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Removal of Reactive Dye by Using Soybean Cake

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Abstract

In this study, soybean cake as an economic adsorbent was used to remove reactive dye from aqueous solution. Effect of initial pH, dose, contact time and particle size were studied. The selected conditions are 2, -100 mesh, 1 g/l and 30 min for initial pH, particle size, adsorbent dosage and contact time, respectively. The equilibrium data and kinetic data were analyzed for adsorption mechanism and characteristic. According to the results, second order kinetic model and Langmuir isotherm model are well fitted to the experimental data obtained for Reactive Black 5 (RB5) adsorption on soybean cake. The monolayer adsorption capacity values were calculated as 250 and 285.7 mgRB5/g for 20 and 60°C, respectively.

Key words: Reactive Black 5, Soybean cake, Adsorption kinetics, Adsorption Isotherm

Soyafasulyesi Küspesiyle Reaktif Boya giderimi

Özet

Bu çalışmada sulu ortamlardan reaktif boyar maddenin gideriminde ekonomik bir adsorbent olarak soyafasülyesi keki kullanıldı. Başlangıç pH'sı, doz, temas süresi ve tanecik boyutunun etkisi incelendi. Başlangıç pH'sı 2, tanecik boyutu -200 meshten geçen tanecikler, doz 1g/l ve temas süresi 30 dakika olarak belirlendi. Adsorpsiyon mekanizması ve karakterizasyonu adsorpsiyon denge verileri ile kinatik verileri kullanılarak incelendi. Soyafasülyesi küspesiyle rekatif siyah 5 boyar maddesinin adsorpsiyonu için yapılan deneylerden elde edilen deneysel sonuçlara göre ikinci dereceden yalancı kinetic model ve Langmuir isotherm modellerine uyduğu görüldü. Tek tabak adsorpsiyon kapasitesi 20 °C'de 250 mgRB5/g, 60°C'de 285.7 mgRB5/g olarak bulundu.

Anahtar Kelimeler: Reaktif siyah 5, Soya fasülyesi keki, Adsorpsiyon kinetiği, İzoterm

1. Introduction

Dyes have been extensively used in industries such as textile, paper, food, cosmetics, electroplating, plastic and pharmaceutical [1]. The pollution problems in surface and ground water increases due to increasing industrial application of dyes. Removal of dye from colored wastewater is difficult with conventional methods such as biological, physicochemical treatment because of robust nature of industrial dyes [2]. Reactive dyes are soluble and not easily biodegradable in wastes streams. The extensively used methods for removing of dyes from waters are precipitation, ozonation, biosorption, membrane separation, electrochemical technology, etc [3].

Reactive dyes are important class of the dyes used in industry. Reactive dyes, have azo bonds (-N-N-), have simple application techniques, bright and low energy consumption [4]. In the reactive dyes, the azo based chromophore groups are combined with different types of reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine, difluorochloropyrimidine etc [5]. These constituents of reactive dyes can be harmful to aquatic life even after decomposition treatments.

Adsorption process becomes increasingly common method for colored effluents treatment. Activated carbon, which has a high surface area and high capacity for uptake of adsorbate, is most known adsorbent. But, high cost of activated carbon led to seek for low-cost material for using as adsorbent. There is many study about to searching of low-cost adsorbent for removing dye from wastewaters. These materials are less efficient more than the activated carbon, but they can be found abundant and easy. In a numerous study, the agricultural and industrial by-products such as almond shell [6], leaves[7], wheat bran[8], cotton plant wastes[9], peanut hull[10], etc. were searched to obtain low-cost adsorbent for dye removal.

Soybean, which being consumed as an important food in many countries, is processed to obtain soybean oil on a large scale. During this production process, soybean cake (SC) is obtained as an important by-product at huge amount. SC which is by-product remaining from oil extraction, has functional groups such as $-NH_2$ and –COOH [11]. Each of these groups has reductive and adsorptive properties. SC can be used as a low-cost and abundant adsorbent for industrial wastewater treatment.

In generally, initial dye concentration, initial pH, contact time, adsorbent particle size and temperature are considered as main parameters for any batch adsorption process. The effect of these parameters on dye removing by adsorption must be investigated. The aim of this study was to investigate the removing properties of RB5 from aqueous solution by adsorption on soybean cake at various conditions. Also, it is aimed that to make some mechanistic, kinetic and thermodynamic evaluations for the adsorption process.

2. Materials and Methods

2.1. Adsorbent and adsorbate

The soybean cake used in this study was supplied from Adana, Ceyhan, located in the southern part of Turkey. The material was washed with distilled water and dried in an oven at 80 °C for 24 hours. Dry material was grinded and sieved by using a sieve series. The adsorbent was preserved in a plastic jar. RB5 was supplied from a local textile firm and used any further purification. The chemical structure of the RB5 is given in Figure 1. The general characterization of RB5 are given in Table 1.

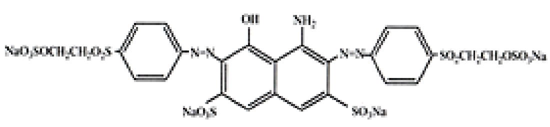

Figure 1. Chemical structure of RB5[12].

Table 1. Properties of RB5 [4]

Generic Name	CI Reactive
Percentage of pure dye	66
Anchor	Vinilsulphone
Chromophore	Azo
λmax, nm	595
Molecule weight, g/gmol	991

2.3. Experimental method

The experiments were conducted in a rotary shaker (150 rpm) by using 250 ml capped conical flasks containing 50 ml of dye solution. In the adsorption experiments, the effects of temperature, dosage, particle size, initial pH and dye concentration were investigated depending on the contact time. The all experiments were carried out in duplicate and mean values were considered as result.

In order to conduct of sorption kinetic experiments, the flasks containing 50 ml of solution having 225 mg/l RB5 and 0.05 g SC were used. The flasks were taken from the orbital shakers at different contact time intervals and the residual concentration of RB5 was determined.

At defined intervals, the aqueous solutions were separated by filtering and concentration of RB5 in solution was assayed with a spectrophotometer (λ_{max}=595 nm).

The adsorption density (q) and adsorption yield (%) were calculated from Eq.(1) and (2), respectively.

$$q = \frac{(C_0 - C) * V}{m} \quad (1)$$

$$Adsorption\ yield, \% = \frac{(C_0 - C)}{C_0} * 100 \quad (2)$$

Where, V (l) is the solution volume, C_0 and C (mg/l) are the initial and final RB5 concentrations, respectively, and m (g) is the dry weight of SC.

3. Results and Discussion

3.1. Effect of initial pH

The experiments were carried out at various initial pH values of solution (1.1 ,1.5, 2, 2.5, 3 and 4) for different time intervals at 20°C as shown in Fig.2. It is shown that RB5 removal is rapid in first 60 min for all investigated initial pH values. After this time, it proceeds slowly and attains to the state of saturation. This may be attributed to a rapid adsorption on the outer surface followed by slower adsorption inside the pores [6]. As initial pH increases from 1.1 to 4, the equilibrium sorption yield of dye decreases from 94.2 to 12.5%. Soybean cake has got functional groups (carboxyl, amine. etc) due to high protein content. So, it cannot favor the adsorption of anionic groups coming from the dye due to the electrostatic repulsion. The adsorbent has a net positive charge on its surface at low pHs, and the negatively charged functional groups located on RB5 would be interacted with surface[13]. Following experiments was conducted at pH 2 due to both high adsorption yield and decreased acid amount. For the further adsorption experiments, pH 2 was preferred due to conducting in the presence of lesser acid amount. Because the acid consumed for the pH adjusting can be considered as high cost and pollution factor.

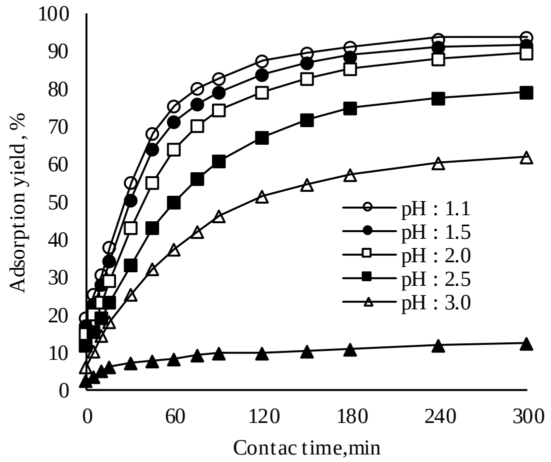

Figure 2. The effect of pH on adsorption on soybean cake (250 ml 225 ppm RB5, 1 g/L dose temperature: 20°C).

3.3. Effect of initial dye concentration on adsorption

The effect of initial dye concentration on adsorption process is shown in Figure 3. Adsorption density (q) increased from 77 to 223 mg/g when the initial RB5 concentration increased from 175 to 300 mg/l. This is attributed to the increase in the driving force of the concentration gradient, as an increase in the initial dye concentration[7].

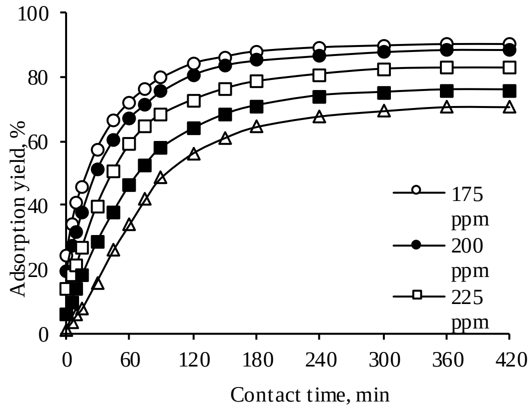

Figure 3. The effect of initial dye concentration on adsorption of RB5 by SC (Conditions ;250 ml, 1 g/l dose, initial pH; 2, temperature; 20°C).

3.4. Effect of adsorbent dose

Figure 4 shows the variation of adsorption yield of RB5 by SC dosage. The dye removal increased as the dose was increased over from 0.5 to 2.0 g/l. The adsorption yield increased from 63.7 to 99.10%, and the adsorption density decreased from 322.6 to 62.91 mg/g for an increase in dose from 0.5 to 2.0 g/l, respectively. Below the 1.0 g/l of dosage, the adsorption yields RB5 significantly decreased. On the other hand, it is clearly shown that adsorption density of RB5 seriously decreased above this dosage value. So, the soybean cake dosage of 1.0 g/l (qe:135.2 mg/g) was selected for further experiments.

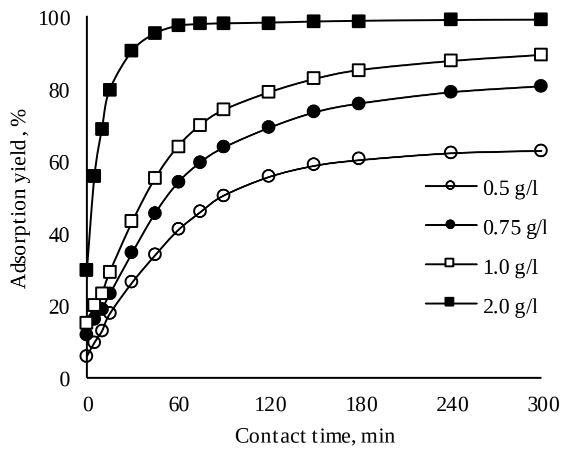

Figure 4. Effect of adsorbent dose on the removal of RB5 by SC. (Conditions ;250 ml, 225 mg/l dye concentration, initial pH; 2, temperature; 20°C).

3.5. Effect of particle size

The adsorption of dye increases as the particle size decreases, because the surface area increases when the particle size decreases [14]. It can be said that the sorption phenomenon was reached to equilibration very quickly (30 min) for the smallest sorbent particle size fraction which is below 150 μm (-100 mesh) (Figure5). The sorbent particle size is an important factor in adsorption kinetics because it determines the time required for transport of sorbate to adsorption sites within the pores [9]. Due to liquid-solid separation difficulties and economic reasons, it is considered that it cannot be preferred the finer particle size fractions.

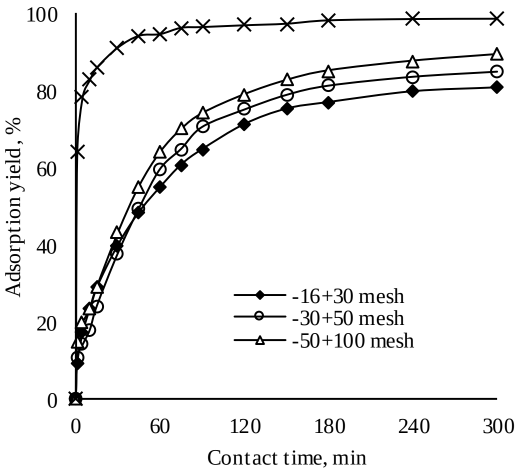

Figure 5. Effect of adsorbent size on the removal of RB5 by SC. (Conditions ;250 ml, 225 mg/l dye concentration, initial pH; 2, dosage 1 g/l, temperature; 20°C).

3.6. Kinetic parameters of adsorption

Kinetic data were analyzed by using pseudo-first order (Lagergren Equation) and pseudo-second order models to evaluate the adsorption mechanism and characteristics. A linear form of the pseudo-first-order kinetic model, known as the Lagergren rate equation, can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \qquad (3)$$

where q_e and q_t (mg/g) are the amounts of RB5 adsorbed per unit weight of SC at equilibrium and at any other time (t), respectively, and k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption rate [10].

The pseudo-second-order kinetic model can be expressed in linear form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}, \qquad (4)$$

where k_2 (g/mg min) is the rate constant of the pseudo-second-order adsorption.

Fig.6 and 7 shows the linearized plots of both models for different temperatures. Also, calculated kinetic parameters and regression coefficients for both models are given in Table 2. As shown from the table, the experimental data are well fitted to pseudo-second order kinetic model. The values of R^2 are higher than 0.99 and the theoretical adsorption capacity values agree with experimental results for this model**,** assumed rate limiting step may have chemisorption.

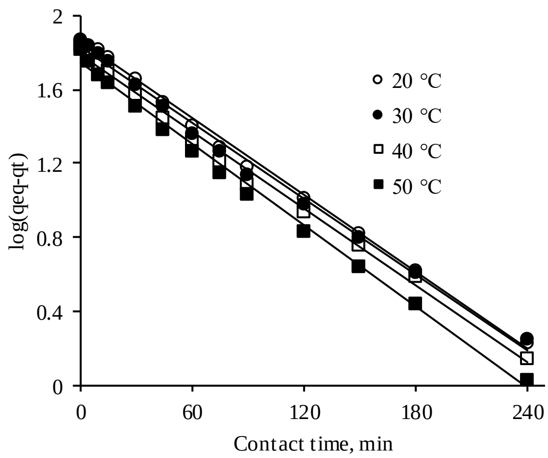

Figure 6. Pseudo- -first order adsorption kinetics of RB 5

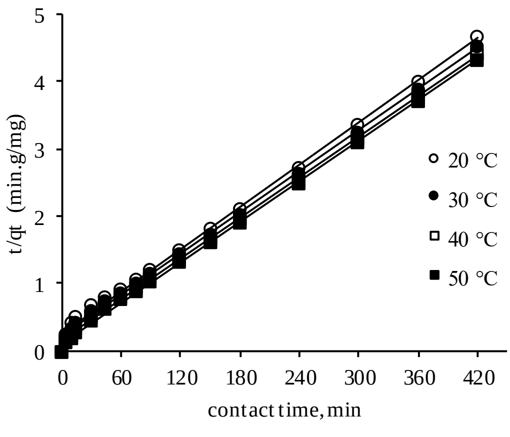

Figure 7. Pseudo-second order adsorption kinetics of RB 5

Table 2. The pseudo-first and second-order reaction rate constants

T (°C)	$q_{e,exp}$ (mg/g)	First order kinetic model			Second order kinetic model		
		$k_{1,ad}$, (l/min.)	$q_{e,cal}$, (mg/g)	R^2	$k_{2,ad}$,*10^3 (g/mg.min.)	$q_{e,cal}$, (mg/g)	R^2
20	89.9	0.0159	71.94	0.967	0.404	96.15	0.996
30	92.8	0.0156	67.30	0.953	0.486	98.04	0.998
40	95.4	0.0159	61.16	0.944	0.650	99.01	0.999
50	97.2	0.0175	56.98	0.943	0.825	100.00	0.999

3.7. Adsorption *isotherms*

The adsorption isotherm models are important for design of adsorption processes. Also, these models can help to understand the nature of the sorption phenomenon. There are several adsorption isotherm model equations in the literature. In this study, two most important models are selected, the Langmuir and Freundlich isotherms. Langmuir isotherm model assumes that the saturation is monolayer. Langmuir equation is given as below:

$$q_e = \frac{bC_e q_{max}}{1 + bC_e} \tag{5}$$

Where q_e is the sorption capacity (mg/g) at equilibrium, C_e the equilibrium dye concentration (mg/l) at equilibrium, q_{max} the maximum adsorption capacity (mg/g) and b sorption constant related to affinity of binding sites or bonding energy (1/mg).

The Freundlich isotherm model, an exponential equation, is given in Eq5. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases by multilayer sorption [15].

$$q_e = K_f C_e^{1/n} \tag{6}$$

Where K_f is roughly represent of the sorption capacity and 1/n is the constant related to the adsorption intensity.

In the experiments conducted to obtain the isotherm data, initial RB5 concentrations were changed from 200 to 550 mg/l while the SC dosage was kept constant (1g/l) at 20, 40 and 60°C. The K_f, n, q_{max} and b values calculated from slops and intercepts of isotherm lines are presented in Table 3.

Table 3. The constants obtained from isotherm models

T (˚C)	Langmuir constants			Freundlich constants		
	q_{max}	b	R^2	K_f	n	R^2
20	250.	0.3	0.99	179.5	15.33	0.835
40	263.	0.5	0.99	186.8	14.90	0.936
60	285.	1.0	0.99	198.3	14.74	0.969

From Table 3, it is seen that the maximum adsorption capacity values increase while b values decrease with increasing temperature. The monolayer adsorption capacity (q_{max}) was founded as 285.71 mg/g for highest temperature value (60°C). A higher value of b implies a shift of the adsorption equilibrium to the right [8]. Increasing b value with temperature indicate that chemical interaction between adsorbent and adsorbate is important. Furthermore, the increase in sorption capacity of soybean cake at high temperature may be related to the enlargement of pore size or activation of the adsorbent surface [16]. The maximum K_f value was founded as 198.36 at 60 ˚C. Adsorption intensity values (n) were obtained higher than 1. High K_f and n values indicate removal of RB5 from aqueous media. The Langmuir isotherm can be used to explain the sorption of dye into soybean cake due to high regression coefficient investigated all temperature in Table3.

3.8. Determination of thermodynamic parameters

The thermodynamic parameters of adsorption process can be obtained by using Langmuir constant at different temperature. These parameters were calculated by using suitable form of Equations 6-8. Gibbs energy values were determined as −30.803, −34.467, and −38.53 kJ/mol for temperatures of 20, 40 and 60 °C, respectively. RB5 adsorption onto SC is the spontaneous nature according to negative value of ΔG. Enthalpy change and entropy change were calculated by using van't Hoff plots (Fig 9). The calculated ΔH° and ΔS° values for RB 5 are 25.77 kJ/ mol and 0.193 k J/mol K, respectively. The positive value of ΔH° indicates that the adsorption process is endothermic in nature.

$$\Delta G^{o} = -RTlnb \tag{7}$$

$$lnb = lnb' - \frac{\Delta H^{o}}{R}\frac{1}{T} \tag{8}$$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \tag{9}$$

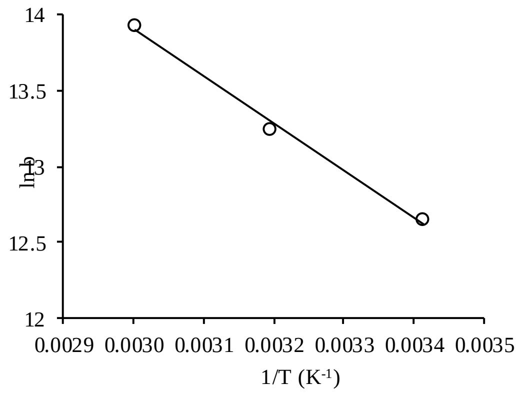

Figure 9. Plot of lnb vs. 1/T

4. Conclusions

The effect of variables such as initial pH, dose, particle size on adsorption process was determined experimentally. The low initial pH (2), lower particle size (-100 mesh) and dose of 1 g/l was selected for adsorption RB5 on SC. The adsorption kinetic, isotherms and thermodynamic parameters calculated various model equations. The adsorption process showed more suitable to Langmuir isotherm. The mono layer sorption capacity was assayed as 250.0, 263.2, 1285.7 mg/g for the temperature of 20, 40 and 60 °C, respectively. SC may be used as adsorbent for removing reactive dye effectively, and economically from wastewater.

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