Kinetics and Equilibrium Studies on Biosorption of CBB by Coir Pith

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Abstract: The biosorption of Coomassie Brilliant Blue by acid treated coir-pith has been investigated in batch mode. Effect of time, Initial Concentration of dye and initial adsorbent concentration on biosorption was investigated. The pseudo-first order kinetic model was applied to the adsorption system and high co-relation co-efficient favored Pseudo-second order reaction. Freundlich’s and Langmuir’s mathematical models were used to describe batch adsorption equilibrium data and the constants were evaluated. The adsorption was found to be favourable in both isotherms. The maximum adsorption capacity was found to be 31.847mg/g. The adsorption capacity for the system was 6.438 and adsorption intensity was 2.8019. The investigation shows that the acid-treated coir pith is better suited for the removal of dyes from the textile industry effluent.

Key words: Biosorption • coco-pith • CBB • Langmuir’s • Freundlich’s isotherms

INTRODUCTION

The inappropriate disposal of dyes in waste water constitutes an environmental problem and can cause damage to the ecosystem [1]. Water pollution by dyes is one of the major pollution sources in India. Wastewater containing dye cause water pollution by lowering light penetration and photosynthesis and toxicity from heavy metals associated with pigments [2]. Conventional biological processes are relatively inefficient for color removal [3]. In recent years, use of microbial biomass for decolorization of textile industry waste water is promising alternative in which some bacteria and fungi are used to replace present treatment process [4]. Though they are effective in treating waste water they suffer some limitations like production of biomass for large scale process and disposing the biomass after the treatment. Thus using agricultural waste products as a potential biosorbert of dyes is being extensively investigated. A variety of agricultural biosorbert have been investigated like sago waste [5], cassava waste [6], peanut skins [7], banana pith [8], sugarcane waste [9], chaff, apple pomace [10], wheat straw [11], rice husk [12], yellow passion fruit waste [13], coconut husk carbon [14], coir-pith carbon [15] just to mention a few. The chemical modification of sorbent with the help of an acid, base, is done for enhancing biosorption [16]. The kinetic and equilibrium parameters of acid treated coir pith have been investigated in the present study.

MATERIALS AND METHODS

Preparation of adsorbent: The coir pith used in the study was obtained from in and around Salem district, Tamil Nadu, India generated as a waste after coir making. They were washed with de-ionized water thrice and was dipped in one molar solution of acid (HCl) for two days and then washed with double distilled water thrice to remove any residue of acid. The pith was then dried at 55°C for a day in oven and used for biosorption studies.

Preparation of dye solution: 0.1 mg/mL (100 mg/L) solution of Coomassie brilliant blue was prepared and stored in brown reagent bottles in dark place to prevent oxidation of the dye solution. The dye solution was prepared and used freshly, before 24 hours of their preparation. A standard graph of Dye concentration versus optical density at 580 ηm was plotted.

Estimation of optimum time and kinetics: One gram of treated coir pith was added to 100 ml of 100 mg/L of dye solution and shaken at a 30°C. Samples were withdrawn at regular intervals of 15 min and their optical density was measured. The plot of Adsorption Capacity versus Time was plotted and the optimum time was found from the graph. The Adsorption Kinetics was found from the time adsorption data.

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The effect of initial dye concentration and adsorbent concentration: 20, 40, 60, 80, 100 mg/L dye solutions were prepared. 0.2 g of adsorbent was added to 50 ml of solution and shaken for 150 minutes at 30°C. The OD was measured and adsorption capacity was found. For the effect of adsorbent concentration, 0.2, 0.4, 0.6, 0.8, 1.0 g of adsorbent was added to 100 mL of 0.1 mg/mL dye solution and shaken for 150 minutes at 30°C. The Absorbance was measured and subsequently the adsorption capacity was determined. From the above measured data, sorption kinetics, Langmuir’s isotherm and Freundlich’s parameters were evaluated. The dye uptake was calculated using the following mass balance equation

\[ q = \frac{V(C_i - C_f)}{S} \]

Where
- \( q \) = Dye uptake (mg dye/g sorbent)
- \( V \) = Volume of Dye solution in contact with sorbent (L)
- \( C_i \) = Initial Concentration of metal in solution (mg/L)
- \( C_f \) = Final Concentration of metal in solution (mg/L)
- \( S \) = Dry weight of the sorbent (g)

Theory and data evaluation

Sorption kinetics: The rate of sorption of a molecule on the adsorbent surface is an important parameter. In batch adsorption system it is necessary to establish time dependence of the process. The Pseudo-second order rate equation developed by Ho et al. 1995 was used [17, 18].

\[ \frac{dq_t}{dt} = K(qe - qt)^2 \]

Where \( k \) is the equilibrium constant (g/ mg.min), \( q_t \) is the amount of dye adsorbed on sorbent at time \( t \) (mg/g) and \( q_e \) is the equilibrium dye uptake (mg/g). Equation can be rearranged as

\[ \frac{1}{q} = \frac{1}{q_e} + \frac{1}{Kqe} \]

A plot of \( t/q \) vs \( t \) will give a linear plot if the sorption data obeys pseudo-second order kinetics. \( h = kq_e^2 \) is described as the initial rate constant as \( t \) approaches zero.

Adsorption isotherms


Freundlich isotherm: The Freundlich’s equation is given by:

\[ q = K_f C_e^{1/n} \]

Where
- \( q \) = Dye adsorbed to the adsorbent at equilibrium (mg/g)
- \( C_e \) = Equilibrium concentration of dye in the solution (mg/mL) in other words \( C_f \)
- \( K_f \) = Empirical constant, indicates the adsorption capacity of the sorbent.
- \( n \) = Constant indicating the intensity of adsorption.

The equation can be rearranged to linear form as given below.

\[ \log q = \log K_f + \frac{1}{n} \log C_e \]

The value of \( K_f \) and \( n \) are obtained by plotting \( q \) vs \( \log C_e \).

Langmuir isotherm: The Langmuir’s equation is given by

\[ q = \frac{Q_{ma} b C_e}{1 + b C_e} \]

Where
- \( Q \) = Dye adsorbed to the adsorbent at equilibrium (mg/g)
- \( Q_{ma} \) = Maximum possible amount amount of dye that can be adsorbed per unit dry weight of sorbent.
- \( C_e \) = Equilibrium concentration of dye in the solution (mg/mL)
- \( b \) = Empirical constant, indicating the affinity of sorbent towards the sorbate.

This equation can be linearised as:

\[ \frac{C_e}{Q} = \frac{1}{Q_{ma} b} + \frac{1}{Q_{ma} C_e} \]

The adsorption constants \( Q_{ma} \) and \( b \) can be obtained by plotting \( 1/q \) as a function of \( 1/C_e \).

RESULTS AND DISCUSSION

The time course profile of sorption of CBB from 100 mL 0.1 mg/mL solution is shown in Fig. 1 and in Table 1. The Concentration decreased to 0.0102 (89.8% Sorption) and beyond that remained constant with time. From the time adsorption data it was found that the optimum time for adsorption is 150 min to obtain
Table 1: Effect of contact time on sorption process

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>CONC (mg/L)</th>
<th>Ce (mg/L)</th>
<th>Adsorption capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.100000</td>
<td>100.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>15</td>
<td>0.043311</td>
<td>43.3110</td>
<td>5.6680</td>
</tr>
<tr>
<td>30</td>
<td>0.035970</td>
<td>35.9701</td>
<td>6.4029</td>
</tr>
<tr>
<td>45</td>
<td>0.029363</td>
<td>29.3634</td>
<td>7.0636</td>
</tr>
<tr>
<td>60</td>
<td>0.025693</td>
<td>25.6929</td>
<td>7.4307</td>
</tr>
<tr>
<td>75</td>
<td>0.021288</td>
<td>21.2884</td>
<td>7.8711</td>
</tr>
<tr>
<td>90</td>
<td>0.015049</td>
<td>15.0487</td>
<td>8.4951</td>
</tr>
<tr>
<td>105</td>
<td>0.013948</td>
<td>13.9476</td>
<td>8.6052</td>
</tr>
<tr>
<td>120</td>
<td>0.012479</td>
<td>12.4794</td>
<td>8.7520</td>
</tr>
<tr>
<td>135</td>
<td>0.011011</td>
<td>11.0112</td>
<td>8.8988</td>
</tr>
<tr>
<td>150</td>
<td>0.010644</td>
<td>10.6442</td>
<td>8.9355</td>
</tr>
<tr>
<td>165</td>
<td>0.010277</td>
<td>10.2771</td>
<td>8.9722</td>
</tr>
</tbody>
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Table 2: Effect of adsorbate concentration on adsorption

<table>
<thead>
<tr>
<th>Conc (mg/L)</th>
<th>Ce (mg/L)</th>
<th>Adsorption capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.1011</td>
<td>9.4494</td>
</tr>
<tr>
<td>40</td>
<td>2.9363</td>
<td>18.5318</td>
</tr>
<tr>
<td>60</td>
<td>8.8090</td>
<td>25.5954</td>
</tr>
<tr>
<td>80</td>
<td>17.6180</td>
<td>31.1909</td>
</tr>
<tr>
<td>100</td>
<td>21.2884</td>
<td>39.3557</td>
</tr>
</tbody>
</table>

Table 3: Effect of adsorbent concentration on adsorption

<table>
<thead>
<tr>
<th>Gm adsorbent (g)</th>
<th>Conc (mg/L)</th>
<th>Adsorption capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>46.2473</td>
<td>26.8763</td>
</tr>
<tr>
<td>0.4</td>
<td>21.6555</td>
<td>19.5861</td>
</tr>
<tr>
<td>0.6</td>
<td>12.8464</td>
<td>14.5255</td>
</tr>
<tr>
<td>0.8</td>
<td>6.2397</td>
<td>11.7200</td>
</tr>
<tr>
<td>1.0</td>
<td>2.5692</td>
<td>9.7430</td>
</tr>
</tbody>
</table>

Fig. 1: Effect of time on adsorption

Fig. 2: Pseudo-first order kinetics. Y = 1.5761 + 0.1020X, R = 0.9991

Fig. 3: Effect of initial dye concentration on adsorption

The effect of initial dye concentration on adsorption is tabulated in Table 2 and illustrated in Fig. 3. The adsorption capacity was found to be increasing with adsorbate concentration. The plot on effect of initial dye concentration on biosorption shows the sorption increases with the initial concentration of the dye. The plot is likely to be linear. The plot of adsorption capacity Vs adsorbent concentration shows that the adsorption capacity reduces with the increase in adsorbent concentration.

The effect of amount of sorbent on adsorption is given Table 3 and in Fig. 4. The Freundlich’s plot and Langmuir plot shown in Fig. 5 and 6 respectively. The regression coefficients are 0.9828 and 0.9080 respectively.
The Freundlich’s isotherm best fitted the data with $n = 2.8019$ and $K_f = 6.438$. According to Kadirvelu and Namasivayam (2000) [15] $n$ values between 1 and 10 represents beneficial adsorption and thus the adsorption of Dye on acid treated coir-pith is also beneficial.

From the Langmuir plot, $q_{\text{max}} = 31.847 \text{ mg/g.}$ and $b = 0.0926 \text{ L/mg (0.295 L/mg)}$. The essential characteristics of the Langmuir isotherm can be expressed as dimensionless constant separation factor or equilibrium parameter given by $R_L$.

$$R_L = \frac{1}{1 + K_L C_o}$$

Where $K_L$ is Langmuir’s Equilibrium Constant which is related to the affinity of binding sites and $K_L = Q_{\text{max}}b$ [22]. $C_o$ is the initial dye concentration.

According to McKay et al. [23], $R_L$ between 0 and 1 indicates favourable adsorption. In the current experiment $R_L$ is found to be 0.0034 and again the adsorption is found to be favourable.

**CONCLUSION**

The adsorption of CBB on coir pith undergoes pseudo-second order kinetics. The maximum dye adsorption is about 0.21 mg/g of acid treated coco-pith. Evaluation by both Langmuir and Freundlich’s isotherm has been found to undergo favourable adsorption. So the acid treated Coir-Pith can be used as a potential source for adsorption of textile dyes. The coir-pith thus can be used to play a vital role in the effluent treatment of Dyeing industries. Developing this adsorption data to textile dyes may help for the survival of many textile industries in India and in many other countries which suffer from water pollution due to dyes.

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**REFERENCES**


