Sawdust as Biosorbent for Removal of Dyes from Wastewaters. Kinetic and Thermodynamic Study

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Abstract: A new waste material, characterized by low cost, availability and ligno cellulose composition, was tested for its ability to remove reactive dyes from aqueous systems or environments. This paper continues our studies concerning utilisation of sawdust as low-cost sorbent for decolourization of different textile effluents which contain synthetic textile dyes with a high molecular weight. In this context, kinetic and thermodynamic studies were carried out in order to establish all favourable conditions to uptake of Orange 16 reactive dye from aqueous solution of pH =1 by using batch technique. The kinetics of adsorption of Orange 16 reactive dye are following a pseudo-second order model. The values of thermodynamic parameters, ΔG and ΔH, were calculated using Langmuir constant (K_L) and showed a spontaneous and exothermic sorption process. The results indicate that waste of wood (like sawdust) is an attractive sorbent for removing reactive dyes from the wastewater.

Keywords: Orange 16 reactive dye, sawdust, sorption, kinetic, thermodynamic study

1. Introduction

The presence of synthetic dyes in the environment can generate serious problems because their possible toxicity and carcinogenicity, heightened by the fact that many dyes formerly were made of known carcinogens (i.e. benzidines). Due to their aromatic structures these compounds are more stable, no biodegradable and difficult to remove from the industrial effluents before their discharges into the urban wastewater sewage system or different emissaries.

The industrial effluents are characterized by complex compositions that make impossible a general available method for removing textile dyes. Several technologies have been developed to remove dyes from industrial wastewater; these include chemical precipitation, coagulation/flocculation process, membrane filtration, oxidation process, adsorption, reverse osmosis, ion exchange, solvent extraction [1-4]. Many of these processes are often complicated and time consuming, generate sludges or other toxic wastes and may be ineffective or expensive for diluted dye solutions.

Sorption has been found to be an efficient and economic method for dyes removal. One of the advantages is the possibility to use a large variety of solid materials: synthetic to natural low-cost materials (natural as well as wasted materials from different industries and agriculture) as suitable sorbents for decolourization of industrial effluents [5].

Sorption onto activated charcoal is a very useful technique, but the high cost implied to obtain this sorbent stimulated the search of cheaper alternatives.

In this context, the overall attention was moved to the non-conventional and low-cost materials which include industrial and agricultural by-products and wastes [2,6,7].

Thus, the sorption of reactive dyes on solid materials based on wood wastes (i.e. special types of sawdust) have been intensively studied and the principal data are sumarized in Table 1.

TABLE 1. Application of sawdust as biosorbent for removal of different dyes

Sorbent	Retained dyes	Sorption capacity, q	Ref.
Wood shavings - untreated	- Methylene Blue - Egacid Orange - Methylene Blue - Egacid Orange	0.056 mmol/g 0.033 mmol/g	8
- chemically treated		0.039–0.091 mmol/g 0.036-0.111 mmol/g	
Pine sawdust	Acid Blue 256	280.3 mg/g	9
Treated wood sawdust	Basic Green 4	74.5 mg/g	10
Wood sawdust	Basic Blue 69 Acid Blue 25	74.4 mg/g 5.99 mg/g	11
Neem sawdust	Basic Violet 3 Basic Green 4	3.78 mg/g 3.42 mg/g	12
Rubber wood sawdust	Bismarck Brown	35 mg/g	13

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The results of these studies suggest that the sorption onto wood wastes is a progression towards a perspective method.
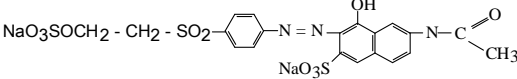
This paper continues our studies concerning utilisation of sawdust as low-cost sorbent for decolourization of different textile effluents which contain synthetic textile dyes with a high molecular weight [14,15]. In this context, kinetic and thermodynamic studies were carried out in order to establish all favourable conditions to uptake of reactive dyes with large molecules.

2. Experimental

2.1. Materials and reagents

The principal material and reagent used in this study are presented and characterized in Table 2.

TABLE 2. Characterization of material and reagent

Material	Characteristics
Sawdust	Represents waste material from the wood processing. *Preparation*: dried in air, sieved and collected the fractions with particle size of 1-2 mm. *Constituents*: like other lignocellulosic materials the major constituents are: cellulose, hemicelluloses and lignin. *Physical properties*: humidity 9.85%; ash: 0.5234 %; density 1211 Kg/m^3 and caloric power 2035 kcal/Kg
Reactive dye -Orange 16	*Concentration of the stock solution*: 500 mg/L. *Working solutions* were prepared by appropriate dilution with bidistilled water of the stock solution. *Concentrations of working solutions*: 24.7 – 197.6 mg/L. *Properties*: MW = 617.54, λ_{max} = 495 nm. *Chemical structure:* $NaO_3SOCH_2 - CH_2 - SO_2$ —⬡— $N = N$ ⬡ $N - C$ O CH_3 with OH and NaO_3S substituents

2.2. Working Method

The effect of contact time against the sorption of Orange 16 reactive dyes onto sawdust was determined by the 'limited bath' technique. A sample of 0.2 g of sawdust was added under stirring to 25 mL of dye solution (i.e. 86.45 mg/L initial dye concentration) into the conical flask (capacity of 250 mL) placed in a thermostatic assembly. The solution pH was adjusted to the value of 1 using the 1N HCl solution, and was measured at a Hach One Laboratory pH Meter, U.S.A. The temperature of solutions was maintained at 20 ^{0}C. After appropriate time intervals (5 - 400 min), volumes of supernatant were taken for determination of residual dye content by absorbance measurements (495 nm) at a SP-830 Plus spectrophotometer, Metertech Inc. Version 1.06.

The amount of sorbed dye, *q* (mg dye/g sawdust), was evaluated by the next equation:

$$q = \frac{(C_0 - C) \cdot V}{G} \tag{1}$$

where, C_0 and C are the initial and residual dye concentration (mg/L), *G* is the amount of sawdust (g) and *V* is the volume of solution (L).

The extent of sorption was expressed by the fractional attainment of equilibrium:

$$F = \frac{q_t}{q} \tag{2}$$

where, q_t and *q* (mg/g) are the amounts of dye sorbed at time *t* and at equilibrium (24 h), respectively.

3. Results and Discussion

3.1. Effect of contact time

The information on the sorption rate is required for selecting optimum conditions of operating in full-scale batch process. Thus, we studied the effect of contact time on removal the Orange 16 reactive dyes from solutions of initial concentrations of 86.45 mg/L, by sorption onto sawdust (Fig. 1).
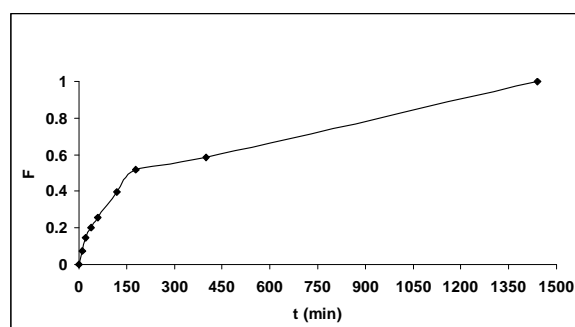

Figure 1. The fractional attainment of equilibrium (F) versus time for sorption of Orange 16 reactive dye onto sawdust: T= 20°C; pH= 1; 4 g sawdust/L, C_0 = 86.45 mg/L

As it can be seen in Fig. 1, the rate of sorbtive removal of this reactive dye is rapid into the first 100 min and after has a constantly proportional increasing until the equilibrium establishment (after more than 4 hours, but usually corresponding to a contact time of 24 hours).

3.2. Kinetic study

Three different kinetic models were used to process the experimental data of Orange 16 reactive dye sorption onto sawdust (Table 3).

The kinetic parameters related to each model were calculated from the intercepts and slopes of the corresponding linear plots (Figure 2a,b,c).

The values of kinetic parameters together with their correlation coefficients (R^2) are synthetically presented in Table 4.

TABLE 3. Mathematical equations and the main parameters of the three tested kinetics models

Kinetic model/ Linear form of equation	Model parameters, significance
Lagergren model (pseudo-first order kinetic model) [16] $\log(q_e - q_t) = \log q_e - k_1.t$	k_1 (min^{-1})- the rate constant of the pseudo-first order sorption
Ho and McKay model (pseudo-second order model) [17] $\dfrac{t}{q_t} = \dfrac{1}{k_2 \cdot q_e^0} + \dfrac{t}{q_0}$	k_2 is the rate constant of pseudo-second order sorption (g/mg.min) $h = k_2.q_e^2$ (mg/g·min) is the initial sorption rate (mg/g.min) at t value close to zero
Intra - particle diffusion model [18] $q_t = k_p \cdot t^{0.5} + c$	k_p is the rate constant for intra-particle diffusion (mg/g.min$^{0.5}$) c is an experimental sorption constant
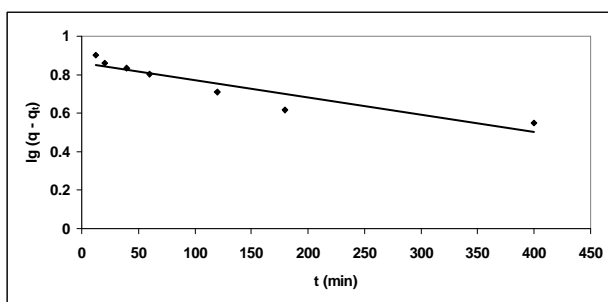
Figure 2a. Pseudo-first order sorption kinetics of Orange 16 reactive dye onto sawdust: T= 20°C; pH= 1; C_0 = 86.45 mg/L; 4 g sawdust/L
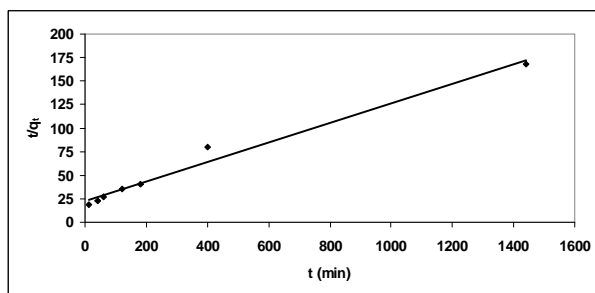
Figure 2b. Pseudo-second order sorption kinetics of Orange 16 reactive dye onto sawdust: T= 20°C; pH= 1; C_0 = 86.45 mg/L; 4 g sawdust/L
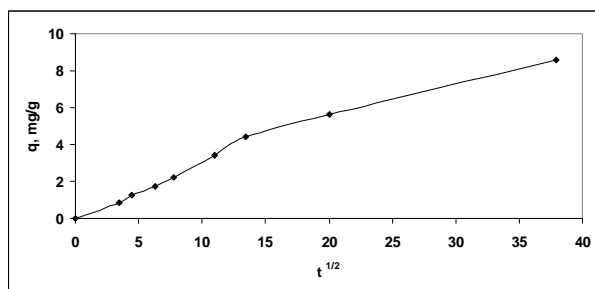
Figure 2c. Intra-particle diffusion model for the Orange 16 reactive dye sorption onto sawdust: T= 20°C; pH= 1; C_0 = 86.45 mg/L; 4 g sawdust/L

In this context, it can be mentioned that the R^2 values are below 0.90 suggesting the fact that the Lagergren model is not the most indicated model (the best fitted model) for the obtained kinetic data; also the estimated values of q_0 are not in a good agreement with the performed experimental data.

TABLE 4. The kinetic parameters of Orange 16 reactive dye sorption onto sawdust wastes

Kinetic model	Parameters	Value
Lagergren model - pseudo-first kinetic model	k_1 (min^{-1})	0.02073
	R^2	0.8682
	q_0 (mg/g)	7.231
Ho model - pseudo-second kinetic model	k_2 (g/mg.min)	0.431x10^{-4}
	h (mg/g.min)	0.044
	q_0 (mg/g)	9.62
	R^2	**0.9823**
Intra-particle diffusion model	k_p mg/g.min$^{0.5}$	0.2217
	R^2	0.9633

The pseudo-second order model (i.e. Ho model) assumes that the sorption follows a second order sorption mechanism and the rate limiting step can be the chemical sorption involving valence links or covalent links between sorbent and adsorbate [17]. The value of correlation coefficients higher than 0.9 for this model shows a good compliance with the pseudo-second order kinetic model. Also, the good correspondence between the calculated and experimental values of sorption capacity indicates that the kinetic data are in very good agreement with the pseudo-second order rate equation.

The intra-particle diffusion model assumes that sorption is a multi-step process involving transport of adsorbate from aqueous solution to the sorption sites of the sorbent and the diffusion into pores is the slow rate determining process. From Figure 2c it is observed that, after saturation of the surface (into the first 40 min), a linear equation form of the q vs $t^{0.5}$ is obtained indicating the diffusion of adsorbate species through the internal porous structure of the sawdust.

3.3. Thermodynamic study

The aim of thermodynamic study is to establish the thermodynamic parameters that can characterize the sorption process of Orange 16 reactive dye onto sawdust material. The thermodynamic parameters, usually free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), have an important role to determine spontaneity and heat change for the adsorption process.

In order to evaluate the effect of temperature on the Orange 16 reactive dye sorption onto sawdust, the apparent thermodynamic parameters were determined using the values of binding Langmuir constant, K_L (L/mol) at 2°, 20°, and 45°C, previously determined [19], and also the following two equations.

$$\Delta G = -RT \ln K_L \qquad (4)$$

$$\Delta G = \Delta H - T \cdot \Delta S \qquad (5)$$

where R is the universal gas constant and T is the absolute temperature.

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The calculated values of the thermodynamic parameters are synthetically presented in Table 5.
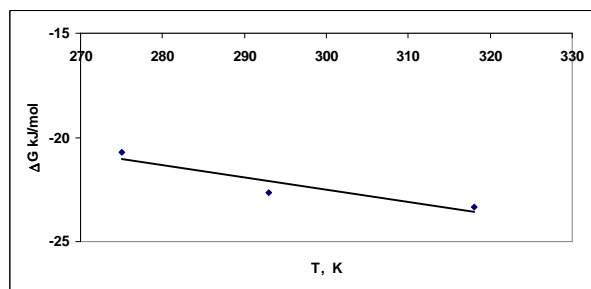

Figure 3. The plot of ΔG versus T

TABLE 5. The thermodynamic constants of the sorption process of Orange 16 reactive dye onto sawdust

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
278	-20.725		
293	-22.625	- 4.8115	- 59
318	-23.352		

The negative value of ΔG indicates the spontaneous nature of dyes sorption onto sawdust. The values of ΔG decreases with an increase in temperature showing that the spontaneity of the sorption process depends directly proportional of temperature.

The negative values of ΔH (-4.815 kJ/mol) calculated from the slope of linear dependence ΔG *vs.* T (Figure 3) reveal the exothermic behaviour of sorption process of Orange 16 reactive dye onto sawdust.

Therefore, the magnitude of ΔH and ΔG gives some informations about the nature of sorption process [20]. The literature data [21-25] show that a physical sorption is characterized by values of ΔH no more than 4.2 kJ mol^{-1} and ΔG lower than 40 kJ mol^{-1}. According to the calculated data from Table 5, the sorption of Orange 16 reactive dye onto sawdust in acidic media is rather physical adsorption than chemisorption.

These observations are confirmed by the other research results included in one of our previous study [15].

Finally, it can be said that the sorption mechanism of sorption of Orange 16 reactive dye onto sawdust is a combined one of adsorption and ionic exchange. The links and forces involved in adsorption can range from weak van deer Waals forces to electrostatic attractions between the ionized sulfonyl groups of the dye molecule and positively charged surface of biosorbent.

4. Conclusions

The ability of sawdust as biosorbent to retain the reactive dyes with high molecular weigh was investigated for Orange 16 reactive dye using kinetic and thermodynamic experimental data.

The kinetics of Orange 16 reactive dye sorption onto sawdust were studied using the pseudo-first, pseudo-second order and intra-particle diffusion kinetic models.

The results indicated that the pseudo-second order equation provided the best correlation with the experimental data. Also, this fact suggests that chemical sorption instead of mass transfer is the rate-controlling step for the sorption process.

The thermodynamic parameters of the sorption process were also evaluated. The negative value of ΔG confirms the spontaneous nature of sorption process. The negative value of ΔH indicated that the sorption process is exothermic.

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