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Removal of Rhodamine-B from Aqueous Solution by Adsorption Using Water Hyacinth Ash

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The use of cheap and ecofriendly adsorbents have been studied as an alternative substitution of activated carbon for the removal of dyes from wastewater. Adsorbents prepared from water hyacinth ash are used to remove the rhodamine-B from aqueous solution. The effect of various experimental parameters has been investigated using a batch adsorption technique to obtain information on treating effluents from the dye industry. The extent of dye removal increased with decrease in the initial concentration of the dye and also increased with increase in contact time and amount of adsorbent. Adsorption data were modeled using the Freundlich adsorption isotherm and first order kinetic equation Lagergren equation.

Key Words: Rhodamine-B, Water hyacinth ash, Adsorption.

INTRODUCTION

Dye industries and many other industries which use dyes and pigments discharge wastewater, characteristically high in colour and organic content. Presently, it is estimated that about 10,000 of different commercial dyes and pigments exists and over 7×10^5 tons are produced annually world wide[1].

Dyes are widely used in textile, rubber, paper, plastic, leather, food industries, *etc*. Colour stuff discharged from these industries poses certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibiting sun light penetration into the stream and affecting aquatic ecosystem[2]. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade[3]. There are various conventional methods of removing dyes including coagulants[4], oxidizing agents[5], ultra-filtration[6], electrochemical[7] and membrane separation[8]. However these processes are costly and cannot effectively be used to treat the wide range of dye-wastewater. In contrast, an adsorption technique is by far the most versatile and widely used. Activated carbon (powdered or granular) is the most widely used adsorbent because it has excellent adsorption efficiency for the organic compound. But commercially available activated carbon is very expensive.

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In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. These include rice husk, orange and banana peels, chitin, fly ash, saw dust, bagasse pith, *etc.*[9-13].

In this study water hyacinth ash is used as an adsorbent to remove rhodamine-B from aqueous solution. Water hyacinth is available in the rivers and ponds in India. Therefore water hyacinth ash can be used as a cost effective adsorbent for the removal of rhodamine-B from aqueous solution.

The present study is undertaken to evaluate the efficiency of a carbon adsorbent prepared from water hyacinth for the removal of rhodamine-B in aqueous solution. The adsorption study was carried out systematically involving various parameters such as initial concentration, adsorbent dose and contact time. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. The applicability of kinetic and mass-transfer models for the adsorption of rhodamine-B on to water hyacinth ash are also reported.

EXPERIMENTAL

Preparation of dye solution: An accurately weighed quantity of rhodamine-B (S.D. Fine Chemicals, India) was dissolved in double distilled water to prepare stock solution (500 mg/L). Experimental solution of the desired concentration was obtained by successive dilutions. Concentrations of the aqueous solutions of dye were monitored on UV /Visible spectrophotometer, Model SL-164 (M/sElico) over a wavelength of 543 nm.

Preparation of adsorbent: The water hyacinth was collected from the local ponds. It was washed thoroughly with water for several times to remove earthy matter and all the dirt particles. It was then dried in an oven at a temperature of 90 ºC for *ca.* 16 h. The dried sample was then burned for *ca.* 1 h. The remaining was then crushed, sieved and stored in plastic bottle for use.

Adsorption experiment: The adsorption experiments were carried out in a batch process. The known weight of the adsorbent material was added to 50 mL of the dye solution with an initial concentration of 10 to 90 mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120 rpm. The samples were withdrawn from the shaker at the predetermined time intervals and adsorbent was separated from the solution by centrifugation at 4500 rpm for 5 min. The absorbance of the supernatant solution was estimated to determine the residual dye concentration[14], measured at 543 nm with an ELICO double beam UV-Vis spectrophotometer (model SL-164). Finally the suitability of the adsorption model to the equilibrium data was investigated from rhodamine-B adsorbent system. The percentage removal of the dye and the amount adsorbed (mg L^{-1}) were calculated using the following equations:

$$\text{Percentage removal} = (C_o - C_f)/C_o \times 100$$

$$\text{Amount adsorbed} = (C_o - C_f)/m$$

where C_o and C_f are the initial and final concentration (mg L^{-1}) of dye and m is the mass of the low-cost adsorbent (g L^{-1}).The effect of initial concentration, adsorbent dosage and contact time were investigated. Each experimental point is the average of three independent runs and all the results were reproducible within ± 3 % error limit.

RESULTS AND DISCUSSION

No changes appeared either in the adsorption spectrum or in additional peaks formed for the dye solution after shaking it with the adsorbent. This indicated that there were no breakdown product(s) of the dye and also supported the fact that the dye removal from the solution in this study was through the mechanism of adsorption.

Effect of initial concentration: The influence of the initial concentration of rhodamine-B in the solutions on the rate of adsorption on water hyacinth ash was studied. The experiments were carried out at fixed adsorbent dose (10 g/L) in the test solution, 29 ± 1 ºC room temperature and at different initial concentrations of rhodamine-B (10, 30, 50,70 and 90 mg/L). The relevant data are given in Table-1. Table-1 reveals that the percentage adsorption decreases with the increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of adsorbent increases with increase in dye concentration. It means that the adsorption is highly dependent on the initial concentration of dye[15]. This is because at lower concentration, the ratio of the initial number of dye molecule to the available surface area is low, subsequently, the fractional adsorption becomes independent of the initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence, the percentage removal of dye is dependent upon the initial concentration. This was similar to the one reported in literature[16].

TABLE-1
EFFECT OF VARIOUS PARAMETERS ON THE REMOVAL OF RHODAMINE-B

Adsorption system					
Initial dye conc. (mg/L)	Dye removal (%)	Adsorbent dosage (g/100 mL)	Dye removal (%)	Contact time (min)	Dye removal (%)
10	99.9	0.5	82.0	5	89.1
30	97.8	1.0	89.0	15	92.5
50	95.0	1.5	95.0	25	95.0
70	93.0	2.0	98.0	35	97.3
90	91.5	2.5	99.9	45	99.7
–	–	–	–	55	99.7

Effect of adsorbent dosage: The adsorption of rhodamine-B on water hyacinth ash were studied by changing the quantity of adsorbent (0.5-2.5 g/100 mL) in the test solution while keeping the initial dye concentration (30g/L), temperature (29 ± 1 ºC) constant. As shown in Table-1, the percentage removal of rhodamine-B increased with the increase in adsorbent dosage. Increase in the adsorption with adsorbent dosage can be attributed to increased surface area and availability of more adsorption sites[17,18]. Table-1 shows the effect of adsorbent dosage on the removal of water hyacinth ash.

Effect of contact time: In the adsorption system contact time plays a vital role irrespective of the other experimental parameters affecting the adsorption kinetics. In order to study the kinetics and dynamics of adsorption of rhodamine-B by water hyacinth ash the adsorption experiments were carried out at different contact times (5-55 min) at constant initial concentration of dye (50 mg/L) with a fixed dose of adsorbent (10 g/L). It is found that the removal of rhodamine-B increases with increase in contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of rhodamine-B on the available adsorption sites on adsorbent material[19]. The results show that the equilibrium time required for the adsorption of rhodamine-B on water hyacinth ash is 45 min. The percentage removal of dye on water hyacinth ash at 45 min of contact time reveals that water hyacinth ash has maximum removal efficiency of 99.7 %. The relevant data are given in Table-1.

Adsorption isotherm: Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent for different pollutants. Equilibrium data can be analyzed using commonly known adsorption isotherm, which provide the basis for the design of adsorption systems. The most widely used isotherm equation for modeling of the adsorption data is the Freundlich equation[20], which is given by:

$$Q_e = K_f \, C_e^{1/n}$$

where K_f and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity respectively.

The linearized form of Freundlich isotherm can be written as:

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

The value of K_f and n can be calculated by plotting ln q_e *versus* ln C_e.

Fig. 1 shows the Freundlich curves for rhodamine-B adsorption on water hyacinth ash.The isotherm constants and correlation coefficients are shown in Table-2. It has been stated by Mckay *et al.*[21] that magnitude of the exponent n gives an indication of the favourability and capacity of the adsorbent/adsorbate system. Values of $n > 1$ represents favourable adsorption condition according to Trey ball[22]. In this case the observed exponent is $1 < n < 10$ showing beneficial adsorption[23].

TABLE-2
EQUILIBRIUM CONSTANTS FOR RHODAMINE-B ONTO WATER HYACINTH ASH

Freundlich isotherm parameters		
K	n	r
2.6189	1.9904	0.9999

Adsorption kinetics: In order to study the rate constant for rhodamine-B-water hyacinth ash system, the well known Lagergren first order rate equation was employed. The first order rate equation is:

$$\log (q_e - q_t) = \log q_e - (K_{ad}/2.303)\ t$$

where q_e and q_t (both in mg g^{-1}) are the amounts of rhodamine-B adsorbed at equilibrium time and at any time t, respectively. The straight-line plot of log (q_e-q_t) *vs.* t (Fig. 2) indicates the validity of Lagergren equation for the present system and explained that the process follows the first order kinetics. The values of K_{ad} calculated from the slope of the plots, was 0.0055 min^{-1} for water hyacinth ash at 10 g/L dosage.

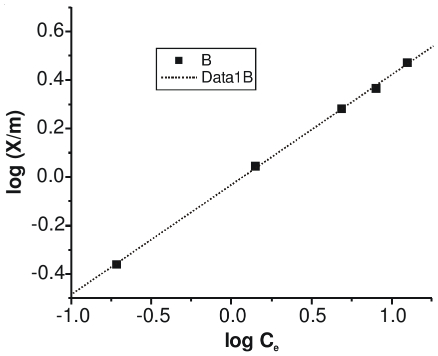

Fig. 1. Freundlich adsorption isotherm of rhodamine-B using water hyacinth ash

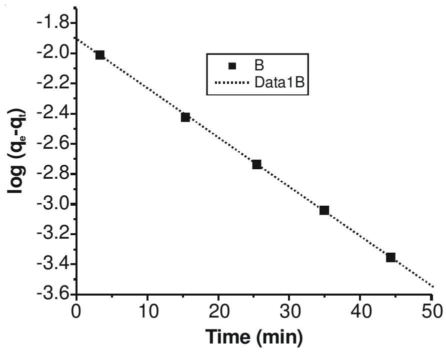

Fig. 2. Lagergren plot for removal of rhodamine-B

Intra-particle diffusion study: The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in a intra-particle diffusion plot. Besides adsorption at the outer surface of the adsorbent there is also a possibility of intra-particle diffusion of dye molecule from bulk of the outer surface into the pores of water hyacinth ash. This possibility was exposed by plotting the amount of dye adsorbed against square root of time, $t^{0.5}$. According to Weber and Morris[24], an intra-particle diffusion coefficient K_p is defined by the equation:

$$Q = K_p\ t^{0.5}$$

where Q (mg g^{-1}) is the amount of rhodamine-B adsorbed at any time t and K (mg g^{-1} min) is the intra-particle diffusion rate constant. The shape of the q *versus* $t^{0.5}$ plot is curved (Fig. 3) at a small time limit which might be due to mass transfer effect[25]. There are two separate regions in the curves. The initial curved portion reflects film or boundary layer diffusion effect and the linear portion to the intra-particle diffusion effect[26]. The values of K_p were obtained from the slope of the straight lines and was 1.765 mg g^{-1}.

Fig. 3 shows that intra-particle diffusion is slow and rate determining step. The linear portions of the curves (Fig. 3) do not pass through the origin. This indicates that mechanism of dye removal on water hyacinth ash is complex and both, the surface adsorption as well as intra-particle diffusion contribute to the rate determining step[27].

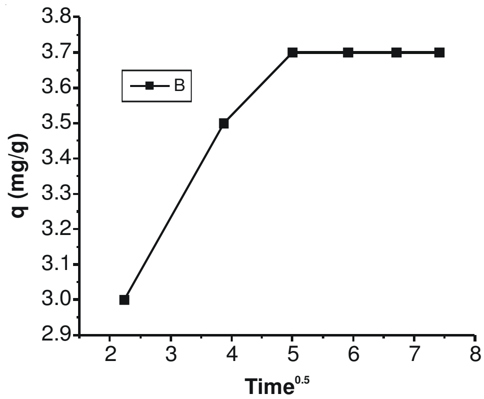

Fig. 3. Intraparticle diffusion effect for the adsorption of rhodamine-B on water hyacinth ash

Conclusion

In this study, the adsorption of rhodamine-B from aqueous solution was investigated using water hyacinth ash as an adsorbent. The results indicated that adsorption capacity of the adsorbent was considerably affected by initial dye concentration, contact time and adsorbent dosage. The results show that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. Higher adsorption percentages were observed at lower concentrations of rhodamine-B. Equilibrium data fitted very well in a Freundlich isotherm equation and Lagergren first-order kinetics model. This study proved that water hyacinth ash is an attractive option for dye removal from dilute industrial effluents. As water hyacinth is easily available in the river and pond it has potential to be used for the small scale industries which produced dye as their effluent, after it was being pretreated with water hyacinth ash.

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