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Comparison and analysis of two natural adsorbents of Sorghum and Ziziphus nummularia pyrene for the removal of erythrosine dye from aquatic environments

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A B S T R A C T

One pollutant which seriously threatens water resources is dye. Therefore, finding a suitable method to separate the dye in water resources is very important. An adsorption process that uses low cost adsorbents is considered as an efficient strategy for this purpose. In this study, Erythrosine dye removal from an aquatic environment using natural absorbents, namely Sorghum and Ziziphus nummularia pyrene, was reviewed. The effects of different parameters such as pH, contact time, initial density, and the adsorbent amount in the batch system were investigated. The results indicated that increased temperature has no significant effect on the removal of Erythrosine dye, and the highest adsorption was achieved in the first 30 min of adsorbent- dye contact time. Also, most of the adsorption occurred at pH values of 4-8. Moreover, the highest amount of dye removal was observed in a concentration of 20 mg/L for the Ziziphus nummularia pyrene adsorbent and 5 mg/L of the Sorghum adsorbent. Also, the Langmuir and Freundlich equations were used to analyze the adsorption process, where both the Sorghum and Ziziphus nummularia pyrene adsorbents showed a better agreement with the Langmuir isotherm.

1. Introduction

Nowadays, increasing importance has been attached to the issue of preserving water resources. The consequences of rapid population growth including the excessive use of limited water resources and the associated water pollution due to a variety of agricultural, biological and industrial activities have added to the problem of water shortages in recent years. Environmental pollution from dyes and the contamination of water supplies have proved to be a considerable challenge for the modern world. The discharge of colored wastewater from textile, paper, plastics, cosmetics and food industries into the waterways can be considered as the first detectable sign of contamination. Since light and heat do not affect the stability of most dyes and impedes biological decomposition, it is difficult to remove them from water; therefore, in most countries, the removal of textile dyes from industrial wastewater proves to be a major problem for environmental management even though environmental laws are enforced [1]. There are many different methods for reducing the toxicity of dyes including coagulation, oxidation, membrane separation, electrochemical methods, and aerobic and non-aerobic microbial decomposition. However, these methods have some limitations. Among the different methods, adsorption is more economical and also removes high amounts of the dye. The most commonly used adsorbent is active carbon. However, application of active carbon has some limitations such as its high cost. Therefore, adsorption via agricultural products can be an economical and practical method for the removal of most pollutants such as dyes, heavy metals, fennel, and gasses [2]. Erythrosine is one of the most well-known dyes generally

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employed in cosmetics, food, medicine, and textile industries. Erythrosine is a water-soluble dye from the Zanten category. It is a highly poisonous dye which can cause many different kinds of health problems such as allergies, triode illness, cancer and DNA behavioral abnormalities. A large number of qualitative studies have already been carried out in regard to Erythrosine dye removal, and these studies have attracted attention among different researchers [3-4]. In the present study, two natural adsorbents, Sorghum and Ziziphus nummularia pyrene, were applied to remove Erythrosine dye from the effluent. They are low-priced and available from agricultural wastes. In addition, the abilities of these adsorbents have been analyzed and compared. The main issues considered in the present paper are as follows:

1. Analysis of contact time, pH, initial density of the dye, temperature and heat adsorption in the removal of Erythrosine dye.
2. Determination of the best isotherm and Kinetic model for the dye adsorption under study.

2. Materials and methods

2.1. Sorbents

In this study, Sorghum and Ziziphus nummularia pyrene procured from agriculture wastes were used as adsorbents for the removal of Erythrosine dye. Sorghum and Ziziphus nummularia pyrene were obtained from a farm in the city of Garmsar and from agriculture wastes in the city of Behbahan, respectively. Initially, the obtained wastes were extensively washed with tap water to remove the initial impurities, sprayed with distilled water, and dried at room temperature to a constant weight. Then they were ground into small fine particles by a home type grinder and particles with sizes of $35 < d \leq 60\mu m$ were obtained; these particles were used directly for the adsorption experiments without any pre-treatment.

2.2. Chemicals

Erythrosine (empirical formula $C_{20}H_8I_4O_5$; molecular weight= 835.89) is a commercial Nitrozo dye containing -NO-groups. The mentioned dye was purchased from Merk (Germany). The test solutions containing the required dye concentration were prepared by diluting 100ppm of stock solutions of dye which was obtained by dissolving a weighed quantity of 0.05 g of Erythrosine dye in 0.5 L of distilled water. The concentration range of the prepared dye solutions was between 5 and 100 mg/L.

2.3. Sorption studies

Sorption studies were conducted in a routine manner via the batch technique. A number of Pyrex flasks containing a definite volume (100 ml in each case) of Erythrosine dye solution with the desired concentration and pH were placed in a thermostatic rotary shaker. In the batch experiments, 0.3 g of sorghum and 0.5 g of Ziziphus nummularia pyrene were treated with 100 ml of dye solution. The flasks were agitated at a constant shaking rate of 300 rpm for 30 min to ensure that equilibrium was reached. The dye solutions were separated from the sorbents by filtering. Uptake values were determined as the difference between the initial dye concentration and the one in the supernatant. The effects of the experimental parameters on the adsorption capacity of the adsorbent in the experiments were investigated.

Equation (1) was used to calculate the removal efficiency of the dye from the solution. To calculate the adsorption capacity or the amount of dye adsorbed per unit weight of adsorbent, Equation (2) is commonly used

$$R = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

which C_o and C_e are initial concentration and dye concentration at time t, in terms of milligrams per liter V is volume of solution in terms of Liter, and M is the mass of sorbent in term of gram [5]. All the experiments were carried out in duplicates and the average values were used for further calculation. For the calculation of average value, the percent relative standard deviation for samples was calculated.

2.4. Analysis of Erythrosine

The concentration of unadsorbed Erythrosine dye in the adsorption medium was measured colorimetrically using a spectrophotometer (UNICO2100). The absorbance of the green dye was at 527 nm, where the corresponding maximum adsorption peak existed.

3. Results and discussion

3.1. Analysis of contact time

The known density of the dye material (100ppm) has been exposed to certain amounts of adsorbent (0.3 g of sorghum and 0.5 g of Ziziphus nummularia) with the adjusted pH of solution, and then the resulting mixture was stirred with a magnetic stirrer. The percentages of dye adsorption at different contact times of 5 to 90 minutes have been investigated. The results show that an increase in contact time from 5 to 20 minutes quickly increases the amount of adsorption, which can be ascribed to the increase in the active sites on the adsorbent. This incremental trend continues for 30 minutes and then reaches a constant level. Therefore, the time of 30 minutes has been considered as the optimal time for both adsorbents, as shown in Figure 1.

3.2. Analysis of the initial concentration

Solutions of different initial Erythrosine concentrations (5, 10, 20, 25,50ppm) were shaken for 30 min at ambient temperature with an adjusted solution pH to investigate the effect of the concentration on the removal of Erythrosine. Obviously, the total amount of adsorbed Erythrosine always increased with an increase in the initial Erythrosine concentration. Figure 2 shows the effect of pollutant concentration on dye removal using Erythrosine. As it can be observed from this figure, the optimal concentration of the pollutant for the adsorption of sorghum and Ziziphus nummularia were found to be 5ppm and 20ppm, respectively. At a lower concentration, the exposed surface of adsorbent to the dyes was higher while this exposure was reduced as the concentration was increased. Therefore, removal efficiency decreased with an increase in initial concentration. The results indicated that the maximum amounts of adsorption were 93.7% and 92% for Ziziphus nummularia and sorghum, which was reduced to 91% and 75.6%, respectively, when initial concentration was increased.

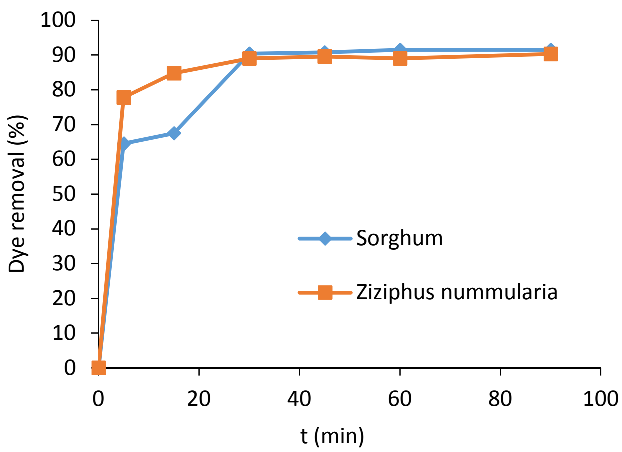

Fig. 1. Comparison of optimization of contact time of two adsorbents

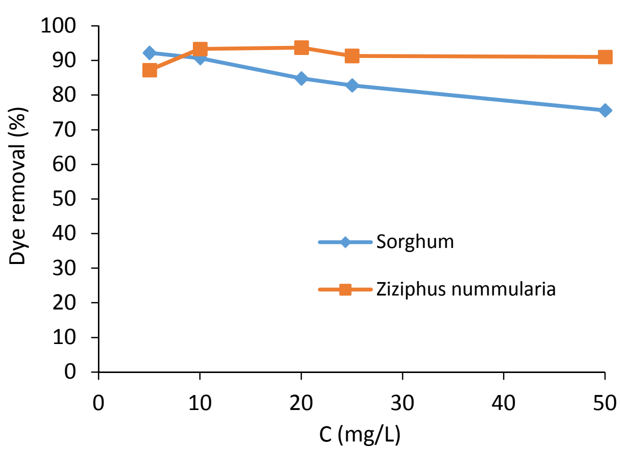

Fig. 2. Comparison of pollutant density optimization for two adsorbent

3.3. Effect of adsorbent dose

Different weighed amounts of Sorghum (0.1-1g) and Ziziphus nummularia (0.025-1) adsorbents were added to the dye solution of 5 mg/L and 20 mg/L, respectively. Subsequently, they were stirred for the optimal time achieved in the previous stage (30 min) using a magnetic stirrer. After sifting the mixture, the remaining pollutant concentration in the solution was measured by a spectrophotometer device; resultantly, the optimal gram of sorghum and Ziziphus nummularia adsorption were found to be 0.3 gr and 0.1gr, respectively. The results are shown in Figure 3.

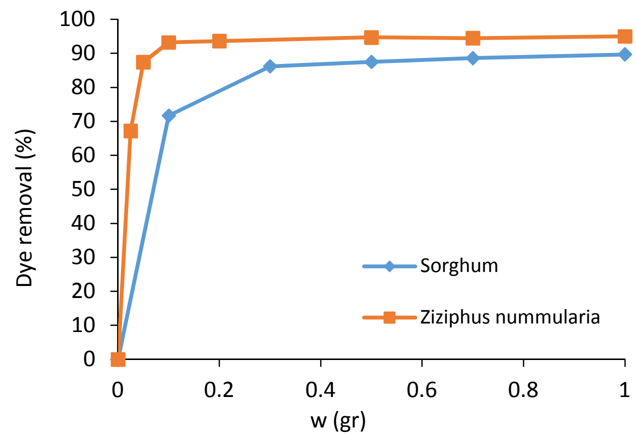

Fig. 3. Optimal comparison of adsorbent dose

3.4. Effect of pH

The pH of aqueous solution is an important controlling parameter in the adsorption process. Variations in pH result in the variations in the adsorption load, degree of homogeneity of adsorbent material and homogeneity of active absorbent groups [6]. Studies on the effect of Ziziphus nummularia adsorbent on the Erythrosine dye removal from aqueous environments have been carried out in the pH range of 2-10. Sodium hydroxide and hydrochloric acid were used to adjust the pH. The effect of pH on the Erythrosine dye adsorption process is shown in Figure 4. According to this figure, the best percentage of dye removal was achieved in the neutral range. Furthermore, a pH = 2 was not considered due to the color change and wavelength variation.

3.5. Adsorption isotherm

Adsorption is a process of mass transformation where the different compounds may compete to reach a balance. The initial effective forces in the adsorption between the adsorbent and the adsorbate are electrostatic attraction and electrostatic repulsion, which can be physical or chemical. As recorded in the literature, different equations have been formulated to explain the balance between the adsorbate and the adsorbent, among which are Langmuir, Freundlich and others [7].

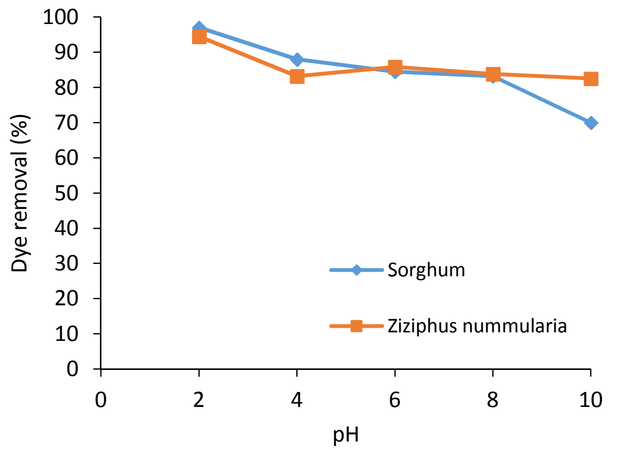

Fig. 4. Optimization of pH comparison

3.5.1. Freundlich isotherm

The equation of the Freundlich isotherm [8-9] is as follows:

$$Lnq_e = \frac{1}{n} LnC_e + LnK_F \quad (3)$$

where q_e is the amount adsorbed per unit mass of the adsorbent at equilibrium condition in terms of mg/g, C_e is equilibrium concentration of the pollutants in terms of mg/L, K_F is adsorption capacity at unit concentration and 1/n is intensity of adsorption. 1/n signifies the type of isotherm that if 1/n = 0, then it is irreversible; 0< 1/n <1 is desirable; and 1/n > 1 is undesirable.

3.5.2. Langmuir isotherm

The Langmuir isotherm [10] is:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (4)$$

where q_e and C_e are defined as before, q_0 is the amount of sorbent required for single-layer capacity per unit mass of the adsorbent in terms of mg/g and the constant b is related to the binding energy in terms of mg/l. The basic characteristic of a Langmuir isotherm is a non-dimensional constant called the equilibrium parameter (R_L) [11], which can be defined through the following equation:

$$R_L = \frac{1}{(1 + bC_0)} \quad (5)$$

In the above equation, C_o is the initial concentration of dye in terms of mg/L; R_L indicates the type of isotherm according to which if R_L = 0, it is irreversible; 0< R_L <1 is desirable; R_L=1 is linear; and R_L > 1 is undesirable [12-13].

3.5.3. Temkin isotherm

The Temkin model [14-15] is another adsorption isotherm model constructed to describe the adsorption phenomenon. The corresponding equation can be expressed as follows:

$$q_e = (\frac{RT}{b})LnA + (\frac{RT}{b})LnC_e \quad (6)$$

$$\frac{RT}{b} = B \quad (7)$$

$$q_e = B_T LnA_T + B_T LnC_e \quad (8)$$

In the above equation, A is in terms of L/gr and B is in terms of J/mol. They are both Temkin's constants which are determined by plotting q_e versus LnC_e. The parameters of the Langmuir, Freundlich and Temkin isotherms and the regression correlation coefficients (R^2) are listed in Table 1. According to Table 1, the adsorption was better fitted by Langmuir (R^2 = 0.998–0.999) when compared to Freundlich (R^2 = 0.953–0.941) and Temkin (R^2 = 0.911–0.977) models. Thus, adsorption happened in a single layer or on a fixed number of adsorption sites in the surface of the adsorbent. Also, all locations had the same adsorption energy and were based on the assumption that the adsorbent structure was homogeneous.

Table 1. Isotherm coefficients of Erythrosine Dye adsorption

	Langmuir model		
b (L/mg)	Q_0 (mg/gr)	R^2	Adsorbent
0.2329	101	0.998	Ziziphus nummularia
0.1551	17.857	0.999	Sorghum
	Freundlich model		
n	K_f (mg/g)	R^2	Adsorbent
1.5723	3.4452	0.953	Ziziphus nummularia
1.675	2.846	0.941	Sorghum
	Temkin model		
B	A	R^2	Adsorbent
43.52	1.642	0.9107	Ziziphus nummularia
3.748	1.546	0.9774	Sorghum

3.6. Kinetic studies

The term 'kinetic' shows the motion or the change. In the present study, kinetics refers to the rate of a reaction as the change in the concentration of the reactant or product over time. Kinetic tests are usually performed at several concentrations of adsorbent. By conducting kinetic experiments under different conditions, the contributory factors in the adsorption rate and adsorption rate-limiting step can be identified. For the analysis of the adsorption kinetics, the first and second order kinetics models can be used.

3.6.1. First order kinetic model

To express the adsorption rate of the dissolved substances from the aqueous solution, the first equation is employed. The equation can be stated as follows:

$$\frac{dq}{dt} = K_1(q_e - q_t) \tag{9}$$

By integrating both sides of the above equation for t = 0 to t = t and q = 0 to q = q_e as boundary conditions, the following linear form is obtained [16]:

$$Ln(q_e - q_t) = Lnq_e - K_1 t \tag{10}$$

This equation was applied to describe the adsorption kinetics of different systems.

3.6.2. Second order kinetic model

Another equation for kinetic analysis of adsorption is the quadratic equation, which can be expressed as follows:

$$\frac{dq}{dt} = K_2(q_e - q)^2 \tag{11}$$

K_2 : Quadratic equation rate constant of absorbent (g mol^{-1} min^{-1}). By integrating the above equation for t = 0 to t = t and q = 0 to q = q_i as boundary conditions, the following equation can be obtained [17]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

By plotting t/q_t versus t, a straight line is obtained, from which the slope and the intercept are 1/q_e and 1/$K_2q_e^2$, respectively. Consequently, the equilibrium adsorption capacity, q_e, and the adsorption rate constant can be determined.

3.6.3. Elovich model

The Elovich model is shown as follows [18-19]:

$$q_t = \frac{1}{b} Ln(ab) + \frac{1}{b} Lnt \tag{13}$$

where a is the initial adsorption rate in terms of $mg.g^{-1}.min^{-1}$; b is related to the extent of surface coverage and activation energy for chemisorption(g/mg); and q_t is the amount of the adsorbed dye at time t in terms of mg/g. By plotting q_t versus Ln (t), the values of a and b are obtained.

3.6.4. Richie Kinetic Model

The Richie Kinetic Model is expressed as follows:

$$\frac{1}{q_t} = \frac{1}{K_r q_e t} + \frac{1}{q_e} \tag{14}$$

In the above equation, K_r is the rate constant in terms of min^{-1} whereas q_e and q_t are defined as before. By plotting 1/q_t versus 1/t, the values of q_e and K_r are obtained [20]. The corresponding kinetic parameters obtained from the above models are listed in Table 2. However, the correlation coefficient (R^2) obtained from the second-order adsorption kinetic model was higher than that from the other kinetic models, suggesting that the pseudo-second-order equation was more appropriate to simulate the experimental kinetic data. The pseudo second-order model was based on the assumption that the adsorption rate was linearly related to the square of the number of unoccupied sites and the adsorption rate between adsorbent and adsorbate appeared to be controlled by the chemical adsorption.

Table 2. Calculation of Kinetic parameters for the first and second order reaction

	First order Kinetic model	
R^2	K_1 (min^{-1})	q_e (mg/g)
0.4887	0.00005	65.313
0.6184	13.818×10^{-5}	16.428
	Second order Kinetic model	
R^2	K_2 ($mg.g^{-1}min^{-1}$)	q_e (mg/g)
0.9999	0.05192	35.714
1	0.601	1.535
	Richie Kinetic model	
R^2	K_r (min^{-1})	q_e (mg/g)
0.9783	1.146	36.496
0.9957	1.009	1.529
	Elovich Kinetic model	
R^2	b (g/mg)	a ($mg.g^{-1}.min^{-1}$)
0.9025	0.4455	503.048
0.9278	12.048	1.722

4. Conclusions

To investigate the effect of natural adsorbents of Ziziphus nummularia pyrene and sorghum on the amount of Erythrosine dye removal, several important and influential factors including contact time, dose of adsorbent, dye initial concentration, temperature, and pH were analyzed. Through pH analysis, it was observed that the dye removal for both types of adsorption does not depend on pH; thus, all the tests were performed in neutral pH. With an increase in the adsorbent dosage and also an increase in contact time, the adsorption amount increased. This can be attributed to the fact that as the amount of adsorption dose increased, larger surface was available for removal and more sites could be placed in the environment for adsorption. The analysis of the initial concentration effects indicated that with the increase in the density of the pollutant, the amount of dye removal for the sorghum adsorption decreased while this amount increased for Ziziphus nummularia pyrene. This indicated the different capabilities of natural adsorptions for dye removal. The data obtained from the tests were analyzed using the Langmuir and Fernedlich models. According to the results, the data were best fitted by the Langmuir model.

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