**Removal of Congo Red Dye from Aqueous Solution by Using Limonia acidissima Shell as Adsorbent**

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This research paper highlights the removal of a congo red from aqueous medium by using *Limonia acidissima* shell. Various factors such as initial dye concentration, dosage of adsorbent, time contact, effects of temperature and pH were studied. The characterizations of adsorbent were done by XRD and FTIR analysis. The equilibrium data analyzed using Freundlich, Langmuir, Temkin and Dubinin Radushkavich isotherm models. Out of four adsorption isotherm, the R² value of Langmuir isotherm model was the highest. The maximum monolayer exposure from Langmuir isotherm model was determined to be 84.48mg/g, the separation factor (R_L) indicating favorable sorption is 0.76. The kinetic results inveterate that pseudo-first-order kinetic model explained the removal of Congo red dye by *Limonia acidissima* shells in a better way. The rate constant of 2.8 mg/g min⁻¹ was shown by intra-particle diffusion model. Thermodynamic parameters like Gibb’s free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) illustrated that Congo red dye adsorption onto *Limonia acidissima* shells was realistic, spontaneous and endothermic.

**Keywords:** Congo red, *Limonia acidissima* shell, Isotherms, Adsorption capacity, Kinetics.

**INTRODUCTION**

In the era of industrialization, large quantities of various dyes can be used in many industries, like paper and pulp manufacturing, textiles, printing, food products, leather treatment, etc. [1]. The effluent contains various colourful materials from industries, which further mixed with the surface and groundwater system. It causes a problem to human health such as kidney, liver, brain, and central nervous system due to toxic and carcinogenic dyes [2]. Therefore, it is required to eliminate dye contamination. Due to complex aromatic structures, it can't easily degrade [3]. Therefore, it is necessary to design an appropriate treatment method.

Recently, various methods have been developed which includes biological treatment, reverse osmosis, coagulation, flocculation, chemical oxidation, photodegradation [4] and adsorption [5] for the wastewater treatment containing colour impurities. Among this adsorption is one of best technique due to its effortlessness operation and lower cost compared to other processes. Recently, great attention has been focused on use of agricultural waste for elimination of dyes from wastewater. Several reports on adsorbents includes sawdust [6], hardwood, bagasse [7] and corn cobs [8]. The wood apple shell (*Limonia acidissima* shell) is an indigenous and ordinary fruit cultured in India. It is used in different culinary preparations, and a large amount of outer shell is discarded as waste. The wood apple shell (*Limonia acidissima* shell) carries lignocellulosic material [9]. This study aims to eliminate of Congo red dye from the aqueous solution by using *Limonia acidissima* shells with number of parameters like pH, time, initial dye concentration, time and temperature influence on adsorption behaviour, adsorption isotherm, adsorption kinetics and thermodynamics properties.

**EXPERIMENTAL**

The Congo red dye purchased from Lab Chemie (CAS no. 573-58-0). NaOH and HCl were bought from Merck, India. Wood apple shell (*Limonia acidissima*) derived from an economically available and ecological vegetable source.
The physico-chemical analysis of sample was done by Fourier transforms infrared spectroscopy (Thermo Scientific Nicolet) and X-Ray diffractometer (Rigaku Miniflex). The concentration of dye of solution was determined by UV-visible spectrophotometer (Rigol-3000).

**Preparation of adsorbent (Limonia acidissima):** The Limonia acidissima shells were collected from the region of Karnal and Sonipat (India) and washed thoroughly with double distilled water (2 times) to remove dust particles. The clean Limonia acidissima shells were dried in sunlight for 2 days and remaining moisture removed by over-night heating in oven at 80 °C. The dried Limonia acidissima shells were grinded and sieved by using different sizes (150 and 300-micron) by sieve shaker. The 300 μm sized particles of Limonia acidissima shells were collected and used for further experiments.

**Adsorption:** The experiments were investigated batchwise to identify the effect of operation parameters like pH (2 to 12), time contact (20-140 min), adsorbate concentration (50, 60, 70, 80, 90 and 100 mg/L), adsorbent dose (0.5-50 mg) and temperatures (303, 313, 323 and 333 K) during the study. All the experiments were performed at laboratory temperature (30 ± 5 °C), except when effect of temperature was examined. All beakers were shaked for 120 min with a speed of 100 rpm by using an orbital shaker. The absorbance of supernatant (dye remained in solution after the adsorption) was determined by UV spectrophotometry (Rigol-3000) at 497 nm. All experiments were carried out thrice. The amount of retained dye (qe) at equilibrium was estimated by following equation:

\[ q_e = \frac{(C_o - C_e)V}{m} \]  
(1)

where \( C_o \) and \( C_e \) (mg/L) are initial and equilibrium concentrations of Congo red dye, \( V \) (L) is the volume of solution, \( m \) (g) is the weight of Limonia acidissima shells.

**Kinetics and Adsorption parameter:** The adsorption of diffusion through a boundary, the pseudo first-order rate model and pseudo second-order rate model were investigated. The pseudo first-order rate model can be expressed as shown in eqn. 2 [10,11].

\[ \ln (q_e - q_t) = \ln q_e - K_1 t \]  
(2)

where \( q_e \) (mg g\(^{-1}\)) and \( q_t \) (mg g\(^{-1}\)) are the adsorbed amounts of Limonia acidissima shells at equilibrium and at time ‘t’, respectively; \( K_1 \) (min\(^{-1}\)) is the adsorption rate constant. The graph plot between \( \ln (q_e - q_t) \) against \( t \) gives the value of \( K_1 \) and \( q_e \) from the slope and the intercept of graph. The linearized pseudo second-order rate form [12] (eqn. 3) and intra-particle diffusion model (eqn. 4) were tested.

\[ t = \frac{1}{K_2 q_t^2} + \frac{1}{K_2 q_t} \]  
(3)

\[ q_t = K_d t^{1/2} + C \]  
(4)

where \( K_1 \) (g mg\(^{-1}\) min\(^{-1}\)) is the adsorption rate constant for pseudo second-order rate model and \( q_t \) (mg g\(^{-1}\)) can be calculated from the slope and intercept of graph between \( t/q_t \) and \( t \). And \( K_d \) (mg g\(^{-1}\) min\(^{0.5}\)) is the intra-particle diffusion rate constant and \( C \) is the intercept.

**Adsorption isotherm:** To uptake adsorption isotherm, including Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (DR) isotherm models were determined to explain Congo red dye-Limonia acidissima shells interaction. The Langmuir isotherm forms can be written according to the eqn. 5:

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \]  
(5)

The graph plot (C_e/q_e versus C_e) gives higher absorption capacity \( q_m \) (mg/g) and the Langmuir adsorption constant \( K_L \) (L/mg). The study of feasibility of adsorption by using separation factor (\( R_L \)) is shown in eqn. 6:

\[ R_L = \frac{1}{1 + K_L C_o} \]  
(6)

where \( K_L \) (L/mg) and \( C_o \) (mg/L) are the Langmuir isotherm constant and initial concentration of Congo red dye, respectively. The \( R_L \) value between 0 and 1, gives the favorability of adsorption process [13]. The Freundlich model was determined the interaction relationship between Congo red and Limonia acidissima shells particles by eqn. 7:

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  
(7)

where \( q_e \) (mg/g) and \( C_e \) (mg/L) are the quantity of Congo red dye retained at equilibrium and concentration at equilibrium of dye solution, respectively. The degree of sorption \( K_f \) and intensity of adsorption 1/n were obtained from the gradient and intercept log \( q_e \) versus log \( C_e \) [14]. Furthermore, if n > 1, this represents a favourable adsorption isotherm [13]. The Temkin isotherm model [15] was determined the relationship between adsorbent and adsorbate interaction as shown in eqn. 8:

\[ q_e = B \ln AT + B \ln C_e \]  
(8)

The equilibrium binding energy \( A_T \) (L/mol) and heat of adsorption \( B \) determine from the gradient and intercept of graph between \( q_e \) against \( \ln C_e \). The linear Dubinin-Radushkevitch adsorption isotherm [16] eqn. 9 may be written as:

\[ \ln q_e = \ln q_m - (\beta \varepsilon^2) \]  
(9)

where \( \beta \) (mol\(^2\)/kJ\(^2\)) and \( q_m \) (mg/g) are the adsorption energy and degree of adsorbent: \( \varepsilon \) is the Polanyi potential was estimated by eqn. 10:

\[ \varepsilon = RT \ln \left(1 + \frac{1}{C_e}ight) \]  
(10)

where T (K) and \( R \) (J/mol K) are the temperature and gas constant. A linear graph plot between \( \ln q_e \) versus \( \varepsilon^2 \), gives \( \beta \) and \( q_m \) from the slope and the intercept, respectively.

**Adsorption thermodynamic parameters:** Adsorption thermodynamic properties like Gibb’s free energy change (\( \Delta G^° \)), enthalpy change (\( \Delta H^° \)) and entropy change (\( \Delta S^° \)) were calculated using the subsequent equations:

\[ K_c = \frac{C_o}{C_e - C_s} \]  
(11)

where \( K_c \) is the constant, \( C_o \) (mg/L) are the initial ion concentration and the amount of Congo red dye adsorbed at equilibrium, respectively.

\[ \Delta G^° = -RT \ln K_c \]  
(12)
The values ($\Delta H^\circ$) and ($\Delta S^\circ$) were calculated by using gradient and intercept of a graph called Van't Hoff equation, $\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$ (13).

The results and discussion:

**Characteristic of Limonia acidissima:** The FTIR spectrum of *Limonia acidissima* shells (Fig. 1) was used to study the functional group. The band at 3600-3200 cm$^{-1}$ is recognized due to O-H and N-H stretching groups. The absorption band at 1598 cm$^{-1}$ is assigned to weak-stretching aromatic ring of C=C. The band at 1427 cm$^{-1}$ are also observed, which are axial deformation and bending of C-H of alkane dye structure. The XRD model was used to analyze the crystalline nature of *Limonia acidissima* shells (Fig. 2). The characteristic diffraction at around 18º-25º

was detected in all diffractograms. The diffraction in spectrum, showed no obvious crystalline peak in the 10-70º scanning range thus indicated the amorphous phase of *L. acidissima* shells.

**Effect of initial concentration:** The initial dye concentration and its effect on Congo red adsorption is understood by Fig. 3. To evaluate desired initial Congo red concentration, the initial concentration ranged from 50-100 mg/L, maintaining the temperature, adsorbent dosage and time at 303 K, 0.05 g and 120 min, respectively. The graph indicates that the percentage of elimination of Congo red dye decreases with increase Congo red dye concentrations; though the amount of adsorbed dye increases. Because increasing the concentration of dye, the surface area and their active sites of *Limonia acidissima* shells become saturated hence the removing percentage decreases [17].

**Effect of contact time:** Behaviour of Congo red dye on *Limonia acidissima* shells was studied to conclude an optimal contact time. It is observed (Fig. 4) that in a series of experiments...
in which, initial concentration of Congo red dye, contact time, temperature and amount of adsorbent were 50 mg/L, 20-140 min, 303 K and 0.05 g, respectively. As can be seen in Fig. 4, Congo red dye adsorption is fast at the beginning and thereafter it almost constant as the equilibrium reached. This is due to fact that covering the active surface of Limonia acidissima shells by Congo red dye molecules which leads to saturation of Limonia acidissima shell surface [17].

**Effect of Limonia acidissima shells dosage**: Desired dosage of Limonia acidissima shells used for adsorption of Congo red dye is shown in Fig. 5. It is evident that the dye concentration (50 mg/L) were contacted with varying dosage of Limonia acidissima shells (0.5-50 mg) for 120 min at 303 K. Due to a maximum number of active adsorbent sites availability, the removal percentage of Congo red elimination of dye is increased with the increase in adsorbing Limonia acidissima shells [18].

**Adsorption isotherms**: Experimental data collected at 303 K and a particular initial concentration of 50 mg/L were used on standard isotherm models applied in the aqueous solution viz., Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (DR). The Langmuir adsorption isotherm is more suitable for describing adsorption equilibrium ($R^2 > 0.9707$). Therefore, it is assumed that Congo red dye covers 84.48 mg/g. The $R^2$ value 0.76 calculated from eqn. 6 in the range 0 to 1, favoured adsorption of Congo red dye on Limonia acidissima shells [13]. Freundlich isotherm is about to know the same system, is mostly explained the adsorption isotherms model at multiple sites.

The intensity of adsorption value is $n > 1$ (1.896) shows a favourable and heterogeneous adsorption of Congo red dye on Limonia acidissima shells. Temkin's isotherm explained the heat of adsorption of all molecules and the interaction of Congo red dye on Limonia acidissima shell surface. The amount of free energy (E) used to distinguish between physical ($< 8$ KJ/mol) and chemical adsorption ($8-16$ KJ/mol) on the basis of ion- exchange. The free energy (E) of adsorption was found to be 0.117 (KJ/mol), which favoured the physical adsorption. Table-1 summarizes values of the isotherm parameters. The best uptake isotherms are preferred based on the correlation coefficient of Langmuir and Freundlich adsorption isotherms.

**Kinetic adsorption**: The asset mechanism is determined by a kinetic model that provides useful data to increase adsorption efficiency and broaden process possibilities. Rate constant was calculated by using the pseudo first-order rate model, pseudo second-order rate model and the intra-particle-diffusion model. The data obtained by Congo red dye at Limonia acidissima shells based on a primary liability dynamics model in which adsorption dynamics does not coincide well with the model of first principle as shown in Fig. 6. These results explained that the pseudo-second-order (0.9735) is higher than pseudo-first-order model (> 0.9141) for Limonia acidissima shell. The results obtained through Fig. 7 indicated that the adsorption data is well represented by pseudo-second-order rate model. Its degree can be limited to the adsorption rate in the specific surface area, which is attributed due to the lack of internal circulation. Of course, hypothetical behavior may include valence by separating electrons between anions and cations. In an intra-particle diffusion model for solid and liquid phase adsorption processes, the behaviour of dissolved substances is generally studied by external mass transfer or dispersion within the particles. The particles distribution model by intra-particle diffusion model [18]. To see the mechanism associated with the sorption is shown in Fig. 8. Table-2 provides the parameters and coefficients of pseudo first-order rate model and pseudo second-order rate model and intraparticle diffusion model.

**Effect of temperature and thermodynamics adsorption studies**: Experiments were conducted in batches conditions

**TABLE-I**

<table>
<thead>
<tr>
<th>Adsorption Isotherm Model</th>
<th>Parameters of Congo red dye</th>
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</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
<td>$Q_e$ (mg g$^{-1}$), $K_L$ (L mg$^{-1}$), $R^2$</td>
</tr>
<tr>
<td></td>
<td>84.78, 0.0260, 0.7680, 0.97077</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td>$1/n$, $K_F$ (mg g$^{-1}$), $R^2$</td>
</tr>
<tr>
<td></td>
<td>0.5271, 1.8968, 6.1308, 0.9600</td>
</tr>
<tr>
<td>Temkin Isotherm</td>
<td>$A_T$ (L mg$^{-1}$), $b_T$, B, $R^2$</td>
</tr>
<tr>
<td></td>
<td>4.2715, 123.533, 20.392, 0.9703</td>
</tr>
<tr>
<td>Dubinin Radushkevich Isotherm</td>
<td>$q_e$ (mg g$^{-1}$), $K_v$ (mol$^{-1}$ KJ$^{-1}$), $E$ (KJ mol$^{-1}$), $R^2$</td>
</tr>
<tr>
<td></td>
<td>10.62, 3.6091 x 10$^5$, 0.117, 0.8928</td>
</tr>
</tbody>
</table>
at particular temperatures viz., 303, 313, 323 and 333 K. The adsorption of Congo red increased from 60.2 to 70.9 mg/g with increase in temperature. This indicates that this is an endothermic process. The rise in temperature leads to increase in active sites of adsorbent [19]. The different thermodynamic properties were determined such as $\Delta G^\circ$, $\Delta S^\circ$ and $\Delta H^\circ$. The van't Hoff equation shows a linear form of $\log (K_c)/T$

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Value</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_e$ (mg g$^{-1}$)</td>
<td>10.66</td>
<td>0.9141</td>
</tr>
<tr>
<td>$K_1$ (min$^{-1}$)</td>
<td>0.0346</td>
<td></td>
</tr>
<tr>
<td>Pseudo second-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg g$^{-1}$)</td>
<td>0.6745</td>
<td>0.9735</td>
</tr>
<tr>
<td>$K_2$ (g mg$^{-1}$ min$^{-1}$)</td>
<td>0.0096</td>
<td></td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_d$ (g mg$^{-1}$ min$^{-1}$)</td>
<td>2.8583</td>
<td>0.9496</td>
</tr>
<tr>
<td>$C$ (mg g$^{-1}$)</td>
<td>1.1211</td>
<td></td>
</tr>
<tr>
<td>$\Delta H^\circ$ (J mol$^{-1}$)</td>
<td>6.637</td>
<td></td>
</tr>
<tr>
<td>$\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>14.208</td>
<td>0.9980</td>
</tr>
<tr>
<td>Thermodynamic Properties</td>
<td>$\Delta G^\circ \times 10^2$ (kJ mol$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>303 K</td>
<td>10.93</td>
<td></td>
</tr>
<tr>
<td>313 K</td>
<td>11.05</td>
<td></td>
</tr>
<tr>
<td>323 K</td>
<td>11.24</td>
<td></td>
</tr>
<tr>
<td>333 K</td>
<td>11.37</td>
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</tbody>
</table>

(Fig. 9), which was further used for calculating the thermodynamic parameters with eqn. 12. The $\Delta H^\circ$ and $\Delta S^\circ$ positive values indicate endothermic environment and randomness of Congo red-Limonia acidissima shell solution of the adsorbents internal structure. The negative value of $\Delta G^\circ$ suggested a favourable adsorption at various temperatures [20].

**Comparison of adsorption capacity of congo red dye with various adsorbents:** Various materials as adsorbents have been investigated for the elimination of Congo red dye. Table-3 summaries the maximum adsorption capacity from Langmuir isotherm model by numerous adsorbents. So, it is clear from Table-3 that the *Limonia acidissima* shell as waste material exhibits the higher adsorption capacity in case of Congo red dye adsorption.

**Conclusion**

The potential of *Limonia acidissima* shells as adsorbent in the elimination of Congo red dye in batch mode is investigated. The several parameters likes dosage, temperatures, initial concentration and contact time were evaluated in order to check the efficiency of *Limonia acidissima* shell as adsorbent towards Congo red dye. Highest adsorbent capacity (60.2 mg/g) of *L. acidissima* shells on congo red dye were achieved at pH 4 within 120 min. Various adsorption isotherm models viz. Langmuir, Freundlich, Temkin and Dubinin-Radushkevitch isotherms were studied. The maximum amount adsorbed 84.48 mg/g by
Langmuir isotherm was achieved. All of them, Freundlich isotherm model is best fitted. In addition, the kinetic of the overall adsorption were investigated by pseudo first-order and pseudo second-order. The pseudo second-order model favoured the adsorption of Congo red dye on Limonia acidissima shells. The fast adsorption of Congo red dye on Limonia acidissima shells showed by intra-particle diffusion. The thermodynamics parameters indicate an endothermic process for adsorption process. The positive value of $\Delta S^o$ confirmed greater stability of adsorption process of Congo red on Limonia acidissima shells.

**CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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