USE OF INDUSTRIAL WASTE BASED ON LIGNINE REMOVAL FROM AQUEOUS SOLUTION BY SORPTION

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The batch equilibrium of Brilliant Red HE-3B reactive dye sorption on industrial lignin was investigated in order to explore its potential to be use as low cost sorbent for wastewater treatment. Sorption isotherms were determined at 20^0 C and the experimental data obtained were modeled with the Langmuir and Freundlich isotherm equations. Also, it was studied the influence of some operating variable: initial dye concentration, sorbent mass, pH, temperature. For determination the sorption equilibrium concentrations of dye were used a UV-vis spectrophotometry analytical method. The results indicate that the industrial waste based on lignin can be an attractive option for reactive dye, like Brilliant Red HE-3B, removal from dilute aqueous solutions

Key words: *dye, lignin, sorption, wastewaters*

Dyes - a large and important group of industrial chemicals, were used in the various industries such as textile, leather and dyeing, pulp and paper, food and cosmetics. The discharged colored industrial effluents are generally considered to be toxic to fish and other wildlife at the concentrations likely to be present and disturbing the equilibrium of aquatic biota. In this context, the actual tendencies are to elaborate very strict settlements concerning wastewater disposal, to develop new technologies for textile effluent depollution and to replace the synthesis of organic dyes with natural products with no toxicological, allergen and mutagen risk, named environmentally-friendly materials. Many different and complicated molecular structures of dyes make very difficult to choose a technique for wastewaters treatment. Some methods have been employed to remove dyes from industrial effluents, such as chemical precipitation, membrane technologies, adsorption, flocculation, foam flotation, biological processes, oxidation and photocatalytic degradation; many of these methods have certain efficiency but require considerable operational costs [1-5]. Sorption appears to offer the best prospect for wastewaters treatment and promises to be effective for dyes removal. It has been found to be more efficient to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and the possibility to use like sorbent a large category of materials such as: materials with ion exchange properties, activated charcoal, natural or synthetic zeolite, ash, lignino-cellulose materials which are presented in nature or are secondary products from industrial or agricultural transformation [1-3, 6-8].

This paper presents the results about the evaluation the analytical sorption potential of lignin like sorbent in retention by batch sorption of reactive dye Brilliant Red HE-3B from synthetic aqueous solution. Operating variable studied were initial dye concentration, sorbent mass, pH, temperature. Sorption isotherms were determined at 20^0 C and the experimental data obtained were modeled with the Langmuir and Freundlich isotherm equations. The sorption equilibrium concentrations were determined by UV-vis spectrophotometry analytical method.

MATERIALS AND METHODS

Sorbent materials.

The *lignin* represents a macromolecular compound much more reactive than cellulose because of its functional groups (hydroxylic, both phenolic and aliphatic). The lignin used like sorbtive materials can be the main by-product of the pulp industry and also can represent a product obtained from renewable resources [9].The experiments were carried out with alkali lignin (offered by Granit Co.) L_1 (from *Wheat straw* 100-W-A) with characteristics present in *Table 1.*

Table 1

The characteristics of Lignin sample [9]

Characteristics	L_1 (100-W-A)	Characteristics	L_1 (100-W-A)
Acid insoluble lignin, %	90	pH (10% dispersion)	2.7
Acid soluble lignin, %	1	Mw	3510
COOH, mmole/g	3.8	T softening, ^{0}C	170
Aromatic OH, mmole/g	1.7-1.8	Solubility in furfuryl alcohol, %	88.5
OH/C9 groups chemical method	1.02	Solubility in aqueous alkali, pH 12, %	98.5
Ash, %	2.5		

The *reactive dye* bifunctional monochlortriazine Brilliant Red HE-3B from BEZEMA (*Fig. 1*, MW =1463, adsorption maximum, λ_{max} = 530 nm) was used as commercial salt. Working solutions (in concentrations of 20-300 mg/L) were prepared by appropriate dilution with bidistilled water of the stock solution (500 mg/L).

S*orption studies.*The sorption of dye on tested sorbent was studied at desired temperature by employing the batch method. A known volume (25 mL) of dye solutions of varying initial concentrations was contacted with a fixed dose of sorbent (0.35 g) for a specified period of contact time in a thermostatic bath. The initial solution pH was adjusted to the required value by adding dilute HCl solutions and measured with a Radelkis OP-271 pH/Ion analyzer. After equilibrium, the concentration of the dye in the residual solution was determined spectrophotometrically with an UV-VIS Digital Spectrophotometer, model S 104D /WPA. The sorption capacity of the lignin was evaluated by means of the amount of dye sorbed: $q = (C_0 - C) \cdot V \cdot 10^{-3} / G$, (mg of dye/g of lignin) and by percent of dye removal: $R\% = (C_0 - C) \cdot 100 / C_0$, where C_0 and C are the initial and the equilibrium (residual) concentration of dye in solution (mg/L), *G* is the amount of lignin (g) and *V* is the volume of solution (L).

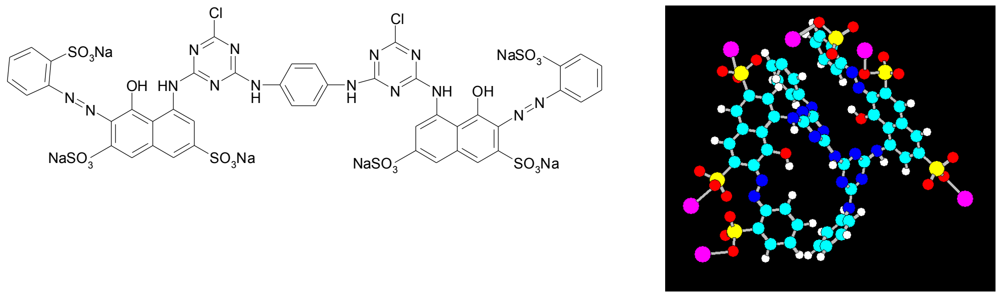

Figure 1 **Bis (monochloro-*s*-triazine) reactive dye (Brilliant Red HE-3B, C.I. Reactive Red 120)**

RESULTS AND DISCUSSION

Effect of pH. The pH of the solution represents an important parameter for controlling the sorption process. The variation of dyes removal percent (R, %) as a function of initial pH of solution, presented in *Figure 3a*, shows that the considered anionic dye is retained from acidic media of pH $\leq$ 2. This behaviour may be correlated with the variation of the lignine surface charge in function of the solution pH. The value of pH_{PZC} (pH of zero charge) for lignine, determined by method proposed by Nouri and Haghseresht [10], was of 3.5 (*Fig. 3b*). At values of pH < pH_{PZC} the lignine surface is positively charged and susceptible to electrostatic interactions with polar portions of Brilliant Red HE-3B reactive dye molecule (dissociated sulphonic groups). At pH > pH_{PZC} values, the sorbent surface is negatively charged and is not available to bind anionic dyes.

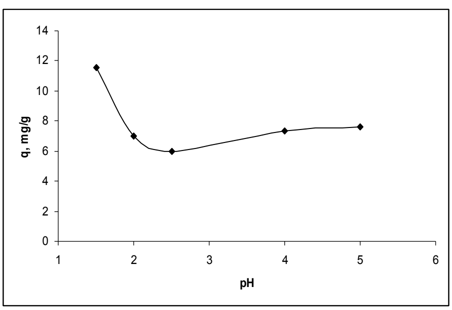

Figure 3a **Effect of pH on the sorption of dye on lignin**

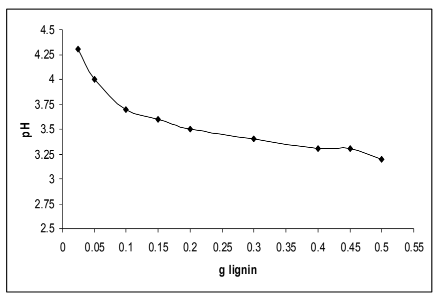

Figure 3b **The value of pH_{PZC} (pH of zero charge) for lignin**

Effect of sorbent dosage. The results, presented in *Figure 4*, showed that the percentage removal of dye increased with the increase in sorbent dose. This can be attributed to increase sorbent surface area availability of more sorption sires that resulting from an increase of sorbent amount. In the same time, amount of dye sorbend per unit mass of lignin decreased with increase in sorbent dose.

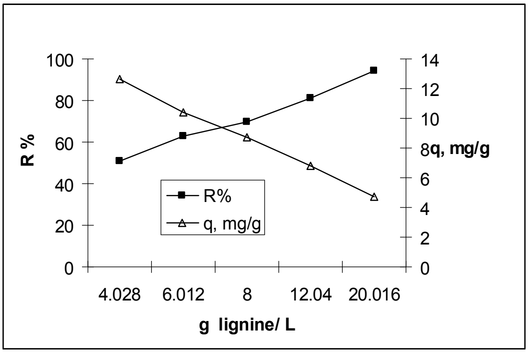

Figure 4 **The influence of amount of sorbent on the sorption of dye on lignin: 100mg/L, pH 1.5, 20^{0}C**

Effect of temperature. The dye sorption onto lignin sorbent is dependent of temperature (*tab. 2*). The data presented in *Table 2* shown that the sorption capacities of lignin increased with increasing temperatures from 5 to 45^{0}C, which indicates that the sorption process is endothermic.

Table 2

The temperature influence into dye sorption on lignin (pH 1.5, dose of sorbent 14g/L)

Temperature ($^0C \pm 2^0C$)	C_0 (mg/L)	q (mg/g)	Temperature ($^0C \pm 2^0C$)	C_0 (mg/L)	q (mg/g)
5	100	5.040	5	150	7.16
20		5.845	20		7.94
45		6.590	45		9.28

Effect of initial dye concentration. The sorption capacity of lignin for reactive dye sorption was determined at the favourable pH in solutions with different initial dye concentrations. The results presented in *Figure 5* shows that the percent of dye removal (R, %) onto lignin decrease with an increase in initial dye concentration, but the amount of dye retained increases with increasing of initial concentration.

Sorption isotherms. The sorption isotherm - the equilibrium relation between the concentration of the sorbate on solid phase and in aqueous phase - is characterized by some constant values, which express the surface properties and affinity of the sorbent. It can also be used to compare the sorbtive potential of different sorbents for the same and different pollutants.

The experimental data of sorption equilibrium for this sorbent were analyzed using two of the most widely used models for adsorption isotherm:

• the **Freundlich** [11], which is an empirical equation based on sorption on heterogeneous surface. It is given as:

$$q = K_F \cdot C^{1/n} \qquad (1)$$

where K_F parameter is related to the adsorption capacity and n is a measure of sorption energy; a favorable sorption corresponds to a value of $1 < n < 10$. For n =

1, K_F = K and isotherm is linear. K_F and n can be calculated by plotting log q versus log C.

- the **Langmuir** [11] model, which is valid for monolayer sorption onto a surface with a finite number of identical site, and is expressed by following equations:

$$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C} \qquad (3)$$

where K_L is related to intensity of the sorption process and q_0 is the maximum value of sorption capacity (corresponding to complete monolayer coverage). The Langmuir constants can be calculated by plotting 1/q versus 1/C.

The parameters related to each isotherm, calculated from the intercepts and slopes of the corresponding linear plots (*Figure 6a and 6b*) together with their correlation coefficients (R^2) are presented in *Table 1*.

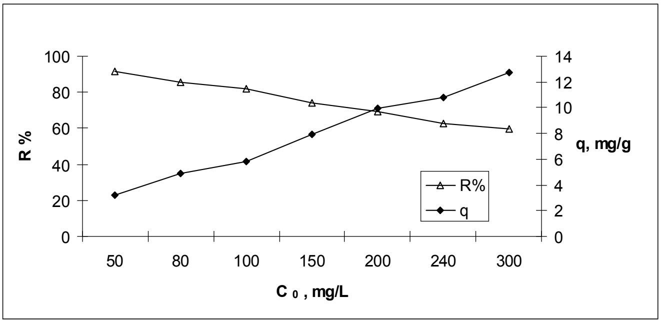

Figure 5. **The influence of initial dye concentration of the sorption process**

The correlation coefficients (R^2) for the Langmuir isotherm are highest comparatively to the coefficient values performed for the Freundlich model. Therefore, the Langmuir isotherm is the best fitting isotherm for the sorption of Brilliant Red HE-3B reactive dye on lignin sorbent at room temperatures.

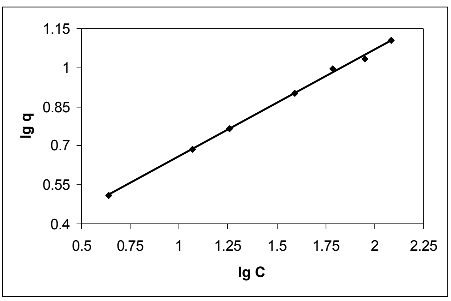

Figure 6a **The linearized form of Freundlich isotherm of the reactive dye Brilliant Red HE-3B sorption on lignin at 20^0C , pH = 1.5, 14 g lignin /L**

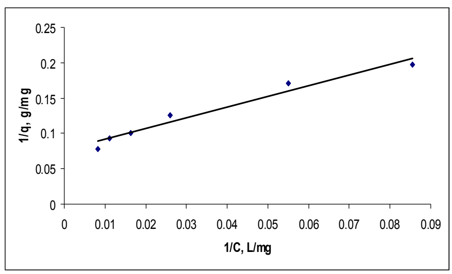

Figure 6b **The linearized form of Langmuir isotherm of the reactive dye Brilliant Red HE-3B sorption on lignin at 20^0C, pH = 1.5, 14g lignin /L**

Table 3

The characteristic parameters of reactive dye Brilliant Red HE-3B sorption onto lignin sorbent

T (^{0}C)	Freundlich isotherm			Langmuir isotherm		
	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2	q_0 (mg/g)	K_L (L/mg)	R^2
20 ±2	1.778	2.44	0.963	12.05	0.0505	**0.998**

CONCLUSIONS

The sorption of reactive dye Brilliant Red HE-3B from aqueous systems onto pure lignin like sorbent is a function of initial dye concentration, temperature, amount of sorbent and pH of solutions. The results of this study show that the tested material has a moderated capacity for dye molecules uptake comparative with other literature information's. Experimental results provide promising perspective for the utilization of lignin (waste material for wood industry or renewable from vegetables wastes) as sorbent in reducing pollution of textile effluents.

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