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Investigation of Crystal Violet Adsorption from Aqueous Media onto Acid-Modified Lignocellulosic Biomass: Kinetic and Thermodynamic Perspectives

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Abstract

Throughout this study, sulfuric acid–treated eucalyptus leaves (SEL) were evaluated as an inexpensive adsorbent for the adsorption and effective removal of CV (Crystal Violet) from aqueous system. The various parameters impacts, involving contacting duration, adsorbent amount (dosage), initial adsorbate concentration, pH on the adsorption phenomenon were investigated under batch conditions. The pseudo-second-order kinetic model provided a better match with the experimental observations compared to the pseudo-first-order model. Among the isotherm models evaluated, the Langmuir isotherm provided a Showed a superior fit compared to the proposed model, suggesting monolayer adsorption on the adsorbent surface. The evaluated thermodynamic parameters showing the process of adsorption was spontaneous, random, and endothermic in nature. Furthermore, the magnitude of the calculated standard enthalpy change supported the predominance of physical adsorption.

Key Words

Adsorbent; Crystal Violet dye; Sulfuric Acid–Treated Eucalyptus Leaves; Adsorption Thermodynamics

1. Introduction

During industrial dyeing operations, nearly 10–15% of the applied dyes are misplaced to wastewater streams. From streams of wastewater these dyes in effluents disrupts water-based ecological system by depleting dissolved oxygen and limiting light penetration, which in turn suppresses photosynthetic activity in aquatic organisms [1]. Exposure to crystal violet (CV) can cause multiple health complications, such as irritation of the eyes, skin, and digestive system, along with phototoxic sensitivity. Prolonged or high-level exposure may result in serious conditions, including respiratory and renal failure [2].

For CV detoxification from wastewater conventional removal techniques used such as flocculation and coagulation [3], ion exchange [4], separation through electrochemical and membrane [5]. Compared to other treatment techniques, adsorption offers a highly effective and economically viable removal process [6]. The present study focuses on the reduction Crystal Violet dyes by implementing sulfuric acid (H_2SO_4)-modified eucalyptus leaves as an adsorbent.

2. Experimental Methodology

2.1. Treated EL process with using of sulfuric acid (SEL)

Eucalyptus leaves cleansed by single-distilled water for removing dirt, sun-dried and dried by using the hot air oven for 8 hr at 70°C. A predetermined mass of eucalyptus leaves (EL) with a particle size of −30 +36 BS was mixed with 98% H_2SO_4 at an EL to acid weight ratio of 5:1, followed by the addition of the required volume of double-distilled water. Further the mixture is kept in the hot air oven at 70°C for 3hr. Subsequently, the H_2SO_4-treated eucalyptus leaves (SEL) were washed with 0.1 M NaOH solution, followed by repeated rinsing with hot highly purified distilled water until filtrate pH achieve 6.5–7.0. Following washing, the sulfuric acid–treated eucalyptus leaves (SEL) were oven-dried at 70 °C for 8 h and finally stored in an air-impermeable container (airtight) for subsequent experiments.

2.2. Experimental procedures

The experimental work was carried out under batch operation in 250 mL conical flasks containing 100 mL of Crystal Violet (CV) solutions of known initial concentrations. To adjust the solution pH 0.1 N NaOH or 0.1 N HCl was used. At a constant speed by 150 – 160 r.p.m. of incubator-cum-shaker contained with conical flasks were shaken at 25 ± 2°C. The capacity of adsorption (q_t) and removal percentage (%R) was evaluated with using

$$q_t = \frac{(C_0 - C_t).V}{m} \quad (1)$$

$$\%R \text{ of CV ions} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

3. Results Evaluation and discussion

3.1. Analysis of adsorbent characteristics

The texture of surface of SEL was examined using a ZEISS EVO 18 SEM operated at an accelerating 15 kilo Voltage and a magnification of 2,000×. The Scanning Electron Microscope (SEM) micrographs of the untreated and CV-loaded adsorbents (Figures 1(a) and 1(b) shows the existence of a porous and irregular surface and delivering active sites for the adsorption of Crystal Violet. The characterization of functional group of SEL was determined by Thermo – Fisher

Scientific Nicolet i35 (iD3 ATR) (FT – IR) with ranging 4000 – 400 cm-1 resolution. The shifts in the wavenumbers of the major FTIR peaks for the fresh and loaded adsorbents are displayed in Table 1. A prominent broad band at 3456 cm^{-1} indicates the availability of O–H stretching vibrations arising from hydrogen-bonded alcohol and phenol groups. Peak describing the group of alkanes at 2925 cm-1. At 1648 cm-1 strong peak substantiate that carbonyl group is also present. Aliphatic amines are represented at 10591cm-1 by the peak. Observations clarify that the presence of Hydroxyl groups facilitate are known to exhibit a high affinity toward various pollutants. Apart from that, the formation of hydrogen bonds takes place between the carbonyl groups and Crystal Violet (CV) influencing the CV absorption.

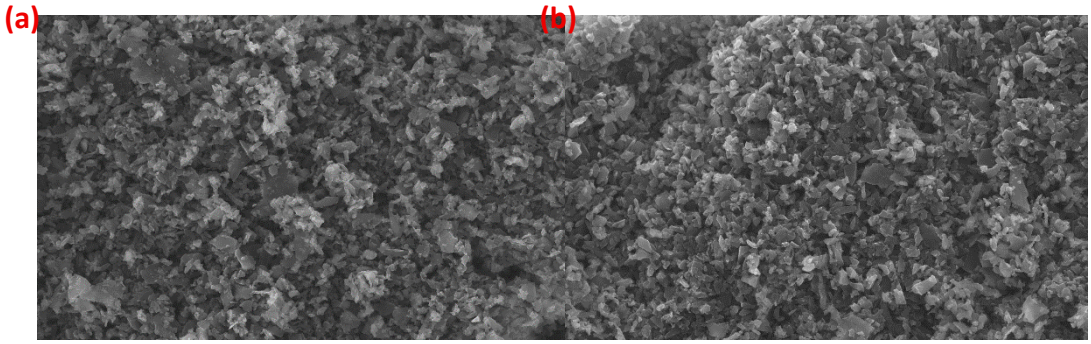

Figure 1 Scanning electron microscopy (SEM) of the adsorbents. (a) SEL. (b) CV loaded SEL

Table 1 FT-IR study of SEL in natural form and CV loaded form

Frequency (cm^{-1})		Groups
Before adsorption	After adsorption	
3456	3418	OH stretching
2925	2924	CH stretching
2350	2186	P-H Phosphine sharp
1648	1615	C=O stretching
1059	1037	C-N stretching

3.2. Influence of pH

Figure 2. illustrate that, when initial pH ranges between 2-7, the removal percentage (%) of CV (Crystal Violet) increases, the H_3O^+ ions complete with CV ions when the solution's initial pH is lower, causing the surface pore area of adsorbent. Rising the initial pH of the CV solution promoted stronger electrostatic interactions together with hydrogen bonding between the adsorbent surface along with dye molecules [7]. Therefore, for SEL to conduct the absorption experiments, the optimal experimental Potential of hydrogen (pH) value was selected is about 7.

3.3. Influence of contact duration

For an initial of CV concentration is about 100 ppm, the influencing in the contact time was studied, at 298K, the mass of an adsorbent is about 1 $g \cdot L^{-1}$ with having pH is about 7. Up to 180 min of adsorption time for fast adsorption kinetics as showing by figure 3. The fast initial uptake of adsorbate is primarily due to the availability of a large number of unoccupied surface active adsorption sites [8].

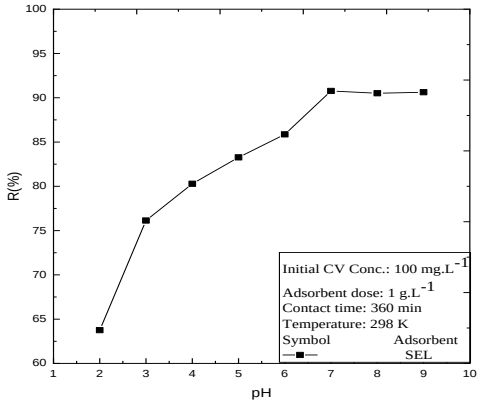

Figure 2 Percentage of removal of CV variation with pH.

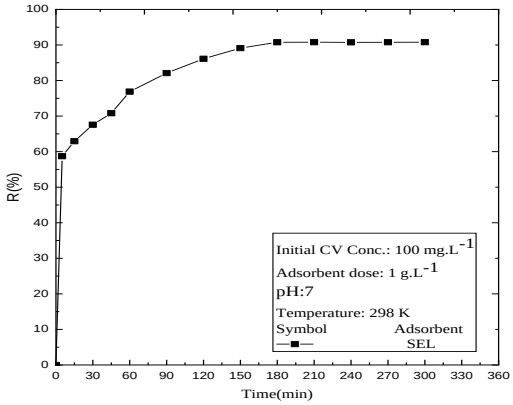

Figure 3 Percentage of removal of CV variation with time

3.4. Influence of adsorbent mass

Figure 4 describing that, increasing in percentage removal rapidly ranges between 1g.L^{-1} to 2 g.L^{-1} by increases the adsorptive surface area which is unoccupied. Rising the removal of percentage R(%) could not lead by increasing in the mass of adsorbent. The observed trend can be associated with the progressive adsorption site's saturation, resulting from the accumulation and aggregation of previously adsorbed particles [9].

3.5. Influence of initial adsorbate concentration and temperature

As per Figure 5, increasing in percentage adsorption and became highest at a 100 of ppm, rising the initial Crystal Violet concentration. Thus, as a result of increasing in CV concentration with the ratio of pore area (adsorptive) to the decreasing in CV concentration. At the different concentration of initial CV, the temperature rising, the removal percentage of CV was identified to be increases, illustrated by Figure 5. At elevated temperatures, the adsorption phenomenon of CV is promoted due to the enhancement of stronger interactions between the molecules of adsorbate (dye) and the available binding sites of the solid surface (adsorbent). The enhancement in adsorption phenomenon is due to the kinetic energy of solute at elevated temperature and increased surface activity [10].

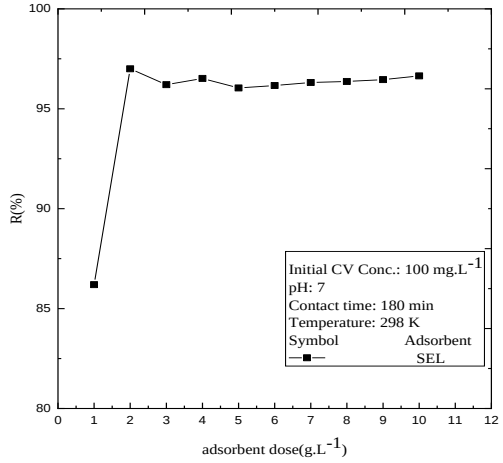

Figure 4 Percentage removal of CV variation with adsorbent mass.

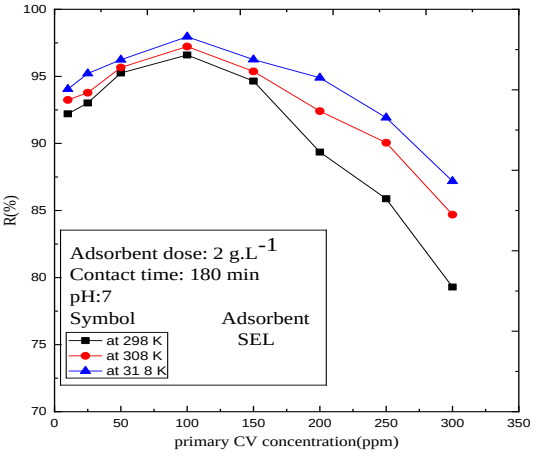

Figure 5 Effect of initial Crystal Violet concentration on removal efficiency at

various temperatures.

4. Reaction Kinetics

4.1. Pseudo first order and Pseudo-second order model

The kinetic parameters for the pseudo-first-order model and the pseudo-second-order model has been represented in the *Table 2*. The higher correlation coefficient signifies that the pseudo-second-order model provides a better representation of the adsorption process.

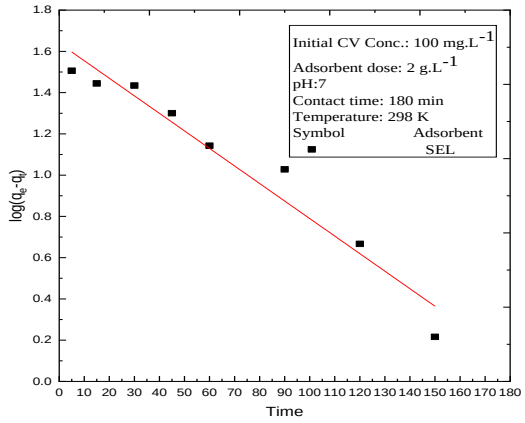

Figure 6 Plot of log (q_e-q_t) vs. t for pseudo-first-order model

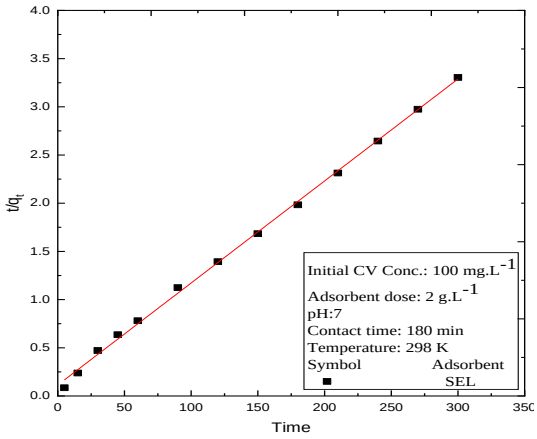

Figure 7 Plot of t/q_t vs. t for pseudo-second-order model

5. The Adsorption Isotherm

5.1. The Freundlich and the Langmuir isotherm

The non-linear expressions corresponding to the Freundlich and Langmuir isotherm models are provided in *Table 3*. Favourability for adsorption is determined from the value of separation factor (R_L) is varies between 0 to 1.

6. Thermodynamic studies

From equation (3), the thermodynamic equilibrium constant, K_c^0 has been obtained and by using the equations (4) and (5), the parameters of thermodynamic is established.

$$K_C^0 = \left(\frac{q_e . m}{c_e} \right) \quad (3)$$

$$\Delta G^0 = -RT \ln K_C^0 \quad (4)$$

To calculate the enthalpy (ΔH^0) and the entropy (ΔS^0), the intercept of the plots of ln K_c^0 vs. 1/T and the slope were used.

$$\ln K_C^0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (5)$$

If the value of heat adsorption ranges between 2.1 to 20.9 kJ·mol^{-1} signifying the physical adsorption, in opposition to this, if the values range from 20.9 to 418.4 kJ·mol^{-1} indicates chemical adsorption (chemisorption) [11]. In table 5, various thermodynamic property's values which were calculated and give conclusion that the phenomenon of adsorption was random, endothermic and spontaneous in the nature. Calculated value of standard enthalpy change supports the physical adsorption.

7. Safe disposal of used biosorbents

The possibility of CV molecules leaching from the exhausted bio-adsorbent prevents its unregulated disposal into the environment. The spent adsorbent containing adsorbed CV was ashed at 800 °C. A 5 mg portion of the resulting ash was then dispersed in 25 mL of double-distilled water to achieve a solid-to-liquid ratio of 1:5. At a normal room temperature, after uninterrupted stirring for 1 day, UV spectrophotometer used by the inspection of filtrate that signifying absence of Crystal Violet's traces. Therefore, it could be concluded that, process of incineration has ability to remove all the CV (Crystal Violet) from ash that will be utilizable to land fill.

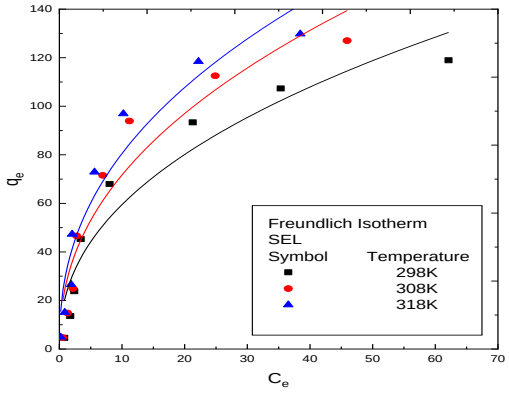

Figure 8 Plot of q_e vs. C_e for Freundlich isotherm model

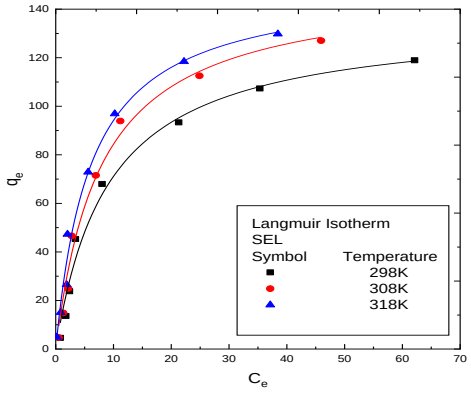

Figure 9 Plot of q_e vs. C_e for Langmuir isotherm model

Table 2 Kinetic parameters for the bio-adsorption of CV on SEL (with ANOVA)

Parameters	Values
$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	
k_1(min^{-1})	0.0195755
q_e(mg g^{-1})	43.60838
R^2	0.94599
ANOVA (Single factor)(Alpha=0.05)	
F	12.042
P-value	0.00375

F_{crit}	4.600
$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{t}{q_e}$	
k_1(mg g^{-1} min^{-1})	0.00098035
q_e(mg g^{-1})	94.51795
R^2	0.99854
ANOVA (Single factor)(Alpha=0.05)	
F	21.65136
P-value	0.0001
F_{crit}	4.259677

Table 3 Different isotherm constants

Freundlich isotherm model $q_e = K_f.C_e^{1/n}$			
Temperature(K)	K_f (mg g^{-1})/(mg L^{-1})	n	R^2
298	22.122	2.3276	0.91074
308	26.254	2.2921	0.9021
318	30.620	2.3811	0.92549
Langmuir isotherm model $q_e = \frac{q_m.K_L.C_e}{1+K_L.C_e}$			
Temperature(K)	q_m(mg g^{-1})	K_L	R^2
298	136.02299	0.1096	0.9816
308	150.22433	0.12816	0.98327
318	151.08912	0.16544	0.98639
Separation factor $R_L = \frac{1}{1+K_L.C_0}$			
Temperature(K)	$R_L(C_0=10)$	$R_L(C_0=50)$	$R_L(C_0=100)$
298	0.47709	0.15432	0.08361
308	0.43828	0.13498	0.07237
318	0.37673	0.10785	0.05699

Table 4 Statistical analysis for isotherms

F	P-value	F_{crit}	Conclusion
23.87748	$1.29x10^{-05}$	4.051748565	P-value<0.05(Significance)

Table 5 Thermodynamic properties for the bio-adsorption of CV onto SEL

Initial CV concentration (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol.K)	-ΔG° (kJ/mol)		
			298 K	308K	318K
50	9.52	51.04	5.6884	6.1988	6.7092

100	20.66	91.21	6.5229	7.4350	8.3471

8. Conclusion

When initial concentration is about 100 of ppm, the percentage removal of CV is found out by 97%, the dosage of adsorbent at 2 $g \cdot L^{-1}$, pH is about 7 and up to 180 minutes of contacting time. As compared to pseudo-first-order model, pseudo-second-order model is better compatibility with experimental data findings. Peak adsorption capacity is about 151.08 $mg \cdot g^{-1}$ for the Langmuir. Monolayer adsorption is more applicable than the Freundlich, suggested by Langmuir adsorption isotherm. Thermodynamic various property's value indicates that process of adsorption is random, endothermic and spontaneous in nature. Value of standard enthalpy change (calculated) supports the physical adsorption. P-values below 0.05 were obtained during the analysis of kinetic and isotherm data, indicating strong statistical support for the fitted models.

Nomenclature

ΔG^0, Gibbs free energy (kJ mol^{-1});
ΔH^0, Enthalpy (kJ mol^{-1});
ΔS^0, Entropy (J (mol K^{-1}) $^{-1}$);
K_L, Langmuir constant (L mg^{-1});
C_o, Initial CV concentration in solution (mgL^{-1});
C_t, Final CV concentration in solution (mgL^{-1});
k_1, Pseudo-first-order (Lagergren) rate constant (min^{-1});
k_2, Pseudo-second-order rate constant (g mg^{-1} min^{-1});
K_c^0, Thermodynamic equilibrium constant;
K_f, Freundlich constant [(mg g^{-1})/ (mg L^{-1})] $^{1/n}$;
m, Mass of the adsorbent per unit volume (g L^{-1});
n, Freundlich constant, intensity of adsorption [(mg g^{-1})/(mg L^{-1})]$^{1/n}$;
q_e, Amount adsorbed (mg) per g of the adsorbent, at equilibrium (mg g^{-1});
q_m, Maximum capacity of adsorption (mg g^{-1});
q_t, Amount adsorbed (mg) per g of the adsorbent at time t (mg g^{-1});
t, Time (min);
T, Temperature (K);
V, Volume of the solution in L;

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