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Adsorption Potential of Bio-Sorbent Derived from *Millingtonia Hortenesis Leaves* for Sorptive Eradicaton of Crystal Violet Dye from Aqueous Media in Eco-Friendly Way

Kalaiselvi D.[1*], Sangeetha V.[2], Basker A.[3], Kandavelu[4] and V Saravanan D.[4]
[1 and 4]Department of chemistry, Sri Shakthi Institute of Engineering and Technology, Coimbatore, INDIA
[2]Department of Chemistry, Kongunadu Arts and Science College, Coimbatore, INDIA
[3]Department of chemistry, Kalaignar Karunanidhi Institute of Technology, Coimbatore, INDIA
[4]Department of chemistry, National College, Tiruchirappalli, INDIA

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Abstract

In this article millingtonia hortenesis leaves, one of the herbal plant materials, available in plenty quantity in india, was chosen as an biosorbent to clutch out crystal violet dye in aqueous media. An equilibrium feature of leaves was scrutinized by executing the experiments in batch adsorption mode. Adsorption models like Langmuir, Freundlich and Temkin were examined to portray briefly the reaction sequences at its equilibrium phase. Langmuir equation was found to have the highest value of R^2 compared with other models. Furthermore, it was found that leaves have an adsorptive capacity of 40 mg/g and show favorable adsorption of CV dye with separation factor ($R_L < 1$). In addition, pseudo-first- order, pseudo-second order and intra-particle diffusion were used to study the kinetics of MB adsorption onto leaves. Adsorption process undergoes pseudo-second order kinetic as bear out by its towering R^2value and also inferred by the low value of sum of squared error (SSE percentage). Results pointed out that intra-particle diffusion model could never orients and the adsorption process is spontaneous as indicated by the negative value of the ΔG^o.

Keywords: Adsorption, crystal violet, Equilibrium, kinetics, thermodynamics.

Introduction

Nowadays tremendous growths in civilization of urban areas possess a threatening alarm to a developing country like India and also worldwide. One such example to quote for such enhancement is the use of dyes in various fields of textiles, food, cosmetics, paper, paints, pharmaceuticals and several other industries. The swelling of environmental concerns pressurised us to frame an innovative remediation to such issues[1]. Thus adsorption processes will hopefully explore as a greener solution to the crisis of environmental soil and water pollution in the mere future since adsorption is considered as one of the subsist effectual technique for relinquishing the dissolved dyes in waste water. So it is very imperative to ensure proper treatment of wastewater prior to discharge by making use of plentiful plant wastes as carbon precursors. Moreover these methods are proving to be potential alternatives to the classical and traditional methods of pollution prevention because of low cost, simple design, sludge free operation and superior colour removal etc.

Crystal violet (CV) or Genetian violet is consistently used in plenty quantity for colouring cotton and silk in textile industries and also quite often used as pigments in the field of paint industry and printing inks. This dye also finds its usage in animal husbandry and veterinary practice as a referee in bacteriostatic tarnishes. CV is considered to have low metabolized ratio and have the persistent capacity in a wide variety of environments. That's why universally this dye falls under the category of recalcitrant molecule. Additionally this dye is well thought-out to have stuff of cytotoxicity and carcinogenic character.

The intention behind this current research is to check out the competence of Millingtonia Hortenesis leaves eradication against crystal violet in aqueous solution. The biosorption data was ensured for its reliability by assortment through isotherm models such as Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm conversely on the other hand the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were also deliberated in this paper in order to be more familiar with biosorption kinetics of dyes on this leaves.

Material and Methods

Preparation of Biosorbent: Fresh and Mature millingtonia hortenesis leaves were taken from the surrounding area and cleaned several times to seize out any adherent dirt constituents. The leaves were shaded under mild sunlight and later on oven dried at 100°C for 2 h. Then it is grounded and trampled in a chopper and sieved to get fine particles of constant size and preferred to use as such without any pre-treatment for CV biosorption[2].

Sorbate and Reagents: CV ($C_{25}H_{30}N_3Cl$) received from scientific company as shown in figure-1 was utilised as such in its commercial quality for better clarity ($C_{25}H_{30}N_3Cl$). Stock solution of this dye was set ready for carrying out adsorption process by dissolving 1g of the dye in 1000ml of distilled water. Furthermore operational solutions of the desired concentrations were taken for analysis by successive dilutions of dye at appropriate intervals. The initial concentration of dye was ascertained. Two replicates per sample were done for prompt analysis of the sample and the average results are presented for better clarity. The pH which is the influential factor for any batch process was analysed by adding very dilute concentration of 0.1HCl or 0.1 NaOH.

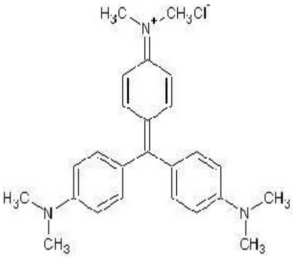

Figure-1
Structure of crystal violet

Results and Discussion

Batch biosorption studies: Predetermined amounts of adsorbent say 150mg was added to 10ppm of dye solution in 250 mL volumetric flasks and agitated at 150 rpm on thermostatic orbital shaker for 120 min. Experiment solution were taken out from the flasks by using syringe at predetermined time periods and the dye solutions were quenched off by subjecting the experimental solutions for centrifugation at 2000 rotation per minute for about 5 min. Then the residual solution after separation was calculated to find out its optical density.

The amount of dye adsorbed, q_e(mg/g) and percentage exclusion of dye were deliberated by using the subsequent Equation as given below.

$$q_e = \frac{(C_o - C_e)}{W} V \qquad (1)$$

Where, C_o (mg/L) and C_e (mg/L) are dye concentrations prior to and soon after of adsorption process, respectively; V (L) is the volume taken for experimental consideration, and m (g) is the actual amount of adsorbent used.

Biosorption Isotherms: In the analysis and design of a biosorption process, isotherms afford as vital segment for providing information in relation to the biosorption course. Furthermore the actual feasibility of adsorption, the distribution of molecules between liquid and solid phase can be established by adsorption isotherms and it is very familiar for illustrating the mechanism of biosorption route, to stand out the exterior properties of sorbent and also in validating the accurate potential of this prepared biosorbent towards adsorbate in aqueous media of low concentration. The isotherm study is also momentous for optimizing and modelling the efficacy of adsorbent towards any dye solutions[4].

The adsorption of adsorbate onto the MH leaves was modelled using a variety of isotherm. All the isotherm model fittings of this study were analysed ranging from 20 to 100 mg/l of CV concentration at equilibrium time.

Langmuir isotherm model is frequently ascertained under supposition to put forth for the prediction of homogeneous monolayer adsorption.

The equation for these models are given as

$$\frac{1}{q_e} = \frac{1}{Q_0 K_L C_e} + \frac{1}{Q_0} \qquad (2)$$

Where, Q_0 signifies monolayer coverage capacity (mg/g), C_e quotes for equilibrium solute concentration in the liquid phase (mg/L), q_e denotes the adsorption capacity (mg/g) and K_L stands for isotherm constant (L/mg). Plot of $1/C_e$ versus $1/q_e$ is graphically represented in figure-2. The various constant values are depicted in table-1.

The Freundlich isotherm model express rapport that considers only the unique heterogeneous adsorption due to the multiplicity of adsorption spots in the periphery of prepared biosorbent.

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \qquad (3)$$

Where, q_e emphasis dye concentration (solid) at equilibrium (mg/g), Ce is dye concentration at equilibrium (mg/L), K_f is the isotherm invariable and n is the isotherm constant associated with the adsorption intensity[6]. The graph is plotted between log q_e versus log Ce as shown in figure-3 and the parameters evaluated were given in table-1. Further the assessment of this model was found to hold the value of n greater the representing the effectiveness of biosorbent.

Temkin isotherm model well thought-out the indirect possessions of adsorbate interactions and keenly emphasized the reason that these category of interactions may decrease the heat of adsorption upon coverage on the periphery of adsorbent[7]. The model is given by the following equation:

$$q_e = BT \ln A + B \ln C_e \qquad (4)$$

Where, B = RT/b, b is the constant associated with warm condition (J/mol), A is the invariability parameter of this model (L/g), R is the gas constant (8.314 J/mol K), T is the temperature (K).

So, by plotting q_e versus ln C_e reveals the invariable parameters A and B of the isotherm as shown in figure-4**.** The subsequent values are shown in table-1.

Dubinin-Radushkecivh (D-R) isotherm was authenticated to make a precise distinction linking physical and chemical adsorption. The linear form of this isotherm equation is given by[8]:

$$\ln q_t = \ln q_m - K\varepsilon^2 \qquad (5)$$

$$\varepsilon = RT\ln\left[1 + \frac{1}{C_e}\right] \qquad (6)$$

Where R is the gas constant (8.314 J/(mol K)), and T (K) is the temperature, q_m (mg/g) is the maximum adsorption capacity based on this isotherm and K is related to mean adsorption energy (E in kJ/mol) given by:

$$E = \frac{1}{\sqrt{2K}} \qquad (7)$$

A plot of $\ln q_e$ versus $\boldsymbol{\varepsilon^2}$ as shown in Figure 5 will furnish the utmost adsorption capacity of q_m (mg/g). If the E value is flanked in the range of 1 - 8 kJ/mol, indicates a physical adsorption while for chemical adsorption the E value must be greater than 16 kJ/mol. If the *E* value falls between 8-16 kJ/mol, then the most likely adsorption mechanism involved is ion substitution. Thus the estimated mean adsorption energy (E) value for this study was found to have a value of 28.9 kJ/mol proving chemisorptions.

Biosorption Kinetics: Adsorption kinetics elucidates extremely glowing information concerning principally the reaction impending skill of the dye just around the exterior ingredient of the adsorbent. Following several models were undertaken to interpret the mechanism implanted in this course.

The integrated form of first model is articulated in the mathematical term as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}\,t \qquad (8)$$

Where, k_1 (min^{-1}) is the rate constant of this model and q_t is the adsorption capacity at time't' (mg g^{-1}).

The parameters of this model are elaborated well in table-2. In several cases this model does not coincides exactly over the entire assortment of contact time and is commonly correlated to the introductory segment of the adsorption route. Moreover, larger discrepancies among calculated ($q_{e,cal}$) and experimental ($q_{e,exp}$) values of the equilibrium adsorptive capacity proposed that the adsorption of CV on this prepared plant leaves denial well with the first model of kinetics.

Kinetic data were further scrutinized for its effectiveness with the second kinetic model. This model is established with the postulation that the rate-limiting stage is chemical sorption or chemisorption[10].

The equation for this model is given as follows:

$$\frac{t}{q_e} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (9)$$

Where, k_2 [g mg^{-1} min^{-1}] is the rate constant of this model and q_t is the adsorption capacity at time't' (mg g^{-1}).

The plot of t/qt versus t was computed as shown in figure-7. At all of the considered initial concentrations, this model showed an excellent healthy conformity with experimental statistics (R^2>0.99). The calculated values ($q_{e,cal}$) also confirms stuck between experimentally observed values ($q_{e,exp}$) as revealed in Table 2. This finding implies that the adsorption kinetics pursues this model[11-12]. Further equilibrium adsorption capacity ($q_{e,cal}$) amplified with rising initial concentration, which is endorsed by the powerful lashing strength of the solution at elevated concentrations. Additionally, the rate constants (k_2) values dwindles from (0.247-0.237) which can be attributed to have lower competition for the adsorption surface spots at minor concentration.

Kinetic data was further scrutinized using the intra-particle diffusion model.

The intra-particle diffusion equation is given as:

$$q_t = K_{int}t^{0.5} + C \qquad (10)$$

Where k_{int}, the intra-particle diffusion rate constant and and C is the intercept is listed in table-2. The value of C narrates the depth of the periphery of the adsorbent. The outsized value of C implies the outcome of the boundary layer. The plots of q_t versus $t^{1/2}$ should be linear if this model is caught up in the analysis, and if these lines circumvent from side to side in its initial stage then this model absolutely be influential factor. The graph clearly revealed the impression that this model never goes behind that. The plot of q_t versus $t^{0.5}$ using the initial kinetic data up to 120 min gave R^2 values of 0.97 and 0.98 for the carbon prepared from leaves.

Activation Energy and Biosorption Thermodynamics: The fundamental idea for finding the thermodynamics parameters affords an immense magnitude of adsorption track since it facilitate one to assess spontaneity and heat change of the adsorbed species[16]. Thermodynamic studies were manipulated, at temperatures 300-320K, CV concentration ranging from of 20-100 mg L^{-1}, and adsorbent dosage 0.15g L^{-1} The adsorption of dye at elevated temperatures was found to be less significant at lesser temperature range since the enhanced value of temperature would definitely boost the mobility of the large dye ions and also generates an inflammation on the exterior side of adsorbent, which in turn smooth the progress of huge dye molecules to penetrate further[17-18].

Thermodynamic factors can be intended from the subsequent equation.

$$\Delta G^{o} = -RT\ln K_d \qquad (11)$$

Where R is the universal gas constant (8.314 $Jmol^{-1} K^{-1}$), T the temperature (K), and K_d is the distribution coefficient.
The K_d value was intended using the subsequent Equation

$$K_d = \frac{q_e}{C_e} \quad (12)$$

Where q_e and C_e are the equilibrium concentrations of CV on the adsorbent and in the solution, respectively. The enthalpy change (ΔH^o) and entropy change (ΔS^o) can be calculated from the equation below.

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \quad (13)$$

This equation can be written as

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (14)$$

The values of ΔG^o, ΔH^o, and ΔS^o for the adsorption of CV at 300°c onto leaves were given in table-3**.**

Conclusion

The adsorption of CV dye onto MH leaves was examined to envisage the effectiveness of this plant precursor. The 150g/l prescribed amount of biosorbent confirms the discolouration of dye in aqueous media. The adsorption equilibrium is achieved in 120 minutes. Among the three different isotherms equilibrium statistic value of Langmuir model fits well with the ongoing progression of analysis made. The monolayer saturation capacity of the prepared biosorbent 40mg/g was comparable with diverse adsorbents evaluated before for the same dye removal. The aptness of Langmuir form put forward ahead to the monolayer coverage of dye in contrast to the freundlich model. The kinetic model enlightens the pseudo second-order model. The thermodynamic parameter very well elaborates the spontaneity and established the affinity for this dye removal. Thus the present work revealed that the plant leaves might be possibly replacing the conventional activated carbon material for the removal of CV dye from aqueous solutions.

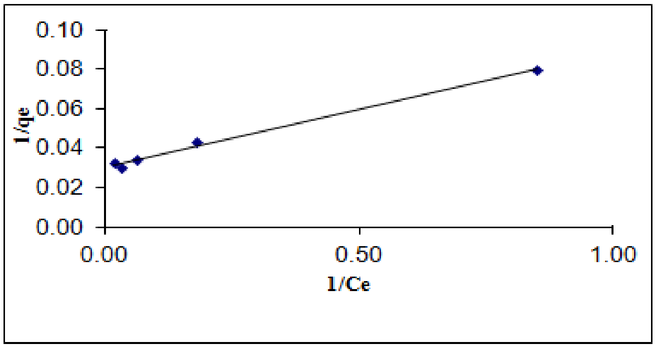

Figure-2
linearlised Langmuir isotherm plot for the adsorption of CV dye onto MH leaf powder.

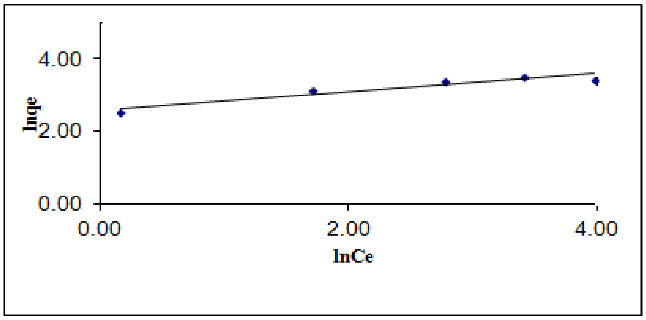

Figure-3
linearlised Freundlich isotherm plot for the adsorption of CV dye onto MH leaf powder

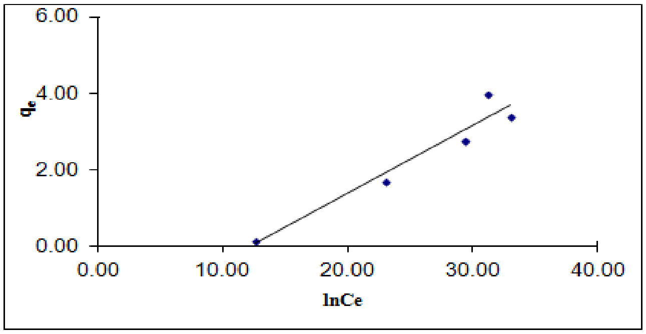

Figure-4
Tempkin isotherm plot for the adsorption of CV dye onto MH leaf powder

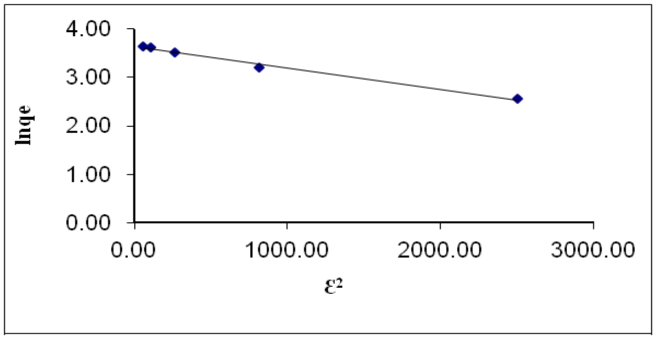

Figure-5
D-R isotherm plot for the adsorption of CV dye onto MH leaf powder

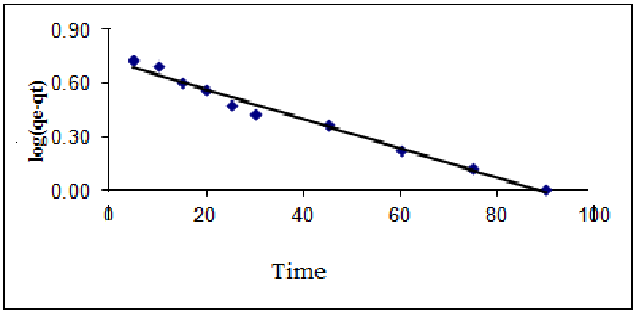

Figure-6
Pseudo first order plot for the adsorption of CV dye onto MH leaf powder

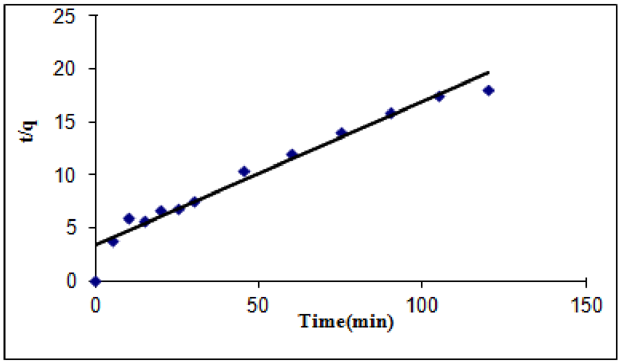

Figure-7
Pseudo Second order plot for the adsorption of CV dye onto MH leaf powder

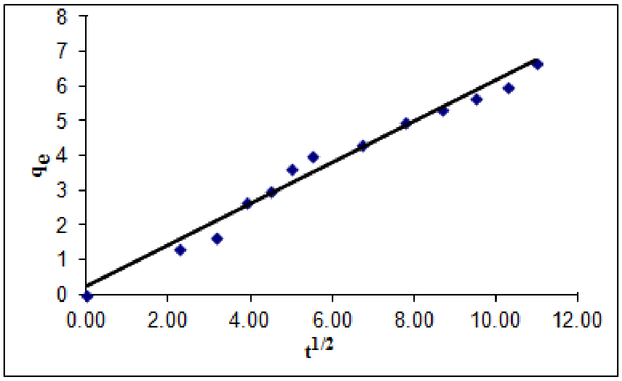

Figure-8
Intraparticle Diffusion plot for the adsorption of CV dye onto MH leaf powder

Table-1
Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm constants and correlation coefficients

Langmuir Isotherm	Freundlich Isotherm	Tempkin Isotherm	D-R Isotherm
Q_0 (mg g^{-1}) 33.33	k_f (mg g^{-1}) 13.37	A_T(L/mg) 11.50	q_m(mg/g) 3.47
R_L 0.09	n 3.99	b_T 5.32	K_{ad} (mol^2/kJ^2) 6.22x10^{-4}
R^2 0.99	R^2 0.90	B 468.47	E(KJ/mol) 28.90
		R^2 0.93	R^2 0.97

Table-2
Pseudo first-order, pseudo second-order and Intraparticle Diffusion constants at different concentrations of CV

Kinetic Models	**Model Coefficients**	**Initial Concentration**	
		10 mg/l	**20 mg/l**
Pseudo first order	q_e(mg g-1)	6.67	12.55
	q_{calc}(mg g-1)	117.6	90.90
	$k_1 min^{-1}$	1.35	0.86
	R^2	0.98	0.97
Pseudo-second order	q_{calc}(mg g-1)	7.92	23.0
	k_2(g $mg^{-1} min^{-1}$)	0.247	0.237
	R^2	0.99	0.98
Intraparticle diffusion	k_{int}(mg $g^{-1} min^{-0.5}$)	2.92	0.480
	C	1.725	0.742
	R^2	0.97	0.98

Table-3
Thermodynamics parameters of CV adsorption at 20 mg/l initial concentration

Conc.(mg/l)	**T (K)**	**K_P**	**ΔG^o (KJ mol^{-1})**	**ΔS^o (J mol^{-1} K^{-1})**	**ΔH^o (KJ mol^{-1})**
20 mg/l	300	10.6	-5.8	277.7	89.2

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