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A study on the use of a waste by-product from saw-mill in the removal of basic dye from aqueous solution: kinetics and thermodynamics

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ABSTRACT

In the present study, an attempt has been made to use oak sawdust, a waste lignocellulosic by product from sawmill, as a potential adsorbent for basic dye (Astrozone Blue FGRL) removal from aqueous solution. The effects of contact time and temperature on Astrozone Blue FGRL (AB) adsorption by oak (*Quercus coccifera*) sawdust were studied. The experimental data at four initial dye concentrations (25, 50, 100 and 200 mg/L) were analyzed by the pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion kinetic models. Thermodynamic parameters, enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) were calculated for the uptake of AB, and indicated that the adsorption was a spontaneous and endothermic process. Kinetic studies of the data showed that the adsorption follows the pseudo-second-order kinetic model.

Keywords: Adsorption; Basic dye; Astrozone blue FGRL; Kinetic; Oak sawdust

1. Introduction

Since dyes have inert properties, dye removal from wastewaters containing dyes is difficult. If they exceed the tolerance limit in water, these unwanted chemicals will cause health problems. Therefore, the removal of dye from wastewater is very important, and urgent action needs to be taken to protect both the public health and the environment [1].

Treating such wastewaters by conventional treatment methods is difficult. Biological oxidation and chemical precipitation are the most commonly used methods. However, these processes are effective and economic only on condition that the solute concentrations are relatively high [2]. The process of adsorption has an advantage over the other treatment methods because of its clean process and complete removal of dyes even from dilute solutions [3]. Although this process is one of the cost effective and efficacious methods of treating polluted water, it has high cost and troublesome procedure for the regeneration of the conventional adsorbent that is used [4]. Therefore, there is still a need for the development of cheaper and equally effective substitutes.

Up to now, various low cost materials have been investigated as alternative adsorbents for activated carbon in the removal of Astrozone Blue FGRL (AB) as a basic dye from aqueous solution, which were macroalga *Caulerpa lentillifera* [5], dried biomass of Baker's yeast [6], sepiolite, fly ash, apricot shell activated carbon [7], agricultural waste dried Seagrape (*Caulerpa lentillifera*) [8], and sepiolite (meersium) [9].

In our previous study, the adsorption of AB by oak (*Quercus coccifera*) sawdust was investigated, and the results of this preliminary study were discussed in the extent of the effects of the adsorbent dosage, pH and initial dye concentration. The equilibrium isotherm analysis of AB adsorption by oak sawdust was also reported [10]. However, in our previous work, the study on the kinetics of oak sawdust for adsorption of AB was not carried out. The effect of varying temperature on the adsorption of AB was not investigated. Herein, the effects of contact time and temperature on the adsorption of AB from aqueous solution using oak sawdust were studied. The kinetics of adsorption of AB at four initial dye concentrations (25, 50, 100 and 200

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mg/L) was discussed using the pseudo-first-order model, the pseudo-second-order model, the Elovich model, and the intra-particle diffusion model. The thermodynamic parameters of adsorption were also calculated and discussed.

Sawdust, which is an abundant by-product of the wood industry, is easily available at zero or negligible price. It is known that it contains lignin, cellulose, hemicellulose [11–13] and some functional groups such as hydroxyl, carboxyl, amide and phenolic groups in its structure, which make the adsorption processes possible [11–12]. Sawdust is highly available and low-cost in Turkey; oak sawdust costs approximately US$ 0.07–$0.10/kg [14].

2. Materials and methods

2.1. Adsorbent and adsorbate

Oak (*Quercus coccifera*) sawdust was obtained from a local sawmill in Istanbul, Turkey. It was washed several times with distilled water and dried at 105°C. Then, it was sieved to the desired particle sizes and stored in dark glass bottles for further use. No other chemical or physical treatments were used prior to the adsorption experiments.

Basic dye, Astrozone Blue FGRL (AB) was provided from Dystar, Turkey and not purified prior to use. This dye consists of two main components which are C.I. Basic Blue 159 and C.I. Basic Blue 3. The ratio of the two components is 5:1 (w/w), respectively. The structures of these two dye components are shown in Fig. 1.

Stock solution (1000 mg/L) was prepared freshly by dissolving the AB in distilled water and then diluted to the required dye concentration.

2.2. Adsorption studies

Batch adsorption experiments were conducted by adding a fixed amount (5 g/L) of adsorbent into 250 mL Erlenmeyer flasks containing 100 mL of dye solution. The Erlenmeyer flasks were agitated in a horizontal bench shaker (Nüve SL-350) at 200 rpm. The samples (the reaction mixtures) were centrifuged at 1000 rpm for 5 min and then the supernatant was analyzed for the AB concentration remaining in the solution by spectrophotometer (Perkin Elmer UV/VIS Spectrometry) at a maximum wavelength of 599 nm.

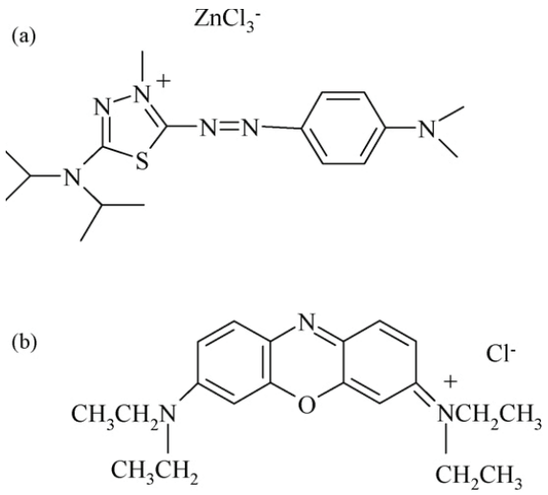


Fig. 1. Chemical structures of (a) C.I. Basic Blue 159 and (b) C:I. Basic Blue 3.

The contact times of 5, 15, 30, 45, 60, and 75 min were tested in conjunction with the initial dye concentrations of 25, 50, 100, and 200 mg/L. In the experiments on the effect of temperature, the temperature was held at 293, 303, 313 and 323K in a contact time of 15 min and initial dye concentration of 50 mg/L.

The original pH of the solution was 4.0. The experiments were carried out at this pH. All the adsorption experiments were conducted in duplicate, and the results are given as average values.

The adsorbed dye amount (mg/g) was computed as follows:

$$q_t\,(\text{mg/g}) = (C_0 - C_t) \times V/M \tag{1}$$

where C_0 and C_t are the initial and any time t dye concentrations (mg/L), V is the solution volume (L), and M is the adsorbent mass (g).

2.3. Theory

2.3.1. Kinetics

The Lagergren pseudo-first-order [Eq. (2)] [15] and the pseudo-second-order (Eqs. (3), (4)) [16] equations in linearized forms, and the intra-particle diffusion equation (Eq. (5)) [17] are expressed respectively as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{3}$$

$$h = k_2 q_e^{\,2} \tag{4}$$

$$q_t = k_{id}t^{1/2} + C \tag{5}$$

where k_1 (1/min) and k_2 (mg/g min) are the pseudo-first-order and the pseudo-second-order rate constants of adsorption, q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption at any time t (mg/g), h (mg/g min) is the initial adsorption rate from the pseudo-second-order kinetics, k_{id} is the intra-particle diffusion constant (mg/g $\text{min}^{1/2}$), and C is the intercept.

The Elovich model is valid for systems with heterogeneous surface and it is suitable and applicable for chemisorption kinetics. The linearized expression of the Elovich model is presented by the following equation [18]:

$$q_t = \frac{1}{\beta}\ln\alpha\beta + \frac{1}{\beta}\ln t \tag{6}$$

where α is the initial adsorption rate (mg/g min) and β is related to the extent of the surface coverage and the activation energy for chemisorptions (mg/g).

2.3.2. Thermodynamic

The thermodynamic parameters such as the change in free energy (Δ*G*), enthalpy (Δ*H*) and entropy (Δ*S*) were calculated using the following equations:

$$\Delta G = -RTInK_d \quad (7)$$

$$InK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

where K_d is the distribution coefficient for the adsorption. Δ*H*, ΔS and Δ*G* are the changes in enthalpy, entropy, and Gibb's free energy, *R* is the gas constant, and *T* is the absolute temperature.

3. Results and discussion

3.1. Effect of initial dye concentration and contact time

The adsorption behavior of AB at different initial concentrations on oak sawdust was determined as a function of contact time. The results are shown in Fig. 2. It is evident from this figure that adsorption of AB rapidly increased up to 10 min of contact time and then practically became constant up to 15 min, except for the initial concentration 25 mg/L. This rapid increase may result because initially adsorption sites were void and the dye molecules easily interacted with these sites. Also, this phenomenon suggests that the adsorption process could be ion-exchange in nature. It can be said that the molecules of AB bind with various negatively charged organic functional groups present on the surface of the oak sawdust [19]. A similar phenomenon was observed for the adsorption of AB from aqueous solution on macroalga *Caulerpa lentillifera* [5], dried biomass of Baker's yeast [6], sepiolite, fly ash, apricot shell activated carbon [7], and sepiolite(meersium) [9].

From Fig. 2, it is clear that the amount of adsorbed dye (mg/g) was higher at higher concentrations than lower concentrations. The increase in the adsorption of AB with an increase in the initial concentration may be due to the increasing concentration gradient. As known, the increase of dye concentration could accelerate the diffusion of dye molecules onto the adsorbent [20]. Similar trend for dye adsorption has been reported by various researchers [5,7,20,21].

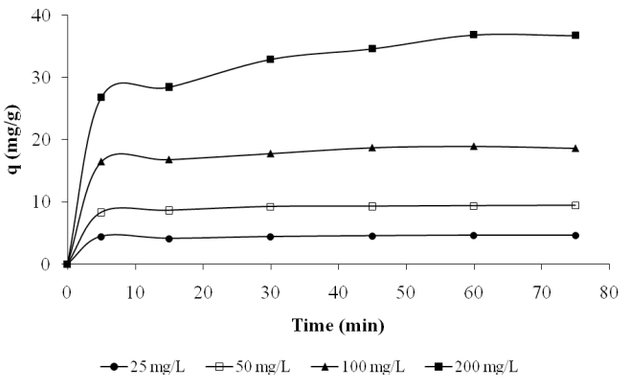


Fig. 2. Adsorption of AB on oak sawdust at various contact times and initial AB concentrations (*m*: 5 g/L; pH: 4.0; T: 20ºC, room temperature).

3.2. Adsorption kinetics

In order to understand the mechanism of the adsorption process, the kinetic data were studied in terms of the pseudo-first-order model, pseudo-second-order model, Elovich model, and intra-particle diffusion model. The parameters and coefficients of these kinetics models applied to the experimental data are given in Table 1.

The correlation coefficients with high values at the dye concentrations employed (25, 50, 100 and 200 mg/L) for the pseudo-first-order kinetic model indicates that the adsorption of AB onto oak sawdust is acceptable for this model (Fig. 3). However, it must be considered that the plots of $log\ (q_e - q_t)$ vs. *t* at different initial concentrations (25, 50, 100 and 200 mg/L) were created for four data points. For the pseudo-second-order kinetic model, the plots of t/q_t vs. *t* at different initial concentrations are presented in Fig. 4. The correlation coefficients for the pseudo-second-order kinetic model were greater than 0.9990, thereby indicating the applicability of the pseudo-second-order kinetic equation to the experimental data. Other researchers revealed that the adsorption of AB on sepiolite, fly ash, apricot shell activated carbon [7], and sepiolite (*meersium*) [9] could be well described by the pseudo-second-order model. This model suggests that the rate limiting step may be chemical adsorption or chemisorptions, which may involve valence forces through sharing or exchange of electrons between the dye and the adsorbent.

Elovich plot for adsorption of AB on the oak sawdust is shown in Fig. 5. The kinetic constants (α and β) obtained from the slope and the intercept of the plot of q_t vs. *ln t* are given in Table 1. As can be seen from Fig. 5, the plot of q_t vs. *ln t* does not give a very good linear relationship (R^2:

Table 1
Kinetic parameters for the removal of AB by oak sawdust

	Dye	Concentrations (mg/L)		
	25	50	100	200
Pseudo-first-order				
k_1 (1/min)	0.026	0.070	0.060	0.039
q_e (mg/g)	0.364	1.618	4.440	13.295
R^2	0.6010	0.9758	0.9424	0.9911
Pseudo-second-order				
k_2 (g/mg min)	0.112	0.153	0.139	0.017
q_e (mg/g)	4.632	9.124	18.975	38.314
h (mg/g min)	2.403	12.737	50.047	24.955
R^2	0.9998	0.9997	0.9999	0.9996
Intra-particle diffusion				
k_{id} (mg/g $min^{1/2}$)	0.145	0.127	0.190	0.904
C (mg/g)	3.385	8.061	17.433	30.460
R^2	0.9415	0.8765	0.9104	0.9344
Elovich equation				
α (mg/g min)	2.774	6.302	12.120	16.403
β (g/mg)	1.105	0.522	0.261	0.128
R^2	0.8347	0.8697	0.8760	0.9403

R^2: Correlation coefficient

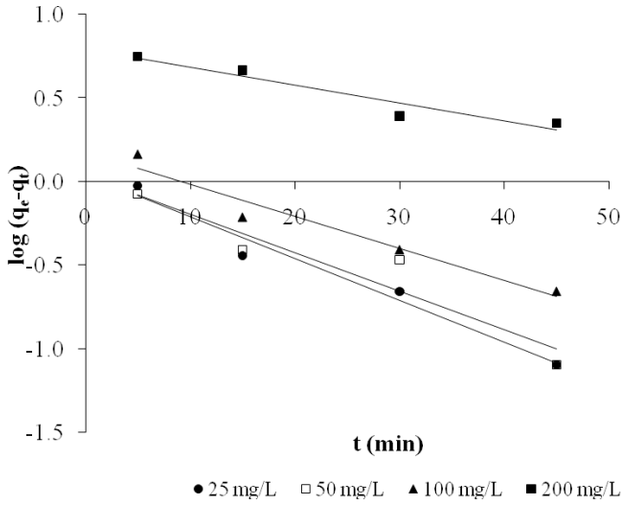


Fig. 3. Pseudo-first-order adsorption kinetics of AB on oak sawdust at various initial concentrations.

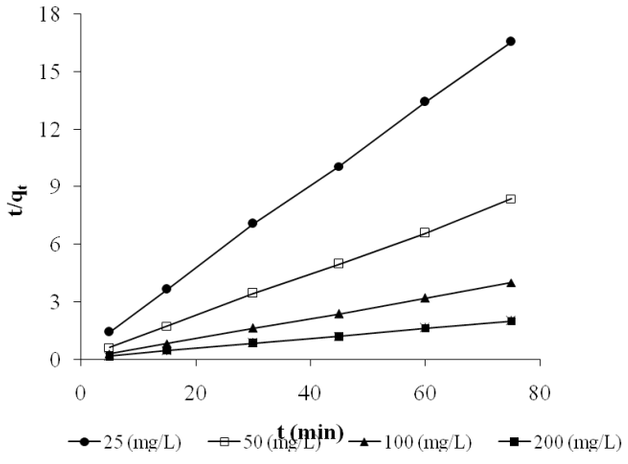


Fig. 4. Pseudo-second-order adsorption kinetics of AB on oak sawdust at various initial concentrations.

0.8347–0.9403). As stated by Riahi et al. [22], Elovich model gives a good correlation for adsorption on highly heterogeneous surfaces, and also shows that along with surface adsorption chemisorption is also a dominant phenomenon taking place. However, in a highly heterogeneous system along with surface adsorption, chemisorptions, ion exchange, precipitation and intra-particle diffusion occur concurrently. Consequently, it can be said that chemisorption does not appear to be a dominant phenomenon in the adsorption of AB on oak sawdust.

In this study, the intra-particle diffusion kinetic model was also tested. The plots of q_t vs. $t^{1/2}$ for the different initial AB concentrations are shown in Fig. 6. The parameters and correlation coefficients of the intra-particle diffusion model are given in Table 1. The k_{id} (intra-particle diffusion constant) values of AB adsorption increases with increased initial concentration. This may be due to the increase in driving force at higher concentrations, which will increase the diffusion rate of the molecular dye in pore [23,24].

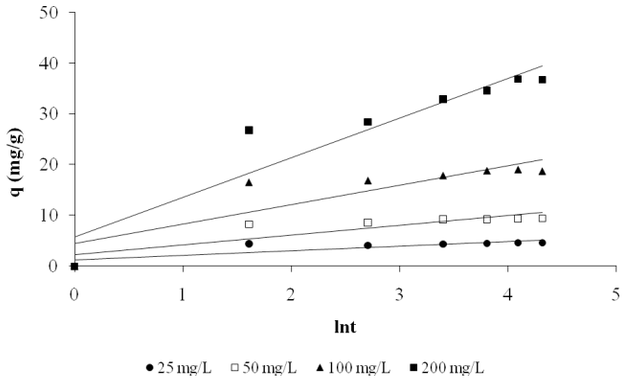


Fig. 5. Plot of Elovich equation for adsorption of AB on oak sawdust at various initial concentrations.

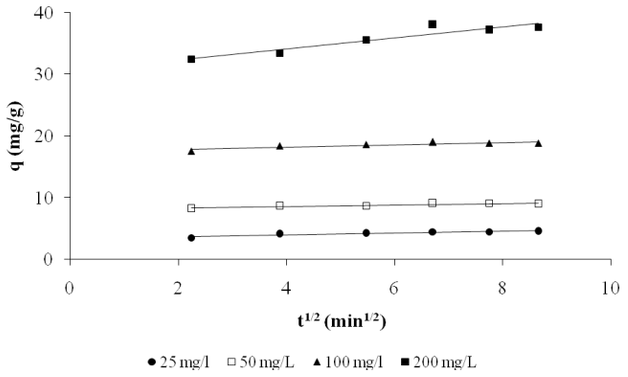


Fig. 6. q vs $t^{1/2}$ plot for adsorption of AB on oak sawdust at various initial concentrations.

As can be seen from Fig. 6, the plots were linear over the whole time range. However, they did not pass through the origin. Therefore, intraparticle diffusion is not the only rate limiting mechanism. It can be said that the AB removal by the oak sawdust is a complex process, and both the intraparticle diffusion and the external films contribute to the rate-limiting step [25,26]. In addition, since the correlation coefficients of the intra-particle diffusion model are lower than those of the second-order kinetic model (Table 1), it can be said that the pseudo-second-order adsorption mechanism is predominant and the overall rate of the AB adsorption process appears to be controlled by the chemical reaction [27,28].

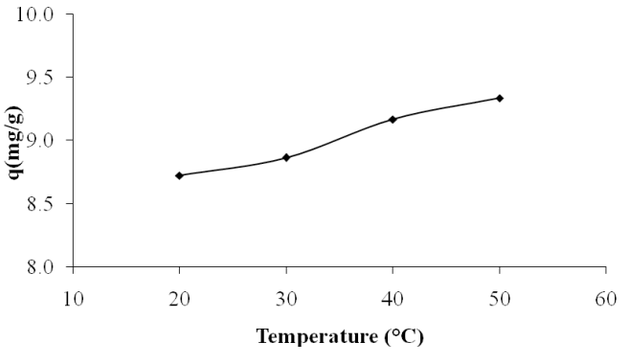
3.3. Effect of temperature

It is known that most of the wastewaters from textile industries are produced at relatively high temperatures. Thus, the effect of temperature on dye removal must be considered as an important factor for the real application of the adsorbent. In this study, the adsorption of AB on the oak sawdust was studied and gently increased by increasing the temperature (Fig. 7a). This was confirmed by other investigators studied AB adsorption from aqueous solution [6,7]. Thermodynamic parameters obtained

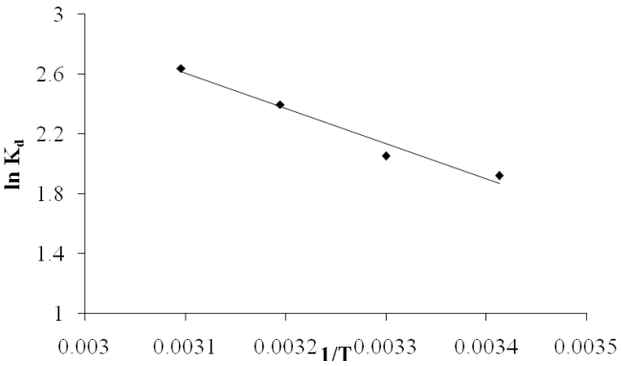
from Fig. 7b for the adsorption of AB on oak sawdust are given in Table 2.

As can be seen from Table 2, the negative value of Gibb's free energy (Δ*G*) suggested that the adsorption process was spontaneous and that the degree of spontaneity of the reaction increased with increasing temperature [14,29]. The increase in ΔG with increasing temperature also indicated that the adsorption was more favorable at high temperatures, supporting the suggestion that the adsorption capacity of sawdust for AB increases with increasing temperature.

The positive value of Δ*H* (19.440 KJ/mol) confirmed that the adsorption was endothermic [14, 29]. The positive value of Δ*S* (81.770 J/mol K) indicated the increasing randomness at the solid/liquid interface during dye adsorption on oak sawdust. Besides, the positive value of ΔS suggested that the dye adsorption caused disorder in the system.



(a)



(b)

Fig. 7. (a) The effect of temperature on AB adsorption on oak sawdust; (b) Thermodynamic study (C_0: 50 mg/L; *t*: 15 min; *m*: 5 g/L; pH: 4.0).

Table 2
Thermodynamic parameters for AB adsorption on oak sawdust

Temperature (K)	Δ*G* (KJ/mol)	Δ*H* (KJ/mol)	Δ*S* (J/mol K)
293	–4.519	19.440	81.770
303	–5.336		
313	–6.154		
323	–6.972		

4. Conclusions

The utilization of oak (*Quercus coccifera*) sawdust (waste lignocellulosic by product) for the basic dye (Astrozone Blue FGRL) removal from industrial wastewaters was investigated in the light of the kinetics and the thermodynamic data obtained by batch studies. Our results demonstrated that the Astrozone Blue FGRL (AB) removal was affected by contact time, initial concentration of AB, and temperature. The amount of the adsorbed dye (mg/g) increased with the increase in the initial dye concentration and temperature. The adsorption kinetics of AB to oak sawdust obeyed pseudo-second-order adsorption kinetics very well. The order of the best-fit kinetic models was found to be pseudo-second-order > pseudo-first-order > intra-particle diffusion > Elovich. The thermodynamic parameters (Δ*G*°, Δ*H*°, and Δ*S*°) suggested that the AB dye adsorption on oak sawdust was a spontaneous and endothermic process with increased randomness at the solid-solution interface.

The present study showed that the oak sawdust can be used as an inexpensive and efficient adsorbent material for the removal of AB from aqueous solutions. Oak is a common tree in Turkey and its sawdust is easily available in large quantities at zero or negligible price. When comparing the cost of activated carbon with oak sawdust, the AB removal by the oak sawdust from industrial wastewaters is expected to be economic, since the adsorbent is a waste/by product from sawmill. Consequently, adsorption of AB on sawdust can be considered as a simple, efficient and economic method for AB removal from wastewater. Dye loaded adsorbent can be burned in an energy cogeneration plant. As stated by Argun et al. [14], it is a renewable resource, and does not need to be regenerated.

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