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Reuse of Solid Waste in Adsorption of the Textile Dye

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Abstract

This work presents the study of the reuse of a regenerated spent bleaching earth (RSBE). The RSBE material was tested in the removal of a basic textile dye presents in aqueous solution. The effect of physicochemical parameters such as stirring speed, initial concentration, contact time and temperature have been invested and thermodynamic nature of the adsorption process was determined by calculating the ΔH° , ΔS° and ΔG° values

The results obtained show that the adsorption mechanism was described by the Langmuir model and the adsorption capacity, q_{\max} (72.41 to 82.37 mg.g⁻¹), increases with temperature (20-50 °C). The thermodynamic parameters show a presence of a strong affinity between two phases (liquid-solid) and an endothermic equilibrium adsorption process. However, the phenomenon of the adsorption kinetic follows the pseudo second order kinetic model.

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1. Introduction

The method of elimination of dyes using a variety of activated carbon is widely studied, but it was economically expensive [1]. Therefore much interest has focused on methods of adsorption by using natural materials and upgraded waste [2].

Virgin bleaching earth (VBE) was a strong acid-activated bentonite [3]. When VBE was used in oil refining, it would change from white to brownish and it became a waste called spent bleaching earth (SBE). Generally, SBE contains approximately 20–30% of oil. The regeneration of this waste is made

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possible by various methods developed by existing works in literature and gives back to the SBE its adsorption capacity before use [4]. This material is called regenerated spent bleaching earth (RSBE). The works results have shown that the regenerated waste is effective for the textile dyes removing [5].

In Algeria, the refinery units' emit thousands of tons of bleaching earth waste per year, without making any treatment, which, over the years, pose an acute problem of management and storage, without forgetting the harmful effects that they create. To minimize the risk of pollution and in order to alleviate the pollution problems, we recently studied a new regeneration method [6]. The results obtained allowed to show an increase in surface area of the regenerated material (RSBE), by developing porosity comparable to the material not used (VBE). So, the main purpose of this study was to test the adsorption capacities of RSBE in the water treatment containing basic dye used in the textile industry.

2. Experiment

2.1. Materials

The basic dye used as adsorbate in the present study is Asucryl red GRL 200%, which was supplied from AlFaditex (textile company of Bejaia, Algeria). It is a product commercialized by AZUTEX ($C_{18}H_{21}N_6Br$; CI 110825; molecular weight (MW) = $400.9 \text{ g}\cdot\text{mol}^{-1}$, $\lambda_{\text{max}} = 532 \text{ nm}$). The spent bleaching earth (SBE) used in this study was provided by the unit of edible oil refining, unit of COGB-Label of Bejaia (Algeria). It is a bentonite from Maghnia deposit (Algeria). Regenerated Spent Bleaching Earth employed as adsorbent in the present study was prepared as described before [6]. It will be noted RSBE.

All chemicals used were analytical grade.

2.2. Stirring speed effect

The effect of the stirring speed (w) was studied by shaking 0.1g of the RSBE material with 100 ml of aqueous solution initially containing $50 \text{ mg}\cdot\text{L}^{-1}$ of dye at the temperature of $20 \text{ }^\circ\text{C}$, pH of 6 and for fixed stirring speeds of 50, 100, 200 and 300 rpm

2.3. Kinetic study

The experiments of adsorption kinetics were carried out at $20 \text{ }^\circ\text{C}$ in a batch process. For each experiment, 100 mL of the basic dye solution at specified concentrations were continuously stirred with 0.1 g of the adsorbent (RSBE) during different time intervals (5-120 min). The suspensions were then centrifuged and the basic dye concentrations in the supernatant, $C_t \text{ (mg}\cdot\text{L}^{-1})$, were measured with UV-visible spectrophotometer (Model: OPTIZEN 3220 UV) at 532 nm wavelength. The amount of adsorbed dye per unit mass of adsorbent at time t , $q_t \text{ (mg}\cdot\text{g}^{-1})$, was then determined by the following equation:

$$q_t = \frac{(C_0 - C_t) V}{m} \quad (1)$$

Where $C_0 \text{ (mg}\cdot\text{L}^{-1})$: initial concentration of basic dye solution; $C_t \text{ (mg}\cdot\text{L}^{-1})$: liquid phase concentration of the basic dye solution at time t , V : solution volume (mL); m : mass of adsorbent (g)

2.4. Sorption isotherms

Adsorption isotherms were determined at 20, 30, 40 and 50°C by shaking 0.1g of the adsorbent (RSBE) with 100 mL of dye solution with concentration from 25 to 125 mg.L⁻¹ for 60 min. After shaking at 300 rpm, the solution was separated from the solid by centrifugation. The remaining concentrations in the supernatants were determined by UV-visible spectrophotometer at 532 nm.

3. Results and discussion

3.1. Influence of stirring speed

The adsorption capacity of the material RSBE depending on contact time for different agitation speed w (rpm), is illustrated by the curves drawn in Fig.1.

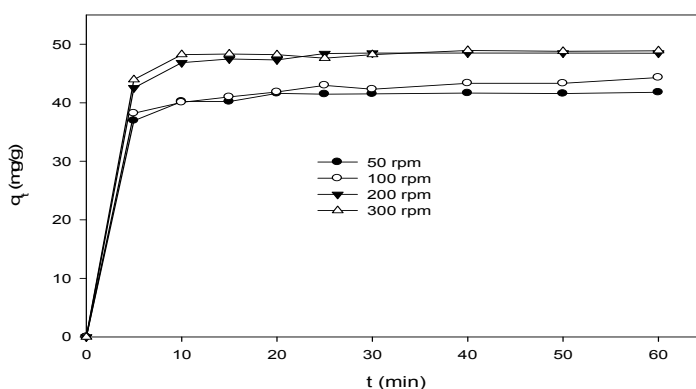


Figure 1: Influence of the stirring speed on the textile dye adsorption by RSBE ($C_0 = 50 \text{ mg.L}^{-1}$, $m=0.1 \text{ g}$, $V = 100 \text{ mL}$, $T = 20^\circ\text{C}$)

The curves have two distinct gaits; fast at the beginning then the adsorption rate decreases to reach a level corresponding to equilibrium after 30 min of contact material-dye solution. The Fig. 1 shows that the amount of the adsorbed dye remains unchanged beyond a stirring speed of 200 rpm. The low levels observed for agitation speeds of 50 and 100 rpm (42.0 mg.g^{-1}) are due to incomplete dispersion of particles of the adsorbent which results in an agglomeration of particles of the adsorbent and thus a decrease in the contact area between the adsorbent and the adsorbate resulting in increased resistance to mass transfer inside the film liquid-solid interface [7]. Beyond the stirring speed of 200 rpm the amount of dye adsorbed remains unchanged (48.4 mg.g^{-1}). For safety and for the rest of our work we maintain a stirring speed of 300 rpm. Similar cases have been reported by the works of literature for dye adsorption on mineral matrices [8].

3.2. Adsorption Kinetic

The Lagergren's first-order kinetic model and the Ho's pseudo-second-order model are the most frequently used in the literature [9,10]. The plots drawn according to Lagergren equation (no mentioned in this paper) are not linear for the RSBE adsorbent [11]. Thus, the kinetic adsorption data were analyzed by the second order model. The pseudo second order kinetic equation based on the adsorption capacity can be defined as in the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

Where k_2 is the pseudo-second order rate constant ($\text{g.mg}^{-1}.\text{min}^{-1}$), which is determined from the plots t/q_t versus t . furthermore, the initial adsorption rate (h) that is obtained from this model can be expressed as in the following equation:

$$h = k_2 q_e^2 \quad (3)$$

In order to check the validity of the above models in describing the kinetic data, the least-squares correlation coefficient (R^2) and normalize standard deviation s (%) were calculated for each experiment. The s value is done by the following expression:

$$s = 100 \sqrt{\frac{\sum \left[\frac{(q_{t,\text{exp}} - q_{t,\text{cal}})}{q_{t,\text{exp}}} \right]^2}{n-1}} \quad (4)$$

where $q_{t,\text{exp}}$ (experimental value for amount of adsorbed basic dye at equilibrium) and $q_{t,\text{cal}}$ (calculated value for amount of adsorbed basic dye at equilibrium) are the measured and calculated dye adsorbed at time t , respectively, and n is the number of data points. Values of the amount of basic dye adsorbed at equilibrium q_e and the rate constant of pseudo second order adsorption k_2 are summarized in Table 1. The results show that the adsorption kinetics was best described by the pseudo second order with the highest correlation coefficient values ($R^2 > 0.99$) and lowest s ($s = 2.79\%$). The q_e values calculated by the pseudo second order model are very close to those determined experimentally. What justifies moreover that the kinetics of the dye adsorption by the RSBE material is pseudo-second order, confirming thus several works of the literature on the adsorption of the basic dyes on the regenerated spent bleaching earth matrices [5]. The amount of adsorbed basic dye per unit of adsorbent mass, q_e (mg.g^{-1}), increases with the increase of the initial concentration C_0 (mg.L^{-1}). This may be attributed to an increase in the concentration gradient between the solute in aqueous solution and solute on the adsorbent surface [12].

Table 1. Kinetic parameters for the adsorption of Asucryl red onto RSBE at various initial concentrations

Adsorbent	Concentration (mg.L^{-1})	$q_{e,\text{cal}}$ (mg.g^{-1})	$q_{e,\text{exp}}$ (mg.g^{-1})	k_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$)	R^2	h ($\text{mg.g}^{-1}.\text{min}^{-1}$)
RSBE	25	23.20	23.36		1	
	50	48.54	47.61	0.250	0.996	589.03
	75	61.35	60.32	$1.24 \cdot 10^{-2}$	0.998	46.67
	100	66.23	64.43	$7.26 \cdot 10^{-3}$	0.999	31.84
	125	74.63	71.74	$7.33 \cdot 10^{-3}$	0.998	40.82

The rate constant k_2 decreases (from 0.25 to $7.33 \cdot 10^{-3} \text{ g.mg}^{-1}.\text{min}^{-1}$) with the increase in the initial concentration of dye, which is coherent with the literature works [13]. With weak concentrations, the ions of the Asucryl red dye could react easily with the adsorption sites, consequently, it results a constant rate greater. At higher concentrations, due to the saturation of adsorption sites, the rate constant for the adsorption of basic dye on the adsorbent material shows a decreasing trend. Also the initial adsorption rate (h) decreases from 589.03 to 31.84 $\text{mg.g}^{-1}.\text{min}^{-1}$, for an increase in the initial concentration of the dye from 25 to 125 mg.L^{-1} . Meanwhile, the initial adsorption rate constant, h , was generally higher for a lower initial dye concentration [14].

3.3. Sorption isotherms

The linear form of the Langmuir model can be represented by the following relation:

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

Values of the maximum adsorption capacities (q_{max}) and the Langmuir isotherm constant (K_L) were calculated and the results are presented in Table 2. The Langmuir model correlation coefficients are higher than 0.99. To confirm the favourability of the adsorption process, the separation factor R_L or Hall parameter, was calculated by the following equation [15]:

$$R_L = \frac{1}{1+K_L C_0} \tag{6}$$

Where the adsorption process to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The examination of the results of Table 2 shows that the maximum quantity of the adsorbed dye, q_{max} ($mg.g^{-1}$), is proportional to the variation of the temperature. This explains the endothermic process of the adsorption with RSBE material. However, the R_L values for the adsorption of Asucryl red GRL dye are less than 1 and greater than zero; therefore the adsorption of the dye for material is favourable. In addition, the R_L values decrease for an increase in initial concentration of dye and tend towards zero for high concentrations simulating that the adsorption process in this case is virtually irreversible. Similar results are obtained by Hameed B.H. on the methylene blue [12].

Table 2. Langmuir isotherm parameters and correlation coefficients

Adsorbent	T (°C)	q_{max} (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R_L					R^2
				25 (mg.L ⁻¹)	50 (mg.L ⁻¹)	75 (mg.L ⁻¹)	100 (mg.L ⁻¹)	125 (mg.L ⁻¹)	
RSBE	20	72.4	0.427	0.083	0.042	0.029	0.022	0.016	0.994
	30	76.92	0.433	0.085	0.044	0.03	0.023	0.018	0.995
	40	79.36	0.481	0.077	0.04	0.027	0.02	0.016	0.997
	50	82.37	0.523	0.071	0.037	0.025	0.019	0.015	0.998

3.4. Thermodynamic study of adsorption

The thermodynamic parameters of the adsorption process, enthalpy ΔH^0 (kJ/mole), entropy ΔS^0 (J.K⁻¹.mol⁻¹) and free energy of Gibbs ΔG^0 (kJ.mol⁻¹), are calculated by using equation 7 below.

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{7}$$

Where K_d : distribution coefficient, R: universal gas constant (8.314 J .mol⁻¹.K⁻¹), T: temperature (K). The representation of the straight lines $\ln K_d$ versus $1/T$ [11] allows deducing the values of ΔH^0 and ΔS^0 (see Table 3).

Table 3. Thermodynamic parameters of the dye adsorption on the RSBE

C_0 (mg.L ⁻¹)	R^2	ΔH^0 (KJ.mol ⁻¹)	ΔS^0 (J.K ⁻¹ mol ⁻¹)	$-\Delta G^0$ (KJ.mol ⁻¹)			
				293	303	313	323
25	0.988	7.737	105.85	23.28	24.34	25.39	26.45
50	0.992	14.860	133.16	24.16	25.49	26.82	28.15
75	0.995	9.316	105.04	21.46	22.51	23.56	24.61
100	0.981	13.739	109.05	18.21	19.3	20.39	21.48
125	0.982	6.368	81.73	17.58	18.4	19.21	20.03

The values of the thermodynamic parameters presented in Table 3 enable us to observe that the variation of enthalpy ΔH° of the system is positive. This indicates that the adsorption process is endothermic. The values of ΔH° are lower than 40 KJ.mol^{-1} implies that the adsorption mechanism is a physisorption [16]. The values of ΔG° (absolute value) increase with the temperature, confirming a spontaneity in the adsorption process of the dye by the RSBE material, while indicating also that the dye adsorption process on the material becomes increasingly favorable [16,17]. The positive value of ΔS° reflects the affinity of material for the basic dye and a possible increase of the degree of disorder at the solid-solution interface during the adsorption [17]. The endothermic nature of the process is confirmed by the positive value of ΔS° which shows that the adsorption process is a combination of the two simple stages: 1- Exchange of solvent molecule (water) adsorbed before. 2- Adsorption of dye molecule (each molecule of dye moves more than one molecule of this solvent) [17].

4. Conclusion

This study shows that a material originating from a waste can be re-used in the remove of a basic textile dye. The study of the influence of various parameters (stirring rate, temperature, contact time and initial concentration) has led to the conclusion that the dye is quickly adsorbed by the RSBE material at least of 30 minutes. The adsorption rate is governed by a pseudo second order kinetic model and the adsorption isotherm of the basic dye obeys to the Langmuir model.

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