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Elimination of Reactive Red 120 (RR-120) Dye from Aqueous Solution by the using of Date Cores Particles

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ABSTRACT

In recent years, textile wastewater treatment has been of special importance due to the potential toxicity, cancinogenic activity, and mutagenicity. The purpose of this study was evaluation of the removal of Reactive Red 120 (RR-120) dye from aqueous solution by date Palm (Phoenix dactylifera) seed particles. Batch adsorption studies carried out to study various parameters included 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. Freundlich and Langmuir isotherms were used to analyze the isotherm. it was found that Langmuir isotherm (R^2=0.9991 and q_m =1.68 mg.g^{-1}) is well fitted with our data. According to Thermodynamic analysis, the process exothermic and natural (ΔH^o= -0.006 J.mol^{-1} and ΔS^o= -13.9 J.$mol^{-1}K^{-1}$). To evaluate the mechanism of adsorption, pseudofirst order and second order kinetic models were used. The adsorption mechanism was found fit the second order (K_2= 0.4 mg.g^{-1}.min^{-1} and R^2= 0.999).

Keywords: Reactive Red 120; Adsorption; Thermodynamic; Date Cores Particles; Kinetic

INTRODUCTION

Synthetic dyes are extensively used in textile, food, paper and cosmetic industries. Dyes have long been used in different types of industries such as, dyeing, textiles, paper, plastics, leather and cosmetics. Wastewaters of these industries contain dye with metals, salts, and other chemicals which may be toxic to aquatic environment. Charges of such wastes in water sources causes damage to ecological balance and affects photosynthetic activity. Hence, the presence of dyes in wastewaters is a major environmental problem as they 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, colorant, and even potentially carcinogenic and toxic, their release into the environment poses serious environmental, aesthetical and health problems [1-8]. Many investigations have been reported using different methods for the removal of dyes from water and wastewater including biological processes, combined chemical and biochemical processes, chemical oxidation, adsorption,

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coagulation, and membrane treatments. Reactive dyes are typically azo-based chromophores combined with different types of reactive groups, e.g., vinyl sulfone, chlorotriazine, trichloropyrimidine and difluorochloropyrimidine. They have poor fixation rates and, hence, it may be hard to remove them from wastewaters because of their low biodegradability and weak absorption in activated sludge. Furthermore, reactive dyes are, in general, the most problematic among other dyes, as they tend to pass through conventional treatment systems unaffected. Furthermore, reactive dyes are resistant to natural biodegradation, due to the aromatic rings in their structure. Among reactive dyes in textile industry, RR-120 is one of the frequently used ones, and is a potential threat to the aquatic environment due to its poor biodegradability [1-13].

The adsorption of Reactive Red 120 onto date cores particles as a low cost adsorbant was studied in batch equilibrium conditions. The effects of different parameters including pH, initial metal ion concentration, contact time, date cores particles dosage and temperature were investigated. The Freundlich and Langmuir adsorption isotherms were used to investigate the adsorption process. Kinetic study was also carried out to evaluate the order of adsorption.

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. Date cores particles 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 corn cob 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, C_o, and its equilibrium concentration, C_e at 298 K. The effect of pH on the Reactive Red 120 adsorption onto date cores particles 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 date cores particles 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 C_0 and C_e are the initial and final concentrations of Reactive Red 120 in solution (mg L^{-1}), respectively [1-14].

$$Q_e = \frac{(C_0 - C_e)V}{W} \qquad (2)$$

where W is the mass of date cores particles (g) and V is the volume of the solution (L). To evaluate the thermodynamic properties of the adsorption process, 0.5 g of date cores particles 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 20 min [1-14].

RESULTS AND DISCUSSTON

The Effect of pH

Solution pH is one of the most important parameters to determine. 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^{o}C. Table 1 illustrate the effect of the pH of the solution on the adsorption percentage of Reactive Red 120, adsorbed onto date cores particles. 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 (C_o=50 mg.L^{-1}, date cores particles =1 g, T=298 K, t=60 min)

pH	%Ae
2	63.40
3	66.70
4	25.21
5	19.30
6	10.72
7	6.36
8	2.75

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^{o}C.The effect of date cores particles dosage on the adsorption percentage of Reactive Red 120 is shown in table 2.

Table 2. The effect of date cores particles dosage on the adsorption percentage (%A) of RR-120 (Co=50 mg.L^{-1}, pH=3, T=298 K, t=60 min)

$W_{\text{date cores particles}}$ /g	%Ae
0.1	36.20
0.2	38.90
0.3	42.12
0.4	48.70
0.5	49.60
0.6	47.80
0.7	47.30

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 ^{o}C) for a period of 60 min. Table 3 show that the adsorption percentage decreases with increasing temperature. Therefore, it may be concluded that the interaction between Reactive Red 120 and date cores particles 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 (C_o=50 mg.L^{-1}, $W_{\text{date cores particles}}$ =0.5 g, pH=3, t=60 min)

T/K	%Ae
298	67.80
308	66.50
318	64.80
328	63.80
338	62.21

The Effect of Contact Time

The effect of contact time, t on the adsorption percentage of Reactive Red 120 onto date cores particles is shown in table 4. A rather fast uptake occured during the first 15 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 [2-15]. 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 20 min.

Table. 4. The effect of contact time, t, on the adsorption percentage (%A) of RR-120 (C_o=50 mg.L^{-1}, $W_{\text{date cores particles}}$ =0.5 g, pH=3, T=298 K)

t/min	%At
5	65.90
10	68.50
15	71.20
20	72.40
25	72.40
30.	72.40

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 date cores particles as a function of initial concentration of Reactive Red 120, shown in table 5.

Table 5. Adsorption data for RR-120 adsorption onto date cores particles (pH=3, t=20 min, T=298 K, $W_{\text{date cores particles}}$ =0.5 g)

Parameter	Value			
C_0 /mg L^{-1}	10	20	30	40
%A	12.90	12.60	14.40	16.90
Ce / mg L^{-1}	4.82	7.60	9.48	9.88
Q_e / mg g^{-1}	0.13	0.27	0.43	0.68
lnCe	2.2	2.85	3.25	1.48
lnQe	-2.05	-1. 3	-0.84	-0.39
1/Ce /L mg^{-1}	0.12	0.06	0.04	0.03
1/Q_e /g mg^{-1}	7.75	3.68	2.32	1.48

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 [5-20]:

$$lnQ_e = lnP + \frac{1}{n} lnC_e \qquad (3)$$

where P (L.g^{-1}) 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 Ce (table 5 and fig. 1) 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 [5-20]:

$$\frac{1}{Q_e} = \frac{1}{bQ_m}(\frac{1}{C_e}) + \frac{1}{Q_m} \qquad (4)$$

where Q_m (mg g^{-1}) is the maximum dyes to adsorb onto 1 g adsorbent and b (L.mg^{-1}) is the Langmuir constant related to adsorption capacity and energy of adsorption. The slope and intercept of plot of $1/Q_e$ versus $1/C_e$ are shown in fig. 2 that were used to calculate the values of b and Q_m (table 6).

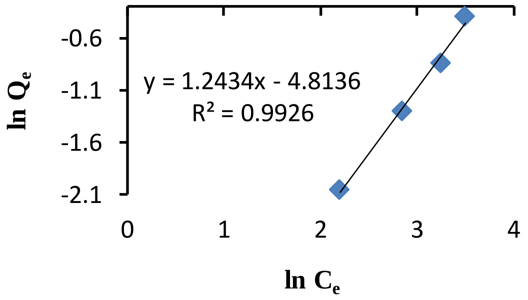

Fig. 1. Freundlich isotherm for RR-120 adsorption onto date cores particles.

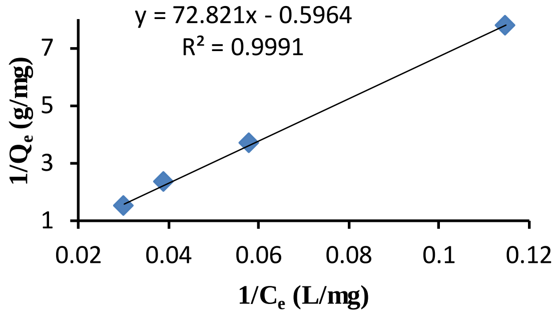

Fig. 2. Langmuir isotherm for RR-120 adsorption onto date cores particles.

Table 6. The resultant values for the studied isotherms in connection to RR-120 adsorption onto date cores particles at 298 K

Isotherm	Parameter	Value
	P /(L mg^{-1})	0.00812
Freundlich	n	0.80000
	R^2	0.99260
	b / (L mg^{-1})	0.00820
Langmuir	Q_m /(mg g^{-1})	1.68000
	R^2	0.99910

Thermodynamic Parameters

The thermodynamic parameters of adsorption process can be determined from the variation of thermodynamic equilibrium constant, K_o [2-21], where K_o is defined as follows:

$$K_0 = \frac{a_S}{a_e} = \frac{Q_e}{C_e} = \frac{C_0 - C_e}{C_e} \qquad (5)$$

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:

$$\Delta G^0 = -RTlnK_0 \qquad (6)$$

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

$$lnK_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (7)$$

In order to obtain the values of ΔH^o and ΔS^o, lnK_o against 1/T was plotted (table 7, fig. 3).

Table 7. The effect of temperature on K_o values (C_o=50 mg.L^{-1}, pH=3, $W_{\text{date cores particles}}$ =0.5 g, t=30 min)

T/K	lnK
298	0.794
308	0.690
318	0.610
328	0.570

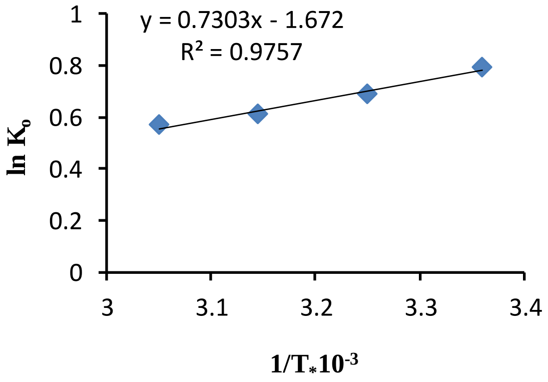

Fig. 3. The effect of temperature on equilibrium constant values.

Table 8. Thermodynamic parameters for adsorption RR-120 onto date cores particles

T /K	ΔG°/kJ.mol^{-1}	ΔH°/J.mol^{-1}	ΔS° /J.mol^{-1} K^{-1}
298	-1.97	-0.006	-13.900
308	-1.77		
318	-1.61		
328	-1.55		

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 date cores particles is an exothermic 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.

Adsorption Kinetics

Various models have been used to analyze the kinetics of the sorption process. The pseudo-first-order rate equation of the Lagergrenis, one of the most widely used for the biosorption of solutes from a liquid solution and is represented as equation (8):

$$\ln(1-\frac{Q_t}{Q_e}) = -K_1 t \ldots \qquad (8)$$

Another model for the analysis of biosorption kinetics is pseudo-second-order. The rate law for this system is expressed as equation (9):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e} + \frac{t}{Q_e} \ldots \qquad \ldots(9)$$

where Q_t and Q_e are the mg of solute sorbed/g biosorbent at any time and at equilibrium, respectively, and K_1 and K_2 are the rate constants of pseudo-first-order sorption and pseudo-second-order sorption, respectively. Pseudo first order and pseudo second order kinetics models were tested [3-18].The rate of adsorption process is shown in figs 4 and 5.

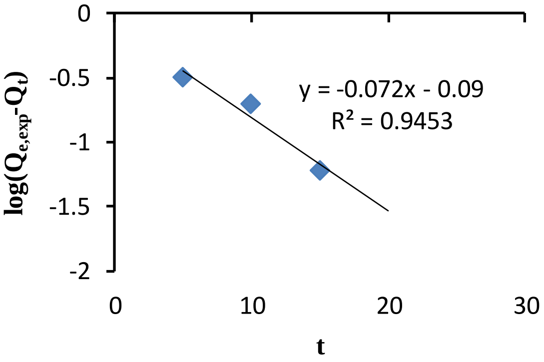

Fig. 4. Pseudo -first -order for adsorption process RR-120 onto date cores particles.

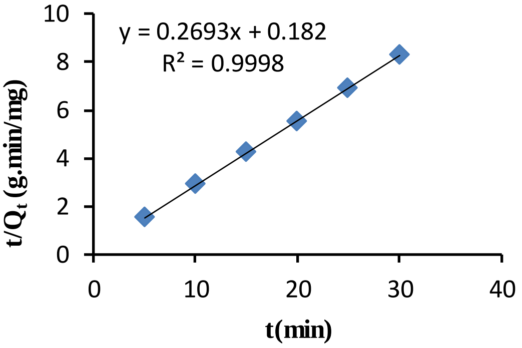

Fig. 5. Pseudo -second -order for adsorption process RR-120 onto date cores particles.

CONCLUSION

The results of this work show that date cores particles is an effective adsorbent for the removal of Reactive Red 120 from aqueous solutions. Results showed that the Langmuir isotherm model was fitted well with adsorption data, thus, indicating the applicability of monolayer coverage of Reactive Red 120 on date cores particles surface. Thermodynamic analysis revealed that the adsorption process is exothermic and spontaneous in nature (ΔH^o= -0.006 J.mol^{-1} and ΔS^o= -13.9 J.mol^{-1}K^{-1}). The results shows that the pseudo second order obtained the better fit for adsorption process Reactive Red 120 onto date cores particles.

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