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Removal of Reactive Red 120 from Aqueous Solutions Using Albizia lebbeck Fruit (Pod) Partical as a Low Cost Adsorbent

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ABSTRACT

Synthetic dyes are using extensively in various industries such as textile, leather tanning, plastic, pulp and paper. Since this dyes are mainly toxic and even carcinogenic, discharging dye containing wastewater into the environment generates serious environmental and health consequences. Therefore, in this research investigated and evaluated the removal effect of Reactive Red 120 (RR 120) from aqueous solutions using Albizia lebbec fruit (pod) partical as a low cost adsorbent to decline mentiined undesirable consequences .In past batch adsorption investigations carried out to study various parameters including contact time, initial concentration of Reactive Red 120, pH, and adsorbent dosage. The concentration of dye was measured using a UV-vis Spectrophotometer at the wavelength of 520 nm. For analyzing data equilibrium, used from Freundlich and Langmuir isotherm models. It was found that Langmuir isotherm (R^2=0.9992 and q_m =1.45 mg/g) is well fitted with our data. According to thermodynamic analyzing, the process exothermic and inherent spantaneous that's it: ΔH^o=9.75 J.mol^{-1}and ΔS^o=38.13 J.mol^{-1}K^{-1}.

Keywords: Reactive Red 120; Adsorption; Thermodynamic; Albizia lebbeck fruit (pod) partical

INTRODUCTION

Dyes due to natural coloring have a pollutant appearance and destroys the transparency and aesthetic quality of surface waters even at relatively low concentration [1-4]. Dye and dye stuffs are extensively used in various areas such as textile, plastic, food, cosmetic, carpet and paper industries. Wastewaters of these industries contain dye with metals, salts, and other chemicals which may be toxic for aquatic environment. Other charges of such wastes, damaging to water sources and ecological balance and affects photosynthetic activity. Hence, the presence of dyes in wastewaters is a major environmental problem as they as are generally resistant to degradation by biological treatment methods. Textile wastewater contaminated with azo reactive dyes needs to be treated by physical and chemical means before discharging. Azo dyes account for about 70% of dyes used in the textile industry, and since dyes are stable, recalcitrant and even potentially carcinogenic and toxic, their released into the environment that poses serious environmental, aesthetical and health consequences [5-9]. Many investigations have been reported application of various procedures for the removal of dyes from water and wastewater including biological processes, combined chemical and

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biochemical processes, chemical oxidation, adsorption, coagulation, and membrane treatments [10-13].

The adsorption of Reactive Red 120 onto Albizia lebbeck fruit (pod) partical as a low cost adsorbant was studied in batch equilibrium conditions. The effects of different parameters including pH, initial ion metals concentrated, contact time, corn cob dosage and temperature were investigated. Langmuir and Freundlich isotherm models were used to analyze the equilibrium data.

EXPERIMENTAL

Apparatus and Materials

An AA 680 model atomic absorption spectrometer (Shimadzu Co.) was used to measure the concentration of Reactive Red 120 in the studied solutions, a 820 A model pH meter (Metrohm Co.) was used to measure pH of solutions and a thermostatic orbit incubator shaker neolab model (India) was used to measure contact time in the solutions. All chemical materials used in this study were of analytical grade. Albizia lebbeck fruit (pod) partical prepared by chemical activation with KOH was characterized as cobalt nitrate, and purchased from Merck Company.

Batch Adsorption Experiments

Batch adsorption experiments were carried out to determine the Reactive Red 120 adsorption isotherm onto Albizia lebbeck fruit (pod) partical and its thermodynamic properties. Reactive Red 120 stock solution (100 mg.L^{-1}) was prepared by dissolving the appropriate quantity of Reactive Red 120 in deionized water. Adsorption isotherms were obtained by using initial Reactive Red 120 concentration, M_o, and its equilibrium concentration, M_e at 298 K. The effect of pH on the Reactive Red 120 adsorption onto Albizia lebbeck fruit (pod) partical was evaluated in a pH range of 2-8. The pH of solutions was adjusted by 0.1 M HCl or 0.1 M NaOH solutions. For every experiment, 100 ml of the solution with Reactive Red 120 concentration of 10 mg.L^{-1} was mixed with 50 mg of Albizia lebbeck fruit (pod) partical in a 250 ml glass conical flask which was shaken in a thermostatic orbit shaker at 220 rpm for 60 min. The mixture was filtered through a 0.45 μm membrane filter. The filtrate was measured by atomic absorption then, the adsorption percentage (%A) was determined as:

$$\%A_e = \frac{A_0 - A_e}{A_0} \times 100 \qquad (1)$$

Q_e, amount adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}) was calculated using the following equation. Where M_o and M_e are the initial and final concentrations of Reactive Red 120 in solution (mg L^{-1}), respectively.

$$Q_e = \frac{(M_0 - M_e)V}{W} \qquad (2)$$

where W is the mass of Albizia lebbeck fruit (pod) partical (g) and V is the volume of the solution (L). To evaluate the thermodynamic properties of the adsorption process, 0.3 g of Albizia lebbeck fruit (pod) partical was added into the 100 ml solution with pH of 3.0 and initial Reactive Red 120 concentration ranging from 50 mg. L^{-1} in every experiment. Each solution was shaken continuously for 60 min [9-11].

RESULTS AND DISCUSSTON

The Effect of pH

Solution pH is one of the most important parameters to determine [7-14]. Batch studies at different pH (2-8) were conducted by soaking the adsorbent in 50 mg.L^{-1} of Reactive Red 120 in each microcosm. Each container was agitated

(156 rpm) for 1 h at 25°C. Table 1 and fig. 1 illustrate the effect of the pH of the solution on the adsorption percentage of Reactive Red 120, adsorbed onto Albizia lebbeck fruit (pod) partical. The best results were obtained at pH=3 for Reactive Red 120.

Table 1. The effect of initial pH of the solution on the adsorption percentage (%A) of RR 120 (M_o=50 mg.L^{-1}, $W_{Albizia\ lebbeck\ fruit}$ =1 g, T=298 K, t_c=60 min)

pH	%Ae
2	83.21
3	97.00
4	84.28
5	81.03
6	79.56
7	78.30
8	74.21

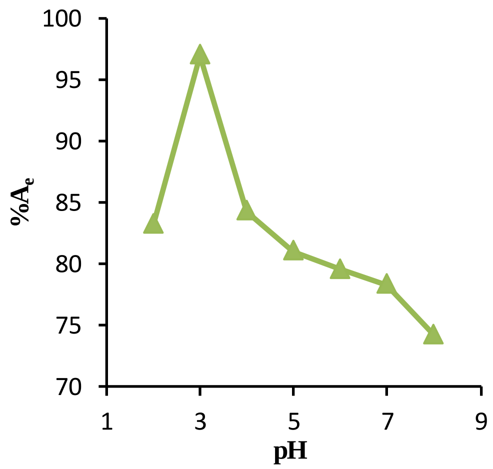

Fig. 1. The effect of initial pH of the solution on the adsorption percentage of RR 120 (M_o=50 mg.L^{-1}, W $_{Albizia\ lebbeck\ fruit}$ =1 g, T=298 K, t_c=60 min).

The Effect of Adsorbent Dosage

Microcosms with different adsorbent doses (0.1-0.7 g) were amended with 50 mg.L^{-1} of Reactive Red 120 in aqueous solutions. The rate of adsorption was monitored at the following optimum conditions: pH of 3, for 1 h at 25°C.The effect of Albizia lebbeck fruit (pod) partical dosage on the adsorption percentage of Reactive Red 120 is shown in table 2 and plotted in fig. 2.

Table 2. The effect of Albizia lebbeck fruit dosage on the adsorption percentage (%A) of RR 120 (Mo=50 mg.L^{-1}, pH=3, T=298 K, tc=60 min)

$W_{Albizia\ lebbeck\ fruit}$/g	%Ae
0.1	60.61
0.2	62.30
0.3	66.50
0.4	65.81
0.5	65.81
0.6	65.81
0.7	65.81

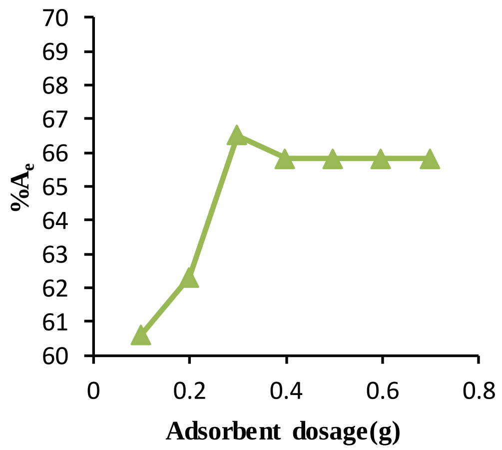

Fig. 2. The effect of Albizia lebbeck fruit dosage on the adsorption percentage (%A) of RR 120 (Mo=50 mg.L^{-1}, pH=3, T=298 K, tc=60 min).

The Effect of Temperature

The same preparation was made, except for the varying temperature conditions. The microcosm which was maintained at pH 3 was incubated at different temperatures (25-65 °C) for a period of 60 min. Table 3 and fig. 3 show that the adsorption percentage decreases with increasing temperature. Therefore, it may be concluded that the interaction between Reactive Red 120 and Albizia lebbeck fruit (pod) partical is exothermic in nature. Adsorption decrease may be due to the increase of the electrostatic repulsion between the Reactive Red 120 [10-12].

Table 3. The effect of temperature on the adsorption percentage (%A) of RR 120 (M_o=50 mg.L^{-1}, W $_{Albizia\ lebbeck\ fruit}$ =0.3 g, pH=3, t_c=60 min)

T/K	%Ae
298	65.23
308	68.92
318	71.00
328	73.00
338	72.32

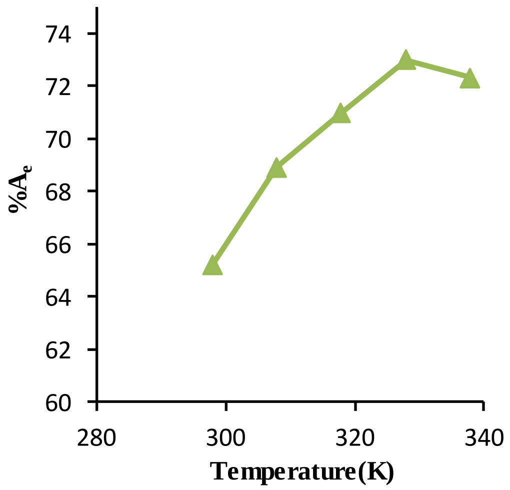

Fig. 3. The effect of temperature on the adsorption percentage of cobalt ion onto Albizia lebbeck fruit (M_o=50 mg.L^{-1}, W $_{Albizia\ lebbeck\ fruit}$ =0.3g, pH=3, t_c=60 min).

The Effect of Contact Time

The effect of contact time, tc, on the adsorption percentage of Reactive Red 120 onto Albizia lebbeck fruit (pod) partical is shown in table 4 and plotted in fig. 4. A rather fast uptake occured during the first 25 min of the adsorption. It became slower as the adsorbed amount of Reactive Red 120 reached its equilibrium value. It can be seen that the adsorption process is rapid due to the availability of very active sites on the adsorbent surface at initial stage. This may be due to the special one atom layering the structure of Reactive Red 120 [13]. At first, adsorption capacity was a slow process then, increased rapidly, it attained equilibrium and saturation gave constant adsorption value. The optimum contact time was obtained at 30 min.

Table. 4. The effect of contact time, t_c, on the adsorption percentage (%A) of RR 120 (M_o=50 mg.L^{-1}, W $_{corn\ cob}$ =0.3 g, pH=3, T=328 K)

tc/min	%At
5	73.42
10	75.60
15	79.56
20	81.32
25	82.60
30.	84.16
35.	84.16

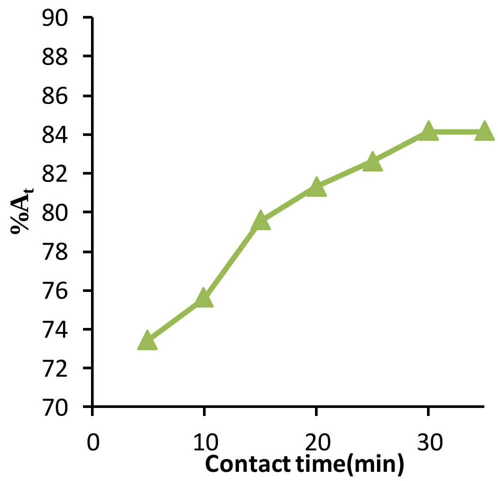

Fig. 4. The effect of contact time on the adsorption percentage of RR 120 onto Albizia lebbeck fruit (M_o=50 mg.L^{-1}, W $_{Albizia\ lebbeck\ fruit}$ =0.3 g, pH=3, T=328 K).

Adsorption Isotherm

An adsorption isotherm is characterized by certain constant values, which express the surface properties of the adsorbent and so on the percentages adsorption of Reactive Red 120 onto Albizia lebbeck fruit (pod) partical as a function of initial concentration of Reactive Red 120, shown in table 5.

Table 5. Adsorption data for RR 120 adsorption onto Albizia lebbeck fruit (pH=3, t_c=30 min, T=328 K, $W_{\text{Albizia lebbeck fruit}}$ =0.3 g)

Parameter	Value			
M_0 /mg L^{-1}	10	20	30	40
%A	51.80	62.00	68.40	75.30
Me / mg L^{-1}	4.82	7.60	9.48	9.88
Q_e / mg g^{-1}	0.86	2.07	3.42	5.02
LnMe	1.60	2.03	2.25	2.30
LnQe	-0.15	0.73	1.23	1.61
1/Me /L mg^{-1}	0.21	0.13	0.11	0.10
$1/Q_e$ /g mg^{-1}	1.20	0.50	0.30	0.20

Adsorption isotherms represent the relationship of the amount of dyes adsorbed with the adsorbent dose. These provide information about the mechanism of adsorption and the adsorptivity of the composite towards the dyes of interest. In this study, Langmuir and Freundlich isotherms were investigated. The Freundlich isotherm is an empirical equation used to model multilayer adsorption on heterogenous adsorbents, with the assumption that sites of adsorption exponentially increase with an increase in the heat of absorption. The linear form of Freundlich isotherm is given by the equation [5-10]:

$$LnQ_e = LnP + \frac{1}{n} LnC_e \quad (3)$$

where P (L/g) and n are the Empirical Freundlich constant or capacity factor and adsorption intensity. The values of P and n are determined from the intercept and slope of a plot of Ln Q_e versus Ln Me (table 5 and fig. 5) that were used to calculate the values of P and n (table 6)).

Monolayer adsorption onto the surface of the adsorbent is assumed by the Langmuir isotherm. In this model, it is assumed that binding of dyes onto the adsorbent is homogeneous, and that adsorption will no longer take place once equilibrium has been established. Also, this model predicts an equal distribution of dyes between the liquid and solid phases. The linear form of the Langmuir isotherm is described by the following equation [5-10]:

$$\frac{1}{Q_e} = \frac{1}{bQ_m}\left(\frac{1}{C_e}\right) + \frac{1}{Q_m} \quad (4)$$

where Q_m (mg g^{-1}) is the maximum dyes to adsorb onto 1 g adsorbent and b (L/mg) is the Langmuir constant related to adsorption capacity and energy of adsorption. The slope and intercept of plot of $1/Q_e$ versus $1/M_e$ are shown in fig. 6 that were used to calculate the values of b and Q_m (table 6).

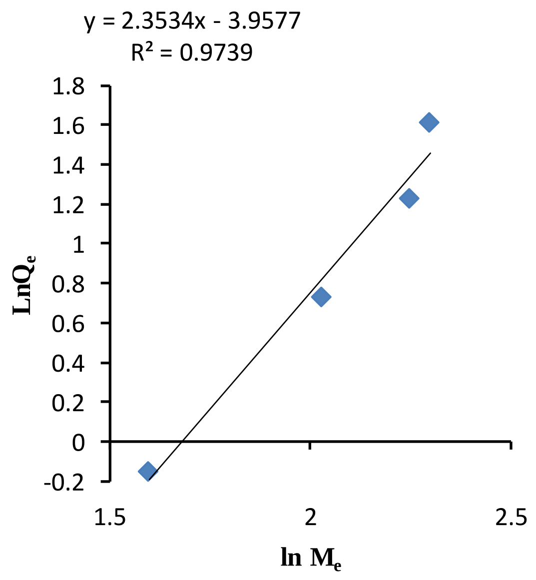

Fig. 5. Freundlich isotherm for RR 120 adsorption onto Albizia lebbeck fruit.

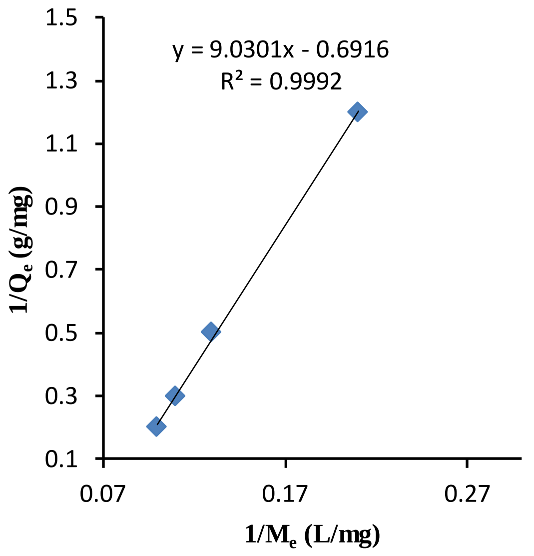

Fig. 6. Plot of $(1/Q_e)$ versus $(1/M_e)$ for RR 120 adsorption onto Albizia lebbeck fruit.

Table 6. The resultant values for the studied isotherms in connection to RR 120 adsorption onto Albizia lebbeck fruit at 328 K

Isotherm	Parameter	Value
	P /(L mg^{-1})	0.0200
Freundlich	n	0.4300
	R^2	0.9739
	b / (L mg^{-1})	0.0800
Langmuire	Q_m /(mg g^{-1})	1.4500
	R^2	0.9992

Thermodynamic Parameters

The thermodynamic parameters of adsorption process can be determined from the variation of thermodynamic equilibrium constant, K_o [10-18], where K_o is defined as follows:

$$K_0 = \frac{a_S}{a_e} = \frac{Q_e}{M_e} = \frac{M_0 - M_e}{M_e} \quad (5)$$

where a_S and a_e are the activity of adsorbed Reactive Red 120 and the activity of Reactive Red 120 in solution at equilibrium, respectively. The adsorption standard free energy change (ΔG^0) is calculated according to:

$$\Delta G^{0} = -RTLnK_0 \quad (6)$$

The average standard enthalpy change (ΔH^o) and the average standard entropy change (ΔS^o) are obtained from the plot of equation (7):

$$LnK_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

In order to obtain the values of ΔH^o and ΔS^o, LnK_o against 1/T was plotted (table 7, fig. 7).

Table 7. The effect of temperature on K_o values (M_o=50 mg.L^{-1}, pH=3, $W_{Albizia\ lebbeck\ fruit}$ =0.3 g, t_c=30 min)

T/K	LnK
298	0.63
308	0.80
318	0.90
328	1.00

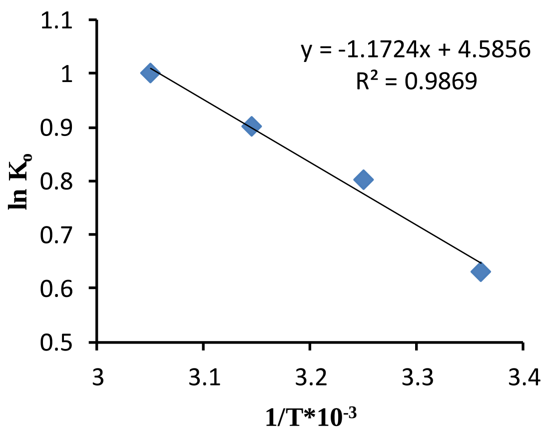

Fig. 7. The effect of temperature on equilibrium constant values.

Table 8. Thermodynamic parameters for adsorption RR 120 onto Albizia lebbeck fruit

T /K	ΔG^o/kJ.mol^{-1}	ΔH^o/kJ.mol^{-1}	ΔS^o /J.mol^{-1} K^{-1}
298	-1.60	9.75	38.13
308	-2.05		
318	-2.40		
328	-2.73		

The obtained values of thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) are listed in table 8. The positive value of ΔH^0 suggests that the interaction of adsorbed Reactive Red 120 with Albizia lebbeck fruit (pod) partical is an endothermic process, which is supported by the decreasing of the amount of Reactive Red 120 adsorption with increasing temperature. The positive value of ΔS^o showed an increased randomness during Reactive Red 120 adsorption. The negative values of ΔG^0 reveal the fact that the adsorption process is spontaneous.

CONCLUSION

The results of this work showed that Albizia lebbeck fruit (pod) partical is an effective adsorbent for the removal of Reactive Red 120 from aqueous solutions. Results showed that the Langmuir isotherm model was well fitted with adsorption data, thus, indicating the applicability of monolayer coverage of Reactive Red 120 on Albizia lebbeck fruit (pod) partical surface. Thermodynamic analyzing revealed that the adsorption process is endothermic and spontaneous in nature.

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