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Sorption study of C.I. Acid Red 88 from aqueous solutions onto sawdust

N. Modirshahla[1], M. A. Behnajady[1], A. Shamel[2,*], H. Eskandari[2]

[1] Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran
[2] Department of Chemistry, Ardebil Branch, Islamic Azad University, Ardebil, Iran

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ABSTRACT

The present study deals with the decolorization of C.I. Acid Red 88 (AR88) as a model contaminant from textile industry using sawdust as an adsorbent. The effects of initial AR88 concentration, adsorbent dosage, pH, contact time and stirring rate were studied in a batch mode. The variation of pH from 3 to 10 showed no considerable change in decolorization rate. The desired conditions for decolorization of 84.46% were obtained to be 20 min of contact time, stirring rate of 400 rpm with 30 g L^{-1} of adsorbent. Freundlich, Redlich-Peterson and Langmuir adsorption models were used for the mathematical description of the equilibrium data and the equilibrium process confirmed well with all the models attaining correlation coefficients 0.970, 0.969 and 0.958, respectively. The results also revealed that the adsorption kinetics obeys pseudo-second order and it was concluded that intra-particle diffusion model is not the rate determining step.

Keywords: Adsorption sawdust; Isotherm; C.I. Acid Red 88; Decolorization

INTRODUCTION

Synthetic dyes are the important pollutants of the environment. Azo dyes, one of the major class of synthetic dyes used in textile industries are characterized by presence of one or more azo bonds (-N=N-) in association with one or more aromatic systems. They are known to be toxic and carcinogenic. They are mostly non-biodegradable and resistant to treatment by many conventional methods [1].

Recently sorption processes have proved to be an effective method for the removal of pollutants from wastewaters. Some adsorbents such as activated carbon [2], kaolin [3], perlite [4] have been utilized to eliminate the dye, and inexpensive and readily available adsorbents are attracting considerable interest.

In the present study, the experiments were carried out to decolorize Acid Red 88 (AR88) by adsorption technique using sawdust as an adsorbent. Some operational parameters were studied and equilibrium data were tested with Langmuir, Freundlich and Redlich-Peterson isotherms.

EXPERIMENTAL

Materials and methods

Acid Red 88 (AR88) (C. I. 15620, FW: 400.39, λ_{max}: 506 nm supplied by Across organics, USA) was used as an adsorbate and its structure is shown in Fig. 1. The pH of the solution was adjusted to desired value using 0.1 N HCl and 0.1 N NaOH.

Sawdust from aspen tree was washed with distilled water and dried in the oven at 80 °C and bottled for experimental purposes. The experiments were performed on AR88 solutions with concentration of 50 mg L^{-1}. At the beginning of each run 50 mL, solution of desired concentration of the dye was fed into a 150 mL pyrex glass reactor and then 0.1 g of adsorbent was introduced and stirred for certain times at known speeds, then filtered for spectrophotometric analysis.

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[*] Corresponding author: ali0029@gmail.com

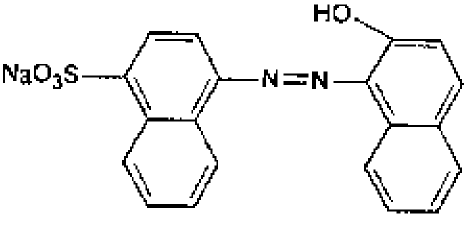

Fig. 1. Structure of AR88.

Chemical analysis

The dye concentration was determined by spectrophotometry at λ_{max}= 506 nm according to Beer-Lambert's law, using a Ultrospec 2000, Biotech Phrmacia UV/Vis spectrophotometer. The equation used to calculate the decolorization efficiency in the experiments was:

$$CR\% = \frac{(C_0 - C)}{C_0} \times 100 \qquad (1)$$

where C_0 and C were the initial and present concentrations of the dye in the solution (mg L^{-1}), respectively.

In order to study the adsorption isotherm 0.1 g of sawdust was kept in contact with 50 mL of dye solution at different concentrations at pH= 6.77 for 48 hours to ensure that equilibrium has been reached. The percentage of removal of dye and equilibrium adsorption uptake, q_e (mg/g) was calculated using the following relationship [5]:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (2)$$

where q_e is the amount adsorbed (mg of adsorbate/ g of adsorbent). C_o is the initial sorbate concentration (mg L^{-1}), C_e is the equilibrium sorbate concentration (mg L^{-1}), V is the volume of the solution (L) and W is the mass of the adsorbent (g). Equilibrium data were examined using polymath program to compare theoretical and experimental values.

RESULTS AND DISCUSSION

Adsorption studies

Effect of contact time

In order to find out the optimum contact time 1.5 g of adsorbent was added to 50 mL of the dye with concentration of 50 mg L^{-1}. The mixture was stirred at different times and left for 24 h. Fig. 2 shows the adsorption percent at different times which indicates that increasing the contact time up to 20 min, will increase the adsorption process but after that it gradually decreases due to desorption phenomena.

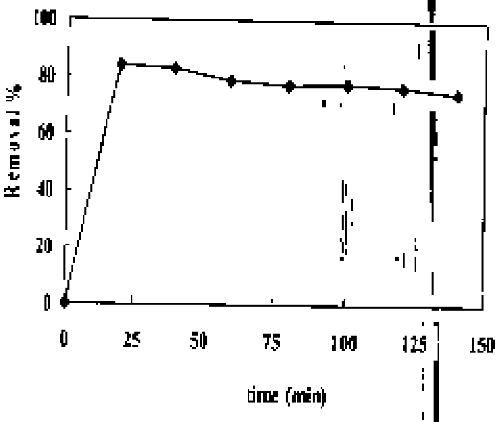

Fig. 2. Effect of contact time on the removal

Effect of pH

It is obvious that pH of the dye solution controls the adsorption process particularly the adsorption capacity since it will be able to change the surface charge of the adsorbent. The adsorption of AR88 by sawdust was studied over pH range of 3 to 10 at 25 °C. Initial dye concentration was 50 mg L^{-1} and the adsorbent dose was kept at 1.5 g/50 mL of the dye solution. Fig. 3 shows the effect of pH on the adsorptive removal of AR88 by sawdust. It can be seen as pH increases from 3 to 10, the removal percent decreases from 85% to 75%. It seems that in aqueous solution, the acid dye is first dissolved and the sulphonate groups of the dye (D-SO_3Na) are dissociated and converted to anionic dye ions [5].

$$D - So_3Na \xrightarrow{H_2O} D - SO_3^- + Na^+ \qquad (3)$$

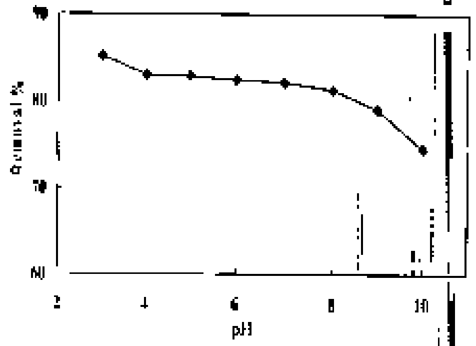

Fig. 3. Effect of pH on the removal.

Since in alkaline solution hydroxyl ions exist therefore inter ionic repulsion between similarly charged particles would retard the adsorption process. This is also in agreement with the findings in the literature [2].

Effect of adsorbent concentration

The effect of sawdust dosage on the removal of AR88 is shown in Fig. 4. The removal percent enhanced with sawdust dosage up to a certain limit and it almost remained constant. This can be explained because of the availability of more surface area for adsorption.

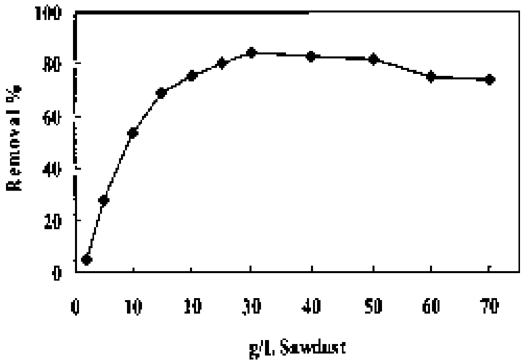

Fig. 4. Effect of sawduct dosage on the removal.

Effect of stirring rate

Agitation is an important parameter in the adsorption process since the distribution of dye in the solution is influenced and the formation of external boundary film could be seriously affected. Fig 5 shows the removal percent of AR88 by sawdust at different stirring speed (100 to 1000 rpm) within contact time of 20 min and rest time of 24 h. The results reveal that the removal increases up to 100 rpm but remains almost constant after that. It may be due to the kinetics of adsorption which follows surface diffusion at low speeds which is quite fast but at higher speeds the inter particle diffusion mechanism may occur which is slow process

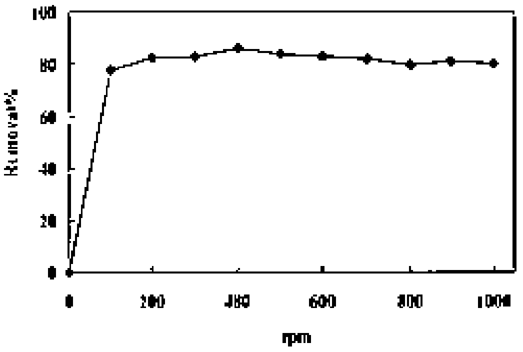

Fig. 5. Effect of stirring rate on the removal.

Adsorption isotherms

Adsorption properties and equilibrium characteristics generally called adsorption isotherms, describe the interaction between adsorbate and adsorbent. These isotherms provide information about the optimum amount of adsorbents, and also they can determine the adsorption capacity of the adsorbent.

The results revealed that using 0.1 g of adsorbent in 50 mL of AR88 with concentration of 50 mg L^{-1} after 48 h shows that the concentration of dye in the solution remains almost unchanged which indicates the constant rate of adsorption and desorption.

The experimental data were tested with well-known Langmuir, Freundlich and Redlich-Peterson isotherm models at a temperature of 21 $^{\circ}C$ and at pH= 6.77.

The basic assumption of Langmuir isotherm is the formation of monolayer of adsorbate on the surface of adsorbent and no further adsorption occurs [6] and Freundlich model indicates the extent of heterogen layer on the surface of adsorbent and Redlich-Peterson equation can be applied either in homogenous or heterogeneous systems due to involved parameters [7]. The equation of Langmuir isotherm [5] is represented as below.

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{4}$$

and Freundlich model [5]:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

and Redlich-Peterson [7]:

$$q_e = \frac{A C_e}{1 + B C_e^{x}} \tag{6}$$

All three models were tested with obtained data and shown in Figs 6, 7 and 8. The correlation coefficients (R^2) for Langmuir, Freundlich, and R-P models were 0.958, 0.970, and 0.969 respectively which indicates that the adsorption process could be explained by all models. But careful observation may describe Freundlich better than others. This means that heterogeneous occupation of the surface may be predominated and also physisorption occurs rather than chemisorption [3].

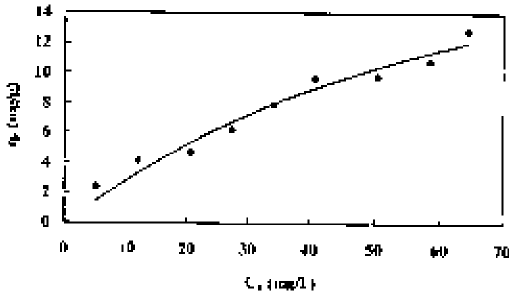

Fig. 6. Langmuir adsorption isotherm for AR88 on sawdust.

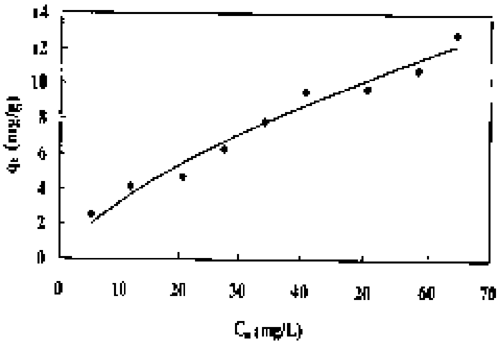

Fig. 7. Freundlich adsorption isotherm for AR88 on sawdust.

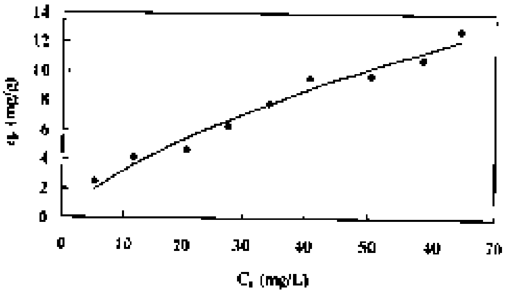

Fig. 8. Redlich-Peterson adsorption isotherm for AR88 on sawdust.

Adsorption kinetics

In the present study three following kinetic equations were examined for the experimented data in order to evaluate the kinetic mechanism which governs the adsorption process.

Pseudo-first order kinetic model

The pseudo-first order equation can be shown in a non-linear form as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad (7)$$

Where q_t and q_e are the amount of adsorbed dye (mg/g) at contact time t and at equilibrium, and k_1 is the pseudo-first order rate constant (time^{-1}) and in linear form as (lagergen, 1898):

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (8)$$

The plot of $\ln(q_e - q_t)$ versus t did not show a straight line except for first few hours. This behavior indicates that the rate of uptake is quite high at the early stages of process and follows pseudo-first order but it does not obey as the process progresses . The findings show that experimental value of q_e was 7.9 mg/g which was not in agreement with calculated value of 3.83 mg/g. also correlation coefficient (R^2) reveals that the above model cannot be considered as a suitable mechanism for the process.

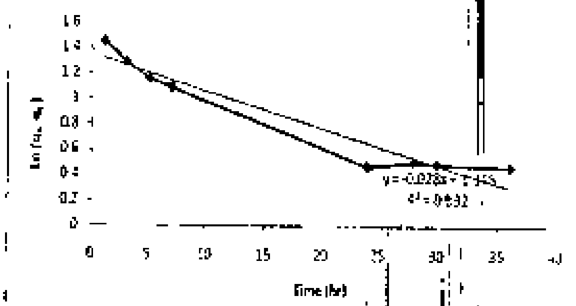

Fig.9. Pseudo-first-order kinetic.

Pseudo-second order kinetic model

The pseudo-second order kinetic model is represented by the following equation [9].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

where k_2 is the rate constant of pseudo-second order adsorption (g/mg min). As shown in Fig. 10.

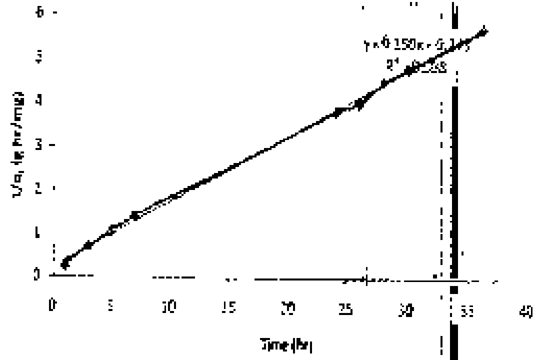

Fig.10. Pseudo-second-order kinetic.

plotting $\frac{t}{q_t}$ against t gives a straight line and a high value of correlation coefficient Indicates that the adsorption process is a pseudo-second order. ($r^2 = 0.9982$).

Intraparticle diffusion model.

The observed data was also analysed by the intraparticle diffusion model. This model is expressed by the equation given below:

$$q_t = k_{id}t^{1/2} + c \qquad (10)$$

where k_{id} is the intraparticle diffusion rate constant (mol g^{-1} $min^{-1/2}$). According to equation (10) a plot of q_t versus $t^{1/2}$ should be a straight line with a slope of k_{id} if process mechanism obeys the intraparticle diffusion model.

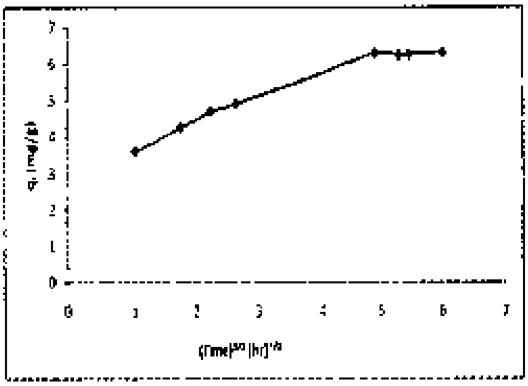

Fig.11. Intraparticle diffusion model.

Fig. 11 slows an initial curved portion followed by a linear portion ending with a plateau.The initial portion is attributed to the adsorption on the external surface of the adsorbent and then the involvement of diffusion into the interior body which appears in the later portion of the plot. since none of the portions of plot passes through the origin it can be concluded that the adsorption is a multi-step process and intraparticle diffusion should not be considered the sole rate limiting step [9], and some degree of boundary layer control could be taken into account [8].

CONCLUSION

The results show that sawdust as a low cost adsorbent could be considered a suitable substitution for expensive ones. The isotherm studies indicate that the adsorption obeys Freundlich model more precisely than Redlich-Peterson and Langmuir isotherm models, therefore heterogeneous layer may be considered to be predominant. The findings also reveal that the adsorption mechanism follows pseudo-second order and the adsorption is multi-step process where intra-particle diffusion model cannot be considered a sole rate determining step.

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