Sorption of acid red 138 from aqueous solutions onto rice bran

S. Hashemian1*, S. Dadfarnia2, M. R. Nateghi1 and F. Gafoori1

1Islamic Azad University, Yazd branch, Department of chemistry, Iran.
2Yazd University, Department of chemistry, Iran.

Accepted 23 January, 2008

The capability of rice bran for removal of Nylomine Red (Acid Red 138) an anionic monoazo direct dye, from aqueous solutions was studied. The effect of various experimental parameters such as treatment of the bran, particle size, contact time, stirring speed, temperature and pH of solutions were studied, and the optimal conditions were selected. The dye sorption onto rice bran increased in the presence of inorganic salt. It was found that the rice bran with a mesh of 20 and activated with saturated sodium chloride have higher adsorption capacity. The optimum reaction time, at a speed of 30 rpm, is 60 min. At initial pH of 2 and at room temperature, AR 138 was removed more effectively. The isothermal data for biosorption followed the Langmuir and Freundlich models.

Key words: Acid dye, rice bran, adsorption.

INTRODUCTION

In textile industries large amounts of water and chemicals are used for dyeing process. The wastewaters of this process usually consist of a number of contaminants including acids, bases, dissolved solids, toxic compounds and organic dyes. The dye compounds not only esthetically are displeasing, but also impede light penetration in the pans, thus upsetting the biological treatment process within the treatment plant. In addition, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities.

Water soluble dyes such as acid dyes and reactive dyes are not easily removed in conventional physico-chemical coagulation methods, and are not biodegradable (Mohan et al., 1999). A number of materials such as natural clay and activated carbon have been used as sorbent for dye removal (Acemioglu, 2004). Activated carbon is the most popular and widely used adsorbent but it is expensive and its cost increase with the quality. In addition its regeneration with refractory technique results in a 10 – 15% loss of the sorbent and its uptake capacity. Therefore, there is a growing interest in finding low-cost, easily available materials for the dye removal for industrial waste (Gong et al., 2007; Namasiyayam et al., 1998; Namasiyayam et al., 1996; Montanher et al., 2005; Hashemian, 2007).

Many investigations have been done on the feasibility of low cost material, as the sorbent for removal of various dye from wastewater including; waste coir pith (Namasiyayam and Kavitha, 2002), modified clays (Bouberka et al., 2005), oxihumolite (Janos et al., 2005), fly ash (Wang et al., 2005), Na-bentonite (Ozcan et al., 2004), kaolinite (Heidmann and Christl, 2005), giant duck weed (Waranusantigul et al., 2003), eolith (Amagan et al., 2004), chitosan (Juang and Tseng, 1997), and powdered peanut hull (Gong et al., 2005). Among these materials, some biosorbents showed extraordinary properties for dye removal.

Bran is a byproduct from the milling of corn, consisting of the large kernel. It is used mainly as fertilizer or fuel (Farajzadeh and Vardast, 2003). Rice bran contains different vitamins, carbohydrates, potassium, nitrogen and phosphorus compounds. These compounds are environmentally friendly and are nutritious to the plants. Therefore the use of bran to eliminate pollution from water and wastewater is interesting.

The purpose of this work was to investigate the capability of rice bran as a biosorbent for removal of anionic dyes from aqueous solution and a rapid inexpensive sys-
Figure 1. Chemical structure of acid red 138.

tem for removal of dyes from textile industry has been developed.

MATERIALS AND METHODS

Preparation of rice bran

All chemicals and reagents used in this work were of analytical grade purity. The rice bran was from Mazandran farm, the north of Iran and was extensively washed with water to remove soil and dust, and was air dried. The rice bran was dried in an oven at 65°C for a period of 3 h. Finally, it was ground and sieved (meshes 2-35). The chemical modification of rice bran was made according to the similar method previously described by Vaughan et al. (2001). Natural rice bran was mixed with 1 M of chemical component (NaOH, HCl, H₂SO₄, HNO₃, H₃PO₄, HClO₄, and NaCl) at the ratio of 1:10 (bran/comp, w/v) and stirred for 24 h. After stirring, the modified rice bran was washed with distilled water to remove residual acids and alkali, and then the wet modified rice bran was dried at 50°C until constant weight and preserved in a desiccator as sorbent for further use.

Preparation of dye solutions

Nylomine red (C-2B) or Acid Red 138 (AR 138- Na₂C₃O₃H₃₈N₃O₈S₂) is an anionic monoazo direct dye that contains OH and SO₃ function groups and has a color index of 18073. AR138 was obtained from Aldrich chemical. AR 138 has a molecular weight of 632.5 g. The structure of AR 138 is shown in Figure 1.

AR138 (Disodium 5-Acetyl Amino3-(4Dodcylephenyle Az0) 4-hydroxynaphthalene 2, 7 disulphide) was used without further purification. The dye stock solutions were prepared by dissolving accurately 1 g of dyes in distilled water and diluting to one liter in volumetric flask. The working solutions were daily prepared by proper dilution.

Instrumentation

Powder XRD was obtained with a SEISERT (Ger) 3003 PPS (Zicert Co) with Ni-filtered Cu- Kα radiation. Dye absorbance was measured at 515 nm with spectrophotometer (Shimadzo, model 16 A Japan). pH measurement was done with a Horiba pH meter (M13, Japan).

The percent of sorbed dye was calculated from the following equation

% Sorbed dye = [(A₀ – A)/A] × 100

Where A₀ is the absorbance of sample before addition of the sorbent and A is the absorbance of sample after treatment with rice bran.

RESULTS AND DISCUSSION

Table 1. Rice bran characterization.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>17</td>
</tr>
<tr>
<td>Fiber</td>
<td>14.32</td>
</tr>
<tr>
<td>Total proton binding ligands (µmol/g)</td>
<td>10</td>
</tr>
<tr>
<td>Humidity</td>
<td>10.42</td>
</tr>
<tr>
<td>Ash</td>
<td>12.18</td>
</tr>
<tr>
<td>Protein</td>
<td>14.70</td>
</tr>
<tr>
<td>SiO₂</td>
<td>6.15</td>
</tr>
<tr>
<td>Iron</td>
<td>4</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2</td>
</tr>
<tr>
<td>Calcium</td>
<td>5</td>
</tr>
<tr>
<td>Copper</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Treatment of the bran

The characterization of rice bran from XRD is shown in Table 1. A high fiber and starch content was found. This is a very interesting characteristic for removing of dyes. In order to investigate the effect of chemical modification on the AR 138 dye sorption of rice bran, the removal capacities modified rice bran sorbing of AR 138 dye from aqueous solution were compared. The results obtained are shown in Table 2, and shows that the treatment of bran with NaCl are very interesting and can remove close to 90 percent of AR 138 dye from aqueous solutions. Therefore for further study, the bran activated with sodium chloride was used. It looks the rice bran surface has functional groups such as hydroxyl, amine, phosphate and silicate to able bind with NaCl, and then remove the AR 138 from aqueous solutions. The attraction of ions causes the dye removal from water.

Studying the effect of NaCl concentration on treatment of bran

The bran was mixed with different concentration of NaCl solution (0.05 M to saturate) for 1 h. It was then washed with distilled water and was used for dye removal from the aqueous solutions. The results are given in Table 3, and as can be seen, the capability of the resultant sorbent increase with an increase in concentration of NaCl up to 5 M, at then levels off. The results also showed that at higher than 1 M of NaCl concentration, the increasing percent of dye removal is negligible, and activation of rice bran was done to 1 M. Therefore in further study the rice bran was activated with 1 M NaCl solution.
Table 2. Effect of chemical modification on the AR 138 dye sorption of rice bran (1 M of each compound, 60 min contact time and room temperature).

<table>
<thead>
<tr>
<th>Component</th>
<th>NaCl</th>
<th>NaOH</th>
<th>H₃PO₄</th>
<th>HClO₄</th>
<th>HNO₃</th>
<th>H₂SO₄</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye removal (%)</td>
<td>91</td>
<td>80</td>
<td>70</td>
<td>68</td>
<td>73</td>
<td>75</td>
<td>82</td>
</tr>
</tbody>
</table>

Table 3. Effect of concentration of NaCl on activation of rice bran conditions.

<table>
<thead>
<tr>
<th>Concentration of NaCl (mol/l)</th>
<th>Saturated</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0.5</th>
<th>0.2</th>
<th>0.1</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye removal (%)</td>
<td>91.8</td>
<td>91.8</td>
<td>91.7</td>
<td>91.5</td>
<td>91.2</td>
<td>91</td>
<td>82</td>
<td>79</td>
<td>75</td>
<td>70</td>
</tr>
</tbody>
</table>

**Effect of particle size of rice bran**

In order to investigate the effect of the size of bran on its capability for dye removal, the bran was ground and sieved with meshes varying between 2 to 35. The results of this investigation are shown in Figure 2. Although the smaller particles had better capability, but some problem in milling, gradation and filtration of the bran, a particle mesh 20 was used through this study.

**Effect of contact time**

To evaluate the effect of contact time between the dye and bran, the stirring time at constant rpm (130) was varied between 0 and 120 min. The results are shown in Figure 3. As it is shown, the sorption is very fast and equilibrium between the aqueous solution and bran is established in less than 60 min. In further studies the stirring time of 60 min was selected to guarantee the equilibration state.

**Effect of stirring speed**

The effect of stirring speed was studied by varying the stirring speed between 50 to 300 rpm at constant concentration and stirring time 60 min. For an rpm of the 130, the sorption of the dye on bran reaches it maximum. It is due the attractive force between dye and adsorption site increased to 130 rpm, but in higher rpm, the dye molecules do not have enough time for contact with sorbent active sites.

**Effect of pH**

The effect of sample pH on the sorption process was investigated. Experiments were performed using various initial pH in the range of 2 to 12. The results are given in Figure 4. As demonstrated, the sorption is highly depended on solution pH, which can be due to the surface charge of the sorbent. In acidic media (low pH) the active site on the sorbent is positively charged and can sorb the reagent dye AR138, as the result of electrostatic attrac-
Figure 4. Effect of pH of solutions on the sorption of AR 138 by rice bran.

The well-known expression of the Langmuir model is:
\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}}K_l + \frac{C_e}{q_{\text{max}}}
\]

Where \( q_e \) is the equilibrium dye concentration on adsorbent (mg g\(^{-1}\)), \( C_e \) is the equilibrium dye concentration in solution (mg dm\(^{-3}\)), \( q_{\text{max}} \) is the monolayer capacity of the adsorbent (mg g\(^{-1}\)) and \( K_l \) is the Langmuir adsorption constant (dm\(^3\) mg\(^{-1}\)).

The Freundlich equation is:
\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

Where \( q_e \) is the equilibrium dye concentration on adsorbent (mg g\(^{-1}\)), \( C_e \) is the equilibrium dye concentration in solution (mg dm\(^{-3}\)), \( K_F \) (dm\(^3\) g\(^{-1}\)) and \( n \) are the Freundlich constants characteristic of the system, respectively. A plot of \( C_e / q_e \) versus \( C_e \) gives a straight line of slop \( 1 / q_{\text{max}} \) and intercept, \( 1 / q_{\text{max}}K_l \).

Table 4 gives the \( q_{\text{max}} \) and \( K_F \) value in Langmuir equation, the \( K_F \) and 1/n values in Freundlich equation and the correlation coefficients of two equations. From the results in Table 4, it could be concluded that the sorption isotherm of AR138 dye followed the Langmuir and Freundlich models. The \( r^2 \) values were found to be in the range of 0.958 to 0.98 for Langmuir isotherm and higher \( r^2 \) values from 0.9907 to 0.9977 for Freundlich model. The best fit of equilibrium data in Freundlich model expression confirms the monolayer coverage of AR138 onto rice bran particles (Vadivelan and Kumar, 2005).

Sorption of AR138 onto rice bran (Figure 6) was employed to generate the intercept value of \( K_F \) and the slop of 1/n. The correlation coefficients show almost per-
fect agreement between the experimental data and the Freundlich model, which indicate the heterogeneity of the adsorption sites on the bran particles. The results also indicated that higher values of 1/n were obtained at higher temperatures. These trends show higher adsorption of AR138 at lower temperatures for rice bran results.

### Conclusion

The present study showed that the rice bran can be used as an adsorbent for the removal of AR138 from aqueous solutions. Rice bran was easily available in large quantity and the treatment method of biosorbent seemed to be economical. The amount of dye sorbed was found to vary with initial solution pH, adsorbent dose, particle size of rice bran, contact time and treatment of the bran. The isothermal data of biosorption followed both Freundlich and Langmuir models and monolayer sorption capacity of AR138 onto rice bran.

### References


Mater. 2-3: 207-211.


