Adsorptive removal of Crystal Violet from aqueous solution by Kokum (*Garcinia Indica*) leaf powder: Equilibrium and Thermodynamic studies

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ABSTRACT
In this paper, adsorptive removal of Crystal Violet dye from aqueous solution using kokum leaf powder was carried out in batch process. The effect of contact time, adsorbent dose, pH, initial concentration and temperature have been studied. The linear regression coefficient R^2 was used to evaluate the best fitting equilibrium isotherm model. Experimental data were best fitted by both Langmuir and Freundlich isotherm models. From the experimental data, it was found that maximum monolayer adsorption capacity of kokum leaf powder was found to be $q_m = 109.89$ *mg/g*. The pH of solution is an important factor to control the dye adsorption. The adsorption of Crystal violet dye increases with increase in pH and increase in temperatures. The values of R_L and thermodynamic analysis indicated that adsorption was spontaneous, endothermic and favorable and increased randomness during adsorption of Crystal violet on Kokum leaf powder. Thus Kokum (*Garcinia Indica*) leaf powder was found to have effective adsorption capacity for the removal of Crystal violet dye from aqueous solution.

Keywords: Crystal violet, Kokum leaf powder, adsorption, Freundlich isotherm, Langmuir isotherm.

INTRODUCTION: Crystal violet is a basic mono azo dye widely used for dyeing of cotton, wool silk, nylon, paper and leather etc. Basic dyes like Crystal violet are the brightest soluble dyes having very high tinctorial value which produce intense colouration even in less than *1 mg/L* concentration of solution[1]. Most of the coloured dyes are synthetic, formed by aromatic rings in their structure which make them inert and non-biodegradable when discharged in water sources. These coloured dyes are not only aesthetic, carcinogenic but also prevent light penetration and disturb the aquatic life[2-3] Therefore it is necessary to remove these dyes before their discharge into water sources. Various studies have been carried out by researcher to remove coloured contaminants and other pollutants. These removal methods include adsorption, coagulation, electro osmosis, ion exchange, membrane filtration etc. in which adsorption is found to be effective and most widely used method but due to its high cost and regeneration issue still there has been search for new alternatives of cost effective adsorbents. A large number of low cost adsorbents were prepared such as Asoka leaf powder[4], Almond tree bark[5], Azardichta indica leaf[6], orange peel7 ,Coconut shell[8], guava leaf powder[9] , sunflower stalk[10], rice husk[11,12] , saw dust[13] were used for the removal of colour from wastewater.
In present study, the Kokum leaf powder (KLP) as the low cost adsorbent for the removal of Crystal violet dye from waste water has been evaluated

MATERIALS AND METHODS

Preparation of kokum leaf powder as adsorbent (KLP)

Kokum leaves were dried in shadow, crushed and boiled in distilled water to remove colour and suspended dust. It was filtered and residue was treated with 20% formaldehyde followed by dilute sulphuric acid for 30 minutes. The residue was further washed with distilled water to remove free acid and dried at 100-120 ^{0}C for 8 hours, powdered, sieved to desired size and used for the study.

Preparation of Crystal violet dye solution

The Crystal violet dye solutions of 10 to 50 mg/L concentration were prepared in distilled water using 1000 mg/L stock solution. The pH of solution was adjusted with 0.1 N HCl or 0.1 N NaOH solutions

Batch adsorption experiment

To study the adsorption of Crystal violet by Kokum leaf powder the batch adsorption experiments were carried by mixing 50 mL of 50 mg/L solution of Crystal violet dye with 1.0 g of KLP adsorbent. The effect of contact time, solution pH, adsorbent dose, initial dye concentration and temperature were evaluated. After desired time interval, sample solutions were filtered and residual dye concentration was determined using UV/VIS Spectrophotometer (Elico -1245) at 590 nm as $\lambda_{max.}$ .The equilibrium isotherm study was carried by mixing of 1.0 g adsorbent dose with various dye concentration of 10-50 mg/L for 60 minutes as equilibrium time at pH 6. The dye solutions were mixed at different time interval in the temperature range of 30 to 60 ^{0}C and residual dye concentration is determined by spectroscopic method.

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time on adsorption of CV by Kokum leaf powder was studied by using 50 mg/L of CV dye solutions was treated with 1.0 g of kokum leaf powder for 5 to 90 minutes at solution pH 6. The dye % removal with contact time has been shown in Figure 1 indicated that % dye removal was increased from 37.42 to 88.13 with increased contact time. The equilibrium was attained at 60 minutes .Similar results were reported by other researchers [14].

Effect of dye solution pH

To study the effect of solution pH on dye removal capacity of KLP was evaluated in the pH range of 2 to 10 with 50 ml dye solution for 50 mg/L concentration, 1.0 g adsorbent dose, 60 minutes contact time and 30 ^{0}C temperature. Figure 2 showed that 44.20 % of Crystal violet dye was removed at 2 pH and at pH 6, it was found to be 88.13 % and equilibrium was attained at pH 6. Similar results were reported by other workers[15]

Effect of dye initial concentration

The effect of initial dye concentration of CV (10 to 50 mg/L) on adsorption was studied with 50 mL volume, adsorbent dose 1.0 g /L, pH 6. From figure 3, it was observed that % removal of dye was decreased from 92.15 to 88.13 % whereas the amount of dye adsorbed increased with increase in concentration. It is attributed to surface activity and formation on monolayer for given range of concentration. Similar observations were reported by other researchers[16]

Effect of adsorbent dose

The effect of adsorbent dose was studied by taking 50 mL of 50 mg/L dye solutions and adsorbent dose was varied from 0.2 to 1.4 g. the removal of CV was 44.46 to 88.13 when treated with different doses of KLP as shown in Figure 4. The increase in dye removal % with increased dose may be due to presence of more active sites on adsorbent surface[17]. The maximum dye removal was found at 1.0 g of adsorbent dose

Effect of temperature

The effect of temperature on removal of CV, batch mode experiment was carried out from 30 to 60 ^{o}C Figure 5, showed that, dye removal % increased from 88.13 to 92.18 % with increase in temperature[18].

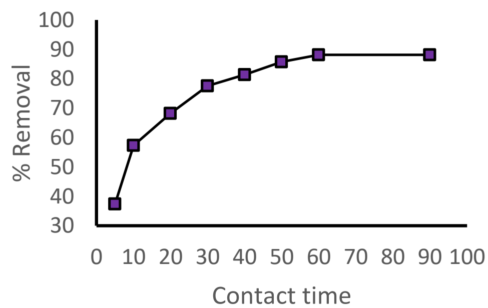

Fig. 1 Effect of contact time on adsorption of Crystal violet by KLP

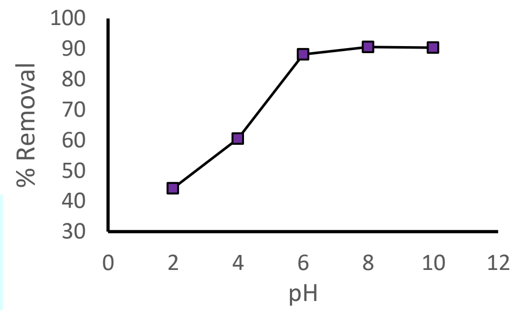

Fig. 2 Effect of pH on adsorption of Crystal violet by KLP

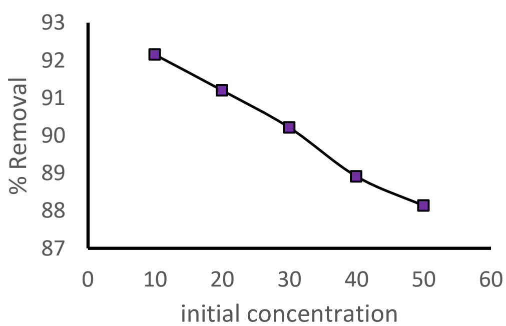

Fig. 3 Effect of initial concentration on adsorption of Crystal violet by KLP

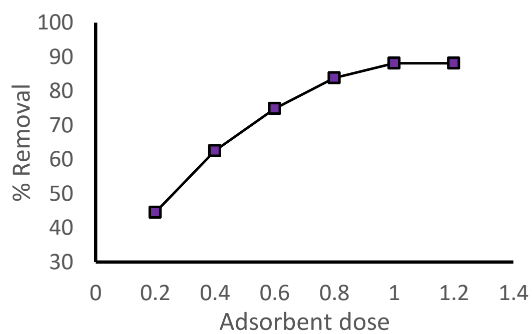

Fig. 4 Effect of adsorbent dose on adsorption of Crystal violet by KLP

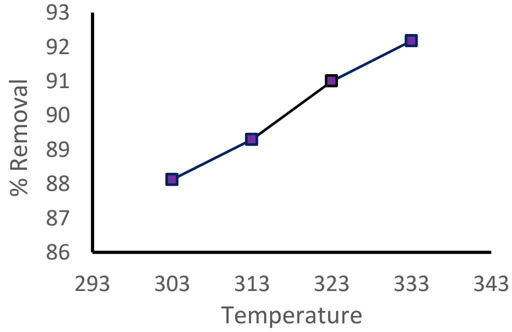

Fig. 5 Effect of temperature on adsorption of Crystal violet by KLP

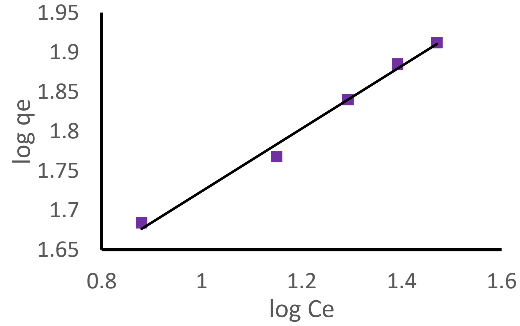

Fig. 6 Freundlich isotherm for adsorption of Crystal violet by KLP

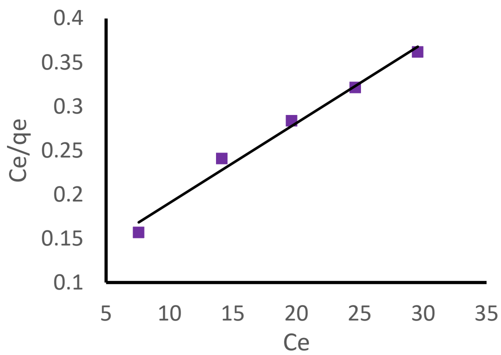

Fig. 7 Langmuir isotherm for adsorption of Crystal violet by KLP

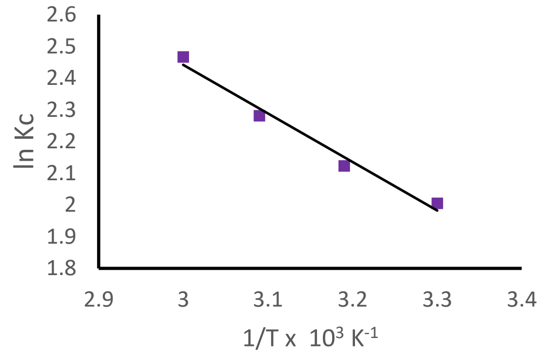

Fig. 8 Van't Hoff's plot of $ln\,K_0$ vs $\frac{1}{T}$ for adsorption of Crystal violet by KLP

Adsorption isotherms

The adsorption of CV by Kokum leaf powder was analyzed by the simple isotherm models given by Freundlich and Langmuir. The linearized form of Freundlich isotherm can be given by[19]

$$lnq_e = lnK_F + \frac{1}{n}\,lnC_e \quad (1)$$

Where q_e is the amount adsorbed (mg/g), C_e is dye equilibrium concentration (mg/L) K_F and n are Freundlich constants for adsorption capacity and adsorption intensity[20] (Table1).The linear relationship between ln q_e vs ln C_e plotted parameters indicates applicability of Freundlich isotherm model (Figure 6)

The linear form of Langmuir isotherm is written as

$$C_e/q_e = 1/q_m\,b + 1/q_m\,C_e \quad (2)$$

Where C_e is equilibrium concentration of adsorbate (mg/L), q_e is the amount adsorbed (mg/g), q_m and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption respectively. The Langmuir constants are evaluated from slope, intercept and correlation coefficients (Table 1) from the plot of C_e/ q_e vs C_e (Figure7) .The higher R^2 indicate that adsorption of CV by KLP show the applicability of Langmuir isotherm model. The dimensionless separation factor $R_L = 1/(1+bC_i)$ is measure of adsorption [21].The R_L values between 0 to 1 indicative of the feasibility of adsorption process

Thermodynamics Parameters

The change in standard free energy ΔG^0, enthalpyΔH^0 and entropy ΔS^0 (Table 2) were evaluated by following equations[22]

$$K_c = \frac{C_0 - C_e}{C_e} \quad (3)$$

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

$$\ln K_c = \Delta S^0/R - \Delta H^0/RT \quad (5)$$

Table: 1 Langmuir and Freundlich parameters for adsorption of Crystal violet on KLP

Langmuir constants			Freundlich constants		
q_m (mg/g)	b (L/mg)	R^2	K_f	n	R^2
109.89	0.0 912	0.985	21.306	2.528	0.990

Table: 2 Thermodynamic parameters for adsorption of Crystal violet dye by KLP

K_c				R_L	$-\Delta G^0$ kJmol⁻¹	ΔH^0 kJmol⁻¹	ΔS^0 Jmol⁻¹
303	313	323	333				
7.431	8.353	9.799	11.778	0.180	5.885	12.730	58.493

CONCLUSIONS

In this study, the adsorption of Crystal violet by Kokum leaf powder is best fitted by both Langmuir and Freundlich isotherm models with high R^2 (0.97 to 0.998). Monolayer adsorption capacity (q_m) was found to be 109.89 *mg/g* .The thermodynamics parameters indicate that adsorption process is spontaneous, endothermic and favorable with increasing disorder at solid -solution interface during adsorption. Therefore Kokum leaf powder can be used as better alternative for the expensive adsorbents.

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