRID		176	19.27	
	Parameters	$K_T(\text{mg g}^{-1})(\text{L mg}^{-1})$		576.5	912.5
		$a_T (\text{L mg}^{-1})^d$		0.9688	0.0866
d			0.1480	0.3077	
Koble-Corrigan	R^2		0.8138	0.7582	
	MPSD		161	59.98	
	HYBRID		130	17.99	
	Parameters	$A_K(\text{mg g}^{-1})(\text{L mg}^{-1})^p$		0.9882	5.944
		$B_{KC} (\text{L mg}^{-1})^p$		0.9308	0.9075
		p		0.009477	0.00518

Langmuir constants for the adsorption CV by a number of adsorbents are presented in Table 3. These include the published values as well as the Langmuir constants obtained in the present study.

Table 3 : Comparison of adsorption capacity of various adsorbents for adsorption of CV computed by non-linear regression (NLR)

Source of Carbon	Dye	Chemical used for activation	Temperature of carbonisation	Langmuir Adsorption Capacity mg g ⁻¹	Reference
<i>Calotropis procera</i> leaf	CV	-	Room temperature	4.14	[16]
Lignite	CV	ZnCl ₂	700 °C	60.8	[17]
Clay nanocomposite	CV	-	Room temperature	55.8	[9]
<i>Thevetia peruviana</i>	CV	H ₃ PO ₄	800°C	129.9	[18]
<i>Eichornia crassipes</i>	CV	NiCl ₂ AC-Ni	250°C	59.69(NLR)	Present study
<i>Eichornia crassipes</i>	CV	CoCl ₂ AC-Co	250°C	92.06(NLR)	Present study

IV. CONCLUSION

The present study shows that activated carbon derived from *Eichornia crassipes* can be used as a low cost adsorbent for the removal of CV from waste water. The temperature used for carbonisation is comparatively low and the raw biomass easily available. Its adsorption capacity and kinetics of AC-Ni and AC-Co are comparable or in some cases superior than other low cost adsorbents. It can be used as an economically viable alternate to commercially available activated carbon.

It may be concluded that the adsorption of CV by the prepared carbons is governed by the formation of monolayer. The adsorption of CV involves adsorption sites of different energies on the heterogeneous surface of the prepared carbons. The results reveal that Langmuir's model fits better to the equilibrium data among the two parameter isotherms and Koble Corrigan model gave the best fit for the adsorption of CV. The adsorption of CV on AC-Ni and AC-Co is exothermic in nature. The adsorption process occurs under favourable adsorption conditions through physisorption in the activated carbons.

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