Adsorption Studies of Direct Red 28 Dye onto Activated Carbon Prepared from Low Cost Material

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ABSTRACT

An experimental investigation on the removal of direct red 28 dye from wastewater by using rice-husk carbon as low cost adsorbent was carried out in a laboratory.

Batch type experiments were conducted to study the influence of different parameters such as adsorbent dose, contact time, pH, initial concentration of dye and particle size of adsorbent. The removal data have been analyzed using Langmuir and Freundlich isotherm models. The adsorption process was in conformity demonstrated use of rice husk to obtain low cost adsorbent for dye removal from aqueous solution.

Keywords: adsorption, low cost adsorbent, isotherm, dye.

1. INTRODUCTION

Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics, etc., to colour their products. The dyes are in variably left as the major waste in these industries. Due to their chemical structures, dyes are resistant to fading on exposure to light, water and many chemicals, therefore, are difficult to be decolorized once released into the aquatic environment (Mckay et al., 1979; Poots and Mckay, 1996). Many of the organic dyes are hazardous and may affect aquatic life and even the food chain (Chua et al., 2005) such as, Congo red dye. It is a secondary diazo, water soluble, yielding aired colloidal solution (Bhattacharya and Sharma, 2004). The removal of dyes from industrial waste before they are discharged into the water bodies is therefore very important from health and hygiene point of view and for environmental protection (O’Neill et al., 1999). Various techniques have been employed for the removal of dyes from wastewaters (Choy et al., 1999; Khattri and Singh, 2000). Conventional physical and chemical methods are either costly, or produce concentrated sludge, or may not capable of treating large volumes of effluent without the risk of clogging (Robinson et al., 2001).

Natural materials that are available in abundance, or certain waste products from industrial or agricultural operations, may have great potential as an inexpensive sorbents.

Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. The abundance and availability of agricultural by products make them good sources of raw materials for activated carbon. Many carbon aqueous materials such as bark, coal, lignite, coconut shells, wood, dead biomass, sea weed, pecan shell and peat are used in the production of commercial activated Carbons (Bailey et al., 1999; Bansode et al., 2003). with the exponential demand in the use of rice as a staple food, the rice husk which is a waste product is available in abundance for in excess of any local uses and thus, has posed disposal problems (Guo et al., 2000). Rice husk possesses a granular structure, is insoluble in water, has chemical stability and high mechanical strength. The typical composition and chemical composition of rice husk is given elsewhere (Damel, 1976; Rahman and Ismail, 1993; Rahman et al., 1997). The rice husk, as the commodity waste, can be activated and used as an adsorbent in water purification or the treatment of industrial wastewater. It would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to the existing commercial carbons. Rice husk, an agricultural waste, contains about 20% silica, is suitable for the production of activated carbon and has been reported as a good sorbent for many metals and basic dyes (Marshall et al., 1993; Mansaraly and Ghaly, 1998; Guo et al., 2002).
2. EXPERIMENTAL

2.1. Materials and methods

2.1.1. Preparation of sorbent

Rice husk (RH) was obtained from local rice mills and was washed several times with tap water followed by filtration. The cleaned rice husk was oven burning completely at 300 °C, then cooled. The rice husk activated carbon (RHC) used in this study was washed with distilled water to remove water soluble materials present in the carbon prior to the adsorption study and then sieved to (100-1000) µm size which was used without further treatment. The main constituents of rice husk are: 64-74% volatile matter and 12-16% fixed carbon and 15-20% ash (Govindarao, 1980; Rhman et al., 1997; Nakbanpote et al., 2000). The rice husk composition are: 32.24% cellulose, 21.34% hemicellulose, 21.44% Lignin, 1.82% extractives, 8.11% water and 15.05% mineral ash. The mineral ash is 94.5-96.34 % SiO₂.

2.1.2. Preparation of adsorbate

Direct red 28 dye is namely Congo red (CR) is an anionic azo dye having IUPAC name as 1-napthalenesulfonic acid, 3, 3-(4, 4-biphenylenebis (azo)) bis (4-aminodisodium) salt. The chemical structure of dye used in this study is described in Figure (1).

![Figure 1: Structure of Congo red Dye.](image)

The physiochemical properties of the CR dye can be shown by Table (1)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₃₂H₂₅N₆Na₂O₆S₂</td>
</tr>
<tr>
<td>Molecular weight(FW)</td>
<td>696.68g/mol</td>
</tr>
<tr>
<td>C.I. Name</td>
<td>22 120</td>
</tr>
<tr>
<td>Absorption maxima</td>
<td>498nm</td>
</tr>
<tr>
<td>Nature</td>
<td>Anionic dye</td>
</tr>
</tbody>
</table>

The dye was obtained from local supplier and its stock solution was prepared in distilled water. All the test solutions were prepared by diluting the stock with distilled water.

Dye solution was prepared by dissolving accurately weighted dye in distilled water at a concentration of 1gm in 1000ml of water (1000ppm). Concentrations of the dye solutions were determined by measuring the absorbance of the solution at the characteristic wavelength(λ max =498nm using a double beam UV-Vis spectrophotometer(UV/VIS-1650 PC SHIMATZU). Final concentration was then determined from the calibration curve already prepared by plot of absorbance versus concentration at maximum wavelength of 498nm. Solution pH was adjusted by adding either 0.1N HCL or NaOH.
The concentration of dye solution was determined by a spectrophotometer operating in the visible range on absorbance mode. Absorbance values were recorded at the corresponding maximum absorbance wavelength and dye solution was initially calibrated for concentration in terms of absorbance units.

2.1.3. Batch adsorption studies

All the experiments were carried out at room temperature in batch mode to investigate the effect of different parameters such as adsorbent dose, contact time, pH, initial dye concentration, particle size of adsorbent, and adsorption isotherm study using a series of conical flask with capacity of 250ml filled with 100ml of CR solution.

All samples were agitated by a rotary shaker at constant agitation.

After shaking the flasks for predetermined time intervals, samples were filtered and analyzed.

The concentration of final sample is measured by spectrophotometric determination. The amount of CR dye adsorbed was calculated from the following equation (Ho et al., 1996):

\[ q_e = \frac{V}{W} (C_0 - C_e) \]  \hspace{1cm} (1)

Where \( q_e \) is the amount of dye adsorbed per unit weight of RHC (mg/g), \( C_0 \) the initial concentration of (CR) (mg/l), \( C_e \) the concentration of (CR) in solution at equilibrium time (mg/l), \( V \) the solution volume (l), \( W \) is the activated carbon dosage (g).

The adsorption behaviors of the samples were studied by evaluating the percentage removal efficiency of CR from the relation.

\[ \text{Removal efficiency} \% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \% \]  \hspace{1cm} (2)

Where \( C_e \) is the initial concentration of (CR), \( C_e \) is the solution concentration after adsorption at any time.

3. Adsorption isotherm models

**Langmuir and Freundlich model**

The analysis of isotherm data is useful for design purpose. In present study the equilibrium data were treated by Langmuir and Freundlich isotherms. The Langmuir isotherm can be represented by the following Equation (Langmuir, 1918).

\[ q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \]  \hspace{1cm} (3)

Where \( q_e \) is the amount adsorbed per unit mass of sorbent at equilibrium (mg/g), \( q_m \) is the maximum adsorption capacity (mg/g), \( C_e \) is the equilibrium dye concentration (mg/l) and \( K_a \) is the adsorption equilibrium constant. The plot of \( \frac{C_e}{q_e} \) versus \( C_e \) (Eq.4) is linear which show that the adsorption of dye onto rice husk carbon follows Langmuir isotherm model (Low and Lee, 1997).

\[ \frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \]  \hspace{1cm} (4)

The essential characteristics of Langmuir isotherm can be express by a dimensional constant called equilibrium parameter, \( R_L \) (Hall et al., 1966) that is defined by:

\[ R_L = \frac{1}{(1 + bC_0)} \]  \hspace{1cm} (5)

where, \( b \) is the Langmuir constant and \( C_0 \) is the initial concentration. The value of \( R_L \) indicates the shape of the isotherm to be either un favorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favorable (0 < \( R_L < 1 \)) or irreversible (\( R_L = 0 \)).

The Freundlich isotherm was also applied for the adsorption of dye by rice husk carbon (Freundlich, 1906).
\[
\log q_e = \left( \frac{1}{n} \right) \log C_e + \log k_f
\]

where, \(q_e\) is the amount adsorbed per unit mass of adsorbent at equilibrium (mg/g), \(C_e\) is the equilibrium dye concentration of the solution (mg/l). \(k_f\) and \(n\) are the Freundlich constants, \(n\) gives an indication of the favorability and \(k_f\) \([\text{mg/g(l/mg)}^{1/n}]\). The values of \(K_f\) and \(n\) can be obtained from the plot of \(\log q_e\) versus \(\log C_e\) and they equal to the intercept and slope of the plate respectively. The value of \(1/n\) is smaller than 1 points out the normal adsorption.

If \(n=1\), then the partition between the two phases are independent of the concentration. On the other hand, \(1/n\) being greater than 1 indicates cooperative adsorption (Mohan and Karthikeyan, 1997).

4. RESULTS AND DISCUSSION
4.1. Adsorption of dye
The adsorption of dye were investigated in the study using different parameters such as adsorbent dosage, contact time, PH, initial dye concentration and particles size of adsorbent.

4.1.1. Effect of adsorbent dosage
The effect of adsorbent dosage was investigated by changing the amount of adsorbent (1 - 3gm per 100ml) in the test solution while keeping other parameters are constant (initial concentration of 50 mg/l and 500µm particle size of adsorbent).

The percentage removal of dye was found (50 – 87.5)% Figure (2).

The increase in removal of dyes with adsorbent dose due to the introduction of more binding sites for adsorption. Similar results have been reported by the other investigators(Malik, 2003; Taha and Samaka, 2012; Taha and Samaka, 2013).

By this study, it was observed that the economical dose with good removal occur at the dose of 2 g / 100 ml for rice husk carbon (RHC) and that is 80 %.

![Figure 2](image2.png)

**Figure 2.** Effect of Adsorbent Dosage in the Removal of CR by (RHC) at Initial Concentration of 50 mg/l and 500µm Particle Size of Adsorbent

4.1.2. Effect of contact time
This experiment was done to determine the equilibrium time for the adsorption. To perform this experiment, different mixing time ranging from 20 to 160 minute. The adsorbent dose used was obtained from the best value received from previous experiment. Other factors were fixed as mentored later.

Figure (3) explains the effect of contact time. It is clear that the extent of adsorption is rapid in the initial stages (20 min.) and the adsorption of the dye increases with increasing contact time and becomes slow till
saturation is reached. The final concentration of CR did not significantly after 100 min. This shows that equilibrium time occur at 100 min. It is due to saturation of active sites which do not allow further adsorption to take place. Similar results for different ionic dyes were reported by (Hashemian et al., 2008; Gupta et al., 2006; Tebrez et al., 2009).

The curve is single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of CR dye on the surface of the adsorbent (Senthikumar et al., 2005; Banat et al., 2000; Taha and Samaka, 2012; Taha and Samaka, 2013).

![Figure 3](image1.png)

**Figure 3.** Effect of Contact Time for Adsorption of CR onto (RHC) at Initial Dye Concentration of 50 mg/l, Adsorbent Dose of 2g, and 500 µm Particle Size of Adsorbent

4.1.3. Effect of pH

The influence of pH on adsorption of CR dye was studied over the pH range (4-10). For this 50mg/l of CR solution containing 2gm/100ml adsorbent was used and 500 µm particle size of adsorbent. The results obtained are presented in Figure(4), which describes that there was no significant change in the percentage removal or dye uptake over the entire pH range of (4-10).

Other studies for different ionic dyes were also found to be independent of pH (Low et al., 1995; Hu et al., 2010).

This indicates there is such a strong interaction between the dye and ARH that nighters H⁺ nor OH-ions could influence the adsorption capacity. In other words, the adsorption of CR dye on RHC does not involve an ion – exchange mechanism.

But in pH 2 the removal was maximum for all adsorbent but in this case can not be used as favorite condition because it was observed the shift of the wavelength for the CR dye at this pH value.

![Figure 4](image2.png)

**Figure 4.** Adsorption of CR by Rice Husk Carbon as a Function of Solution pH at Initial Concentration of 50 mg/l and Adsorbent Dosage of 2 g with 500 µm Particle Size of Adsorbent
4.1.4. Effect of initial dye concentration

These studies were performed by changing the initial dye concentration in the range of (10–100 mg/l) with optimum conditions received from previous experiments with fixed other factors.

From Figure (5), it can be seen that the amount of dye Adsorbed(mg/g) increased with increased initial dye concentration, because important driving force can be obtained by increasing in dye concentration to overcome all mass transfer resistance of the dye between the aqueous and solid phases (Ho et al., 2005). A similar results were cited by (Lata et al., 2007). Hence a higher initial concentration of dye will enhance the adsorption process.

![Figure 5](image1)

**Figure 5.** Effect of Initial Concentration on Adsorption Capacity of CR onto (RHC) (500 µm Particle Size of Adsorbent and 2gm Adsorbent Dose)

4.1.5. Effect of particle size of adsorbent

The variation of the rate of adsorption of the substrate with different particle size of adsorbent is another method that is useful for the characterization of the rate – limiting mechanism of a particular system.

In present investigations different particle sizes of adsorbent(100, 300 , 400 ,500, 600 , 1000) mm were taken at the optimum conditions received from previous experiments.

The experimental data show that amount of CR adsorbed decreases with increase in particle size of the adsorbent. This indicate that the smaller the (RHC) particle size for a given mass of (RHC) , the more surface area is available and as a consequence the greater the number of binding sites available((Quek et al., 1998; Ponnusami et al., 2009). The results of this study are shown in Figure (6).

![Figure 6](image2)

**Figure 6.** Effect of Particle Size on Adsorption Capacity of CR onto (RHC) at Initial Dye Concentration of 50 mg/l and Adsorbent Dose of 2gm
4.2. Modeling of adsorption isotherm data

The adsorption isotherm were developed from the data collected. Equilibrium adsorption data were fitted to the linear form of Langmuir and Freundlich equation (Eq. 4,6). Table (2) shows that the adsorption of CR dye using rice husk carbon both satisfies of Langmuir and Freundlich isotherm.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir (95% Confidence level)</th>
<th>Freundlich (95% Confidence level)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_m ) (mg/g)</td>
<td>4.29</td>
<td>( K_l ) (mg/g)(l/mg)1/n 2.23</td>
</tr>
<tr>
<td>( K_a ) (l/mg)</td>
<td>1.167</td>
<td>1/n 0.205</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9671</td>
<td>( R^2 ) 0.9713</td>
</tr>
<tr>
<td>Standard error of estimate(S.E.)</td>
<td>0.200</td>
<td>Standard error 0.055</td>
</tr>
<tr>
<td>( R_L ) (0.0085-0.0793)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The plots of linearized form of Langmuir and Freundlich are shown in Figure(7a-b). The Langmuir equilibrium adsorption curves relating solid and liquid phase concentration of CR at equilibrium are given as:

\[ q_e = \frac{4.97 C_e}{1+1.167 C_e} \quad (7) \]

But, the Freundlich equilibrium adsorption curves relating solid and liquid phase concentration of CR at equilibrium are given as:

\[ q_e = 2.23 C_e^{0.205} \quad (8) \]

![Graph showing Langmuir and Freundlich isotherms](image-url)
Figure 7. Linearized Adsorption Isotherm Model of CR onto (a) Langmuir Model (b) Freundlich Model

The Langmuir isotherm model assumes monolayer coverage of adsorbate on a homogeneous adsorbent surface. The well fitting of data with Langmuir isotherm indicates to the homogenous distribution of active sites on the adsorbent surface (Bulut and Aydin, 2006).

The variation of separation factor ($R_L$) with initial CR concentration is shown in Figure (8). The ($R_L$) values for the adsorption of CR onto (RHC) are observed to be in the range of (0 – 1), indicating that the adsorption was favorable process (Bhatnagar, 2007; Hameed, Ahmad, and Aziz, 2007).

From Freundlich isotherm, the value of 1/n, the Freundlich parameter, which was between (0-1) also confirmed that the adsorption was favorable and beneficial as low cost adsorbent (Namasivayam and Yumuna, 1992) A value of 1/n below one indicates a normal Freundlich isotherm while 1/n above one indicative of cooperative adsorption (Hameed et al., 2007).

Figure (9) shows the deviation of these models from the experimental data. It appears that Langmuir and Freundlich models were strongly fitted with these data.

The activated rice husk, studied as adsorbent for removal CR, proved that it works well. The adsorption obeyed both Langmuir and Freundlich isotherms exhibiting heterogeneous surface conditions and monolayer adsorption (Lee et al., 1999).
5. CONCLUSIONS

The findings of the present work reveal that the rice husk which is easily and abundantly available agro waste in our country can be easily converted into good adsorbent by using simple methods of activation. A suitable amount (2 g/100 ml) of the activated rice husk adsorbent could decolourize as much as 92% of the dye from an aqueous solution demonstrated sufficient potential of RHC as an adsorbent for the removal of the dye Congo red, from dye wastewater. The adsorption of the dye was maximum around the natural pH of the aqueous solution of Congo red. This shows that adsorption of the dye could be carried out on RHC without adjusting the pH of the medium. The adsorption obeyed both Langmuir and Freundlich isotherm models and their parameters confirmed that the adsorption of Congo red on activated rice husk was favorable.

6. REFERENCES


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