Equilibrium and Kinetic Studies on Sorption of Crystal Violet Dye from Synthetic Solution onto ZnO Nanoparticles

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Abstract – Current study focused on the removal of crystal violet from synthetic dye solution using synthesized ZnO nanoparticles. The adsorption equilibrium and kinetics were assessed at different process conditions and analyzed. Equilibrium studies are performed using Langmuir isotherm, Freundlich isotherm, D=R isotherm, Temkin isotherm. Kinetic analysis were performed using Pseudo first order, Pseudo second order, intra particle diffusion model and Elovich model. From the results, it has been found that Temkin isotherm fits the data well with highest R^2 value. A maximum uptake of 105.26 mg/g of sorbent is observed from the Langmuir model.

Introduction

Water pollution has caused an increased global demand for pure and safe drinking water- moreover, polluted water results in epidemics in many countries. Waterborne diseases are widely spread due to polluted water [1]. The presence of organic pollutant causes health issues like carcinogenesis in the long run in humans and animals. It is also noted that water pollution has increased mortality [2]. Even though water pollution occurs through various industrial means, the textile industry is one major factor contributing to a large share of pollutants. Dyes from textile industries used in various products to impart colour prove a significant factor. The dye effluents have increased soluble solids, pH, colour, salts, metals, BOD (biological oxygen demand), and COD (chemical oxygen demand) in water bodies [3]. The presence of increased dye amounts poses a threat for biota, as they contain toxic substances like heavy metals and aromatics. For example, the presence of -N=N- bond makes synthetic dyes recalcitrant and carcinogenic; moreover, their complex aromatic structure makes them hardly biodegradable [4] Therefore, it is obligated to treat these textile effluents before hitting the water resources [5].

Textile effluent treatments are performed by chemical, physical, and biological treatment processes. Among these methods adsorption technique is the most sought and among the different adsorbents, activated carbon is widely used. However, activated carbon is ineffective for treating dispersed dyes [6].

In recent years, nanoparticles are widely used as sorbents for water treatment, including carbonaceous ones like graphene, carbon nanotubes (CNTs), activated carbon etc.; metallic nanomaterials like ZnO, TiO_2, etc.; bionanomaterials like chitosan. In particular, ZOn-NPs are the most widely used ones owing to their unique plasmon, optical, and thermal properties. ZOn-

NPs can be synthesized in various shapes [7]. The advantages of using Zinc oxide nanoparticles when compared to other counterparts are their cost-effectiveness, stability under ambient conditions, broad absorption spectrum, chemical stability, non-linear optical behaviour, and antimicrobial properties [8, 9].

In this study, ZnO nanoparticles are used for the sorptive removal of crystal violet dyes and its equilibrium and kinetics studies were performed.

Materials and Methods

Batch adsorption experiments were conducted using 250 mL Erlenmeyer flasks to which 100 mL of known concentration of CV dye solution was added. Along with this solution, 0.41 g/L of ZnO NPs was added. The solution pH is maintained at 4.9 and the temperature was maintained at 29.7^{o}C. Agitation is performed at 126 rpm [10]. The flask was agitated in a temperature controlled orbital shaker at designated speeds to study the effect of initial CV dye concentration. Samples were withdrawn at appropriate time intervals and these samples were centrifuged at 4000 rpm. The supernatant was used for analysis of the residual dye concentration.

The % decolorization was calculated by :

% Decolorization = $(C_i - C_t)/C_i$

Where C_i (mg/L) = initial dye solution concentration

C_t (mg/L) = final dye solution concentration

$q = (C_i - C_t)\ V / M$

q – uptake mg/g; V- Volume of Solution, L; M – Mass of sorbent – g/L

Results and Discussion

The effect of initial dye concentration is studied in the range of 100 – 350 rpm and the results are depicted in Fig.1. From the figure it has been found that increase in initial dye concentration leads to decrease in percentage removal of CV dye from aqueous solution. A maximum removal of 93.5% is attained.

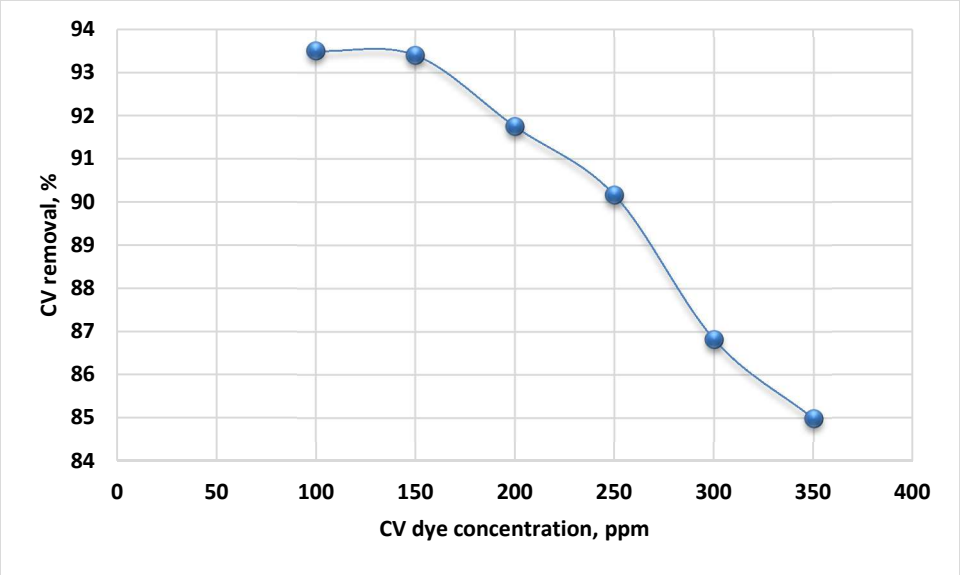

Fig.1. Effect of initial CV concentration on CV removal

Equilibrium study

To perform equilibrium study for CV sorption, the following isotherm models were examined for relating the sorption equilibrium data:

The Langmuir isotherm [11] is characterized by Eq (1):

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \quad (1)$$

C_e - equilibrium concentration (mg/l); q_m - maximum monolayer adsorbing capacity (mg/g); b – Langmuir constant representing the attraction of binding sites (L/mg).

The Freundlich isotherm in linear form [12] is (Eq.2):

$$\text{Log } q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where K_f represents Freundlich isotherm capacity (mg/g); 1/n - adsorption intensity. Linear plot of log q_e vs log C_e produces a straight line with slope K_f and intercept 1/n and presented in table 1. For enhanced adsorption studies the value of 1/n should be between 0 & 1. The 1/n value of 0.5211 confirms the sorption of CV.

The Temkin isotherm [13] is specified by Eq. (3):

$$q_e = B \ln K_T + B \ln C_e \quad (3)$$

where B and K_T denotes Temkin constants (J/mol) and binding energy (L/g) respectively. The plot of q_e vs ln C_e produces a straight line with slope B and intercept B lnK_T and are given in Table 1. The correlation coefficient for Temkin isotherm is 0.997 indicating that the isotherm fits the model well.

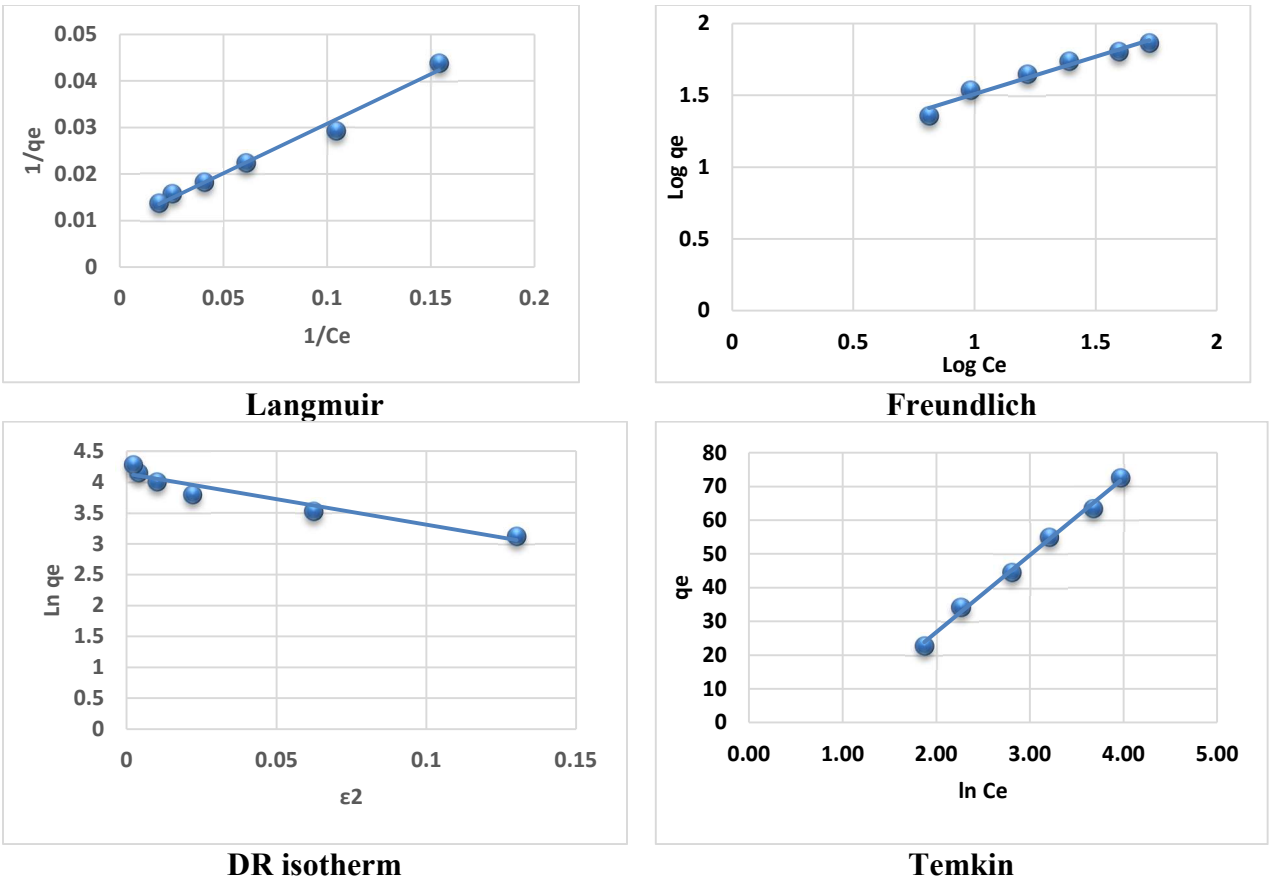

Fig.2. Isotherm plots for CV sorption onto ZnO nanoparticles

Table 1 Equilibrium study results for CV sorption using various isotherms

Isotherm	Parameters	Values
Langmuir	q_m (mg/g)	105.26
	K_L (L/mg)	0.045
	R^2	0.985
Freundlich	K_f (L/mg)	9.712
	1/n	0.5211
	R^2	0.9627
Dubinin- Redushkevich	q_m (mg/g)	62.49
	β (mol^2/ kJ^2)	8.258
	E (kJ/mol)	0.246
	R^2	0.9267
Temkin	B	22.90
	K_T (L/mg)	2.30
	R^2	0.9957

Dubinin-Radushkevich (D-R) [14] isotherm is represented in Eq.(4):

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (4)$$

where ε^2 and β (mol^2/kJ^2) are D-R isotherm constants. ε is RT $\ln(1+1/c_e)$. The D-R constants β and q_m were calculated from the slope and intercept of ln C_e versus ε^2. The plot of the isotherm models are given in Fig. 2 and the isotherm constants and correlation coefficients (R^2) were presented in Table 1. Langmuir isotherm fits the CV sorption well when compared to all other isotherms based on R^2.

Adsorption kinetics

When studying the adsorption kinetics of Crystal Violet (CV) onto ZnO nanoparticles, it's crucial to evaluate multiple kinetic models to understand the mechanism and rate-controlling steps. The adsorption kinetics of Cr (VI) was explored by the Pseudo-first order (PFO), Pseudo-second order (PSO), Elovich and Intra-particle diffusion (IPD) models.

PFO kinetic model is derived based on weak interaction between sorbate and sorbent predominantly prevailing with physisorption. The linear form of PSO kinetics [15] is given by Eq. (5).

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (5)$$

k_1 - rate constant for PSO kinetic model (1/min). The rate constant and correlation coefficient were evaluated from the slope and intercept of the plot between log (q_e-q_t) and t.

PSO kinetic model [16] is based on chemisorption. Linear form of Pseudo – second order kinetics was represented by Eq.(6).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_2 - rate constant of PSO (g/mg min)
t- time (min)

IPD model [17] is given by Eq (7).

$$q_t = k_{id} t^{0.5} + C \quad (7)$$

where k_{id} - IPD rate constant (mg / (g $min^{-0.5}$)) and C - intercept.

Elovich model [18] is specified by Eq (8).

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (8)$$

where α - Elovich constant (mg/g min), β - Elovich exponent (g/mg).

The linearized plots of Eqs. 6, 7, 8 and 9 are presented in Fig. 3. The rate constants, kinetic parameters and correlation coefficients obtained through these plots are listed in Table 2. From the results, it is observed that the correlation coefficient (R^2) of the IPD model was found to be much higher than those of other models indicating that the adsorption mechanism was well suited with IPD model. This shows the possibility that, diffusion into the pores of ZnO nanoparticles controls the adsorption rate.

A linear plot suggests the diffusion-controlled adsorption. The presence of multiple linear regions suggests a multi-step process (external diffusion, intra-particle diffusion, and equilibrium). If the plot passes through the origin, intra-particle diffusion is the rate-limiting step. If not, it suggests that other mechanisms, such as boundary layer diffusion, also influence the process.

Comparing the intra-particle diffusion kinetics with other models helps to determine the roles of diffusion and adsorption rate in the overall process.
Pseudo-first-order kinetics fits well in the early stages of CV sorption where the sorbate concentration is high. But it doesn't describe the entire process, particularly when intra-particle diffusion becomes significant.

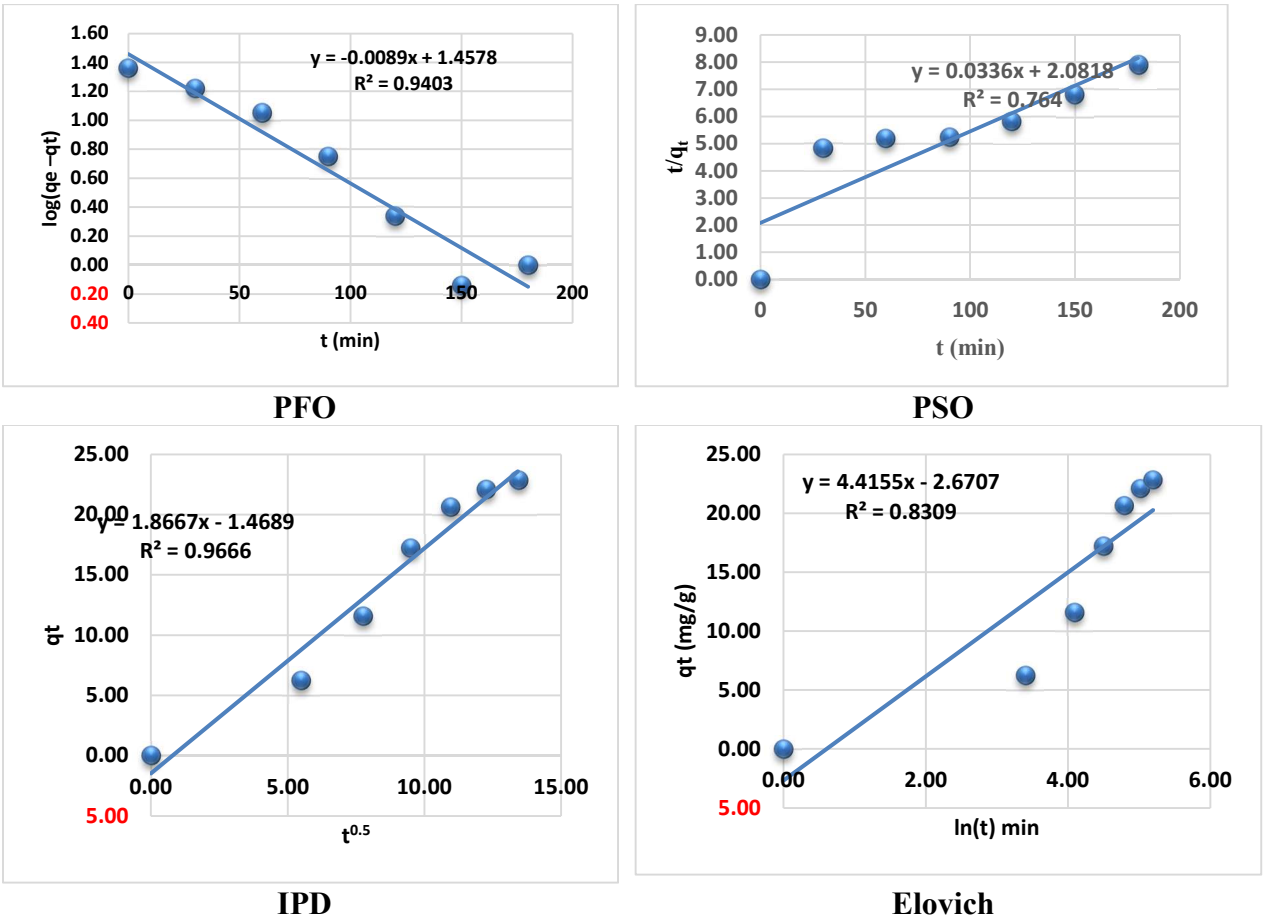

Fig.3. Kinetics plots for CV sorption onto ZnO nanoparticles

The Elovich model assumes a heterogeneous surface, where the activation energy for adsorption changes with surface coverage. This holds good for ZnO nanopsrticles, where surface properties may vary. This model works well for systems where sorption slows down with time, possibly due to site saturation or increased repulsion between adsorbed molecules. While, the

Elovich model accounts for chemisorption, it does not directly consider the diffusion process. In contrast, the intra-particle diffusion model focuses on mass transfer limitations within the adsorbent pores.

From the results, it is observed that the IPD is crucial for understanding the mass transfer and pore diffusion aspects of the adsorption process, especially when ZnO nanoparticles are involved. It also reveals that the diffusion within the pores is the rate-limiting step.

Table 2 Kinetic results for CV sorption

Pseudo first order	K_1 (min^{-1})	0.0089
	R^2	0.9403
Pseudo second order	K_2((g/mg)min)	0.00054
	R^2	0.764
	qe, cal (mg/g)	66.67
Intra particle diffusion	K_{id} ((mg/g)$min^{-0.5}$)	1.8667
	R^2	0.9666
Elovich	α	4.72
	β	0.2265
	R^2	0.8309

Conclusions

In this work, ZnO nanoparticles were successfully employed as an efficient adsorbent for the removal of Crystal Violet (CV) dye from aqueous solutions. The adsorption process was thoroughly investigated through various kinetic and isotherm models, allowing for a detailed understanding of the underlying mechanisms. The IPD kinetic model provided the best fit for the experimental data, suggesting that diffusion into the pores of ZnO nanoparticles plays a significant role, particularly in the later stages of adsorption. This highlights the multi-step nature of the sorption process, with both surface adsorption and intra-particle diffusion contributing to the overall kinetics. Furthermore, equilibrium studies demonstrated that the adsorption data fit well with the Temkin isotherm model. The ZnO nanoparticles present a promising material for environmental remediation, particularly for the removal of CV dye from wastewater. Their high adsorption capacity, fast kinetics, and ease of synthesis make them a viable option for large-scale applications. Further research could focus on the regeneration and reusability of ZnO nanoparticles to enhance their economic feasibility in real-world wastewater treatment systems.

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