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Removal of rhodamine B from aqueous solution by almond shell biosorbent

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Abstract

In the present study, the use of almond shell (*Prunus dulcis*) biosorbent has been investigated to remove the Rhodamine B from aqueous solutions. Almond shell has been selected as an adsorbent because of advantages such as high adsorption capacity, non toxicity, availability and low cost. The effects of contact time, initial dye concentration, adsorbent dosage, particle size and solution pH were studied. The results showed that the removal efficiency increased by increasing contact time, adsorbent dosage and initial dye concentration. In addition, the adsorption was dependant to solution pH and the maximum adsorption was observed at a solution pH of 2.0. The Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption equilibrium data. Freundlich equation fits the experimental data better than the Langmuir and Timken equations do.

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Introduction

The extensive use of dyes and pigments in textile, plastic, food, dyeing, paper, printing, pharmaceutical and cosmetic industries has led to the widespread introduction of these compounds into the environment. The contamination of groundwater and surface water by these compounds become a worldwide environment problem because of the many adverse effects of these pollutants. These compounds color the water and make penetration of sunlight to the lower layers impossible and hence affecting aquatic life. Many of these are toxic, carcinogenic, mutagenic, or even stable to biological degradation (Wong *et al.,* 2003).

Rhodamine B (RB) is one of the most important dyes of the xanthene group, which is a highly water soluble (Fig. 1). It is found as a reddish violet powder and comes under the trade name of D&C Red No. 19. It is harmful if swallowed by human beings and animals, and causes irritation to the skin, eyes and respiratory tract (Rochat *et al.,* 1978). It is widely used in many industrial processes, such as paper dyeing and the production of dye laser. Consequently, it is present in industrial effluents. Some physical properties of RhB are presented in Table 1.

Table 1. Some properties of the Rhodamine B dye.

Properties	Value
Colour Index No.	45170
Molecular formula	$C_{28}H_{31}N_2O_3Cl$
Molecular weight	479.01
λ_{max} (nm)	555
CAS number	81-88-9
Solubility	Very high

Several methods such as coagulation, ozonization, membrane filtration, electrolysis, oxidation and bio-degradation have been widely used for the removal of dyes from water and wastewater (Vasu, 2008). However, these technologies do not always provide a complete and economic solution for some of these wastewater applications and have their merits and limitations in application.

The adsorption process provides an attractive and alternative treatment, especially if the adsorbent is inexpensive and readily available (Sumanjit *et al.,* 2008). Granular activated carbon is the most popular adsorbent, but is expensive. Consequently, several researchers have concentrated their work on low-cost adsorbent materials (Gopinath, 2012; Gupta and Suhas, 2009).

Almond is a common tree in Iran and almond shell, being a low-cost and easily available adsorbent, could be an alternative for more costly wastewater treatment processes.

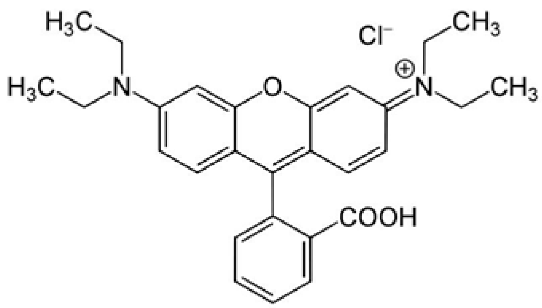

Fig. 1. Chemical structure of Rhodamine B.

In this study, the potential of almond shell, as a agricultural waste, for treating RhB contaminated water, simulated a textile wastewater, was evaluated and the effect of operating conditions such as initial concentration, solution pH, adsorbent dose, and particle size on the process performance was investigated. Furthermore, the isotherms at 25°C were established and the fit of Freundlich, Langmuir and Temkin models to the experimental data points were evaluated.

Materials and methods

Materials

The almond shell was taken from local natural resources. Before use, it was washed with deionised water to remove surface impurities and dried at 100 °C. The material was ground to a fine powder in a still mill. The resulting material was sieved in the size range of 20-100 mesh ASTM and stored in plastic bottles for further use.

RhB and all other chemicals were of analytical grade and purchased from Merck (Darmstadt, Germany). The pH measurements were made using a pH meter (Hanna pH 211) and deionized laboratory water was used for making aqueous mixtures.

Preparation of simulated dye wastewater

The basic dye, RhB was used as such without further purification to prepare the simulated wastewater. An accurately weighed quantity of RhB was dissolved in double distilled water to prepare the stock solution (500 mg/L). Experimental solutions of the desired concentration were obtained by successive dilutions.

Experimental methods and measurements

In each adsorption experiment, 100 ml of dye solution of known concentration and pH was added to 0.5 g of adsorbent in a 250 ml round bottom flask at 25°C and the mixture was stirred on a rotary orbital shaker at 200 rpm.

The samples were withdrawn from the shaker at predetermined time intervals and filtered through filter paper 0.45µm. The residual dye concentration in the solution was analyzed by a UV-Vis Spectrophotometer (JENWAY 6305 UV/Vis model) at 555 nm. The amount of RhB adsorbed defined as follows:

$$q_e = \frac{(C_i - C_e)V}{M} \qquad (1)$$

Where, q_e is the adsorption capacity in mg/g, C_i and C_e are the initial and equilibrium dye concentration in mg/L, V is the volume of RhB solution in L and M is the weight of the adsorbent in g.

The percentage of dye removal was calculated using Eq. 2:

$$\%Removal = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (2)$$

It is worthy to note that, the experiments were carried out at initial pH values ranging from 2-10; initial pH was controlled by the addition of dilute HCl or NaOH solutions. All experimental conditions were repeated two times and the average values are reported.

Results and discussion

Effect of initial RhB concentration

Adsorption experiments were conducted to study the effect of the initial concentration of RhB on the rate of dye adsorption on almond shell. The experiments were carried out at a fixed adsorbent mass (0.5 g) and at different initial concentrations of RhB (5- 200 mg/L) at 25°C as shown in Fig. 2. It was observed that dye uptake is rapid for the first 15 min and thereafter it proceeds at a slower rate and finally attains saturation.

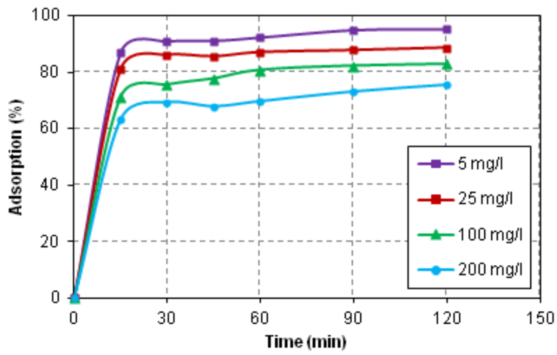

Fig. 2. Effect of initial concentration on the removal efficiency (adsorbent dose = 0.5 g, temperature = 25°C).

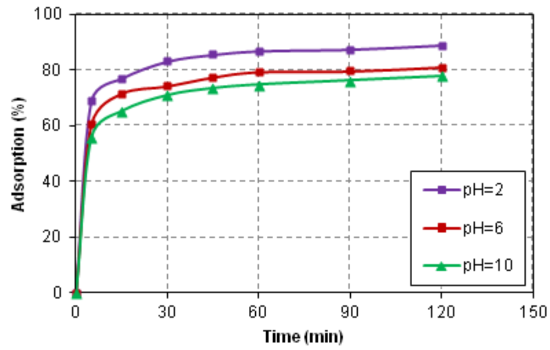

Fig. 3. Effect of pH on the removal efficiency (initial RhB concentration = 100 mg/L, temperature = 25°C, adsorbent dose = 0.5 g).

This may be explained by a rapid adsorption on the outer surface, followed by slower adsorption inside the pores. As the initial RhB concentration increases from 5 to 200 mg/L the equilibrium removal of RhB decreases from 92.2 to 75.7%. This may be due to the fact that at lower concentrations almost all the dye molecules were adsorbed very quickly on the outer surface, but further increases in the initial dye concentrations led to fast saturation of adsorbent surface and thus most of the dye adsorption took place slowly inside the pores. However, the experimental data were measured at 120 min to make sure that full equilibrium was attained.

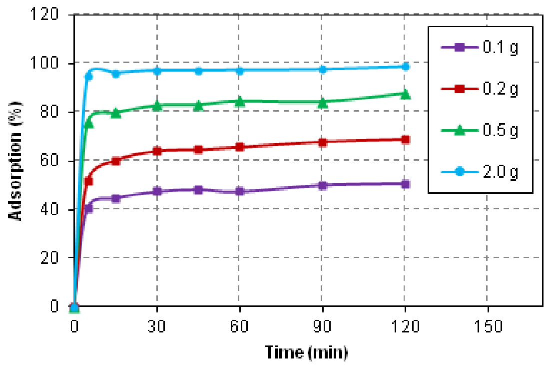

Fig. 4. Effect of adsorbent dosage on the removal efficiency (initial RhB concentration = 100 mg/L, temperature = 25°C).

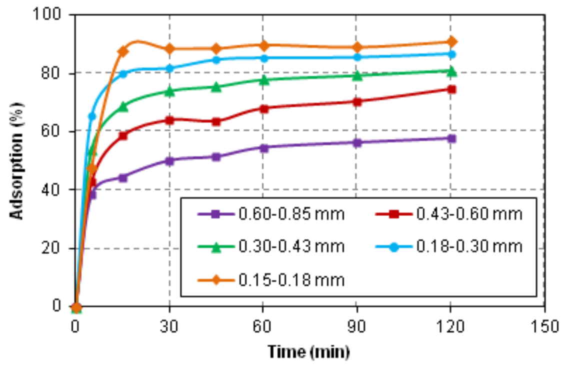

Fig. 5. Effect of particle size on the removal efficiency (initial RhB concentration = 100 mg/L, temperature = 25°C, adsorbent dose = 0.5 g).

Effect of pH

The pH of the aqueous solution is an important controlling parameter in adsorption process. The adsorption studies of RhB on almond shell carried out at pH range 2-10.

As the results show, adsorption of RhB was higher at lower pH and decreased with increasing pH (Fig. 3). Maximum uptake of RhB was about %92.8 which achieved at pH 2.0. Therefore, pH 2.0 was selected as an optimum value.

At pH=2, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent, due to the ionization of functional groups of adsorbent and negatively charged anionic dye. As the pH of the solution increases, the numbers of negatively charged sites increases. A negatively charged site on the adsorbent does not favor the adsorption of anionic dyes due to the electrostatic repulsion (Namasivayam and Kavitha, 2002). Also, lower adsorption of RhB at alkaline pH is due to the presence of excess OH^- ions destabilizing anionic dyes and competing with the dye anions for the adsorption sites. Similar results of pH effect were also reported for the adsorption of acid yellow 36 and Congo red (Namasivayam and Kavitha, 2002, Banat, 1996).

Table 2. Isotherm constants for various adsorption isotherms.

	Langmuir constants	
V_m (mg.g^{-1})	K (L.mg^{-1})	R^2
33.22	0.065	0.945
	Freundlich constants	
n	K_f (mg.g^{-1})	R^2
1.674	2.494	0.993
	Temkin constants	
B	A(L.g^{-1})	R^2
4.454	2.394	0.844

Effect of adsorbent dose

The adsorption of RhB on almond shell was studied by changing the quantity of adsorbent (0.1 - 2 g) in the test solution while keeping the initial dye concentration (100 mg/L) and temperature (25°C) constant at different contact times for 120 min (Fig. 4). Experimental results showed that the percentage removal RhB increases with the increasing amount of adsorbent. This can be explained by the fact that, with increase in the mass of adsorbent the available surfaces for adsorption of RhB also increase.

At equilibrium time, the percent removal increased from 51.7% to 98.7% for an increase in almond shell dose from 0.1 to 2.0 g.

Effect of particle size

Adsorption of RhB on to almond shell was studied at different particle sizes from 0.15 to 0.85 mm. The effect of particle size on RhB adsorption capacity of almond shell is presented in Fig 5. The RhB removal at different particle sizes indicated that the capacity of RhB adsorption at the equilibrium condition increased with the decrease in particle sizes. The relatively higher adsorption with smaller adsorbent particle may be attributed to the fact that smaller particles yield large surface areas and shows that RhB adsorption occurs through a surface mechanism. It can also be observed that smaller particles reach equilibration faster.

Adsorption Isotherm

Isotherms are the equilibrium relations between the concentrations of the adsorbate on the solid phase and in the liquid phase at a constant temperature. The most important factors to design and run an industrial adsorption plant are the knowledge of adsorption kinetics and isotherms. Hence, equilibrium data were analyzed by using the most commonly used isotherms; Langmuir, Freundlich and Temkin isotherm models.

Langmuir isotherm model

The Langmuir model assumes that the uptake of dye occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbate molecules (Aliabadi et al., 2012):

$$\frac{Ce}{x/m} = \frac{1}{KV_m} + \frac{Ce}{V_m} \qquad (3)$$

where C_e is the equilibrium solution concentration, x/m the amount adsorbed per unit mass of adsorbent, m the mass of the adsorbent, V_m the monolayer capacity, and K is equilibrium constant related to the heat of adsorption by Eq. 4:

$$K = K_0 \times \exp(\frac{q}{RT}) \qquad (4)$$

where q is the heat of adsorption.

Freundlich isotherm model

The Freundlich isotherm is empirical for heterogeneous surface energy. It assumes that the adsorption energy of an adsorbate binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied:

$$Ln\frac{x}{m} = LnK_f + \frac{1}{n}LnCe \qquad (5)$$

where K_F (mg.g^{-1}) and $1/n$ are Freundlich constant and exponent, respectively.

Temkin isotherm model

Temkin isotherm is based on the heat of adsorption of ions and is presented in linear form, in Eq. 6:

$$\frac{x}{m} = (\frac{RT}{b})LnA + (\frac{RT}{b})LnCe\ , \quad \frac{RT}{b} = B \qquad (6)$$

Where b is the Temkin constant related to heat of sorption (J/mol), A the Temkin isotherm constant (L/g), R the gas constant (8.314 J/(mol.K)) and T is the absolute temperature (K).

The data obtained from the adsorption experiments conducted at 25°C were fitted to Eqs. (3), (5) and (6) and linear plot (not shown) were obtained for $C_e/(x/m)$ versus C_e, $log(x/m)$ versus log(C_e) and x/m versus ln(C_e), respectively. The theoretical parameters of isotherms along with regression coefficient are shown in Table 2.

The results indicate that the Freundlich equation fits the experimental data better than the Langmuir and Timken equations do.

Conclusions

The present study showed that almond shell, as an agricultural waste, can be used as effective adsorbents for the removal of RhB from aqueous streams. This natural waste is available in large quantity and can be used as an alternative to existing commercial adsorbents. The batch adsorption process was found dependent upon pH of the solution, particle size of the adsorbents, amount of adsorbent and initial concentration of solution. Experiments reveal that highest adsorption of the dye could be achieved at pH=2, while 2 h of contact was sufficient to attain equilibrium. The experimental results were analyzed by using the Langmuir, Freundlich and Temkin equations. The results indicated that the data fit better to the Freundlich equation than to the Langmuir and Temkin equations. Thermodynamic parameters obtained by the adsorption isotherm data confirmed the feasibility of the process. Finally, it can be concluded that almond shell, as an agricultural waste, is a promising adsorbent for the uptake of RhB due to its low cost, easy availability, and high adsorption capacity.

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