EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES OF CONGO RED BIOSORPTION FROM TEXTILE WASTEWATER USING Spathodea Campanulata LEAVES

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ABSTRACT
The aim of the present study is to remove Congo red (CR) dye from their Textile wastewater using Spathodea campanulata leaves powder as biosorbent in a batch study. The variables covered in a batch study were contact time, solution pH, initial CR dye concentration, biosorbent dosage, the average particle size of the biosorbent and temperature. The kinetic and isotherm studies of biosorption of CR dye onto Spathodea campanulata biosorbent was investigated using various kinetic pseudo-first-order, pseudo-second-order and isotherm models (Langmuir, Freundlich, Temkin). The experimental data of biosorption of the dye onto the Spathodea Campanulata biosorbent fitted well with the Langmuir isotherm model. The isotherm reveals that the biosorption of the dye onto Spathodea Campanulata biosorbent was favorable. Thermodynamic parameters such as Gibbs free energy, enthalpy change and entropy change were also estimated for the biosorption of CR dye. The thermodynamic studies indicated that the biosorption of Congo red dye onto Spathodea campanulata biosorbent was spontaneous, feasible and endothermic.

Keywords: Congo red, Spathodea Campanulata, Textile wastewater, Biosorption

INTRODUCTION
Freshwater is a limited resource in many parts of the world. This will become more dearths due to an increase in population, urbanization and climate change. The major fact for this paucity of fresh water is not only due to the demand for water but also due to pollution in a freshwater ecosystem. Due to the pollution created by human beings in this ecosystem, the usable water has decreased drastically and the cost of purifying the water has increased drastically. The main sources of water pollution are point source and non-point source. Point sources include pipeline discharge of pollutants such as domestic sewage discharge, industrial waste effluents from factories or plants to receiving waters. It contrasts non-point pollution results from storm runoff, which transports polluting materials diffusely over land. Colour in the liquid effluents can also decrease the capacity of plants in photosynthesis. Uses of different kinds of shampoos by human beings are a major threat to the water and now a day they act as water pollutants. There are more than 10,000 commercially available dyes with over 7 lakh times of dyestuff being produced annually across the world. The dye-based effluent is a considerable source of non-aesthetic pollution since the presence of a small amount of dye (below 1 ppm) is clearly visible. Many researchers found that colorant may cause problems in the aquatic ecosystem in several ways as follows. Biosorption technique was most favorable procedure among all the physicochemical adsorption, flocculation combined with flotation, membrane filtration, electrokinetic coagulation, ozonation, oxidation, precipitation and Ion exchange methods.

EXPERIMENTAL
Preparation of Dye Solution
Stock solutions of Congo red concentration 1000 mg/L were prepared by dissolving 1 g of 100% Congo red in 1000 ml of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared dye solutions varied between 20 and 200 mg/l was prepared using the stock solution of individual dye.
Preparation of Biosorbent
The green-colored Spathodea campanulata leaves used in the present study were collected from the College of Engineering, Andhra University, Visakhapatnam, India. The collected leaves were washed with deionized water several times to remove dirt particles. The washing process was continued until the wash water contains no dirt. The washed leaves were completely dried in sunlight for 20 days. The dried leaves were then cut into small pieces and powdered using domestic mixie. In the present study, the powdered materials in the range of 53-152 μm particle size was directly used as biosorbent without any pretreatment.

Batch Mode Biosorption Studies
Batch biosorption equilibrium experiments were conducted in 250 ml conical flasks at a constant agitation speed (180 rpm). All the experiments were carried out at room temperature (± 30°C). The concentrations of both the dyes before and after sorption were determined using UV-Vis spectrophotometer by monitoring the absorbance for the dye used.

Effect of Contact Time
The effect of contact time on the biosorption of dye was studied by adding known weight (0.5g) of 53μm Spathodea campanulata leaves powder into Erlenmeyer flasks containing 20 mg/L concentration of Congo red solution at a pH of 7 and temperature 303 K. Immediately this solution was agitated at 180 rpm for the time period of 5 min and then subjected to centrifugation. After centrifugation, the supernatant was carefully decanted and analyzed for residual Congo red concentration. The same procedure was repeated at different time periods such as 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 min. This gives an opportunity for the determination of equilibrium time.

Effect of Solution pH
The effect of solution pH on Congo red biosorption was determined by adding a known amount of Spathodea campanulata leaves powder into 50 ml of Congo red dye solutions of 20 mg/L concentrations individually maintained at different pH (2 to 8) and at a temperature of 303K. These solutions were agitated at 180 rpm for equilibrium time and then residual dye concentrations were measured.

Effect of Initial Dye Concentration
The effect of initial dye concentration on biosorption of dyes was studied by varying concentrations of dye solutions (Congo red) over a range of 20 – 200 mg/L. Spathodea campanulata leaves powder of known weight (0.5 g) was added to the solutions containing different concentrations of Congo red. These solutions were agitated for equilibrium time at a temperature of 303 K, centrifuged and analyzed for final dye concentrations. This procedure was conducted at different temperatures in the range of 283 – 323 K by keeping all other variables constant.

Effect of Biosorbent Dosage
To determine the effect of biosorbent dosage on dye uptake, Spathodea campanulata leaves powder of 0.5 g was added to a series of solutions containing different concentrations (20 – 200 mg/L) of Congo red dye maintained at known pH and temperature. These solutions were agitated for equilibrium time and then un-adsorbed dye concentrations were determined. This procedure was conducted with different biosorbent amounts 1, 1.25, 1.5, 1.75, 2, 2.25, 2.5, 3 and 4 g by keeping all other variables constant.

Effect of Biosorbent Particle Size
To study the effect of biosorbent size on dye removal, Spathodea campanulata leaves powder of known size (53–152 μm) and known weight was added to a series of dye solution (Congo red) controlled at known pH and temperature. These solutions were then subjected to constant agitation for the equilibrium time and decanted supernatants were then analyzed for unadsorbed dye concentrations.
Effect of Temperature
The effect of temperature on dye removal was studied by agitating 0.5 g of *Spathodea campanulata* leaves powder with different concentrations (20 - 200 mg/L) of Congo red dye at a temperature of 283 K and optimum pH. At the end of equilibrium time, solutions were withdrawn and analyzed for final dye concentrations. This procedure was repeated under similar conditions with different temperatures in the range of 283-323 K.

RESULTS AND DISCUSSION
Effect of Contact Time
The percentage of biosorption was determined at different contact times and the results are shown in Fig.-1. The figure reveals that the percentage of biosorption Congo red was steeply increased with an increase in contact time from 5 to 40 min and there after reached plateau after attaining equilibrium 40 min for Congo red. Therefore, the contact time of 40 min is sufficient for the removal of Congo red under the experimental conditions used in this study. The percentage of biosorption of *Spathodea campanulata* leaves as biosorbent for Congo red dye removal was increased from 11 to 64%, with an increase in contact time from 5 to 40 min for an initial dye concentration of 20 mg/L. For 200 mg/L, the percentage of biosorption increased from 7 to 56 % mg/g, respectively with an increase in contact time from 5 to 40 min.

Effect of Solution pH
The solution pH is one of the important controlling parameters of the biosorption process. The effect of solution pH on % biosorption for the removal of Congo red dye was studied From the Fig.-2. It was observed that the increase in solution pH from 2 to 7 for Congo red resulted in an increase in the percentage of biosorption from 44 to 64% for Congo red for an initial concentration of 20 mg/L. For an initial concentration of 200 mg/L, the percentage of biosorption was increased from 36 to 58 % for Congo red with an increase in solution pH from 2 to 7.

![Fig.-1: Effect of Contact Time on % Biosorption of Congo Red Using Spathodea Campanulata Leaves As Biosorbent.](image)

![Fig.-2: Effect of Solution pH on % Biosorption of Congo Red Using Spathodea Campanulata Leaves As Biosorbent.](image)
**Effect of Initial Concentration of Dye**

The effect of initial dye concentration on the percentage of biosorption is shown in Fig.-3. It is evident from the figure that the percentage of biosorption decreased with an increase in the initial concentration of dye from 20 to 200 mg/L at all temperatures. The percentage of biosorption of Congo red decreased from 60 to 36 % and 66 to 42% for Congo red with an increase in initial concentration of Congo red from 20 to 200 mg/L at the temperature of 283 K and 323K, respectively.

![Fig.-3: Effect of Initial Concentration of Dye on % Biosorption of Congo Red Using Spathodea Campanulata Leaves As Biosorbent.](image)

**Effect of Biosorbent Dosage**

The result obtained is shown in Fig.-4, illustrate that the percentage of biosorption was increased with an increase in biosorbent dosage. The percentage of biosorption increased from 64 to 86.5 % from biosorbent dosage 0.5 to 4 g for an initial concentration of Congo red 20 mg/L. For an initial concentration of Congo red 200 mg/L, the percentage of biosorption increased from 56 to 72.5% from biosorbent dosage 0.5 to 4g.

![Fig.-4: Effect of Biosorbent Dosage on % Biosorption of Congo Red Using Spathodea Campanulata Leaves As Biosorbent.](image)

**Effect of Particle Size of Biosorbent**

The result obtained is shown in Fig.-5. The result indicated that the percentage of biosorption was decreased with an increase in average particle size of biosorbent. The percentage of biosorption decreased from 79 to 59 % and 70 to 51% with an increase in average particle size of biosorbent from 53 to 152 µm for an initial concentration of Congo red 20 mg /L and 200 mg/L, respectively.

![Fig.-5: Effect of Particle Size of Biosorbent on % Biosorption of Congo Red Using Spathodea Campanulata Leaves As Biosorbent.](image)

**Effect of Temperature**

The result obtained is shown in Fig.-6, The figure indicated that the percentage of biosorption was increased with an increase in temperature of the solution. This suggests the endothermic nature of the biosorption process. The percentage of biosorption increased from 76 to 82% and 70 to 75.5% with an increase in solution temperature from 283 K to 323 K for an initial concentration of Congo red 20 mg /L and 200 mg/L, respectively.
Equilibrium Studies

Langmuir Adsorption Isotherm

The applicability of Langmuir adsorption isotherm model was analyzed using the experimental data by plotting $C_e/q_e$ versus $C_e$. Figure-7 shows the Langmuir plot for the biosorption of Congo red dye at a temperature 303 K and The separation factor ($R_L$) values at different initial dye concentrations for the dye was determined and shown in Fig.-8. Langmuir constants and maximum biosorption capacity are compiled in Table-1. The high correlation coefficient indicates that the biosorption of dyes onto Spathodea Campanulata leaves biosorbent followed the Langmuir isotherm. The maximum biosorption capacity ($q_m$) values were found to be 11.73 mg/g for Congo red.
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Fig.-8: Separation Factor For Biosorption of Congo Red onto *Spathodea Campanulata* Leaves Biosorbent.

**Freundlich Isotherm**

The experimental data was tested for the fitness of Freundlich isotherm model by using linear graphical method. The biosorption data was analyzed by plotting $\ln q_e$ versus $\ln C_e$ shown in Fig.-9.

Fig.-9: Freundlich Isotherm For Biosorption of Congo Red onto *Spathodea Campanulata* Leaves As Biosorbent.

**Temkin Isotherm**

Temkin isotherm studies were conducted to evaluate the biosorption potentials and to assess the variation of biosorption energies during the biosorption of Congo red dye using *Spathodea Campanulata* leaves as biosorbent. The biosorption data was analyzed according to the linear form of Temkin model and is shown in Fig.10 for the removal of Congo red dye. The linear Temkin isotherm constants $B_T$ and $A_T$, were determined from the slope and intercept of the plots of $q_e$ versus $\ln C_e$. 38-42

Fig.-10: Temkin Isotherm For Biosorption of Congo Red onto *Spathodea Campanulata* Leaves As Biosorbent.
Table-1: Biosorption Isotherm Constants for Congo Red Removal Using Spathodea campanulata Biosorbent.

<table>
<thead>
<tr>
<th>Temperature, T(K)</th>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
<th>Temkin Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
<td>$N$</td>
</tr>
<tr>
<td>283</td>
<td>12.36</td>
<td>0.015</td>
<td>0.99</td>
</tr>
<tr>
<td>293</td>
<td>11.08</td>
<td>0.014</td>
<td>0.99</td>
</tr>
<tr>
<td>303</td>
<td>11.73</td>
<td>0.014</td>
<td>0.99</td>
</tr>
<tr>
<td>313</td>
<td>12.51</td>
<td>0.015</td>
<td>0.99</td>
</tr>
<tr>
<td>323</td>
<td>12.67</td>
<td>0.015</td>
<td>0.99</td>
</tr>
</tbody>
</table>

High correlation coefficient, $R^2$, values suggest that the biosorption process could be due to homogeneous surface coverage. This is in good agreement with the result of Langmuir isotherm for Congo red dye.

**Kinetic Studies**

**Pseudo-First-Order Kinetic Model**

The pseudo-first-order kinetic model was developed based on the solid adsorption capacity. The experimental results were analyzed to test the pseudo-first-order kinetic model and the linear plots of $\ln (q_e - q_t)$ versus $t$ is shown in Fig.-11.

![Fig.-11: Pseudo First Order Kinetic Model For Congo Red onto Spathodea Campanulata Leaves As Biosorbent.](image)

**Pseudo-Second-Order Kinetic Model**

The values of equilibrium biosorption capacity and second order rate constants were determined from the slope and intercept of the linear plot of $t/q_t$ versus $t$ in Fig.-12. The values obtained are tabulated along with the correlation coefficient ($R^2$) values in Table-2 for Congo red dye.

![Fig.-12: Pseudo Second Order Kinetic Model For Congo Red onto Spathodea Campanulata Leaves Biosorbent.](image)
Thermodynamic Studies

Thermodynamic studies provide information about the feasibility of the process and the nature of the biosorption process. In order to estimate the thermodynamic parameters for the biosorption of Congo red dye using *Spathodea Campanulata* leaves as biosorbent, the experiments were conducted and data were analyzed. The values of ΔH° and ΔS° were calculated from the slope and intercept of the linear Van’t Hoff plot i.e ln (q_e/c_e) vs (1/T). These plots are shown in Fig.-13 for Congo red dye. The estimated thermodynamics properties along with the correlation coefficients (R²) are tabulated in Table-3.

**Table-3: Thermodynamic Parameters For the Biosorption of Congo Red onto *Spathodea Campanulata* Leaves As Biosorbent**

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>ΔG° (kJ/mol)</th>
<th>ΔH° (J/mol)</th>
<th>ΔS° (J/mol k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>–3.89</td>
<td>16.02</td>
<td>13.82</td>
</tr>
<tr>
<td>293</td>
<td>–4.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>–4.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>–4.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>–4.44</td>
<td></td>
<td></td>
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</tbody>
</table>

CONCLUSION

The data obtained from the biosorption studies showed that a contact time of 40 min was sufficient for the maximum removal of Congo red dye from aqueous solution using *Spathodea Campanulata* biosorbent. The experimental data of biosorption of the dye onto the *Spathodea Campanulata* biosorbent fitted well with the Langmuir isotherm model. The isotherm reveals that the biosorption of the dye onto *Spathodea*...
Campanulata biosorbent was favorable. The maximum removal efficiency was predicted to be 88.2% at a temperature of 303.62 K, solution pH of 7.11, and initial dye concentration of 19.51 mg/L and biosorbent dosage of 1.66 g.

REFERENCES