Adsorption of Erichrome Black T from Wastewater by *Litchi chinensis*

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Abstract

The efficiency of *Litchi chinensis* peel as a low cost adsorbent for the removal of Erichrome black T from an aqueous solution was studied in batch mode. The examinations are carried out to study the effects of pH, adsorbate concentration, adsorbent dosage, contact time and temperature. The kinetic studies showed that the adsorption reaction is of the pseudo second order kinetics. The thermodynamic parameters were obtained from langmuir, freundlich and DR isotherm models. The Langmuir adsorption capacity ($Q_o$) was found to be 9.94 mg dye per gram of the adsorbent Erichrome black T.

Key words: *Litchi chinensis*, Erichrome black T, Pseudo second order kinetics, Thermodynamics and adsorption.

INTRODUCTION

Water is becoming a threatened resource in the world as of the gap among supply and demand. A study from the United Nations shows that water consumption is increasing at twice the rate of population growth and predicts that by 2025, an estimated 1.8 billion people will live in water-scarce areas. (Tony et al. 2019) Industrial produced dyes are highly toxic and more carcinogenic (Varjani et al. 2020). Discharge of dangerous substances into water bodies pollute the water and make it unfit for aquatic life (Manzoor and Sharma 2020). In additional, the pollutants are stable to light, temperature and microbial attack, making them recalcitrant compounds. Industries are faced with continuing severe enforcement actions by environmental protection agencies, which in turn, motivate scientists to develop novel powerful and low cost techniques for dye removal. In this endeavour, dye removal achievements were acquired by applying biological treatments, coagulation/sedimentation, membrane separation, photocatalytic degradation, and adsorption (Gholami et al. 2016; Balouchi et al. 2020).

Among a number of physical and chemical methods, adsorption process is considered to be one of the best
essential techniques that have been successfully employed for color removal from wastewater (Al-Ghouti and Da'ana 2020). This is a low-cost, easy preparation and many environmental advantages (Murcia-Salvador et al. 2020). Eriochrome black-T (EBT) is the anionic dye. It is used in textile industries of dyeing silk, wool, nylon etc. The EBT is used as an indicator in complexometric titrations for determination of Ca$^{2+}$, Mg$^{2+}$ and Zn$^{2+}$ ions and for biological staining (Moeinpour et al. 2014; Pakdaman and Honarasa 2016). EBT is the stable and non bio degradable dye. It causes carcinogenic and mutagenic problems. Azo dyes are generally used in different industries, because they are soluble in water, have a good distribution of color, are more suitable than natural dyes and their production cost is lower compared to other dyes.(Ngulube et al. 2017; Al-Shabib et al. 2018). Eriochrome Black T (EBT) constitutes an environmental hazard due to the presence of N=N bond (Haghighat et al. 2020). Therefore, it is essential to explore efficient ways to separate hazardous EBT from contaminated streams as it produces naphthylamine. Naphthylamine is a carcinogen. Naphthylamine is a highly toxic substance that can be absorbed through the skin to generate methemoglobin. This leads to blood poisoning. Cost effective and biological adsorbents in recent years are eucalyptus bark (Dave et al. 2011), cotton waste (Ladhe et al. 2011), tridax procumbens (Raveendra et al. 2015), natural and modified orange peel (Salman and Ali 2019), modified wheat straw (Sadeghi et al. 2020), sewage sludge (Gu et al. 2020), etc for the removal of dyes from aqueous solutions. The present study is to determine the removal of EBT from aqueous solution by adsorption technique using Litchi chinensis peel waste as an adsorbent.

MATERIALS AND METHODS

Adsorbate

Eriochrome black T is an azo dye with molecular formula -C$_{20}$H$_{12}$N$_3$O$_7$SNa, having molecular weight of 461.381. It was purchased from Merck. IUPAC name of EBT is Sodium 4-[2-(1-hydroxynaphthalen-2-yl) hydrazin-1-ylidene]-7-nitro-3-oxo-3,4-dihydonaphthalene-1-sulfonate. It appears dark brown in color. In order to prepare stock solution, 1.0 g of EBT was dissolved in one liter of distilled water. The pH of natural solution was 4.9 and it was adjusted to pH 2 and it is the constant throughout all investigations.
Preparation of adsorbent

*Litchi chinensis* fruit was obtained from local market in Kadapa town, Andhra Pradesh, India. The wastage of peel was washed to remove dust particles and dried in hot air oven at 75°C for 48 hours. It was then ground and sieved with uniform particle size 100 μm sieve. The dried sample was used as an adsorbent.

**Batch adsorption**

The batch adsorption studies were conducted in 250 ml conical flasks by agitating 300 mg *Litchi chinensis* peel powder with 50 ml of Eriochrome black T solution of wanted concentration and pH at 180 rpm in a rotary shaker (Kemi). The absorbance of dye concentration was measured by a double beam UV-Vis Spectrophotometer (Lab India UV 3000+) at 530 nm. The pH was evaluated using a pH meter (Elico LI 614 digital pH analyzer). The samples were taken from the rotary shaker at fixed time intervals and the EBT adsorbate solution was isolated from the adsorbent by centrifugation (Remi R-8C) at 4000 rpm for 20 minutes. The absorbance of the supernatant solution was measured. Dye solution of pH was adjusted 0.1 N HCL and 0.1 N NaOH solutions and dose studied with 100 to 500 mg of the adsorbent dose. In adsorption process *Litchi chinensis* peel powder dose was fixed with time. The EBT concentration was assorted (The Langmuir plot was acquired utilizing the equilibrium time curve data).

**Desorption study**

*Litchi chinensis* peel powder was used for the adsorption of 20 and 30 mg l⁻¹ of EBT solution and separated from the adsorbate by centrifugation. The EBT loaded *Litchi chinensis* was filtered using Whatman filter paper and washed with double distilled water to remove any unadsorbed dye. The spent adsorbent was agitated with double distilled water and the pH was adjusted to 2 to 9 for equilibrium time. The concentration of desorbed EBT dye was measured by a double beam UV-Vis Spectrophotometer.

**Characterization of adsorbent**

The raw *Litchi chinensis* peel powdered physical and chemical characteristics were determined with SEM and FTIR.
Scanning Electron Microscope (SEM)

The surface morphology of the *Litchi chinensis* was analyzed by a JEOL JSM-IT500 scanning electron microscope operated at an acceleration voltage of 20 kV.

Fourier Transform Infrared spectroscopy (FTIR)

The surface functional groups and chemical structure *litchi chinensis* was evaluated by an FTIR spectrometer (Perkin Elmer spectrum two) in the transmission mode in the range from 400-4000 cm\(^{-1}\). The adsorbent was mixed with potassium bromide (KBr) and compressed to form disks.

Zero point charge (pH \(z_{pc}\))

The zero point charge (pH\(_{z_{pc}}\)) of *Litchi chinensis* was found to be 7.0.

RESULT AND DISCUSSION

A preliminary investigations were executed to remove EBT at pH 2 using *Litchi chinensis* peel powder.

Characterization of adsorbent

The SEM of *Litchi chinensis* peel is given (Fig 2) The surface was rough and its inside was loose and porous, with large specific surface area and rich pore structure. (Dave et al. 2011; Blaisi et al. 2018; Thitipone et al. 2020; Gu et al. 2020). The FTIR spectrum of *Litchi chinensis* are shown (Fig 3). The peaks at 3654 and 3745 cm\(^{-1}\) indicate the stretching vibration of N-H group, new peaks appeared in the position of 2319, 1634, 1223, 1015 cm\(^{-1}\) respectively in the Eriochrome black T loaded adsorbent. Similar findings are observed (Aziz et al. 2018; Boudouaia et al. 2019; Wen et al. 2019; Al-Zoubi et al. 2020).

Effect of contact time and initial concentration on adsorption of Eriochrome black T

The amount (mg/g) of dye an adsorbed at concentrations of 20, 30, 40, 50 mg/L and at different equilibrium times were studied and results are shown (Fig 4 & Tab 1). The amount of dye removal at equilibrium increased from 3.1 mg/g to 7.0 mg/g for EBT with the increase in dye concentration from 20 to 50 mg/L. In the adsorption process, initially adsorbate molecules have to come across the boundary layer effect before diffusing from boundary layer onto *Litchi chinensis* surface. This is followed by the diffusion of adsorbate into the porous
structure of the adsorbent. This happening will take relatively longer contact time. Similar findings are observed (Sirisha et al. 2019; Fajarwati et al. 2019)

Effect of Dose

The effect of Litchi chinensis dose 100-500 mg on the removal order of absorbate is given (Fig 6). It was noticed that the removal order of EBT directly upgraded with increase in the adsorbent dose from 100 to 500 mg. This can be associated with increase of adsorption active sites with the increase in amount of adsorbent. (Ladhe et al. 2011; Sirisha et al. 2019; Al-Zoubi et al. 2020)

Adsorption kinetic study

In the adsorption kinetic study, three kinetic models were studied i.e., pseudo-first-order, pseudo-second-order, and Elovich models. These two pseudo-first-order and pseudo–second–order kinetic models were applied to examine the controlling the mechanism of Eriochrome black T dye removal from aqueous solutions. The adsorption capacity of Litchi chinensis to different concentrations of adsorbate dye gradually increased with time and then executed an equilibrium. The experimental q_e values and the calculated q_e values of pseudo – second-order values are very near. In this study pseudo – second-order kinetic model data fitted very well with the adsorbent. Similar finding are observed (Moeinpour et al. 2014; sirisha et al. 2019; Salimi et al. 2020) and the adsorption conduct was chemisorptions. The kinetics experimental data are given in the table 1.

Adsorption Isotherms

The adsorption isotherm demonstrates the adsorption demeanour of adsorbate molecules on the surface of the Litchi chinensis peel. Three isotherm models were used to fit the equilibrium data i.e., Langmuir, Freundlich and Dubinin- Radushkevich (DR). In this study it is required to determine the interaction between dye solution and Litchi chinensis at equilibrium. Table 3,4 and figure 7 shows the isotherm parameter and plot. Eriochrome black-T shows very well fitted to the Langmuir isotherm model. Similar findings are observed. (Liu et al. 2014; Moeinpour et al. 2014; Blaisi et al. 2018; Sirisha et al. 2019). All investigations were done at room temperature at 32°C. Langmuir isotherm implied that the surface of litchi is homogeneous and the K_L value indicates the favourable adsorption. The mean free energy of adsorbtion E value 35.360 indicates chemisorption. All investigations were done at room temperature (32°C).
Effect of pH on removal of Eriochrome black T

The effect of pH on the adsorption of Eriochrome black T by litchi peel is shown in figure 8. The solution pH was studied in the range from 2 to 9. The zero point charge (pH_{zpc}) of *Litchi chinensis* was found to be 7.0. The (pH_{zpc}) of 7.0 indicated that the surface of the adsorbent was positively charged at pH less than 7 and negatively charged at pH values above 7 and the highest removal of Eriochrome black T was noticed at pH 2. EBT percent removal decreased virtually linear with the increase in pH from 2 to 9. In acidic pH, the absorbent surface have protonated strong electrostatic interactions if the pH increases the number of positively charged sites decreased which weakened the interactions between the absorbent surface and anionic dye of EBT. In this study electrostatic interactions play a major role (Blaisi et al. 2018). Similar observation was revealed that the pH experiments indicated that the major uptake takes place in the pH range 2–5 for EBT. (Arfi et al. 2017; Aziz et al. 2018; Ahmed et al. 2019; Al-Zoubi et al., 2020)

**Desorption studies**

In this study regenerate the spent adsorbent was explored to control the reusability of the adsorbent after adsorption examinations. And to after understand the mechanism of adsorption of EBT. Efficiency of desorbing eluents was calculated by comparing the amount of EBT desorbed from *litchi chinensis* to the amount of EBT in EBT – loaded adsorbent. Similar finding are observed. (Ahmed et al. 2019; Al-Zoubi et al. 2020)

**Studies of thermodynamics of adsorption**

Thermodynamic parameters for the adsorption of ERiochrome black T onto *Litchi chinensis* peel powder was calculated by the following equation reported (Table 5).

\[
\Delta G^o = -RT \ln K_c
\]  

Where R is gas constant (8.314 J/mol/K), b is equilibrium constant (L/mol) and T is the temperature in (K):

\[
\log K_c = (\Delta S^o/2.303 \times R) - (\Delta H^o/ 2.303 \times RT)
\]

The values of \(\Delta H^o\) and \(\Delta S^o\) were determined from the slope and intercept of van’t Hoff plots log \(K_c\) vs 1/T. Negative values of \(\Delta H^o\) suggest the exothermic nature of adsorption. The negative values of \(\Delta G^o(< - 40 \text{kJ mol}^{-1})\) indicate spontaneous nature of adsorption and beneficial activity under the experimental conditions.
(Anastopoulos et al. 2018; Qian et al. 2018). It involved in strong chemical reaction. The positive value of $\Delta S^o$ with *Litchi chinensis* indicate increased randomness at the solid solution interface during the adsorption process.

CONCLUSION

The study informs that *Litchi chinensis* acts as a good adsorbent for the removal of Eriochrome black T from aqueous solutions. The adsorption kinetics data followed pseudo-second order kinetic model with high correlation coefficient almost reaching a unit value for Eriochrome black T. The removal as a result increases with increase in adsorbent dosage. The use of this low-cost adsorbent can be successfully adopted in treating large amount of dye wastewaters.

Table :1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>First order Kinetic Model</th>
<th>Second order Kinetic Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye</td>
<td>$q_{exp}$ (mg/g)</td>
<td>$K_1$(min$^{-1}$)</td>
</tr>
<tr>
<td>20</td>
<td>3.101</td>
<td>-0.0951</td>
</tr>
<tr>
<td>30</td>
<td>4.414</td>
<td>-0.0948</td>
</tr>
<tr>
<td>40</td>
<td>5.813</td>
<td>-0.0566</td>
</tr>
<tr>
<td>50</td>
<td>7.034</td>
<td>-0.0414</td>
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Table 2.
Adsorption capacities of Eriochrome black T from aqueous solution using different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Q max (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginate/basil seed mucilage Biocomposite</td>
<td>9.52</td>
<td>(Javanbakht and Shafiei 2019)</td>
</tr>
<tr>
<td>Untreated almond shell</td>
<td>6.02</td>
<td>(Şahin et al. 2013)</td>
</tr>
<tr>
<td>Hydrophobic cross-linked polyzwitterionic acid(HCPZA)</td>
<td>15.9</td>
<td>(Saleh et al. 2016)</td>
</tr>
<tr>
<td>Date palm ash/MgA</td>
<td>425.16</td>
<td>(Nawaf et al. 2018)</td>
</tr>
<tr>
<td>Diatom-xerogel (DXC)</td>
<td>47.01</td>
<td>(sriram et al. 2020)</td>
</tr>
<tr>
<td>Epibromohydrin modified crosslinked polyamine resin</td>
<td>42.3</td>
<td>(Manzar MS et al. 2019)</td>
</tr>
<tr>
<td>Graphene</td>
<td>102.04</td>
<td>(Khalid et al. 2018)</td>
</tr>
<tr>
<td>Cold plasma-treated almond shell</td>
<td>18.18</td>
<td>(Şahin et al. 2013)</td>
</tr>
<tr>
<td>NiFe-calcined layered double hydroxides</td>
<td>132.49</td>
<td>(Zubair et al. 2017)</td>
</tr>
<tr>
<td>Activated carbon from waste rice hulls</td>
<td>160.36</td>
<td>(Luna et al. 2013)</td>
</tr>
<tr>
<td>β-Cyclodextrins/polyurethane foam material NiFe2O4</td>
<td>20.17</td>
<td>(Dong, K et al. 2013)</td>
</tr>
<tr>
<td>Eucalyptus bark</td>
<td>52.37</td>
<td>(Dave et al. 2011)</td>
</tr>
<tr>
<td>Bottom Ash</td>
<td>81.52</td>
<td>(Zandipak et al. 2015)</td>
</tr>
<tr>
<td>Litchi chinensis peel</td>
<td>9.94</td>
<td>Present work</td>
</tr>
</tbody>
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Table 3. Langmuir model constants

<table>
<thead>
<tr>
<th>C₀ (mg/L)</th>
<th>Qₒ (mg/g)</th>
<th>b (L/mg)</th>
<th>R&lt;sub&gt;L&lt;/sub&gt;</th>
</tr>
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<tbody>
<tr>
<td>20</td>
<td>0.147</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>9.94</td>
<td>0.289</td>
<td>0.103</td>
</tr>
<tr>
<td>40</td>
<td>0.079</td>
<td></td>
<td>0.079</td>
</tr>
<tr>
<td>50</td>
<td>0.064</td>
<td></td>
<td>0.064</td>
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Table 4. Freundlich model coefficients.

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<thead>
<tr>
<th></th>
<th>k&lt;sub&gt;f&lt;/sub&gt; (mg&lt;sup&gt;1-1/n&lt;/sup&gt; L&lt;sup&gt;1/n&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>n</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>2.656</td>
<td>2.125</td>
<td>0.9825</td>
</tr>
<tr>
<td>Dubinin – Radushkevich</td>
<td>106.866</td>
<td>35.360</td>
<td>0.9698</td>
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</tbody>
</table>

Table 5 Co-efficient of adsorption thermodynamics.

<table>
<thead>
<tr>
<th>Dye</th>
<th>ΔH°(KJ/mol)</th>
<th>ΔS°(J/mol/K)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eriochrome black T</td>
<td>-13.902</td>
<td>52.853</td>
<td>0.9694</td>
</tr>
</tbody>
</table>

Fig. 1: The structure of Eriochrome black T
Fig. 2: SEM images of *Litchi chinensis* before (a) and after EBT adsorption (b).

Fig. 3: FTIR images of *Litchi chinensis* before (a) and after EBT adsorption (b).

Fig. 4: Effect of contact time on Eriochrome black T adsorption.
Fig. 5: Effect of Dose on Eriochrome black T adsorption.

Fig. 6: Second-order kinetics plot for the removal of Eriochrome black-T.

Fig. 7: Comparison of adsorption isotherms of Eriochrome black-T dye.
Fig. 8: Effect of pH on adsorption and desorption of Eriochrome Black T.

Reference:


