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KINETIC AND ISOTHERM MODELING OF ADSORPTION OF DYES ONTO RICE HUSK CARBON

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ABSTRACT
Rice husk carbon (RHC) has the ability to adsorb the dyestuff from aqueous solution. It may be useful low cost adsorbent for the treatment of effluents, discharged from textile industries. The effectiveness of RHC have been tested for the removal of colour from the wastewater samples containing three dyes namely crystal violet, direct orange and magenta. Effect of various parameters such as agitation time, pH, temperature, adsorbent dose and concentration have been investigated in the present study. The adsorption of dyes have been best described by pseudo first order mechanism and Freundlich adsorption isotherms. The rate constant of adsorption (K_{ad}) have been determined, which are found to be 6.8 x 10^{-3}, 8 x 10^{-3} and 10 x 10^{-3} min^{-1} for crystal violet, direct orange and magenta respectively. Similarly the Freundlich constants related to the adsorption capacity (K_f) are found to be 0.74, 0.44 and 0.68 g l^{-1} and intensity of adsorption (n) are found to be 0.41, 0.73 and 0.33 mg g^{-1} for above dyes respectively.

KEYWORDS : wastewater, adsorption, dyestuff, rate constants, Freundlich isotherm.

1. INTRODUCTION

Textile industries discharged a large quantity of highly coloured wastewater effluent which are released into nearby land or rivers without any treatment because the conventional treatment methods are very expensive. On the other hand the low cost technologies don't allow a wishful colour removal and have certain disadvantages. Thus the removal of colour from effluents is one of the major environmental problem. In this concern adsorption process has been found to be more effective method for the treatment of dye containing wastewater. The most efficient and commonly used adsorbent is commercially activated carbon which is expensive and has regeneration problems. Recent investigations focused on effectiveness of low cost adsorbents like pearl millet husk (Selverani, 2000), neam leaf powder (Walker and Weatherly, 1998), coconut husk (Low and Lee, 1990), wheat straw (Robinson *et al.*, 2002; Verma and Mishra, 2006), sewage sludge (Olereo *et al.*,2003), perlite (Dogan *et al.*, 2000), maize cobs (Lin *et al.*,1987), wood (Poots *et al.*,1978), peat (Poots *et al.*, 1976); natural adsorbent (Nassar and Guendi, 1991), banana pith (Namasivayam and Kanchana,1993), chitin (Annadurai and Krishnan, 1996), agricultural waste (Nawar and Doma, 1989) in the removal of dyes from wastewater effluent.

In the present study the adsorption of above three dyes onto rice husk carbon have been investigated. The effect of various parameters such as agitation time, pH, temperature, adsorbent dose and concentration have been investigated in the batch experiments.

2. MATERIAL AND METHOD

Three dyes namely crystal violet, direct orange (both are reactive dyes) and magenta (basic dye) were obtained from Thomas Baker (Chemicals) Ltd. Mumbai, India. The stock solution of these dyes were prepared in distilled water. The adsorbents were prepared by heating rice husk using muffle furnace. The masses obtained from the furnace were treated with concentrated sulphuric acid and washed with water to remove an excess acid and finally dried in sunlight. The physico-chemical characteristics of adsorbents are given in Table1.

Table 1. Physico-chemical characteristics of rice husk carbon

Parameters	Values
Moisture content (%)	15.38
Bulk density (g ml^{-1})	0.68
Surface area (m^2 g^{-1})	98.27
Pore volume (ml g^{-1})	0.12
Average particle size (μm)	85
Ash content (%)	36.81
pH	6.8

2.1. Batch experiments

Dye adsorption experiments were performed by taking 50 ml stock solution of dye (10 mg l^{-1}) and treated with 1 g of dose adsorbent. The variables studied were agitation time, pH, temperature, adsorbent dose and concentration. After desire time of treatment samples were filtered to remove the adsorbent and progress of adsorption was determined spectro photometrically using spectronic-20 (BAUSCH & LOMB) at the wavelength for maximum absorbance (λ_{max}) which are 595, 495 and 510 nm for crystal violet, direct orange and magenta respectively.

2.1.1. Effect of agitation time (15, 30, 45, 60 and 75 min)

The experiments were carried out by taking 50 ml samples of dyes (concentration 10 mg l^{-1}) in separate flasks and treated with 1 g of adsorbent dose at room temperature.

2.1.2. Effect of pH (2, 4, 6, 8 and 10)

The effect of pH was studied in the treatment of 50 ml aqueous solution of dyes with 1 g dose of adsorbent. All the samples were treated for half an hour at fix temperature(room temperature).

2.1.3. Effect of temperature (20, 40, 60, 80 and 100 ^oC)

The effect of temperature was investigated with 1g dose of adsorbent mixing in 50 ml aqueous solution of dyes (concentration 10 mg l^{-1}) and the samples were treated for half an hour.

2.1.4. Effect of adsorbent dose (0.5, 1.0, 1.5, 2.0 and 2.5 g)

The study was carried out with different dose of adsorbent of 85 μm average particle size. The concentrations of samples were 10 mg $l^{-1}$and treated at fix temperature for half an hour.

2.1.5. Effect of concentration: (10, 20, 30, 40 and 50 mg l^{-1})

The samples were treated with constant dose of adsorbent for half an hour at fix temperature.

3. RESULTS AND DISCUSSION

3.1. Adsorption of dyes

The adsorption of dyes were investigated in the study using different parameters such as agitation time, pH, temperature, adsorbent dose and concentration.

3.1.1. Effect of agitation time

The samples of three dyes were taken in separate flasks and treated with 1.0 g dose of adsorbent. The variation in percent removal of dyes with the elapsed time has been shown in Figure 1. It is evident from the figure that RHC treatment resulted in 70% removal of crystal violet in first 15 min, which increased up to 82.5% in 60 min. It also shows that the percent removal of direct orange and magenta are 47% and 54% in 15 min, which increased up to 77% and 84% in 45 min respectively for both the dyes. The optimum time is 45 min for both the dyes at which equilibrium is obtained. The present observations are in conformity with the other investigators(Verma and Mishra, 2004; Khatri and Singh, 2000). The increase in the extent of removal of dyes with increasing time because adsorbate generally formed monolayer on the surface of adsorbent. Thus the removal of dyes from aqueous solution is controlled by the rate of transport of the adsorbate species from the outer sites to the interior sites of adsorbent.

3.1.2. Effect of PH

The aqueous solution of dyes having concentration of 10 mg l^{-1} were treated by 1 g dose of adsorbent for half an hour with varying pH 2 to 10. The pH was maintained with the help of 0.1 N-HCl and 0.1 N-NaOH solution (Figure 2). It is evident from the figure 2, that when the aqueous solution of dyes were treated with RHC, it was found that 80% removal of crystal violet at pH 2 and 85% at pH 10. In case of direct orange the removal was increased from 62 to 85%. The equilibrium reached in the acidic medium at pH 6 for both the dyes. However in case of magenta the removal was observed to be 45 to 73% in the same conditions and equilibrium obtained at pH 8.

The removal of dyes are more at higher pH, because the surface of activated carbons are negatively charged (Helfferich, 1963), the decrease in adsorption capacity in the low pH region would be expected as the acidic medium would lead to an increase in hydrogen ion concentration which would then neutralize the negatively charged carbon surface thereby decreasing the adsorption of the positively charged cation because of reduction in the force of attraction between adsorbate and adsorbent.

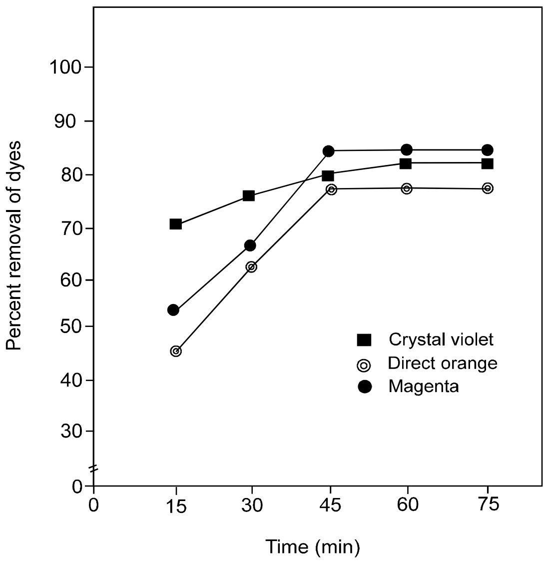

Figure 1. Effect of agitation time in the removal of dyes by RHC

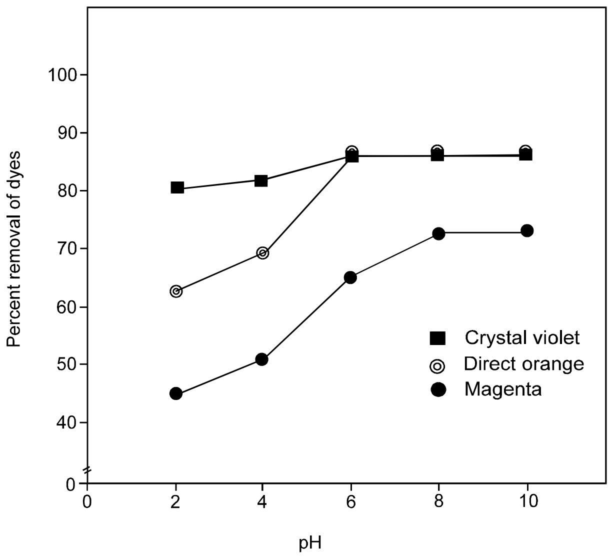

Figure 2. Effect of pH in the removal of dyes by RHC

3.1.3. Effect of temperature

To study the effect of temperature on the removal of dyes the experiments were carried out at temperature varying from 20 to 100 ^{o}C. It was observed that the removal of crystal violet was found to be 80 to 87.5%, removal of direct orange and magenta were found to be 69.2 to 85% and 50 to 80% respectively keeping the other parameters are constant. The results have been shown in Figure 3. It is revealed from the figure 3, that the removal of dyes with temperatures would increase the mobility of the ions of dyes and produces a swelling effect within the internal structure of adsorbent, thus enabling the large molecules of dyes to penetrate further (Mckay, 1982; Hiroyuki *et al.*, 1994a; Admson, 1980; Setheraman, 1973; Saker and Podar, 1994; Mall and Upadhyaya, 1995).The temperature affect the rate of removal of dyes by altering the molecular interactions and the solubility of dyes (Pandey *et al.*,1989). The greater removal of dyes due to increasing temperature may be more interaction between adsorbate and adsorbent (Pandey *et al.*, 1988; Hiroyuki *et al.*, 1994b).

3.1.4. Effect of adsorbent dose

The effect of adsorbent dose was also investigated for the removal of dyes from aqueous solution. The experiments were carried out with adsorbent dose varied from 0.5 to 2.5 g with keeping other parameters are constant. The removal of dyes were found to be 70 to 77.5%, 54 to 69% and 67 to 89% in case of crystal violet, direct orange and magenta respectively (Figure 4). 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 (Namasivayam and Yamuna, 1994; Sarioglu and Atay, 2006).

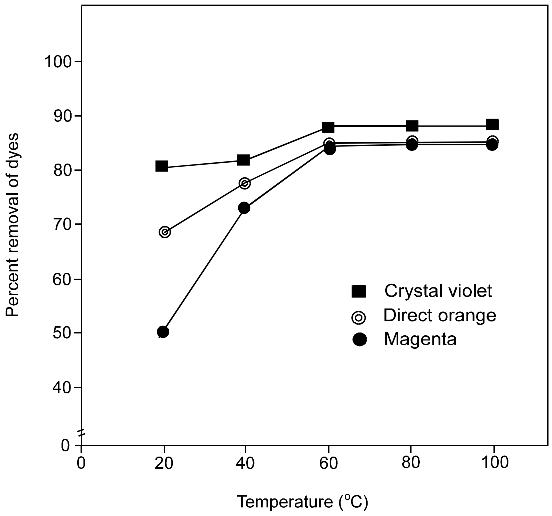

Figure 3. Effect of temperature in the removal of dyes by RHC

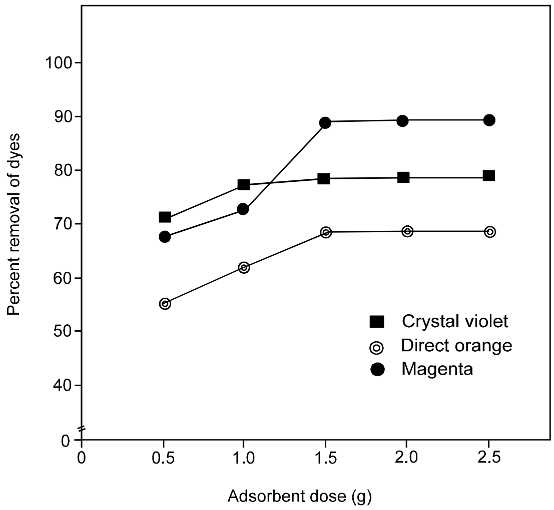

Figure 4. Effect of adsorbent dose in the removal of dyes by RHC

3.1.5. Effect of concentration

The effect of concentration of dyes (10 to 50 mg l^{-1}) have been also tested with constant dose of adsorbent. The removal of dyes decreased from 82.5 to 70% in case of crystal violet, 75 to 47% in case of direct orange and 84 to 54% in case of magenta. The results indicated that the adsorption of dyes are much dependent on concentration of solution. These observations are in close agreement with that reported (Verma and Mishra, 2005; Garg *et al.*, 2003; Gupta *et al.*, 1988) for removal decreases with increase initial concentration of dyes.

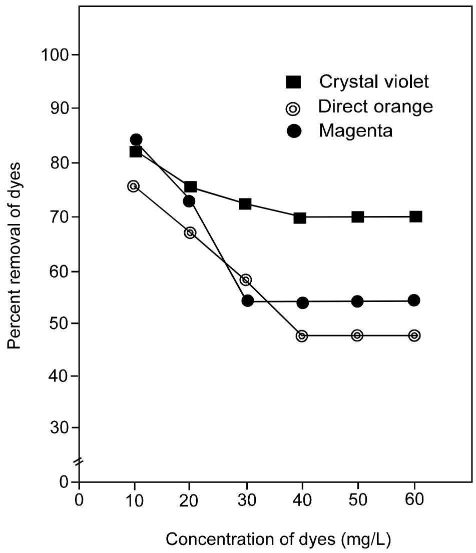

Figure 5. Effect of concentration in the removal of dyes by RHC

3.2. KINETIC MODEL OF ADSORPTION

In order to determine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the first order kinetic model is used to test the experimental data. A simple kinetics of adsorption is given by Lagergren rate equation.

$$\frac{dq_t}{d_t} = K_{ad}\left(q_e - q_t\right) \qquad (1)$$

where K_{ad} is the rate constant of first order adsorption; q_e is the amount of dye adsorbed at equilibrium and q_t is the amount of dye adsorbed at time.

Applying conditions:

$q_t = 0$ at $t = 0$

$q_t = q_t$ at $t = t$

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}t}{2.303} \qquad (2)$$

Based on experimental results, linear plots of log (q_e-q_t) versus t suggest the applicability of Lagergren first order equation (Figure 6). The rate constant was calculated from the slopes and values are given in Table 2. The effect of dye concentration on rate constants (k_{ad}) helps to describe the mechanism of removal of dyes from aqueous solution.

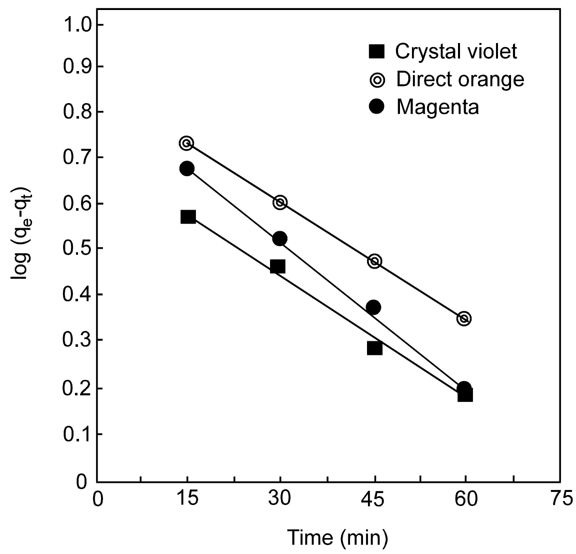

Figure 6. Test of pseudo first order equation for adsorption of dyes by RHC

Table 2. Adsorption rate constant ($K_{ad,}$ min^{-1}) for different dyes

Name of dyes	$K_{ad,}$ min^{-1}
Crystal violet	6.8×10^{-3}
Direct orange	8×10^{-3}
Magenta	10×10^{-3}

3.3. ADSORPTION ISOTHERMS

The distribution of dye between the liquid phase and adsorbent is a measure of the position of equilibrium in the adsorption process and can be generally expressed by a most common theory i.e. Freundlich isotherm model.

3.3.1. Freundlich isotherm model

The equilibrium data obtained with varying dose of adsorbent and fixed concentration of dyes confirm to the Freundlich equation as given below:

$$q_e = \frac{x}{m} = K_f C_e^{1/n} \qquad (3)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_c \qquad (4)$$

where x is the amount of dye adsorbed (g l^{-1}) and m is the mass of adsorbent used, C_e is the equilibrium concentration of dyes, K_f and n are the constants incorporating factors affecting the adsorption process such as adsorption capacity and intensity of adsorption respectively.
The values of K_f and n are obtained from the intercept and slope of the graph plotted between log q_e versus log C_e (Figure 7). The values of n are lie between 0 and 1 (Table 3), indicated that the adsorption is favourable with the Freundlich isotherm model. The similar results were earlier reported by the other investigators (Khan *et al.*, 2004).

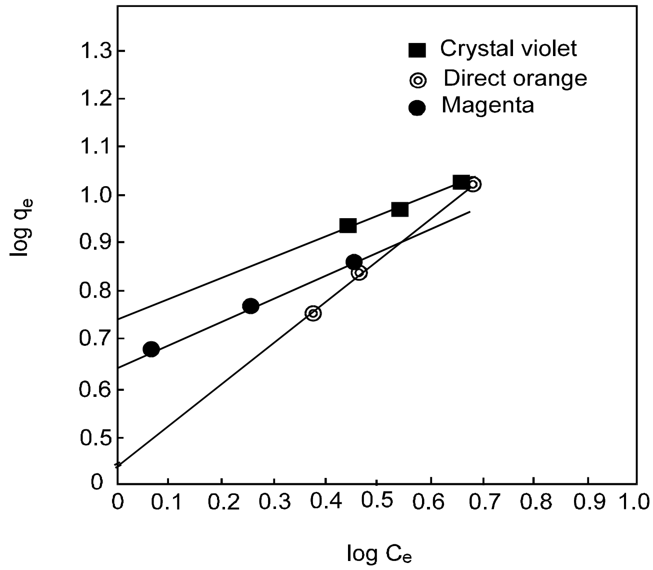

Figure 7. Freundlich isotherm for adsorption of dyes by RHC

Table 3. Values of k_f and n for different dyes

Name of dyes	K_f	n
Crystal violet	0.74	0.41
Direct orange	0.44	0.73
Magenta	0.68	0.38

4. CONCLUSION

The adsorption of dyes namely crystal violet, direct orange and magenta on RHC have been tested by First order kinetic model and Freundlich adsorption isotherm. The values of first order rate constant (K_{ad}) are 6.8 x 10^{-3}, 8 x 10^{-3} and 10 x 10^{-3} min^{-1} for above dyes respectively. The effect of dye concentration on rate constants (K_{ad}) helps to describe the mechanism of removal of dye. Similarly the values of Freundlich constants (n) are 0.41, 0.73 and 0.38 for the above dyes respectively. These values of n are lie between 0 and 1 for all the dyes suggested the applicability of Freundlich adsorption isotherm.
Thus it is concluded that RHC has an ability to adsorb the dyestuffs from aqueous solution and it could be used as a cheap substitute of commercially available adsorbents for decolourising wastewater effluents.

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