BIOSORPTION OF CRYSTAL VIOLET FROM AQUEOUS SOLUTION BY Citrullus lanatus (WATERMELON) RIND

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ABSTRACT

The efficiency of Citrullus lanatus (Watermelon) rind, an agricultural solid waste was investigated in this study as a novel adsorbent for the removal of Crystal Violet (CV) from aqueous solution. Batch mode experiments were conducted to study the effects of contact time, dose of adsorbent, pH and temperature. Equilibrium data were analyzed using the Langmuir and Freundlich isotherms. Different thermodynamic parameters, like Gibb’s free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the adsorption process have also been evaluated. The thermodynamic parameters of CV biosorption indicated that the process is spontaneous and endothermic. Two simplified kinetic models including pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption process. The pseudo-second-order kinetics was the best for the adsorption of CV by Citrullus lanatus rind with good correlation. The results demonstrate that the biosorbent used in this study was found to be a promising material for adsorption of CV from aqueous solutions.

Key Words : Citrullus lanatus rind, Basic dye, Equilibrium, Kinetics, Thermodynamic

INTRODUCTION

Dyes are synthetic organic aromatic compounds that are molecularly dispersed and bound to the substrates by intermolecular forces and have high application potential in the industrial sector as coloring material. Dyes are widely used in industries such as textiles, tanning, plastics, paper, rubber, cosmetics, pharmaceutical and food stuff. Crystal violet is a well-known dye for various purposes like biological stain, dermatological agent, veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus etc. It is a mutagen and mitotic poison and may cause cancer. It is known to be a severe eye irritant and shows harmful effects on inhalation, ingestion or through skin contact. Many treatment processes like coagulation and flocculation, membrane separation, ultra chemical filtration, activated carbon adsorption etc., have been applied for the removal of dyes from wastewater. Adsorption process using commercial activated carbon is the most popular and widely used technique in wastewater reuse methodology. However the higher cost of this material limits its use. Recently a number of researchers have studied the feasibility of using low cost adsorbents like ground nut shell, corn cob, date pits, almond shell, broad bean peels, orange peel as a substitute to the more expensive commercial activated carbon. The biggest advantage of the use of waste materials as adsorbents is their low cost, versatility and easy operations.

In the present study, a new adsorbent Citrullus lanatus (watermelon) rind an agricultural solid waste was investigated for its potential adsorption of a basic dye from aqueous solution. Citrullus lanatus is a vine-like plant of Cucurbitaceae family. This flowering plant produces a special type of fruit known by botanists as a pepo, a berry which has a thick rind (exocarp) and fleshy center (mesocarp and endocarp). To make better use of this cheap and abundant agricultural waste, it is proposed to use the Citrullus lanatus rind as a novel adsorbent for the removal of crystal violet from aqueous solution. The effects of contact time, adsorbent dose, pH and temperature on crystal violet adsorption were evaluated.

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MATERIAL AND METHODS

Adsorbate

Crystal Violet (CV), procured from S. D. Fine-Chem. Ltd. (India) was used as adsorbate. Stock solution was prepared by dissolving 1.0 g of CV in 1L distilled water without further purification. The test solutions were prepared by diluting stock solution to the desired concentrations.

Preparation of adsorbent

*Citrullus lanatus* rinds were collected from the local market as solid waste. It was washed thoroughly with distilled water to remove the dirt adhered at the surface. Then it was sliced, spread on trays and kept under hot sun for 5 days. The dried biomass was ground, sieved (150-300 μm) and stored in an air tight container for further use. No other physical or chemical treatments were given prior to adsorption experiments.

Batch adsorption experiments

Effect of contact time on biosorption

The adsorption of CV onto CLR was carried out at different contact time (5-210 min) with initial dye concentration (C₀) of 10 mg/L and a dose of 1 g/L. The agitation speed was kept constant at 150 rpm. At predetermined intervals of time, solutions were analyzed for the final concentration of CV by double beam UV/vis spectrophotometer (Perklin Elmer Lambda 25) at a wavelength of 587 nm, maximum absorbance.

Effect of adsorbent dose on biosorption

The effect of CLR dose on the amount of CV adsorption was obtained by adding different amounts of CLR (0.1-1.0g) into 250 ml stoppered glass Erlenmeyer’s flask containing a definite volume (50 ml in each case) of fixed initial concentration (10 mg/L) of dye solution at temperature 30°C. The flasks were placed in an isothermal shaker and agitation was provided at 150 rpm for 180 min. After equilibrium, the sorbent was separated from the dye solution by centrifugation and the dye concentrations were measured.

Effect of solution pH

In this study, the effect of pH on adsorption of CV on CLR was studied by mixing 50 mg of adsorbent with 50 ml of dye solution at different pH values (2-12). The pH was adjusted with 0.1N NaOH and 0.1 N HCl solutions and measured by using an Orion EA 940 expandable ion analyzer. Agitation was made for 180 min at a constant agitation speed of 150 rpm. The dye concentrations at equilibrium were determined.

Effect of temperature on biosorption

The effect of temperature on the adsorption characteristics was studied at 30°C, 40°C and 50°C to determine the thermodynamic parameters using a fixed dye concentration (10 mg/L) and dosage (50mg/50ml).

RESULTS AND DISCUSSION

The effect of contact time on dye adsorption

The adsorption of CV on CLR was studied as a function of contact time in order to find out the equilibrium time for maximum adsorption. The influence of contact time on color removal by CLR is presented in Fig. 1. It was observed that the sorption is very rapid initially, which occurs as a result of the presence of large number of active adsorption sites available on the surface of the adsorbent, compared to the number of adsorbate species in the solution and the maximum CV adsorption was reached at an equilibrium contact time at 180 min. The maximum amount of CV adsorbed corresponding to the equilibrium time was found to be 87% for a dose of 1.0 g/L of the adsorbent.

The effect of adsorbent mass on dye adsorption

The effect of CLR dose on the amount of CV adsorption was obtained by adding different amounts of CLR (0.1-1.0g) into 250 ml stoppered glass Erlenmeyer’s flask containing a definite volume (50 ml in each case) of fixed initial concentration (10 mg/L) of dye solution at temperature 30°C. The flasks were placed in an isothermal shaker and agitation was provided at 150 rpm for 180 min. After equilibrium, the sorbent was separated from the dye solution by centrifugation and the dye concentrations were measured.

Effect of solution pH on dye uptake

The solution pH is an important factor in controlling the adsorption of dye onto adsorbent. Adsorption experiments were conducted in the pH range 2.0-12.0 keeping all other parameters constant (CV concentration = 10mg/L, adsorbent dose = 50mg/50mL; stirring speed = 150 rpm; contact time = 180 min; temperature = 30°C). Fig. 3 shows that
the sorption of CV was minimum at pH 2 and increased up to 8.0 and then remained almost constant over the pH range of 8.0-12.0. Lower adsorption of CV at acidic pH was due to the presence of excess H\(^+\) ions competing with the dye cation for the adsorption sites. As the pH of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases. The negatively charged sites favour the adsorption of dye cation due to electrostatic attraction. Similar results were reported for the adsorption of MB on papaya seed\(^{20,21}\) and fallen phoenix tree’s leaves\(^{22}\).

**Effect of temperature on dye uptake**
The effect of temperature on the adsorption of CV on CLR was investigated under isothermal conditions in the temperature range of 30-50\(^\circ\)C. The temperature dependence of CV adsorption on CLR is shown in **Fig. 4**.

The extent of adsorption of CV was found to increase with increase in temperature, indicating the process to be endothermic in nature\(^{23}\). The increased removal of CV may be attributed to the increase of mobility of the CV particles and
Isotherm analysis

Isotherm analysis is basically important to describe how solutes interact with adsorbents and is critical in optimizing the use of adsorbents. In this study, two isotherms were used for describing the experimental results namely the Langmuir and the Freundlich isotherm. The applicability of the isotherm equation is determined by comparing the correlation coefficients, $R^2$. The Langmuir isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solution. The monolayer capacity can be represented in a linear form using equation (1)

$$\frac{1}{X/M} = \frac{1}{q_{\text{max}}} + \frac{1}{b q_{\text{max}} C_e}$$

where, $b$ is the constant that increases with increasing molecular size; $q_{\text{max}}$ is the maximum adsorption capacity (mg/g); $X$ is the weight of substance adsorbed (mg); $M$ is the weight of adsorbent (g); $C$ is the concentration of the dye remaining in solution (mg/l).

Freundlich isotherm is an empirical expression based on biosorption on a heterogeneous surface.
Equation (2) represents the Freundlich isotherm model,
\[
\log q_e = \log K + \frac{1}{n} \log C
\]
(2)
where K and n are Freundlich isotherm constants being indicative of the extent of the biosorption and the degree of non linearity between solution concentration and adsorption, respectively. The plot of ln q_e versus ln C for the biosorption was employed to generate K and n from the intercept and slope values. The linearized plots of Langmuir and Freundlich isotherms obtained are shown in Fig. 5. Parameters of the two isotherms were calculated and listed in Table 1. Based on the values of R^2, it can be concluded that the Freundlich isotherm best-fit the equilibrium data.

Adsorption kinetics
Kinetic models are used to examine the rate of the adsorption process and the potential rate-controlling step. In the present study the adsorption kinetics for the adsorption of CV on CLR has been tested using the pseudo-first-order and pseudo-second-order model. The linear form of the pseudo-first-order kinetic equation is given by equation (3)
\[
\log \left( q_e - q_t \right) = \log \left( q_e \right) - \frac{k_1}{2.303} t
\]
(3)
Where q_e and q_t are the amount of CV adsorbed (mg/g) at equilibrium and at time t (min), respectively. k_1 is the equilibrium rate constant of pseudo-first-order kinetics (min^-1). The value of k_1 at 30o C was calculated from the plot of log \((q_e - q_t)\) vs t (Fig. 6). The R^2 value obtained was relatively small and the experimental q_e value did not agree with the calculated values obtained from the linear plot (Table 2).

The pseudo-second-order equation based on equilibrium adsorption is expressed as
\[
\left( t \right) = \frac{l}{k_2 q_e^2} + \frac{l}{q_e} (t)
\]
(4)
Where k_2 (g/mg min) is the equilibrium rate constant of the pseudo-second-order kinetics. The linear plot of \(t/q_t\) vs t is shown in Fig. 7. The coefficient of correlation (R^2= 0.999) was more than that of the pseudo-first-order kinetics. It also showed a good agreement between the experimental and calculated q_e values (Table 2) indicating the applicability of this model to describe the adsorption of CV on to CLR.

Thermodynamic studies
Thermodynamic parameters reflect the feasibility and spontaneous nature of the adsorption process.

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**Table 1 : Langmuir and Freundlich constants and correlation coefficients for the adsorption of CV onto CLR**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Langmuir isotherm constants</th>
<th>Freundlich isotherm constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_{max}) (mg/g)</td>
<td>b</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>-17.24</td>
<td>-0.213</td>
</tr>
</tbody>
</table>

CLR has been tested using the pseudo-first-order and pseudo-second-order model. The linear form of the pseudo-first-order kinetic equation is given by equation (3)
The thermodynamic parameters such as change in free energy ($\Delta G$) (J/mole$^{-1}$), enthalpy ($\Delta H$) (J/mole$^{-1}$) and entropy ($\Delta S$) (J K$^{-1}$ mole$^{-1}$) were determined using the equations (5) and (6):

$$K_0 = \frac{C_{\text{solid}}}{C_{\text{liquid}}}$$  \hspace{1cm} (5)

$$ln k_0 = \frac{-\Delta G}{RT}$$  \hspace{1cm} (6)

Where $K_0$ is equilibrium constant, $C_{\text{solid}}$ is solid phase concentration at equilibrium (mg/ℓ), $C_{\text{liquid}}$ is liquid phase concentration at equilibrium (mg/ℓ), $T$ is absolute temperature in Kelvin and $R$ is gas constant. $\Delta H$ and $\Delta S$ values are obtained from the slope and intercept of plot $ln K_0$ against $1/T$.

Fig. 8 illustrates Von't Hoff plot of effect of temperature on adsorption of CV on CLR. The observed thermodynamic values are listed in Table 3. The negative value of $\Delta G$ indicates the adsorption is favorable and spontaneous. The high positive values of $\Delta H$ confirm the endothermic nature of adsorption process. The positive values of $\Delta S$ indicate the increased disorder and randomness at the solid solution interface of CV with the adsorbent.

The increase of adsorption capacity of the adsorbent at higher temperatures was due to enlargement of pore size and activation of adsorbent surface$^{31}$.

![Graph showing pseudo-first-order kinetics for the adsorption of CV onto CLR at 30°C.](image)

**Table 2**: Adsorption kinetic model rate constants for CV removal

<table>
<thead>
<tr>
<th>$C_0$ (mg/g)</th>
<th>Pseudo 1$^{st}$ order kinetics co-efficients</th>
<th>Pseudo 2$^{nd}$ order kinetics co-efficients</th>
<th>$q_e$ (exp) (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$q_e$ (cal) 1.9906 0.0138 0.859</td>
<td>$q_e$ (cal) 8.77 0.026 0.999 8.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$ 0.859</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$y = -0.006x + 0.299$
$R^2 = 0.859$
y = -2932x + 14.81
\( R^2 = 0.831 \)

Fig. 7: Pseudo-second-order kinetics for the adsorption of CV onto CLR at 30°C

y = -2932x + 14.81
\( R^2 = 0.831 \)

Fig. 8: Von’t Hoff plot of effect of temperature on adsorption of CV on CLR

Table 3: Thermodynamic parameters of CV over CLR

<table>
<thead>
<tr>
<th>Initial CV concentration (mg/ℓ)</th>
<th>ΔG (J/mole)</th>
<th>ΔH (J/mole)</th>
<th>ΔS (J/K/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303K</td>
<td>-12458.82</td>
<td>-14245.43</td>
<td>2932</td>
</tr>
<tr>
<td>313K</td>
<td>-14245.43</td>
<td>-14841.74</td>
<td>14.81</td>
</tr>
<tr>
<td>323K</td>
<td>-14841.74</td>
<td>2932</td>
<td></td>
</tr>
</tbody>
</table>
CONCLUSION

In the present study, the ability of *Citrullus lanatus* (watermelon) rind an agricultural solid waste to remove CV from aqueous solution was investigated. The adsorption followed Freundlich isotherm. The adsorption capacity was found to be 4.82 mg/g at 30°C. The kinetics of adsorption was found to follow pseudo-second-order kinetic model. The positive value of $\Delta H$ and $\Delta S$ value indicated the endothermic nature of adsorption and the increased randomness at the solid-solution interface during adsorption respectively. The negative value of $\Delta G$ indicated the feasibility and the spontaneous nature of the adsorption of CV onto CLR. The adsorbent used in this study is a cheap, readily available solid waste hence it can be used as an alternative for more costly adsorbents used for dye removal in wastewater treatment process.

REFERENCES


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*Our environmental problems originate in the hubris of imagining ourselves as the central nervous system or the brain of nature. We're not the brain, we are a cancer on nature.*

*Dave Foreman*