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Original Article

Reactive Blue 19 Dye Adsorption Behavior on Jujube Stems Powder from Syntetic Textile Wastewater: Isotherm and Kinetic Adsorption Studies

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Abstract

Introduction: Dyes have complicated structures, they are usually toxic and resistant to biological treatment and enter the environment through industrial waste streams. The present study is aimed to review the isotherm and kinetic adsorption studies of Reactive Blue 19 (RB19) dye onto Jujube stems powder from synthetic textile wastewater.

Materials and Methods: This study was conducted in laboratory scale. Synthetic wastewater was prepared with dissolving RB19 in distilled water. The dye concentration was determined by using UV/Vis spectrophotometer at 592 nm. In this study, we investigated the effects of initial dye concentration, pH, adsorbent dose and contact time. For better understanding of the adsorption process, the experimental data were analyzed with Langmuir and Freundlich isotherm models and kinetic studies.

Results: The results showed that removing RB19 dye with Jujube stems powder as a natural biosorbent had the best efficiency in alkaline environment (pH=10) and by increasing the pH from 3 to 10, the dye removal efficiency increased. By decreasing the initial dye concentration and increasing the time and adsorbent dose, dye removal efficiency increased. In this study, the best fit of the adsorption isotherm data was obtained using the Langmuir model. Kinetic analysis of our results showed that the results well fitted the pseudo-second-order reaction.

Conclusion: We can conclude that Jujube stems powder could be used as a biosorbent for dye removal from aqueous solutions.

Keywords: Adsorption, Jujube Stems Powder, Reactive Blue 19, Kinetics

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Introduction

Industrial development in recent years has caused many problems including pollution[1]. These pollutants include dyes, heavy metals, organic pollutants, etc [2]. Dyes are generally used in textile, paper, cosmetics, food, pharmaceuticals, and leather industries [3,4,5,6]. Due to the large volume of water consumption in textile industry, the production of huge volumes of wastewaters is inevitable [7]. Dyes can be classified into three categories: anionic (direct, acid, and reactive dyes), cationic (basic dyes) and non-ionic [8, 9, 10]. Dyes cause a lot of problems i.e. skin allergies, skin irritations, cancer, mutation, etc [11]. The methods used to remove dye from wastewater are biological coagulation, flocculation, deposition, adsorption, membrane filtration, ozonation, electrochemical techniques, etc [12,13]. However, these methods are still very expensive in developing countries. Generally, physical methods, including adsorption, are effective for removing dyes without producing unwanted by-products [14]. Among all treatment options, adsorption appears to have considerable potential for the removal of color from industrial effluents [12].

Adsorption is found to be an efficient process for the treatment of effluents, because of its low initial cost, easy operation, flexibility, and simplicity of the design [15,16,17]. In the past few years, efforts have been made to remove toxic substances from wastewaters by using low cost adsorbents like Pineapple stems [18], pine-fruit shell [19], eggshell biocomposite beads [20], rubber wood sawdust [21], rice husk, crushed brick, cedar saw dust, clay, etc [22]. The aim of the present work is introducing a new natural adsorbent in dye removal as an organic pollutant tipical.

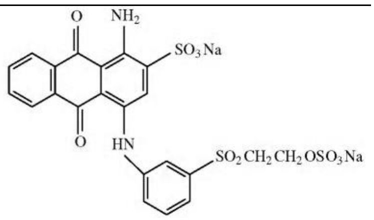
Materials and Methods

Batch experiments were performed in this survey in laboratory scale. The main parameters considered in this study are pH, contact time, initial dye concentration, and adsorbent dose. Absorption of the samples was measured by UV-Vis spectrophotometer, SP-3000 Pulse Model, Japan, and pH was adjusted by HACH pH meter, HQ40d, USA. Reactive Blue 19 dye used in this study was purchased from Dyestar, Germany. The general characteristics of the dye are presented in Table 1. All materials used in this study are purely analytical.

A stock solution of 1000 mg/L was prepared by dissolving an appropriate amount of RB19 in 1000 ml of distilled water.

Jujube stems powder was prepared by boiling and then it was dried at room temperature. For pulverizing the adsorbent, jujube stems were crushed in an electrical mill and sieved by standard sieves (ASTM), (40-60 mesh).

Table 1. General characteristics of Reactive Blue 19 [23]

Chemical structure	
C.I. generic name	C.I.Reactive Blue 19
synonym	Remazol Brilliant Blue R
Molecular Formula	$C_{22}H_{16}O_{11}N_2S_3Na_2$
molecular weight (g/mol)	626.5
wavelength of maximum absorbance (nm)	592

Adsorption studies

Adsorption experiments were carried out by adding some adsorbent to a series of 250 mL Erlenmeyer's flasks. The Erlenmeyer's flasks were then sealed and placed in an orbital shaker (GFL 137) at 120 rpm with a required adsorbent time and different pH (3, 7 and 10). The effect of pH was investigated at initial dye concentration of 25 and 50 mg/L.

pH adjustments have been done using solutions of NaOH and HCl 1 N. The flasks were then removed from the shaker, and all samples were filtered using 0.2 µm membrane filters.

Then the final concentration of dye in the solution was measured at maximum wavelengths of Reactive Blue 19 dye (592 nm) using UV/Vis spectrophotometer.

The amount of dye adsorbed per unit of jujube stems powder mass at equilibrium, q_e (mg/g), was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where C_0 and C_e are the initial and equilibrium concentrations, of the dye solutions in mg/L, respectively, V is the volume of dye solution in liters, and W is the mass of adsorbent used (g) [24]. The percentage of dye removal by adsorbent was calculated using the following equation [25]:

$$R\ (\%) = \frac{C_0 - C}{C_0} \times 100$$

Kinetic studies

Pseudo-first-order kinetic model

Pseudo-first order equation is a simple kinetic analysis of adsorption, given in the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

By applying the initial conditions of t=0 to t and q_t =0 to q_t, it becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

In these equations, k_1 is the pseudo-first-order adsorption rate constant and q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium condition [7,29].

Pseudo-second-order kinetic model

The pseudo-second-order model can be represented by the following equation:

$$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2$$

Where k_2 is the pseudo-second-order adsorption rate constant [7,27].

Isotherm studies

In this study, Langmuir and Freundlich isotherms have been studied. The Langmuir equation is given by the following equation:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

The following equation is a linear form of Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}}$$

In these equations, q_e is the solid phase adsorbate concentration in equilibrium (mg/g), q_{max} is the maximum adsorption capacity on the surface (mg/g), C_e the adsorbate concentration in equilibrium (mg/L) and K_L is the Langmuir constant (L/mg). The essential characteristics of the Langmuir equation can be expressed in a dimensionless factor, R_L, defined as:

$$R_L = \frac{1}{1 + K_L C_0}$$

The Freundlich equation is:

$$q_e = K_F C_e^{1/n}$$

A linear form of the Freundlich equation can be obtained by:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

In these equations, qe and Ce have the same definition and KF is the Freundlich constant (mg/g)(L/mg)1/n and 1/n is the heterogeneity factor [2,7].

Results

Effect of pH

In this study, the initial dye concentration was 25 and 50 mg/l at pH= 4, 7 and 10, respectively and in the presence of 0.6 gr adsorbent dose /100 ml of solution. As shown in Figure 1, by increasing the pH from 3 to 10, the dye removal efficiency increased. The dye removal in initial dye concentration of 25 mg/l for pH= 3, 7 and 10 were 56.8%, 68% and 77%, respectively and in initial dye concentration of 50 mg/l at the same PH levels, the dye removal rates were 48.5%, 55% and 71%, respectively. According to these results, other experiments of this study were carried out at pH=10.

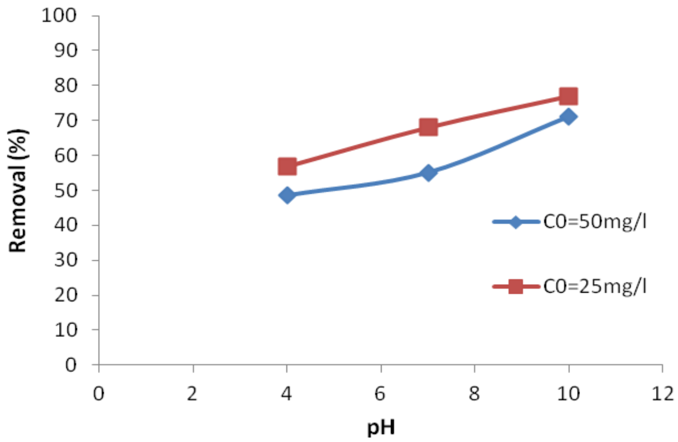


Figure 1. Effect of pH on the RB19 dye removal (initial dye concentration= 25 and 50 mg/l, adsorbent dose = 0.6 gr/100ml, contact time = 24h)

Effect of adsorbent dose

This study was done at initial dye concentration of 25 and 50 mg/l, PH level of 10, and contact time of 24 h. The amounts of adsorbent were 0.2, 0.4 and 0.6 g/100 ml. Figure 2 shows the effect of adsorbent dose on the RB19 dye removal.

The results showed that by increasing adsorbent dose from 0.2 to 0.6 gr/100 mL, the removal efficiency increased. In initial dye concentration of 25 mg/l for adsorbent dose of 0.2, 0.4 and 0.6 gr/100 mL, the dye removal rates were 53%, 76% and 84%, respectively and in initial dye concentration of 50 mg/l for the same adsorbent doses, the dye removal efficiency were 42%, 71% and 80%, respectively.

According to these results, other experiments of this study were carried out at an adsorbent dose of 0.6 g/100 ml.

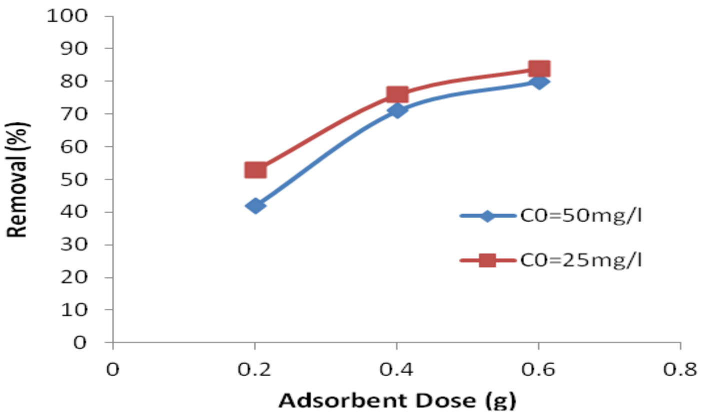


Figure 2: Effect of adsorbent dose on the RB19 dye removal (initial dye concentration = 25 and 50 mg/l and pH=10)

Effects of initial dye concentration and contact time

As shown in Figure 3, by increasing the initial concentration of dye from 25 to 50 mg/l, the removal efficiency of dye decreased. In this study, by increasing the contact time from 15 to 180 min in the initial dye concentration of 25 mg/l, removal efficiency increased from 31% to 65.6% and in the initial dye concentration of 50 mg/L, removal efficiency increased from 24.3% to 59%.

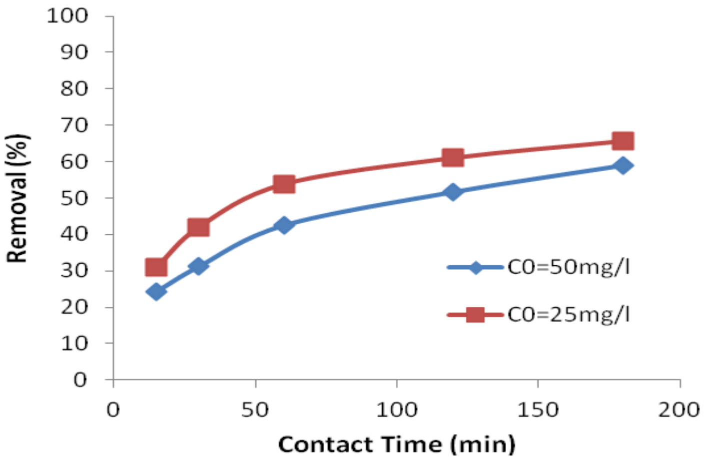


Figure 3. Effects of initial dye concentration (25 and 50 mg/l) and contact time (15 – 150 min) on RB19 dye removal

Adsorption kinetics

To investigate the mechanism of RB19 dye adsorption on jujube stems powder, the pseudo-first-order and pseudo-second-order kinetics were used to find out the adsorption order of reaction. However, they fitted well with second-order reaction. The influence of contact time on dye removal by jujube stems powder is presented in Fig. 4. In this study, R^2 in the pseudo-first-order kinetic for 25 mg/L was (R^2= 0.9329), (R^2= 0.9896) for 50 mg/L of RB19 dye, and in the pseudo-second-order kinetic (R^2= 0.9629) for 25 mg/L and (R^2= 0.9934) for 50 mg/L of RB19 dye.

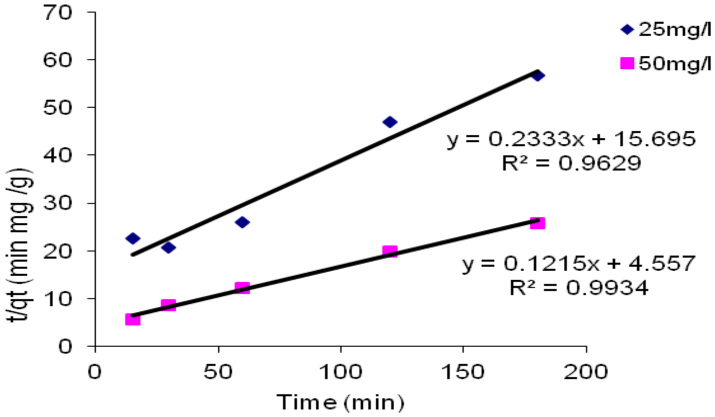


Figure 4. Kinetic results (pseudo-second-order) for the mechanism of RB19 dye (25 and 50 mg/L) adsorption on jujube stems powder

Adsorption isotherms

Adsorption characteristics of Langmuir and Freundlich isotherms are shown in Table 2. In this study, the best fit of the adsorption isotherm data was obtained using the Langmuir model.

Table 2. Values of Langmuir and Freundlich isotherm parameters (C_0=25 and 50 mg/L, pH=10, contact time=24hr)

Langmuir isotherm	**25 mg/l**	**50 mg/l**	**Freundlich isotherm**	**25 mg/l**	**50 mg/l**
b (L/mg)	10.2	18.18	$K(mg/g).(L/mg)^{1/n}$	1.361	2.163
q_{max}(mg/	0.76	0.9	1/n	0.4407	0.455
R^2	0.9	0.91	R^2	0.87	0.89
R_L	0.0039	0.0011			

Discussion

Studying the effects of pH, we found that by increasing pH, the dye removal efficiency increased. In other studies, the dye adsorption was also pH-dependent.

The pH value of the dye solution plays an important role in the whole adsorption process, and particularly influences the adsorption capacity [13]. It affects the ionization degree of the dye and the surface properties of the biosorbent [20].

The interaction between dye and adsorbent depends on the structure of dyes and absorbent. The dyes are complex organic compounds with different functional groups and unsaturated bonds, so they show different levels of ionization at different pHs. Adsorbent surface charge also depends on the pH, because the adsorbent surface has bio-polymers with different functional groups [32].

The study of Gok et al, showed that the amount of adsorbed dye onto modified bentonite as an adsorbent, decreases as the pH increases from 1.5 to 7 and after pH=7, a small increase is observed in adsorption [28].

Sun et al reported that pH had a significant effect on the uptake of dyes. They showed that the removal percentages of reactive red 23 and reactive blue 171 dyes were maximum at alkaline pH (7.5-8.5) [29].

Lima et al considered the application of Brazilian pine-fruit shell as a biosorbent to remove reactive red 194 dye from aqueous solution, they reported that the amount of dye uptake decreases with increasing the pH solutions from 2.5 up to 6. For pH levels above 4.5, practically no dye was adsorbed [19].

Elkady et al have investigated the assessment of the adsorption kinetics, equilibrium and thermodynamic for the potential removal of reactive red dye using eggshell biocomposite beads. They reported that the dye removal decreased from 59.3% to zero after 180 min when pH increased from 1 to 10 [20].

Gulnaz et al (2011) showed that a decrease in pH from 5 to 1 caused a significant increase in the amount of reactive red 198 dye adsorbed by Potamogeton crispus biomass [30]. Also, in the study of Amin, it was shown that the dye adsorbed by different types of carbons was higher at lower pHs. In his study, the optimum pH was attained at pH of 1. As the pH of the solution increased, the adsorbed dye decreased considerably [12].

However, our study showed different results and the adsorbed dye on jujube stems powder in the present study increased by increasing pH, while the best pH was 10.

The results of the present study showed that by increasing the adsorbent dose, the removal efficiency increased. Increasing dye removal efficiency with adsorbent dose could be attributed to increasing adsorbent surface areas and enhancing the number of available biosorption sites for adsorption [19,20,32].

In a study by Garg et al, it was shown that the adsorption efficiency increased from 59.6% to 99.8%, as the adsorbent dose increased from 0.2 to 1 g/100 mL at 250 mg/L malachite green dye concentration after the equilibrium time [31]. Gok et al found that uptake of reactive blue 19 dye increased as the adsorbent was added. In their study, the maximum dye removal occured at the absorbent level of 0.025 g/50mL[28]. Lima et al observed that the removal of the dyes was attained for biosorbent dosage of at least 5 g/L. For higher biosorbent dosages, the dye removal remained almost constant [19]. Akar et al found that when the biomass concentration increased from 0.2 to 3 g/L, the biosorption percentage increased from 2.78% to 84.70% [32]. Similar findings have also been reported by other researchers [33,34].

In this survey, studying the effect of initial dye concentration and contact time showed that by increasing the initial dye concentration, the dye removal efficiency decreased and by increasing the contact time, RB19 dye removal efficiency increased. It was demonstrated that with increasing time, the dye adsorption increased and reached a constant value at equilibrium time [20].

Gok et al, in a study of adsorption behavior of a textile dye of reactive blue 19 from aqueous solutions onto modified bentonite, have reported that the adsorption capacity increased by increasing the contact time and the dye removal was dependent on the dye concentration [28]. Sun et al (2010) reported that dye removal efficiency was higher for low initial dye concentration because of availability of unoccupied binding sites on the adsorbents [29]. Amin (2008) has investigated the removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith. In his study, dye removal decreased with increasing of initial dye concentration [12]. Santhy and Selvapathy (2006) have investigated the removal of reactive dyes from wastewater by adsorption on coir pith activated carbon, their study showed that the removal of dye increased with decreasing dye concentration [13]. The results of these studies agree with the present study.

In the present study, the mechanism of reactive blue 19 dye adsorption on Jujube stems powder, well fitted with second-order reaction. Most studies are cconsistent with our study. For example, in studies of Gok et al (2010), Sun et al (2010), Ozcan et al (2009) and Amin (2008), it was reported that the pseudo-second-order kinetic model coincided very well with their experimental results [2,14,31,32]. But some other studies on parameters like adsorption of reactive dyes by coir pith activated carbon [13] and removal of malachite green dye by adsorption on treated sawdust [31] reported that the biosorption process followed the pseudo-first-order kinetic model.

In the present study, the best fit of the adsorption data was obtained using the Langmuir isotherm model. The equilibrium study of Elkady et al indicated that adsorption data fitted well by both Langmuir and Temkin models [20]. Amin found that adsorption data were modeled using the Langmuir and Freundlich adsorption isotherms [12]. Sun et al reported that Freundlich isotherm described the equilibrium data of acid dyes on fly ash better than Langmuir isotherm, but Langmuir isotherm showed better fit to the equilibrium data of reactive dyes [29]. Adsorption of dyes in Santhy and Selvapathy's (2006) study was found to follow the Freundlich model [13].

Conclusion

The results of the present study showed that by decreasing the initial dye concentration from 25 to 50 mg/l, the removal efficiency of dye decreased and by increasing the time from 15 to 180 min, removal efficiency increased. Also, we found that by increasing the pH from 4 to 10, the dye removal efficiency in both initial dye concentration (25 and 50 mg/l) increased and by increasing the adsorbent dose from 0.2 to 0.6 grams, the removal efficiency increased. Batch's studies demonstrated that the kinetics were well described by the pseudo-second-order model, and the equilibrium was well described by the Langmuir isotherm model. From this study, it can be concluded that Jujube stems powder could be used as an adsorbent for dye removal from textile wastewater.

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