Adsorption of Safranin-T from wastewater using waste materials—activated carbon and activated rice husks

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Abstract

Textile effluents are major industrial polluters because of high color content, about 15% unfixed dyes and salts. The present paper is aimed to investigate and develop cheap adsorption methods for color removal from wastewater using waste materials activated carbon and activated rice husk—as adsorbents. The method was employed for the removal of Safranin-T and the influence of various factors such as adsorbent dose, adsorbate concentration, particle size, temperature, contact time, and pH was studied. The adsorption of the dye over both the adsorbents was found to follow Langmuir and Freundlich adsorption isotherm models. Based on these models, different useful thermodynamic parameters have been evaluated for both the adsorption processes. The adsorption of Safranin-T over activated carbon and activated rice husks follows first-order kinetics and the rate constants for the adsorption processes decrease with increase in temperature.

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1. Introduction

The discharge of highly colored effluents into natural water bodies not only is aesthetically displeasing, but also impedes light penetration, thus upsetting biological processes within streams. The disposal of dyes laden wastewater poses one of the industry’s major problems because such effluents contain a number of contaminants including acid or caustic, dissolved and suspended solids, toxic compound sand coloring pigments. Out of all these contaminants, color is the first to be recognized because it is visible to human eye and is objectionable to the public for hygiene reasons. In addition many dyes are toxic to some organisms causing direct destruction of aquatic communities [1]. Some dyes can cause allergic dermatitis, skin irritation, cancer and mutation in man [2,3]. Safranin-T is one of the most commonly used azine dye, which are amongst the oldest known synthetic dyes (see Scheme 1). Safranin-T is a water-soluble reddish brown powder, which is mainly used as food dye in flavoring and coloring candies and cookies. It is also used for dyeing tannin, cotton, bast fibers, wool, silk, leather and paper [4]. Due to its extensive use in food and textile industries as colorant, Safranin-T was considered as the model compound to represent the dyes that are released in effluents from the textile and food industries.

The conventional methods for treating dye-containing wastewater are coagulation, flocculation, reverse osmosis, and adsorption onto various adsorbing materials [5]. Adsorption over activated carbon is one of the most effective methods employed in the treatment of wastewaters containing different classes of dyes [6]. Many investigations have studied the economic feasibility of using inexpensive alternative materials such as fruit stones [7,8], coconut shells [9,10], fertilizer waste [11,12], peat moss [13], maize cobs [14], coir pith [15], and red mud [16] as carbonaceous precursors for the removal of various toxic pollutants from wastewater.

Adsorption of organic pollutants onto solid/water interfaces has been found to be an efficient and economically cheap method of controlling the extent of water pollution. The most
commonly used adsorbent is activated carbon [17], but it is relatively expensive and difficult to regenerate. The object of the present investigations has been to evaluate the efficiency of removal of Safranin-T dye using activated rice husks and activated carbon. Activated rice husks are an agricultural waste material, which is easily available, cheap, and economically advantageous. In the present study application of activated rice husks for the removal of dyes from aqueous solution has been studied and activated carbon was used as a conventional adsorbent to compare the results. The effects of adsorbent dose, pH, particle size, temperature, initial dye concentration, and equilibrium time have been studied and obtained results are discussed.

2. Materials and methods

The dye Safranin-T (molecular formula $C_{16}H_{11}N_2O_4SNa$) was obtained from M/s Merck and its 0.02 M stock solution was prepared in double-distilled water. To prepare various solutions at desired concentrations from the stock solution, double-distilled water was used for necessary dilutions. All reagents used in the present work were of analytical grade.

Adsorbent activated carbon (AC) was also purchased from M/s Merck and used as received, while rice husk (RH) was a kind gift from the local rice mill. All pH measurements were carried out with a decibel DB 1011 digital pH meter, fitted with a glass electrode and COD digestion apparatus (Spectra Lab-2015 S) was used for determining COD of the solutions. Absorbance measurements were recorded on a Spectronic 20D+ Thermospectronic spectrophotometer over the wavelength range 200–600 nm.

RH obtained was cleaned, thoroughly washed with distilled water, and then dried in an oven. It was next treated with acetic acid and again washed with distilled water. Thereafter, it was treated with hydrogen peroxide (100 volumes) for about 24 h to remove all adhering organic particles and dried at 110°C for 1 h in the vacuum oven. The material was grounded and sieved to desired particle sizes such as 0.425–0.3 mm (36–50 BSS mesh), 0.3–0.15 mm (50–100 BSS mesh), 0.15–0.088 mm (100–170 BSS mesh) and ≤0.088 mm (≥170 BSS mesh). Finally, granules of ARH thus obtained were stored in separate vacuum desiccators until required. However, the procured AC was separated for into similar particle sizes and also kept in desiccators.

Adsorption of Safranin-T was carried out by a batch technique in aqueous suspensions of both the adsorbents and experiments were conducted to observe the effect of various parameters such as pH, temperature, particle size, amount of adsorbent, concentration, and contact time. Adsorption isotherms were recorded at equilibrium conditions for concentration of dyes over the range $1 \times 10^{-2}$–$9 \times 10^{-5}$ M at a fixed pH. The selected concentration range was ascertained after a good deal of examination. Each adsorption study was made in a mechanically agitated 100-ml volumetric flask filled with 25 ml of a dye solution of desired concentration along with a known amount of adsorbent. When the equilibrium was thought to be established, supernatant was carefully filtered through Whatmann filter paper (No. 41) and analyzed spectrophotometrically by measuring the absorbance at $\lambda_{max}$ of 518 nm.

A stock solution (0.01 M) of the dye was prepared in 250 ml distilled water. It was diluted to the required volume and concentration. A known amount of adsorbent was added to the solution. All the contents were agitated for a suitable contact time. Then the contents were filtered with Whatmann filter paper No. 1. The concentration of filtered solution was determined on a Spectronic 20D+ Thermospectronic spectrophotometer at 518 nm.

A batch technique was also applied for the kinetic measurements. In airtight 100-ml conical flasks, a known amount of AC or ARH was added into 25 ml of dye solution. The flasks were then kept in a water bath maintained at a desired temperature and agitated mechanically. After a fixed time interval the adsorbent was separated by filtration and the filtrate thus obtained was analyzed spectrophotometrically to determine the equilibrium concentration of the dye. The kinetic studies were also carried out under different adsorbate concentrations.

3. Results and discussion

3.1. Effect of pH

To determine the optimum pH conditions for the adsorption of Safranin-T over AC and ARH, the effect of pH was observed over the entire pH range (2.0–12.0). The studies were conducted at a fixed concentration of adsorbate ($5 \times 10^{-5}$ M) and contact time (50 min). The results obtained are presented in Fig. 1, which describes maximum adsorption of around 96 and 82% for AC and ARH, respectively, at pH 6.5. Hence, all the succeeding investigations were performed at pH 6.5 for both adsorbents.

3.2. Effect of adsorbent dose

To optimize the adsorbent dose for the removal of Safranin-T from its aqueous solutions, adsorption was carried out with different adsorbent dosages at different temperatures. The amounts of the dye removed by adsorption on AC and ARH are presented in Figs. 2 and 3. The dose of adsorbent was varied from 0.02 to 0.1 g/L for AC and from 0.4 to 2.0 g/L for ARH at fixed pH, temperature, and adsorbate concentration. It is apparent from Figs. 2 and 3 that at all the temperatures, for both the adsorbents, adsorption increases with increase in the amount of adsorbent. Thus in all subsequent studies the amounts of AC and ARH were chosen as 0.10 and 0.05 g, respectively. The half-life of the process
Fig. 1. Effect of pH on the adsorption of Safranin-T over AC and ARH. Dye concentration $5.0 \times 10^{-5}$ M; temperature 40°C; amount of AC 0.10 g and amount of ARH 0.05 g; sieve size 0.3–0.15 mm (for each).

Fig. 2. Effect of adsorbent dose on the uptake of Safranin-T over AC. Dye concentration $5.0 \times 10^{-5}$ M; temperature 40°C; pH 6.5; sieve size 0.3–0.15 mm (for each).

Fig. 3. Effect of adsorbent dose on the uptake of Safranin-T over ARH. Dye concentration $5.0 \times 10^{-5}$ M; temperature 40°C; pH 6.5; sieve size 0.3–0.15 mm (for each).

Fig. 4. Effect of initial dye concentration on the adsorption of Safranin-T over AC and ARH. Temperature 40°C; pH 6.5; amount of AC 0.10 g and amount of ARH 0.05 g; sieve size 0.3–0.15 mm (for each).

was also determined at varying doses for each adsorbent and it was specified that the half-life increases with increasing amount.

3.3. Effect of initial dye concentration

It has been observed that for both the adsorbents, adsorption of the dye increases with increasing concentration at all temperatures. Fig. 4 presents typical dye concentration versus amount adsorbed for AC and ARH adsorption at 40°C. It is observed that with increasing concentration of the dye from $1.0 \times 10^{-5}$ to $9.0 \times 10^{-5}$ M, the percentage removal decreases from 95 to 86% for AC and 84 to 55.4% for ARH.

3.4. Effect of particle size

The variation of the rate of adsorption of the substrate with different particle size of adsorbent is another method that is useful for the characterization of the rate-limiting mechanism of a particular system. In the present investigations different particle sizes were taken at a fixed dose and pH and adsorption of the dye over both the adsorbents was monitored. For both AC and ARH, adsorption increased with increasing particle size. Maximum adsorption (about 98% for AC and 92.8% for ARH) could be achieved at the particle size 0.3–0.15 mm (50–100 BSS mesh). Hence, all further studies were carried out using
0.3–0.15 mm (50–100 BSS mesh) size of granules of both adsorbents.

3.5. Effect of temperature

Adsorption studies were carried out at 40, 50, and 60 °C for AC and ARH. The rate of uptake of dye with AC was found to decrease with increase in temperature, thereby indicating the process to be exothermic in nature. For ARH an increase in adsorption with increase in temperature was observed, signifying the process to be endothermic. Fig. 5 exhibits the effect of temperature on the adsorption of Safranin-T over AC and ARH.

3.6. Effect of contact time

The adsorption experiments were also carried out for different contact times with fixed adsorbent dose and concentration. Fig. 6 presents graphs for the variation in adsorption with respect to time for AC and ARH at 60 °C and indicates that the adsorption gradually increases with increase in contact time. For AC, initially rate of adsorption remains constant and then increases with increasing contact time; maximum adsorption of the dye could be achieved within 15 min. For the ARH, initially the adsorption of the dye increases with increasing contact time and rate of adsorption becomes lower after 30 min; however, maximum adsorption is achieved after 50 min.

3.7. Adsorption isotherms

The adsorption studies were also conducted at a fixed initial concentration of Safranin-T with varying adsorbent dose. The equilibrium data were analyzed by Langmuir and Freundlich isotherms. These isotherms are useful for estimating the total amount of adsorbent needed to adsorb a required amount of adsorbate from solution.

3.7.1. Langmuir isotherm

The Langmuir isotherm has been used by many workers to study the sorption of a variety of compounds. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of the isotherm was analyzed in the light of the model

\[
\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e},
\]

where \( q_e \) is the amount adsorbed (mol/g) and \( C_e \) is the equilibrium concentration of the adsorbate (mol L\(^{-1}\)). \( Q_0 \) and \( b \) are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When \( 1/q_e \) is plotted against \( 1/C_e \), a straight with slope \( 1/bQ_0 \) is obtained, which shows that the adsorption of Safranin-T follows the Langmuir isotherm (Figs. 7 and 8) for both the adsorbents. Langmuir constants are calculated and the values of these constants at 40, 50, and 60 °C are given in Table 1.

3.7.2. Freundlich isotherm

The adsorption data for adsorption over AC and ARH were also found to be fitted to the linear form of the Freundlich equation

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

where \( K_F \) and \( n \) are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. Figs. 9 and 10 were used to calculate the Freundlich constants \( K_F \) and \( n \) for AC and ARH, respectively, and their values are given in Table 1.

3.8. Thermodynamic parameters

Thermodynamic parameters for the adsorption of Safranin-T on AC and ARH were calculated using the following equations
Fig. 7. Langmuir adsorption isotherms of Safranin-T–AC system.

Fig. 8. Langmuir adsorption isotherms of Safranin-T–ARH system.

and the values are given in Table 2:

\[
\Delta G^0 = -RT \ln b, \\
\Delta H^0 = R \left( \frac{T_2 T_1}{T_2 - T_1} \right) \ln \left( \frac{b_2}{b_1} \right), \\
\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}.
\]

The negative values of \( \Delta G^0 \) (Table 2) indicate that adsorption of Safranin-T with both the adsorbents was spontaneous, while positive \( \Delta H^0 \) value indicative of endothermic nature of the processes in case of ARH and negative value of \( \Delta H^0 \) exhibits exothermic nature for AC. The positive \( \Delta S^0 \) values for

Table 1
Freundlich and Langmuir constants for the removal of Safranin-T over AC and ARH

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_0 )</td>
<td>( K_F )</td>
</tr>
<tr>
<td>AC</td>
<td>3.183</td>
<td>1.3315</td>
</tr>
<tr>
<td></td>
<td>1.1875</td>
<td>1.8375</td>
</tr>
<tr>
<td></td>
<td>0.7978</td>
<td>2.9257</td>
</tr>
<tr>
<td></td>
<td>32.061</td>
<td>2.061</td>
</tr>
<tr>
<td></td>
<td>50.505</td>
<td>6.668</td>
</tr>
<tr>
<td></td>
<td>118.25</td>
<td>23.8396</td>
</tr>
<tr>
<td>ARH</td>
<td>0.2117</td>
<td>1.0683</td>
</tr>
<tr>
<td></td>
<td>0.1013</td>
<td>1.1856</td>
</tr>
<tr>
<td></td>
<td>0.07831</td>
<td>1.2422</td>
</tr>
<tr>
<td></td>
<td>4.0139</td>
<td>0.6091</td>
</tr>
<tr>
<td></td>
<td>7.0761</td>
<td>0.3414</td>
</tr>
<tr>
<td></td>
<td>8.6070</td>
<td>0.2697</td>
</tr>
</tbody>
</table>

Note. Dye concentration \( 5.0 \times 10^{-5} \) M; pH 6.5; amount of AC = 0.10 g and amount of ARH = 0.05 g; sieve size = 0.3–0.15 mm (for each).

The adsorbents show increased randomness at the solid solution interface during the adsorption of dye.

3.9. Adsorption kinetics

The adsorption kinetics was evaluated at 40, 50, and 60°C for AC and ARH with different contact times. To determine the specific rate constant of Safranin-T–AC and Safranin-T–ARH systems, the well-known Lagergren first-order rate equation was employed [18]

\[
\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303} t,
\]

where \( q_e \) and \( q_t \) signify the amount adsorbed at equilibrium and at any time \( t \), respectively. For both the systems, the graphs (Figs. 11 and 12) obtained for \( \log(q_e - q_t) \) versus \( t \) exhibit straight lines and confirm the adsorption process to follow first-order rate kinetics in each case. The \( K_{ad} \) values evaluated, for
Table 2
Thermodynamic parameters for the uptake of Safranin-T over AC and ARH

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$-\Delta G^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>9.023</td>
<td>12.100</td>
<td>13.214</td>
</tr>
<tr>
<td>ARH</td>
<td>3.617</td>
<td>5.255</td>
<td>5.959</td>
</tr>
</tbody>
</table>

Note. Dye concentration $5.0 \times 10^{-5}$ M; pH 6.5; amount of AC 0.10 g and amount of ARH 0.05 g; sieve size 0.3–0.15 mm (for each).

Table 3
Rate constant for the uptake of Safranin-T over AC and ARH

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$K_{ad}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>72.08</td>
</tr>
<tr>
<td>ARH</td>
<td>10.13</td>
</tr>
</tbody>
</table>


dye solutions adsorbed by AC and ARH, the COD of decreases from 1180.0 to 316.8 and 498 mg L$^{-1}$, respectively, indicating the lower toxicity of the solutions left after adsorption.

4. Conclusions

On the basis of the results obtained, it can be safely concluded that both AC and ARH act as potential adsorbents for the removal of Safranin-T from wastewater. ARH are a cheap and easily available material that thus can act as a better replacement for AC. Being a waste product, the use of ARH as adsorbent would also solve their disposal problem.

References