RHODAMINE 6G REMOVAL USING PROSOPIS SPICIGERA L. WOOD(PSLW)CARBON-IRON OXIDE COMPOSITE

[R. Dhana Ramalakshmi, V. Jeyabal, M. Murugan]

Reg.No: 12583, Department of Chemistry, Rani Anna Government College for Women, Tirunelveli-627008, Research centre (St. Xavier's College, Tirunelveli-627002), affiliation of Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli-627012, Tamil Nadu, India.

[2] Associate professor, Department of Chemistry, St. Xavier's College, Palayamkottai, Tirunelveli-627002, Tamil Nadu, India.


mail:[1] dhana.ram11@gmail.com, [2] vjnino04@gmail.com, [3] kgsmurugan@gmail.com

Abstract:

Rhodamine 6G, a cationic dye is used to dyeing silk, cotton, wool, bast fiber, paper, leather, and plastic. It is toxic and carcinogenic in nature. Hence it is essential to remove Rhodamine 6G from dyeing industrial discharge and contaminated drinking water resources. In this present work, a waste plant material Prosopis spicigera L. wood is carbonised (by natural process) and its composite with iron oxide, is used for the removal of Rhodamine 6G from aqueous solutions by batch and column methods. The PSLW carbon-iron oxide composite is characterized by FTIR for functional group, scanning electron microscope for surface morphology and potentiometric titration for pHzpc. Batch experiments have been carried out to investigate the influence of sorption parameters such as initial dye concentration, pH, contact time, in the presence of other ions and temperature on the removal of Rhodamine 6G. The batch experiments were carried out at pH 6.0. The adsorption equilibrium fits Langmuir isotherm. The kinetic data follows pseudo second order model. The thermodynamic study indicated that the adsorption of dye is spontaneous and endothermic in nature. In order to apply this process to industrial and domestic applications, column analysis was performed. Column data was analysed using Thomas model.

Keywords: Adsorption, Kinetics, PSLW carbon, Langmuir Isotherm, Rhodamine 6G, Thomas model.

Introduction

Dyes are colored compounds which are widely used in textiles, printing, cosmetics, plastics, rubber and leather industries. These industrial effluents contain a large amount of colored wastewater and pollute the environment. The usage of natural dye which is isolated from natural materials is limited. The discovery of synthetic dyes and its wide range of uses such as fastness and brightness produce a massive industrial effluents[1]. However, synthetic dyes have toxic behavior and adverse effect.
The presence of dyes or their degradation products in water even at low concentration can cause human health disorders like nausea, haemorrhage, ulceration of the skin, damage kidneys, reproductive system, liver, brain and central nervous system[2]. It is difficult to remove these dyes using conventional water treatment method because they are designed to have high water solubility [3]. Many physical, chemical and biological methods are available for the removal of dye from aqueous system. Among various physical methods, adsorption is one of the best method to successively remove them. In sorption technique, adsorbents have a prominent role. The common adsorbents like activated carbon, peat, wood, fly ash, coal and silica are used. Activated carbons are most widely used to remove pollutants from aqueous solutions due to their high surface area, adsorption capacity and easily availability. The adsorption capacity of activated carbon still can be increased by modifying the surface of carbon. One such process is composite formation with iron metal oxides. The magnetic particle technology have received more attention to solve the environmental problems[4]. Compared to other adsorbents, the magnetic composites are good adsorbents because of their large surface area, high adsorption capacity and after adsorption, it can be easily separated from the medium by a simple magnetic process. In our present study, a low-cost adsorbent i.e., Prosopis spicigera L. wood (PSLW) carbon and its iron oxide composite which is used for Rhodamine 6G removal. The effect of pH, contact time, initial concentration, adsorbent dosage, presence of other ions and temperature of Rhodamine 6G solution on PSLW carbon-iron oxide composite were examined. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption isotherms, kinetics and thermodynamic parameters.

MATERIALS AND METHODS

Materials

PSLW plant material used in the present work was collected from the dry land area of Palayamkottai in Tirunelveli district, Tamilnadu state, India. The branch and roots of the plant were cut into pieces and piled up on a firing hearth. Before firing, the heaped wood pieces were enclosed by fresh plantain pith and the whole mass was covered and plastered with layers of wet clay. This arrangement prevented the direct entry of air into wood pieces and hence prohibited burning of wood and its becoming ash. After 48 h of continuous firing and subsequent natural cooling, the activated carbon was obtained. After removing the non-carbonaceous materials the carbon was isolated, crushed and sieved to 75 micron particles. The composite adsorbent was prepared using the slightly modified literature procedure [5],[6]. 20 g of PSLW carbon was suspended in 400 ml of FeCl₃ (7.8 g, 28 mmol) and FeSO₄ (3.9 g, 14 mmol) at 70°C. The above solution was stirred well using a magnetic stirrer for 3 hours. Sodium hydroxide solution (100 ml, 5 mol/L) was added dropwise to precipitate the iron oxides. Again the stirring was continued for another two hours at 70°C. Later the solid material was
separated, washed with de-ionised water until the washings became neutral. Further the washings were tested for iron with 1:10 phenontherline for reddish color or precipitates. The final product was dried in an air oven at 100°C for 8 hours and finally stored in air tight containers.

**Characterisation of the adsorbent**

The standard procedure [7], [8] was adopted to study the characteristics of PSLW carbon-iron oxide composites. Surface functional groups and surface morphology of these adsorbent have been analysed using FT-IR (JASCO FT/IR-4700 type A) and SEM respectively. The morphological studies SEM was performed on Jeol, JSM 6390, Oxford instruments, UK. Potentiometric titration with acid/alkali was made to determine the zero point charge [9].

**Batch Adsorption studies**

The stock solution was prepared by dissolving 1 g of Rh 6G in 1000 mL of distilled water. The stock solution was diluted with distilled water for further experimental studies. A digital pH meter with glass electrode model (Roy instruments RI 501) was used for the measurement of pH of the dye solution. The initial pH of the solution was varied (1-10) using 0.1 M NaOH or 0.1 M H₂SO₄ solutions. Batch adsorption studies were carried out in 10 ml of dye solution. After adsorption, the solution was centrifuged and absorbance was measured at 524 nm using UV–Visible spectrophotometer. The batch experiments were studied to determine the effect of pH (1-10), initial concentration (10, 15 and 20 mg/L), contact time (5-150 min), in the presence of other ions (chloride, carbonate, nitrate and sulphate ions) and temperature (20–50°C).

The amount of adsorbate adsorbed at equilibrium, $q_e$ (mg/g) was calculated as:

$$q_e = \frac{(C_o - C_e)V}{W}$$  \hspace{1cm} (1)

Where, $C_o$ and $C_e$ (mg/L) are the initial and equilibrium concentration of adsorbate respectively. $V$ is the volume of the solution (L) and $W$ is the mass of adsorbent (g).

**Column study**

In column study, 5 g of PSLW carbon-iron oxide composite was packed in a glass column (2.5 cm diameter and 48 cm height) for a bed height of 3.5 cm. The dye solution was dropped into the column at a rate of 2 mL/min from a separatory funnel fixed at a height of 1 meter. Effluents were collected at regular intervals and analysed.

**Results and Discussion**

**Characterisation of adsorbent**
The FTIR spectrum of PSLW carbon and its iron composite (Fig. 2) show that both of their surface have very few bands with very weak intensities. This indicates the presence of meagre amount of acidic and basic groups on their surface. Further the composite formation has little interaction with the surface functional groups. SEM study is used to understand the changes of morphological features during adsorption process. The comparative study of SEM images of free PSLW carbon and PSLW carbon-iron composite (Fig. 3) reveals that the PSLW carbon powder has irregularly shaped particles with porous structure whose size is further reduced in the composites. Further a coating of white patches of iron oxide is seen on the surface of the PSLW carbon.

Fig. 1 structure of Rhodamine 6G

Fig. 2 The FTIR spectrum of (a) pure PSLW carbon (b) PSLW carbon-iron oxide composite (c) Rh 6G loaded carbon
Fig. 3 SEM images of (a) pure PSLW carbon (b) PSLW carbon-iron oxide composite (c) Rh 6G loaded carbon

**Effect of pH**

The adsorbate and the surface charge of the adsorbent in aqueous solution are pH dependent, which makes pH be one of the most important factors affecting dye adsorption onto the adsorbent [10]. Fig. 4 shows, the removal of dye which increases with increase in pH and maximum sorption is noted above pH = 8.0. The maximum adsorption above pH = 8.0 may be due to electrostatic attraction between adsorbent and dye molecule [11], [12]. The pH_{zpc} of the composite is 8.22 and it reveals that the surface of the adsorbent is positively charged. Therefore the adsorption of Rhodamine 6G cationic dye on the PSLW carbon-iron oxide composite above pH = 8.0 may be due to electrostatic interaction. But the desorption study with 0.1 N NaOH shows 90.5 % of the Rhodamine 6G dye is desorped. Therefore the adsorption may involve weak interaction between the dye molecule and the composite. This is evident from the IR spectral study. In the IR spectrum there is no shift in the stretching frequencies of the PSLW carbon composite (Fig. 2c) and the spectrum is only due to the adsorbed Rhodamine 6G molecule. Further SEM analysis after adsorption of Rhodamine 6G onto the composite (Fig. 3c) shows the presence of aggregated larger size particles.
with filled pores. This indicates the asorption of Rhodamine 6G molecule onto the composites. But as an optium pH=6.0 is maintained throughout the adsorption study to apply this process to treat polluted drinking water.

**Effect of initial concentration and contact time**

Fig.5 shows the effect of initial concentration and contact time. The sorption process increases with increase in contact time and attains equilibrium in 150 minutes. The maximum adsorption capacity at three different concentrations of 10, 15 and 20 mg/L are found to be 11.6, 16.4 and 18.3 mg/g respectively for an adsorbent dose 0.5 g/L.

**Effect of Temperature**

Fig.6 depicts that the adsorption capacity of adsorbent increases with increase in temperature due to increase in dye mobility that may occur at high temperature between the adsorbent and the adsorbate [13]. This indicates that the adsorption of dye is an endothermic process [14].

**Adsorption of dye in the presence of other ions**

Adsorption capacity of PSLW carbon-iron oxide composite of the dye was examined in the presence of mixture of chloride, carbonate, nitrate and sulphate ions of concentration 0.001 M each. The adsorption capacity increases with time and equilibrium is reached at 60 min which is similar to that of adsorption of dye in the absence of above ions. But the adsorption capacity decreases and this may be due to competition between the ions and dye molecules for the same number of adsorption sites.

**Thermodynamic behavior**
The thermodynamic parameters, standard free energy ($\Delta G^\circ$), standard enthalpy ($\Delta H^\circ$) and standard entropy ($\Delta S^\circ$) were calculated using equations (2), (3) and (4).

$$\Delta G^\circ = -RT \ln k$$  \hspace{1cm} (2)

$$\ln k = \Delta S^\circ / R - \Delta H^\circ / RT$$  \hspace{1cm} (3)

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$  \hspace{1cm} (4)\hspace{1cm} \text{where, } T \text{ is the temperature (K),} \hspace{1cm} R \text{ is the gas constant (8.314 J/mol k) and} \hspace{1cm} K \text{ is the equilibrium constant. A plot of} \ln k \text{ versus } 1/T \text{ gives a straight line with slope } \Delta H^\circ \text{ and intercept } \Delta S^\circ. \text{ The values of the thermodynamic parameters are listed in table I. The negative value of } \Delta G^\circ \text{ which indicates the adsorption of dye on PSLW carbon-iron oxide composite is a spontaneous process. The positive value of } \Delta H^\circ \text{ shows the adsorption process is endothermic. This reveals that the adsorption capacity increases with increase in temperature. The } \Delta S^\circ \text{ value increases with temperature, which indicates the randomness of adsorption of dye on adsorbent surface. From thermodynamic parameters, the adsorption process is spontaneous and endothermic [15], [16]. Thus, temperature plays a vital role in adsorption of dye on PSLW carbon-iron oxide composite.}

I. Thermodynamic parameters: Adsorbent dose 0.5 g/L

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$- \Delta G^\circ$ (KJ/mol)</th>
<th>$\Delta H^\circ$ (KJ/mol)</th>
<th>$\Delta S^\circ$ (KJ/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>120.34</td>
<td>512.14</td>
<td>2.16</td>
</tr>
<tr>
<td>303</td>
<td>115.88</td>
<td>514.13</td>
<td>2.07</td>
</tr>
<tr>
<td>313</td>
<td>164.46</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>172.40</td>
<td>2.12</td>
<td></td>
</tr>
</tbody>
</table>

Isotherm Analysis

Adsorption isotherm is used to predict the mechanism of sorption process. The adsorption capacity of the adsorbent was examined by Langmuir[17] and Freundlich[18] models. Langmuir and Freundlich models are expressed by equations (5) and (6)

$$C_e/q = 1/Q_b + C_e/Q$$ \hspace{1cm} (5)

$$\log q = \log K_f + 1/n \log C_e$$ \hspace{1cm} (6)
where \( C_e \) is the equilibrium concentration of the adsorbate (mg/L), \( q \) is the amount of dye adsorbed at equilibrium (mg/g), \( Q_o \) and \( b \) are the Langmuir constants which represents the maximum monolayer adsorption capacity and energy of adsorption respectively. \( K_f \) and \( 1/n \) are Freundlich constants related to adsorption capacity and adsorption intensity respectively. Fig. 7 shows the linear plot \( C_e/q \) versus \( C_e \) at different initial concentration and temperature. The slope and intercept of the plot gives the values of \( Q_o \) and \( b \) respectively. The adsorption process follows Langmuir isotherm and not Freundlich isotherm.

\[
R_L = \frac{1}{1 + bC_e}
\] .... (7)

The values of \( Q_o \), \( b \) and \( R_L \) are tabulated in table II. The observed values of \( R_L \) lie between zero to one, which establish the fact that the adsorption process is favorable under the studied conditions.

### II. Langmuir isotherm constants: Adsorbent dose 0.5 g/L

<table>
<thead>
<tr>
<th>( C_0 ) (mg/L)</th>
<th>Temp (°C)</th>
<th>( Q_o ) (mg/g)</th>
<th>( B ) (L/mg)</th>
<th>( R_L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>30</td>
<td>3.2952</td>
<td>0.2517</td>
<td>0.2843</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>5.8213</td>
<td>0.1826</td>
<td>0.2674</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>5.9319</td>
<td>1.1650</td>
<td>0.0412</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>4.4436</td>
<td>0.3425</td>
<td>0.2259</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>3.0463</td>
<td>0.3623</td>
<td>0.2163</td>
</tr>
</tbody>
</table>

Fig. 7 Langmuir plot of Rh 6G adsorption at different concentrations and temperatures
Adsorption kinetics

The kinetics of dye adsorption on PSLW carbon-iron oxide composite was analyzed by pseudo-first order [20] or pseudo-second order [21], [22] kinetic models, given by equations (8) and (9).

\[
\ln(q_e - q) = \ln q_e - K_1t
\]

\[
t/q_e = \frac{1}{K_2 q_e^2 + t/q_e}
\]

Where, \(q_e\) and \(q_t\) is the amount of adsorbate, adsorbed at equilibrium (mg/g) and at particular time intervals respectively. \(K_1\) and \(K_2\) are the rate constants. A plot of \(\ln (q_e - q)\) versus \(t\) gives a straight line slope of \(K_1\) and intercept of \(\ln q_e\). The rate constants (\(K_1\) and \(K_2\)) and calculated equilibrium capacity \(q_{e\,\text{cal}}\) of pseudo first order and second order models were determined from the slope and intercept of linear plots of pseudo first order and second order models at different concentration and temperature.

Fig. 8 shows that the linear plot of pseudo first order and second order models at different concentration and temperature. The summary of kinetic parameters listed in table. III

Fig. 8 Pseudo-second order plot of Rh 6G adsorption at different concentrations and temperatures

### III. Pseudo first order and second order constants at different concentrations and temperatures:

<table>
<thead>
<tr>
<th>C₀</th>
<th>Temp</th>
<th>Pseudo first order constants</th>
<th>Pseudo second order constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>40</td>
<td>5.5816</td>
<td>0.3761</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>4.8655</td>
<td>0.3311</td>
</tr>
</tbody>
</table>
From the experimental data, it is clearly seen that the adsorption of dye follows pseudo second order kinetics. The comparison between \( q_e \text{(cal)} \) and \( q_e \text{(exp)} \) value and the closeness of \( R^2 \) towards unity is closer for pseudo second order kinetics than pseudo first order kinetics. Thus, the adsorption process follows pseudo second order kinetics.

**Pore diffusion**

The intra particle diffusion method is used to study the mechanism of Rh 6G dye adsorption. The plot of \( q \) versus \( t^{1/2} \) gives the information about the mechanism and the slope is the intra particle diffusion constant \( (k_i) \). The \( k_i \) values are listed in Table IV for different concentration and temperature. The \( k_i \) value increases with increase in concentration and temperature and it indicates the increase in boundary layer thickness and it leads to decrease in external mass transfer and increase the internal mass transfer [23].

**IV. The intra particle diffusion constant:** Adsorbent dose 0.5 g/L

<table>
<thead>
<tr>
<th>( C_0 ) (mg/L)</th>
<th>T °C</th>
<th>Intra particle diffusion ( (k_i) ) (mg/g/min^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>30</td>
<td>2.2701</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>3.7976</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>4.5772</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>1.5636</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>1.7036</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>1.8595</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>1.9532</td>
</tr>
</tbody>
</table>

**Column Study**
The column study provides the practical application of this process to industries. The observed data fit to the linearised form of the Thomas model [24], [25] and are given in equation (10).

\[ \log\left(\frac{C_o}{C_e} - 1\right) = Kq_o M/Q - KCq_o C_e \]

(10)

where, \(C_o\) and \(C_e\) are the influent and effluent dyes concentrations (mg/L) respectively. \(K\) stands for the Thomas rate constant (mL/min/mg), \(q_o\) is the maximum solid phase concentration of solute (mg/g), \(M\) is the mass of the adsorbent (g), and \(V\) is the throughput volume (ml/min). The linear plot of \(\log\left(\frac{C_o}{C_e} - 1\right)\) against \(V\) gives the value of \(K\) (slope) and \(q_o\) (intercept). The column study was performed by 10 mg/L dye solution. The concentration of dye is gradually increases with bed volume. The value of rate constant \(K\) (1.712 mL/min/mg) and the solute concentration \(q_o\) (1.95 mg/g) are useful for designing columns on large scale.

**Conclusion**

The present study describes the effective removal of Rh 6G dye from aqueous solution using low-cost PSLW carbon-iron oxide composite as an adsorbent. Batch studies exhibits the adsorption process follows Langmuir adsorption. The thermodynamic parameters show the adsorption process is spontaneous, favorable and endothermic nature. The effective removal of dye can be obtained even at high temperature. The kinetic data indicates the removal of dye follows the pseudo-second order kinetics. In column study, Thomas model is used to assign the dye removal in industrial scale. From the above results, it is concluded that the effective removal of Rh 6G from industrial effluents can be achieved using PSLW carbon-iron oxide composite.

**References**


