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ADSORPTION STUDY OF CRYSTAL VIOLET DYE ONTO *Morus nigra* L. (MULBERRY TREE) LEAVES POWDER: EQUILIBRIUM, KINETICS AND THERMODYNAMICS STUDY

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ABSTRACT

The biosorbents were produced by grinding mulberry leaves to give mulberry leaves powder (MLP) and was utilized for the removal of crystal violet (CV) dye from aqueous solution. To study the effect of various parameters like contact time, concentration, temperature etc batch mode experiments were carried out. Mulberry leaves powder (MLP) was characterized by using Fourier transform infrared spectroscopy (FTIR). The isotherm data fit to some extent into the Langmuir isotherm than that of Freundlich and Temkin isotherms for linear models while as kinetic data fit best to pseudo-second order kinetic model. Intraparticle diffusion studies indicate that more than one mechanism influenced the adsorption process. Gibb's free energy -3.29728 to -1.20599 for (MLP) indicated spontaneous process. Also the enthalpy changes of -19.232 KJ mol⁻¹ of MLP indicated exothermic process. Uptake efficiency (> 95%) recorded at an equilibrium time of 30 minutes shows that MLP was fast and effective adsorbents for the removal of aqueous crystal violet (CV) dye.

KEYWORDS: Mulberry Leaves Powder, Crystal Violet, Isotherms, Kinetics, Thermodynamics

The untreated disposals into the water bodies cause major problem to the environment including flora, fauna and human beings (Bhatnagar et al., 2014). The disposal of dyes and pigments is mainly contributed by many textile industries, cosmetic mills, plastic mills, paper mills, pulp mills, distilleries and tanneries and are prominently responsible for disposal of huge amount of dyes and pigments disposing these effluents untreated proportion (Guo et al., 2014). These disposed dyes and pigments are strongly colored and affect the environment especially aquatic life even at low doses as these effluents block the penetration of sunlight and thus affecting the photosynthesis of aquatic plants (Kagalkar et al., 2010). It is estimated that more than 10, 000 dyes with an annual production of greater than $7x10^5$ metric tons worldwide are commercially available and 5-10% of this dye stuff is lost in the industrial effluents (Sine, 2003). In this present work the crystal violet (CV) dye which is a synthetic cationic dye that transmits violet color in aqueous solution is taken as a model dye. It is widely useful in the textile industry (for dying cotton, wool, nylon, silk etc), printing inks production, and veterinary medicine (as dermatological agent) (Adak et al., 2005). Crystal violet dye also destroys cells, binds to DNA, and could cause gene mutation and cancer (Sabnis, 2010).

Therefore, there is a need of their removal from wastewater before disposal.

The azo dyes have a complex structure and are considered electron deficient xenobiotic compounds, since these characteristics make these dyes resistant to degradation in wastewaters and thus their treatment is a great challenge. The use of conventional treatment methods such as biological degradation, chemical oxidation, coagulation, flocculation, precipitation, membrane filtration, irradiation, ion exchange, ozonation, and solvent extraction have been investigated with changeable degree of success in dye removal (Noorimotlagh et al., 2019). These methods have certain disadvantages like high investment and operating costs, inefficiency in dye removal and thus there is a need for appropriate treatment of wastewater. Adsorption is one of the simple and economical alternative as new materials of low cost and high efficacy are available for this process, therefore remains one of the most widespread treatment technique (Harrache et al., 2019). Agricultural bio-wastes contain high carbonaceous contents (cellulose, lignin and hemicelluloses) and thus have high affinity for organic molecules, therefore being continuously explored for removal of dyes from wastewaters due to their abundance. These biomaterials contain favourable

physical and chemical characters therefore requires no or little processing before use (Rangabhashiyam et al., 2013). The plant wastes like wool fiber and cotton fiber, peanut shell, almond shell, hazelnut shell, algal biomass, fruit stones, plum kernels, banana pith, chitosan, neem husk, tamarind fruit shell, coconut tree sawdust, rice husk, olive stones, plum kernels, palm tree cobs, date pits, fruit stones, cassava peel and sugarcane bagasse have been used as low cost adsorbents. The cost of these biomaterials is negligible compared with the cost of activated carbon or ion-exchange resins. These biomaterials are used to remove various dyes like crystal violet (CV) dye. Some low cost biomaterials used as adsorbents are potato peel (Lairini et al., 2017), rice straw (Abd-Elhamid et al., 2020), jute & sunnhemp (Hussain et al., 2010), juglans regia leaves (Shah et al., 2021), cajanuscajan (red gram) seed husk (Jirekar et al., 2015), husk of green gram (Phaseolus aureus) seed (Jirekar et al. 2014), Cassia siamea (CS), Albizia labbeck (AL), Nerium indicum (NI), Durauta erecta (DE), and potato husk (PH) (Taher et al., 2012), green peas shell (Dandge et al., 2016), masoor seed husk (Jirekar and Farooqui, 2013), black gram seed husk (Jirekar et al., 2015), spines of Taxus bacata (Dar et al., 2011), Vigna unguiculata seed husk powder (Jirekar et al., 2016), elephant grass (Menkiti et al., 2018), bael bark (Kadam and Farooqui, 2018) etc.

The plant leaves contain certain constituents like polyphenols, lignin, pigments and protein making it suitable to provide active sites for binding dyes (Abadian *et al.*, 2015). *Morus nigra* L.(black mulberry) belongs to flowering plant species in the family Moraceae. It is native to southwestern Asia and the Iberian peninsula; however it is also cultivated in Kashmir India as a feed for cattles like sheep etc and its fruits for eatable juice. The aim of our work is to find out the efficient, low cost adsorbents to manage wastewater so we used mulberry leaves to convert them into mulberry leaves powder (MLP) for the adsorption of crystal violet (CV) dye from aqueous solution.

EXPERIMENT

Materials

All the chemicals used in this research work were of analytical grade and used as received. Crystal violet (CV) (99.9 %) Sigma-Aldrich), mulberry leaves powder, leaves of which were collected in local native village (first author) (Dungdara Dawlatpora Kreeri Baramulla Kashmir India).

Instrumentation

Water distillation plant, UV/Vis. Spectrophotometer (Elico double beam SL 244.), pH meter (Equip- Tronics EQ-610), magnetic hot plate stirrer (Macro Scientific Works (R),10A/UA, Jawahar Nagar, Delhi- 110007.), electronic balance, centrifuge,(eltek multispin TC 650 F.), and grinder machine (Usha Mixer Grinder (MG-3576) 750 Watt.) are used throughout the experimental investigations.

Preparation of Leaf Powder

Mulberry leaves were collected from Dungdara Dawlatpora Kreeri Baramulla J&K India where huge number of Mulberry trees exist. These leaves were kept under sun for five days for drying after extensive washing with tap water and then distilled water to remove Suspended impurities. Dried leaves were crushed into fine powder by using grinder. The MLP were washed with distilled water again and again until it became free from dust and color. Dirt free MLP was sun dried for five days and then in an oven at 65 °C until it attained constant weight. For further use in experiments, the adsorbent was stored in an air tight voils.

Adsorption Process

Variation of the color of crystal violet (CV) dye in an aqueous solution by MLP adsorbent under continuous stirring on magnetic stirrer was recorded and studied by UV/Vis. Spectrophotometer. We carried out the experiments by placing 20 ml of the crystal violet dye solution in a 100 ml glass beaker at various initial dye concentrations (5.4, 12.8, 17.3, 27.2, 33.3, 43.9 and 58.7 ppm). Distinctive amounts of adsorbent (MLP) (0.05-0.30 mg) and the effect of contact time were demonstrated at different time intervals (05, 10, 20, 30, 40, 50 and 60 min). The salinity was checked by adding KCl and CaCl₂ to the dye solution in the range of 0.05-0.30 g, temperature was diversed from 25 $^{0}C - 65 {}^{0}C$ and pH was considered in acidic medium only at 2.62, 2.96 and 3.35 as base discolourise the crystal violet (CV) dye solution. Finally, suspension was filtered by whatmann's filter paper and crystal violet dye concentration in filterate was determined with the help of spectrophotometer at 581.5 nm as it is its λ_{max} .

The CV dye percentage removal (% R) is defined as:

$$\% R = \frac{c_{0-C_t}}{c_0} \tag{1}$$

Where, C_o and C_t are the initial concentration and the concentration of CV dye at time t, respectively.

Characterization

The characterization of the MLP adsorbent was carried out by a Fourier transform infrared spectroscopy (FT-IR) covering the range from 400 to 4000 cm⁻¹, carried out in Babasaheb Ambedkar Marathwada University Chemistry Dept. Aurangabad India.

The FTIR spectra of MLP is shown in fig. 1. Several peaks were observed from the spectra (Fig. 1), indicating that mulberry leaves powder is composed of various functional groups which are responsible for binding of positively charged crystal violet (CV) dye. The broad absorption peak at 3271.27 cm⁻¹ corresponds to the O-H stretching vibration of alcohols, phenols and carboxylic acids as in pectin, cellulose, and lignin, thus showing the presence of "free" hydroxyl groups on the adsorbent surface (Pathania et al., 2017). The broad peak is because of macromolecular association by hydrogen bonding (Pavia et al., 1996). The small three peaks at 3759.26, 3714.90 and 1608.63 are probably due to asymmetric, symmetric and bending vibrations of adsorbed water molecules respectively (Kaur, 2009). The absorption peaks at 2922.16 and 2848.86 cm⁻¹ are attributed to the (C-H) asymmetric and symmetric stretching vibrations, respectively (Pavia et al 1996). Three weak peaks are found at 2096.62, 2125.56 and 2164.13 cm⁻¹ which can be described as $-C \equiv C - alkyne$ band. The peaks at 2258.64 cm^{-1} with C=N stretches show nitrile functional group (Wellesley college, 1875). Peak at 1722.43 represents ester and carboxyl groups with C=O stretch (University of Colorado, 1985), the spiky strong peak observed at 1608.63cm⁻¹ is assigned to C=C ring stretch of aromatic rings (Pavia et al., 1996). In addition the band at 1421.54 cm⁻¹ confirm the presence of C=C of aromatic rings (Pavia et al., 1996). The presence of alcohols, carboxylic acids, esters and ethers functional groups were observed through C-O strong stretch in the absorption band at 1,320–1,000 cm⁻¹ frequency with absorption peaks at 1317.38, 1228.66, 1095.57 and 1014.56 cm⁻¹ (University of Colorado, 1985). Alkene small =C-H absorption bend is found strongly in between 1,000 and 650 cm⁻¹ having peaks at 898.83 cm^{-1} .

RESULTS AND DISCUSSION

The structure of crystal violet (CV) dye is specified in fig.2. The conditions of maximum removal for crystal violet (CV) dye from aqueous solution by given adsorbent (MLP) were initially optimized. For optimization effect of contact time, concentration of dye solution, amount of dose of adsorbents, effect of temperature, effect of salt and effect of pH were varied to the large extent. The results of above mentioned parameters for crystal violet (CV) dye were summarized in graphs.

Effect of Contact Time

The effect of the contact time on adsorption of crystal violet (CV) dye by MLP at pH 6.52, concentration 27.2 mg/L, temperature 24 °C and dose of adsorbents 0.05 gm/20 ml as given in fig. 3. This graph indicates that initially there was rapid intake of dye by adsorbent and became constant (at equilibrium) after a particular time. Indeed, it is possible because initially all the sites are vacant and get occupied with the passage of time where it shows equilibrium. It is to be noted that at initial stages adsorption rate is high and slows down with the passage of time because of competition of dye molecules for adsorption on adsorbents (Santos and Boaventura, 2016).

Effect of Initial Dye Concentration

The effect of initial crystal violet (CV) dye concentration was investigated by batch mode experiments at temperature = $27 \,^{\circ}$ C, dose = 0.05 gm/20 ml, pH = 6.52, contact time 30 minutes and the concentration range of 5.4, 12.8, 17.3, 27.2, 33.3, 43.9 and 58.7 mg/L were used as shown in fig.4. The adsorption capacity increased with increase in crystal violet (CV) dye concentration from 2.1 to 20.9 mg/gm. for MLP. This is because at higher concentration there is higher concentration gradient thus greater driving force resulting in higher adsorption capacity (Tan *et al.*, 2008).

Effect of Adsorbent Dose

The percentage removal of crystal violet (CV) dye as a function of adsorbents dose at equilibrium are presented in fig. 5. It was observed in the figure that the percentage removal of dye was first increased from 98.2 to 98.7 % with an increase in adsorbent dose from 0.05 to 0.15 gm./20 ml and then decreases. The increase in the percentage removal of crystal violet (CV) dye with dose of adsorbents could be attributed to increase in the adsorbent active sites. On the other hand, the adsorption capacity was decreased after a particular dose and may be attributed due to hidening of adsorbent sites.

Effect of Salt of Adsorbent

The effect of KCl and $CaCl_2$ dose in the range of 0.05–0.3 gm./20 ml dye solution at temperature 27 °C on the percentage removal of crystal violet (CV) dye solution (27.2 mg/L) was studied as shown in fig. 6 and fig. 7.The dose for this observation was taken 0.05 gm separately for 30 minutes. It is clearly shown in figures

that there is slight variation in the percentage removal of crystal violet (CV) dye by the adsorbent. The graphs shows decrease in percentage removal and may be due to the increase in ionic strength causing screening of surface charges.

Effect of Temperature

Temperature is one of the important parameters affecting mobility and solubility of dye molecules in aqueous solution. It has also impact on the surface properties of adsorbents. For this investigation the parameters like concentration of dye solution, volume, time and dose of adsorbent were taken same as those in contact time. In this search percentage removal of crystal violet (CV) dye decreases from 90.4 to 79.3 % for MLP as shown in fig. 8 showing exothermic processes.

Effect of pH

pH is also one of the important factor that controls the removal of crystal violet (CV) dye by MLP adsorbent. The pH study was performed at a temperature of 26 °C, dose 0.05 gm and volume 20 ml of dye solution for 30minutes. The result shown in the fig. 9 indicates that MLP adsorbent showed good removal capacity in basic medium. However it is not investigated in basic medium as base like NaOH discolourise the crystal violet (CV) dye solution.

Adsorption Isotherms

To study the relationship between the quantity of adsorbed adsorbate (mg) and the adsorbent (gm), adsorption isotherm models were used. The most commonly used isotherm models studied also here are Langmuir (Langmuir, 1918), Freundlich (Freundlich, 1906) and Temkin (Temkin and Pyzhev, 1940). The Langmuir adsorption isotherm is significant for monolayer adsorption and considers that there are identical sites on the adsorbent surface. The Langmuir isotherm is represented by the following linearized forms as given in Eq.(2)

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o b C_e}$$
(2)

Where, C_e = equilibrium dye concentration (mg/L), q_e = amount of CV dye adsorbed per unit mass at equilibrium (mg/gm), q_o = adsorption capacity (mg/gm.) and b = Langmuir constant (L/mg). These values are obtained from the slope and intercept by plotting a graph between '1/ q_e ' versus '1/ C_e ' (fig. 10). The Equilibrium factor or separation factor 'R_L' was used to express important characteristics of Langmuir equilibrium isotherm (Hall *et al.*, 1966), which is given as below:

$$R_L = \frac{1}{1+bC_0} \tag{3}$$

Where, $C_o =$ initial dye concentration (mg/L). Four 'R_L' values are possible for any adsorption: R_L >1 (unfavourable), R_L = 1(linear), R_L = 0 (irreversible) and 0 < R_L < 1 (favourable) (Taher, 2012).The Langmuir constants and R_L values are given in table 1 where R_L values lie between 0 and 1 indicating Langmuir isotherm is favourable.

Freundlich adsorption isotherm describes multilayer adsorptions on heterogeneous adsorbent surface with different functional groups showing different adsorbent-adsorbate interactions and its linear form is expressed as:

$$lnq_e = lnK_f + \frac{1}{n}lnC_e \tag{4}$$

Where, K_f is the Freundlich constant [mg/g $(L/gm)^{1/n}$] related to bonding energy and 'n' is the heterogeneity factor. The plot of lnqe against lnCe gives a straight line with slope and intercepts (fig.11). The value of 'n' lies between 1to10 indicates favourable adsorption. These Freundlich constants are also summarized in table 1.

The Temkin model considered the effects of interaction of the adsorbate and the adsorbing species (Temkin and Pyzhev, 1940). It is because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly rather than logarithmically with coverage due to adsorbate–adsorbent interactions (Temkin and Pyzhev, 1940), the linearized form of equation is as:

$$q_e = BlnA_T + BlnC_e$$
(5)
$$B = \frac{RT}{b_T}$$

Where, b = Temkin constant related to heat of sorption (J/mol.), A = Temkin isotherm constant (L/gm), R = gas constant (8.314 J/mol. K) and T = absolute temperature (K). By plotting a graph between qe versus lnC_e (fig.12) gives a straight line with slope and intercept from which constants can be determined as listed in table 1.

Kinetic Studies

Adsorption kinetics of crystal violet (CV) dye by given adsorbent was also evaluated and analysed by using pseudo-first-order, pseudo-second-order and intra-particle diffusion models in order to explore the mechanism and the momentary behavior of the dye adsorption process.

Pseudo-First-Order and Pseudo-Second-Order Kinetic Models

The linearized integral form of the pseudo-firstorder kinetic model developed by Lagergren is generally expressed as (Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - \frac{\kappa_1}{2.303}t$$
(6)

Where, k_1 = rate constant of pseudo-first-order adsorption (min.⁻¹), q_e = amounts of crystal violet (CV) dye adsorbed by MLP at equilibrium (mg/gm) and q_t = amount of CV dye adsorbed by MLP at time 't' (mg/gm). Plot of log ($q_e - q_t$) against time (t) (fig. 13) resulted with lower correlation coefficients as mentioned in table 2. First order kinetic model showed poor fitting because of having lower correlation coefficients and the values calculated for ' q_e ' from the graph showed an enormous deviation with the experimental data. Experimental data were further investigated by using pseudo-second-order kinetic model (Weber and Morris, 1963) having linearized form as:

$$\frac{t}{q_t} = \frac{1}{K_2 \times q_e^2} + \frac{1}{q_e} \times t \tag{7}$$

Where, k_2 = rate constant for pseudo-secondorder adsorption (g mg⁻¹ min⁻¹). The plot of 't/q_t' against 't' (fig. 14) of Eq. (7) gives a linear line with slope and intercept from which 'q_e' and 'k₂' can be calculated. The graph shows that experimental data had a good fit to Pseudo-second-order kinetic model with higher values of correlation coefficient (R² = 1).

To calculate the initial sorption rate v_o , constant K_2 is used at $t \rightarrow 0$, as follows:

$$\nu_o = K_2 \times q_e^2 \tag{8}$$

Thus the rate constants ' K_2 ', calculated equilibrium uptakes ' q_e ', the initial sorption rate ' v_o ' and the corresponding correlation coefficients ' R^2 ' of crystal violet dye for MLP adsorbent for the given concentration were determined and presented also in Table 2. The elevated agreement between calculated and experimental values proves that the adsorption of crystal violet dye onto MLP perfectly followed pseudo second order kinetic model.

Intraparticle Diffusion Model

Intraparticle diffusion model was proposed by Weber and Morris (Weber and Morris, 1963) and is used for identifying the mechanism of adsorption for design purpose. There are large numbers of adsorption processes where amount of adsorbate adsorbed varies almost proportionately with ' $t^{1/2}$ ' rather than with the contact time (Dawood *et al.*, 2014).

$$K_{id}q_t = t^{0.5} + I (9)$$

Where, q_t = amount of CV dye adsorbed at time t, $t^{1/2}$ = square root of time and K_{id} = rate constant for intra-particle diffusion (mg/g min^{1/2}). I (mg/g) is a constant giving an idea about the thickness of the boundary layer. K_{id} is determined from the slope of the linear equation where 'q_t' is plotted against 't^{1/2}' (fig.15) and constants are given in table 2.

Thermodynamic Studies

Thermodynamic parameters are very important in order to understand the the effect of temperature on adsorption process. The thermodynamic study for adsorption process was carried out at different temperatures from 298.15 K to 338.15 K and Van't Hoff equation (Ijagbemi *et al.*, 2009; Khan et al, 2021) as given below was applied to evaluate the thermodynamic parameters like the ΔG° , ΔH° and ΔS° .

$$lnK_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$
(10)

Where, K_c = equilibrium constant for sorption, R= universal gas constant (8.314 J/mol. K), T = absolute temperature (K).The value of ΔH° and ΔS° can be calculated from the slope and intercept by plotting a graph between 'lnK_c' and '1/T' (fig. 16). The K_c value was determined with the help of following relation:

$$K_{c} = \frac{q_{e}}{C_{e}}$$
(11)

Where, ' q_e ' (mg gm⁻¹) and ' C_e ' (mg L⁻¹) have usual meanings as described in the paper.

Knowing ΔH° , the thermodynamic parameters for adsorption process like ΔG° , and ΔS° can also be obtained by using the following relations:

$$\Delta G^o = -RT ln K_c \tag{12}$$

$$\Delta G^o = \Delta H^o - T \Delta S^o \tag{13}$$

The estimated thermodynamic parameters (ΔG° , ΔH° and ΔS°) and R^2 are presented in table 3.The enthalpy change (ΔH°) for the adsorption of crystal violet (CV) dye onto MLP signifies that MLP adsorbent shows exothermic adsorption process. The ΔG° value was negative at all considered temperatures indicating that the adsorption of crystal violet (CV) dye by MLP is feasible and spontaneous. Similarly, ΔS° is negative for MLP adsorbent for adsorption of crystal violet (CV) dye and may be due to the decrease in randomness of dye molecules at interface.

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Langmuir	Q _o (mg/gm.)	b (l/mg)	R _L	\mathbf{R}^2
	50	0.2666	0.0599	0.9332
Frundlich	1/n	Ν	K _f	\mathbf{R}^2
	0.517	1.934	8.2978	0.79246
Temkin	A _T	В	b _T	\mathbf{R}^2
	9.2415	4.497	554.913	0.88604

Table 1: Langmuir, Frundlich and Temkin isotherm data for crystal violet (CV) dye using MLP adsorbent

Table 2: Kinetic data for crystal violet (CV) dye adsorption onto MLP adsorbent

Pseudo-first-order	\mathbf{R}^2	K ₁	q _e	
	0.6695	0.1589	2.716	
Pseudo-second-order	\mathbf{R}^2	q _e	K ₂	V ₀
	1	10.7422	0.5127	59.1715
Intraparticle diffusion	\mathbf{R}^2	Intercept (I)	Slope	
	0.8157	10.338	0.0543	

Table 3: Thermodynamic parameters



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Figure 1: FTIR of CLP







Figure 3: Effect of contact time on CV adsorption.



Figure 4: Effect of conc. on CV adsorption





Figure 7: Effect of CaCl₂ on CV adsorption



Figure 8: Effect of temp. on CV adsorption



Figure 9: Effect of pH on CV adsorption



Figure 10: Langmuir isotherm plot of CV dye



Figure 11: Freundlich isotherm plot of CV dye



Figure 12: Temkin isotherm plot of CV dye



Figure 13: Pseudo first orde kinetic model



Figure 14: Pseudo second order kinetic model





Figure 15: Intraparticle diffusion model (CV)

Figure 16: Vant Haff plot for CV dye

CONCLUSION

The collected mulberry leaves from which powder was prepared in this study demonstrated a high capacity for CV dye adsorption, removing more than 98% of the dye at an equilibrium adsorption time of 30 minutes, with an equilibrium concentration of 27 mg/L. The experimental data to some extent fit best to the Langmuir isotherm than that of Freundlich and Tempkin isotherm models for linearly regressed data. The Kinetic data fit best to the pseudo- second order kinetic model for linear regressed data while as intraparticle diffusion study reveals that more than one mechanism affected the adsorption process. The calculated thermodynamics parameter like ΔG° and ΔH° shows that the adsorptions of crystal violet (CV) dye onto given adsorbent was favorable, endothermic and exothermic.

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