African Journal of Biotechnology Vol. 7 (5), pp. 600-605, 4 March, 2008
Available online at http://www.academicjournals.org/AJB
DOI: 10.5897/AJB07.765
ISSN 1684–5315 © 2008 Academic Journals

Full Length Research Paper

Sorption of acid red 138 from aqueous solutions onto rice bran

S. Hashemian[1]*, S. Dadfarnia[2], M. R. Nateghi[1] and F. Gafoori[1]

[1]Islamic Azad University, Yazd branch, Department of chemistry, Iran.
[2]Yazd 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 biodegradeble (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; Namasivayam et al., 1998; Namasivayam 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 (Namasivayam 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-

*Corresponding author. E-mail: sa_hashemian@yahoo.com

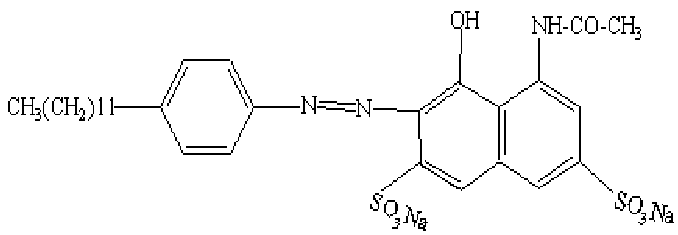

Figure 1. Chemical structure of acid red 138.

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, H_2SO_4, HNO_3, H_3PO_4, $HClO_4$, 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- $Na_2C_{30}H_{38}N_3O_8S_2$) is an anionic monoazo direct dye that contains OH and SO_3 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 Azo) 4-hydroxynaphtalene 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- K_a 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

$$\% \text{ Sorbed dye} = [(A_0 - A)/A] \times 100$$

Where A_0 is the absorbance of sample before addition of the sorbent and A is the absorbance of sample after treatment with rice bran.

Table 1. Rice bran characterization.

Component	Weight (%)
Starch	17
Fiber	14.32
Total proton binding ligands (µmol/g)	10
Humidity	10.42
Ash	12.18
Protein	14.70
SiO_2	6.15
Iron	4
Magnesium	2
Calcium	5
Copper	4.1

RESULTS AND DISCUSSION

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 attracttion 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).

Component	NaCl	NaOH	H_3PO_4	$HClO_4$	HNO_3	H_2SO_4	HCl
Dye removal (%)	91	80	70	68	73	75	82

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

Concentration of NaCl (mol/l)	Saturated	5	4	3	2	1	0.5	0.2	0. 1	0.05
Dye removal (%)	91.8	91.8	91.7	91.5	91.2	91	82	79	75	70

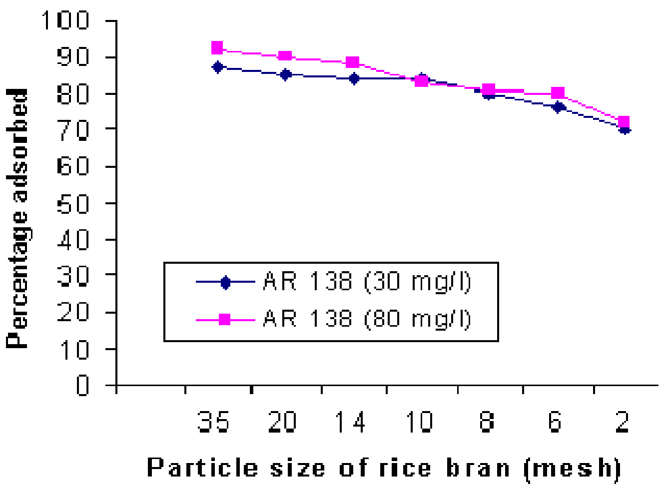

Figure 2. Effect of particle size of rice bran on the sorption of AR 138.

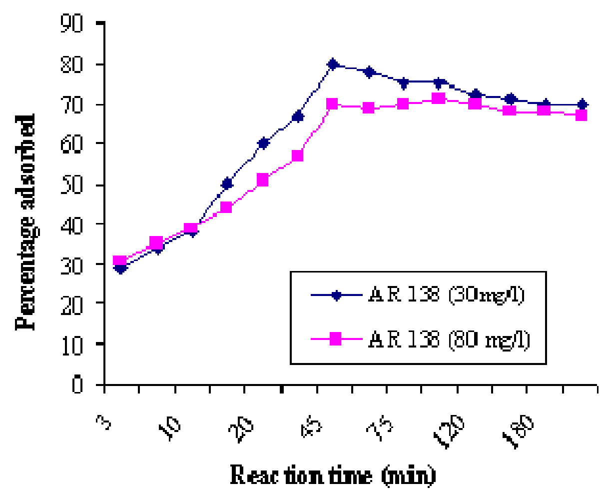

Figure 3. Effect of reaction time on the adsorption of AR 138 onto rice bran.

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 and120 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-

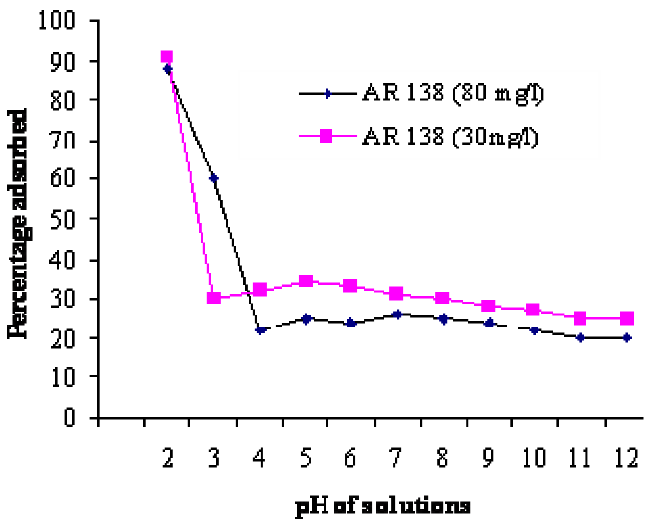

Figure 4. Effect of pH of solutions on the sorption of AR 138 by rice bran.

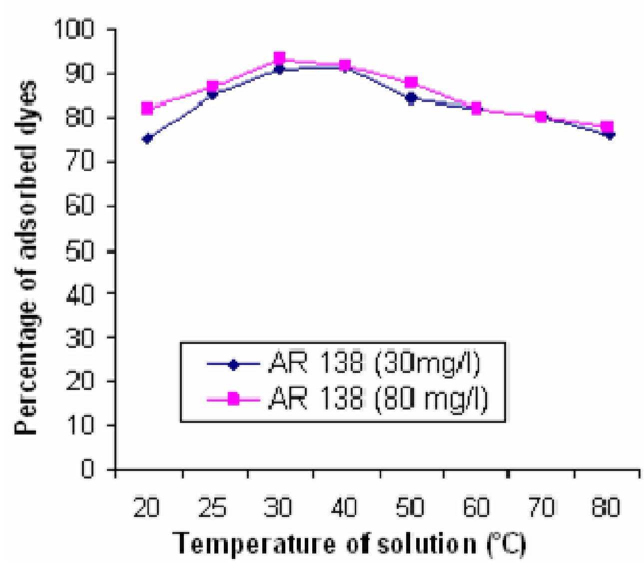

Figure 5. Effect of temperature on sorption of AR 138 (pH 2, particle size 20 mesh and 60 min contact time).

tion between negatively charged dye anions and positively charged adsorption sites and an increasing in dye adsorption. Maximum removal of AR 138 with rice bran was at acidic pH of 2. In basic media the surfaces are probably negatively charged. It may be due to the abundance of $^{-}$OH ions on sorbent which cause repulsion between the negatively charged surface and the anionic dye molecules, and also there are no exchangeable anions on the outer surface of the adsorbent at higher pH values and consequently the adsorption decreases (Ozacar and Sengil, 2003). It is notable that the AR138 is stable in acidic media and with lowering the pH no shift in λ_{max} was observed.

Effect of temperature

The effect of temperature on the amount of dye sorbed onto rice bran (Figure 5) was studied by varying temperature between 20 to 80°C while keeping the amount dye constant (80 mg l^{-}). As can be seen from the Figure 5, when the temperature was increased up to 3°C, the percent of sorption of dye was increased, but a further increase in temperature causes a decrease in % dye sorption. It is due to desorption of AR 138 from sorbent to the solution on high temperature. Nevertheless as the uptake of AR138 by rice bran was fast and quantities at room temperature, further experiment was done at ambient temperature.

Adsorption isotherm studies

Acid Red 138 (AR138) adsorption isotherm at different initial dye concentration was investigated and the data were fitted into the models of Langmuir and Freundlich.

The well- known expression of the Langmuir model is:

$$C_e / q_e = 1/ q_{max}K_l + C_e/ q_{max}$$

Where q_e is the equilibrium dye concentration on adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in solution (mg dcm^{-3}), q_{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:

$$\ln q_e = \ln K_F + 1/n \ln C_e$$

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}), and K_F (dm^3 g^{-1}) and n are the Freundlich constants characteristic of the system, respectively. A plot of Ce /q_e verses Ce gives a straight line of slop 1/ q_{max} and intercept, 1/ $q_{max}K_l$.

Table 4 gives the q_{max} and K_l 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-

Table 4. Langmuir and Freundlich isotherm constants for adsorption of AR138.

T (^{0}C)	Freundlich			Langmuir		
	1/n	K_F	r^2	q_{max}	K_l	r^2
20	0.228	0.516	0.997	0.43	-1	0.98
25	0.240	0.2513	0.990	0.47	0.387	0.966
30	0.256	0.188	0.995	0.58	0.277	0.96
40	0.263	0.189	0.993	0.611	0.413	0.958
50	0.274	0.068	0.996	0.854	-12.03	0.963

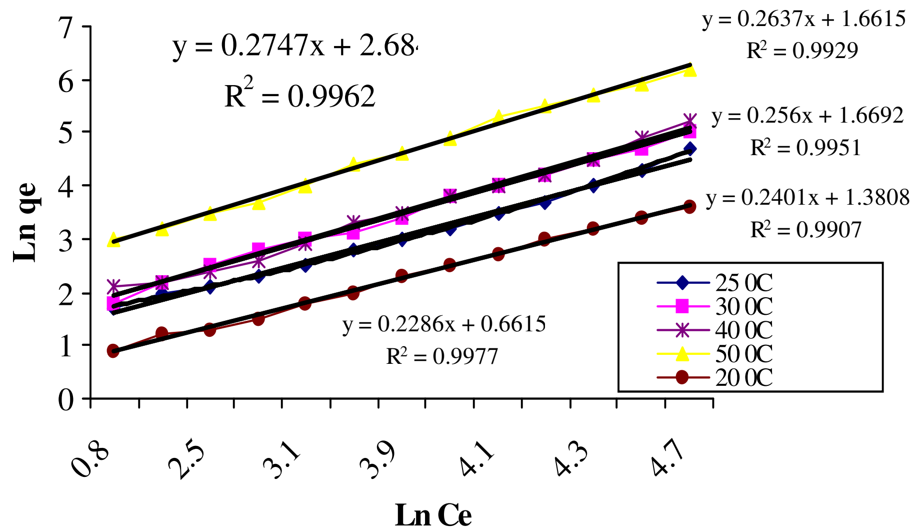

Figure 6. Freundlich plots for the adsorption of AR138 onto rice bran at various temperatures.

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

Acemioglu BI (2004). Adsorption of Congo red from aqueous solution onto calcium-rich fly ash. J. Colloid Interf. Sci. 274:371-379.

Amagan B, Turan M, Celike M (2004). Equilibrium studies on the adsorption of reactive azo dyes into zeolite, Desalination. 170: 33-39.

Bouberka Z, Kacha S, Kameche M, Elmaleh S, Derriche Z (2005). Sorption study of an acid dye from aqueous solutions using modified clays. J. Hazard. Mater. B. 119:117-124.

Farajzadeh MA, Vardast MR (2003). Rice Bran as an Excellent sorbent for Heavy Metals from aqueous Media 1. Optimization of conditions. J. Chin. Chem. Soc. 50: 245-250.

Gong R, Jin Y, Chen J, Hu Y, Sun J (2007). Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw. Dye Pigment 73(3): 332-337.

Gong R, Ding Y, Li M, Yang C (2005). Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution, Dyes Pigments, 64: 187-192.

Hashemian S (2007). Study of adsorption of acid dye from aqueous solutions using bentonite, Main Group Chem., 6(2): 97-107.

Heidmann I, Christl I (2005). Competitive sorption of protons and metal cations onto kaolinite: experiments and modeling, J. Colloid Interf. Sci. 282: 270-282.

Janos P, Sedivy P, Ryznarova M (2005). Sorption of basic and acid dyes from aqueous solutions onto oxihumolite, Chemosphere; 119: 881-886.

Juang R, Tseng R (1997). Adsorption behavior of reactive dyes from aqueous solutions on chitosan, J. Chem. Tech. Biotechnol. 70:391-399.

Mohan VS, Srimurali SP, Karthikeyan M (1999). Color removal of monoazo acid dye from aqueous solution by adsorption and chemical coagulation, J. Environ. Eng. Policy, 1: 149-154.
Montanher SF, Oliveira EA, Rollemberg MC (2005). Removal of metal ions from aqueous solutions by sorption onto rice bran, J. Hazard.

Mater. 2-3: 207-211.
Namasivayam C, Kavitha D (2002). Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, J. Dyes Pigments, 54: 47-58.
Namasivayam C, Muniasamy N, Gayatri K, Rani K, Ranganathan K (1996). Removal of dyes from aqueous solutions by cellulosic waste orange peel, Bioresour. Technol. 57: 37-43.
Namasivayam C, Prabha D, Kumutha M (1998). Removal of direct red and acid brilliant blue by adsorption on to banana pith, Bioresour. Technol 64: 77-79.
Ozacar M, Sengil IA (2003). Adsorption of reactive dyes on calcined alunite from aqueous solutions J. Hazard. Mater. 98(1): 211-224.
Ozcan SA, Erdem B, Ozcan A (2004). Adsorption of acid blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite, J. Colloid Interf. Sci. 280: 44-54
Vadivelan V, Vasanth Kumar K (2005). Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. J. Colloid Interf. Sci. 286: 90-100.
Vaughan T, Seo CW, Marshall WE (2001). Removal of selected metal ions from aqueous solution using modified corncobs, Bioresour. Technol; 78: 133-139.
Wang S, Boyjoo Y, Choueib A, Zhu ZH (2005). Removal of dyes from aqueous solution using fly ash and red mud, Water Res. 39: 129-138.
Waranusantigul P, Pokethitiyook P, Kruatrachue M, Upatham ES (2003). Kinetics of basic dye biosorption bygiant duckweed, J. Environ. Pollut. 125: 385-392.