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 R² 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 qₑₑₑ=e = 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 Rd 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 solution¹. 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 life²³. 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 powder⁴, Almond tree bark⁵, Azardichta indica leaf⁶, orange peel⁷, Coconut shell⁸, guava leaf powder⁹, sunflower stalk¹⁰, rice husk¹¹,¹² saw dust¹³ 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 °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 λₑₑₑₑ. 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 °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 °C temperature. Figure 2 showed that 44.20 % of Crystal violet dye was removed at pH 2 and at pH 6, it was found to be 88.13 % and equilibrium was attained at pH 6. Similar results were reported by other workers15.

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 researchers16.

Effect of adsorbent dose
The effect of adsorbent dose was studied by taking 50 mL of 50 mg/L dye solutions and adsorbent dose 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 surface17. 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 °C Figure 5, showed that, dye removal % increased from 88.13 to 92.18 % with increase in temperature18.
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

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]

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 intensity²⁰ (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

\[ \frac{C_e}{q_e} = \frac{1}{q_m} b + \frac{1}{q_m} C_e \]

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 \( C_e \) (Figure 7). The higher \( R^2 \) indicate that adsorption of CV by KLP show the applicability of Langmuir isotherm model. The dimensionless separation factor \( R_L = 1/(1+bC_e) \) is measure of adsorption process.

Thermodynamics Parameters

The change in standard free energy \( \Delta G^0 \), enthalpy \( \Delta H^0 \) and entropy \( \Delta S^0 \) (Table 2) were evaluated by following equations²²

\[ K_c = \frac{q_m}{K_F} \]

\[ \Delta G^0 = -RT \ln K_c \]

\[ \ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]

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

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<th>Langmuir constants</th>
<th>Freundlich constants</th>
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<td>( q_m ) (mg/g)</td>
<td>( b ) (L/mg)</td>
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Table: 2 Thermodynamic parameters for adsorption of Crystal violet dye by KLP

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<th>( R_L )</th>
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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.

REFERENCES


