Removal of direct dye from aqueous solutions with an adsorbent made from tamarind fruit shell, an agricultural solid waste

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Removal of a direct dye, Congo Red, has been carried out using tamarind fruit shell (TFS) as an adsorbent. Parameters like agitation time, adsorbent dosage and pH effect have been studied. Adsorption followed the first-order rate expression. The equilibrium data fit well with both Langmuir and Freundlich models of adsorption. Desorption experiments confirmed that major mode of adsorption is ion-exchange for the dye.

Keywords: Adsorbent, Congo Red, Dye, Solid waste, Tamarind fruit shell

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Introduction

The removal of dyes from effluent using adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. A number of non-conventional, low cost plant materials (residues), used as adsorbents for dye removal, include fruit waste of Prosopis juliflora, wood, waste orange peel, banana pith, bagasse pith, maize cobs, barley husk, apple pomace and sunflower stalks. Utilization of agricultural wastes is of great significance in India, where more than 200 million tons of agricultural residues are generated annually. The utilization of agricultural waste provides additional employment and income to marginal farmers and landless agricultural labourers, especially in developing countries. The present research is to explore the feasibility of utilizing tamarind fruit shell (TFS) as adsorbent for color removal in textile wastewater. This solid waste is not used for any purpose except firewood in some places.

Materials and Methods

Materials

TFS, collected from a local farmer during the summer of 2001, washed thoroughly with de-ionized water for removing dirt. Dried material grounded to pass through 75 µm mesh sieve, retained on 53 µm, and washed with de-ionized water. Congo Red (C.I.22120; CR), procured from Qualigens Fine Chemicals, India, was purified using salting out method.

\[
\text{Congo red} \quad \text{NH}_4^+ \quad \text{SO}_4^{2-} \quad \text{Na}^+ \\
\text{N} = \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{SO}_4^{2-} \quad \text{Na}^+ \\
\]

Batch Mode Studies

Adsorption experiments were carried out by agitating TFS (125 mg) with dye solutions (25 ml) of desired concentration and pH in a 50 ml screw type Erlenmeyer flask at room temperature (30±1°C). A good contact has been made between adsorbent and dye by agitation at 180 rpm in a Julabo shaking water bath. Dye concentration has been determined spectrophotometrically by monitoring the absorbance at 497 nm using Chemito UV-VIS Spectrophotometer and two 1-cm cells. The wavelength of the maximum absorbance for dye has been selected, and \( \lambda_{\text{max}} \) value is 497 nm. The pH of dye solutions has been determined using pH meter (model LI-120, Elico, Hyderabad, India). The samples were withdrawn from the shaker at pre-determined time intervals and the
Dye solution was separated from the adsorbent by centrifugation at 10,000 rpm for 20 min. The absorbance of supernatant solution was measured. Effect of pH was studied by adjusting the pH of dye solutions using dilute HCl and NaOH solutions. Effect of adsorbent dosage was studied with different adsorbent doses (50-900 mg) and 50 ml of 100 mg/l dye at equilibrium time. Langmuir and Freundlich isotherms have been employed to study the adsorption capacity of the adsorbent.

Desorption Studies
Adsorbent that was used for the adsorption of 100 mg/l of dye solution was separated from the dye by centrifugation. The dye-loaded adsorbent was washed gently with water to remove any unadsorbed dye. Then the spent adsorbent was agitated with 50 ml of distilled water, adjusted to different pH values for 180 min. Desorbed dye was estimated as before.

Results and Discussion
Effects of Agitation Time and Concentration of Dye on Adsorption
The uptake of dye increased with increase in dye concentration and remained nearly constant after equilibrium time (Fig. 1). The dye attained equilibrium at 1, 2, 3, 4 h for dye concentrations of 20, 40, 60, and 80 mg/l respectively. The present dye removal decreased from 87 percent to 58.8 percent as the dye concentration increased from 20 mg/l to 80 mg/l. It is clear that the removal of dyes depends on the concentration of the dye. The removal curves are single, smooth and continuous leading to saturation.

Adsorption Dynamics: Adsorbent Rate Constant
The rate constant of adsorption has been determined from the first order rate expression given by Lagergren16.

\[
\log(q_e - q) = \log q_e - k_{ad} t / 2.303 \quad \ldots(1)
\]

where \( q_e \) and \( q \) are the amounts of dye adsorbed (mg/g) at equilibrium and at time \( t \) (min), respectively and \( k_{ad} \) is the rate constant of adsorption (l/min).

Linear plots of \( \log(q_e - q) \) vs \( t \) for different concentrations of dye (Fig. 2) shows that the adsorption process follows the first order rate expression. The rate constant for intra particle
diffusion $k_e$ has been calculated from the slope of the linear portion (Fig. 3, Table 1).

**Effect of Adsorbent Dosage**

Increase in adsorbent dose increased the percentage removal of dye. For quantitative removal of dye from 50 ml of 100 mg/l, a maximum dosage of 900 is required.

**Adsorption Isotherm**

Langmuir isotherm has been applied for adsorption equilibrium.  

$$\frac{C_e}{Q_e} = \frac{1}{K_L b} + \frac{1}{K_L} C_e$$  

(2)

where $C_e$ is equilibrium concentration (mg/l), $Q_e$ is amount of dye adsorbed at equilibrium (mg/g) and $K_L$ and $b$ are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (l/mg) respectively. $K_L$ and $b$ are determined from the slope and intercept of Langmuir plot, which is made between log $C_e$ and log $Q_e$ and the values are 10.48 mg/g and 0.30 l/mg respectively.

**Effect of Isotherm Shape**

Effect of isotherm shape has been considered with a view to predicting if an adsorption system is “favorable” or “unfavorable”. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, $r$, which is defined by the following relationship given by Hall:

$$r = \frac{1}{1 + b C_0}$$  

(3)

where $C_0$ is the initial dye concentration in solution (mg/l). The parameter, $r >1$, $r=1$, $0<r<1$ and $r=1$ indicates unfavorable, linear, favorable and irreversible isotherm type respectively. The values of separation factor, $r$, range from 0.01 to 0.05 in the concentration range from 20 to 80 mg/l in the present investigations indicate that the adsorption process is favourable.

Freundlich adsorption isotherm model, used to explain the present adsorption phenomenon, is represented by equation:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$  

(4)

$K_f$ and $n$ are constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity). The values $K_f$ and $n$ were calculated from the intercept and slope of the plot, which is made between log $C_e$ and log $Q_e$ and the values are 3.48 and 3.17 respectively. The n values are between 1 and 10 representing beneficial adsorption.

**Effect of pH**

The lower pH of the Congo Red solutions are not taken for the studies because at lower pH the solution turns to a black color due to formation of quinoniod structure. When initial pH of the dye solution has been increased from 5.5 to 12, the percentage removal decreased from 83 to 68. Lower adsorption of the dye at alkaline is provable due to the presence of excess of OH$^-$ ions competing with the dye anions for the adsorption sites. As the pH of the dye solution decreases, the number of positively charged surface sites on the adsorbent favors the adsorption of the anions due to electrostatic attraction. Similar results are observed for the adsorption of Acid Violet by banana pith and orange peel.

The final pH of dye solution after desorption (in absence of dye) was higher than the pH of the dye solution after adsorption (in presence of the dye). This is due to consumption of H$^+$ ions during desorption of alkali metal ions present in the adsorbent. This may also be due to either release of OH$^-$ ions into solution or the consumption of H$^+$ ions in solution.

**Desorption Studies**

Desorption studies help to elucidate mechanism of adsorption and recovery of the adsorbate and adsorbent. Regeneration of adsorbent may make the treatment process economical. Percent desorption increases with increase in pH of the aqueous medium. This is just opposite to pH effect, indicating that ion exchange is probably then major mode of adsorption process.

**Conclusions**

An agricultural solid waste or by-product, tamarind fruit shell, studied as adsorbent for removal of Congo Red, proved that it works well. The adsorption obeyed both Langmuir and Freundlich isotherms. Desorption study shows that the recycling of adsorbent may be possible.

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References

Additions and Corrections

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