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FOOD AND ENVIRONMENT SAFETY

THE INTERACTION BETWEEN BEANS HULLS AND FOOD DYE

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Abstract: *In this study, a local agro – waste, namely beans hulls, was used to identify the interactions between it and the xanthene food dye Red No. 3. Batch experiments were made iIn order to identify if the dye can be adsorbet by the hull components.*
Thus, the investigation started with the influence of different parameters on bean-hull absorption capacity: pH, contact time, initial dye concentration, and temperature. The amount of dye sorbed was found to vary with the initial dye concentration and contact time. The process is favorable at low acid pH (5) value and the optimum sorbent dosage was found to be 20 g L^{-1} sorbent.

Keywords: *beans hull, Red No. 3, sorption parameters.*

1. Introduction

Effluents from industries like food, cosmetic and pharmaceutical contain different kinds of synthetic dyes. Coal-tar dyes can have hazardous effects on the living systems because of their carcinogenicity and toxic nature. Due to their synthetic origins and aromatic structures, with by-products biologically non-degradable, it is rather difficult to treat these effluents (i.e. Red No. 3). Therefore, the removal of dyes from aqueous solution becomes environmentally necessary.
Out of the processes applied for the removal of dyes, sorption is often one of the effective methods because it produces an effluent that is free of harmful substances that can appear in the case of biodegradation and photodegradation i.e. [1, 2].
Red No. 3, also known as Erythrosine, is an organoiodine compound, obtained from fluorone. It is the disodium salt of 2,4,5,7-tetraiodofluorescein used for food coloring [2].
Different studies in view of eliminating Red No. 3 from aqueous solutions have been done considering degradation methods and the researchers supposed that the intermediates formed can be toxic [3-6]. Some examples of adsorbents used for Red No. 3 removal are feathers [7], de-oiled mustard [8], montmorillonite [9], bottom ash and de-oiled soya [10]. Other unconventional biosorbents used for different dye classes' removal are hazelnut shells [11], nut shells [12], pumpkin seed hull [13] or bagasse pith [14].
In this study, the agro – waste beans hull (BH) was used as potential biosorbent for Red No. 3 removal from aqueous solutions because it has a good efficiency when tested for the sorption of lead ions [15] and Acid Red 57 decolorization [16].
Batch experiments were conducted for the study of the influence of some parameters on dye adsorption efficiency, such as:

initial solution pH, initial dye concentration, process temperature and the biosorbent concentration. The results were correlated with thermodynamic parameter (free energy of adsorption (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o)).

2. Materials and Methods

2.1. Materials

The research performed in this section brings information on a representative xanthene dye, (Red No. 3) removal from aqueous solutions by agro-waste (bean hull), in batch mode.
Adsorbate
The acid dye used in this study, Red No. 3, was purchased from Sigma–Aldrich (C.I. Acid Red 51, 45430). A stock solution of 1000 mg L^{-1} was prepared by dissolving an accurately weighed amount of Red No. 3 in 500 mL distilled water. For the experimental assays, dilution of the stock was done to achieve the desired concentration, always when necessary.
Absorbent
Phaseolus vulgaris L. used in the study was purchased from a local farm. The by-product is an herbaceous annual plant botanically classified as a dicotyledonous. Dried pods, no seeds of bean contain aminoacids (arginine, asparagines, tryptophan, tyrosine, lysine, betaine, etc.), vitamin C, salicylic acid, phosphoric acid, minerals [17, 18, 19] (Table 1). Before being used as sorbents, the by-product was washed several times with distilled water to remove any adhering dirt and dried at 40ºC for 24h. The dried sample was crushed using a Retsch GM 200 laboratory mill. No other chemical or physical treatments were used prior to adsorption experiments. Finally, they were sieved and classified. The less 3 mm particles size of beans hulls were used in the experiments study. The sorbent was stored in plastic boxes.

The point of zero charge (pH_{PZC}) of BH was determined by immersion technique and potentiometric mass titrations (PMT) [20].

Table 1.

Chemical composition of bean hull (adapted after Duke [17])

Compound	Amount of compound
Water (%)	58.30
Proteine (%)	7.40
Carbohydrates (%)	29.80
Fates (%)	1.00
Fibers (%)	1.91
Ash (%)	1.63
Calcium (mg/100g)	50
Phosphorus (mg/100g)	160
Iron (mg/100g)	2.60
Thiamine (mg/100g)	0.34
Riboflavin (mg/100g)	0.19
Ascorbic acid (mg/100g)	27
Carotene (mg/100g)	0.057

2.2. Batch sorption study

Batch experiments were performed in Erlenmayer flasks, containing Red No. 3 solution at various concentrations (10, -400 mg L^{-1}) and different amount of sorbents (10 - 30 g L^{-1}). The flasks were incubated at room temperature (25±1ºC) and 150 rpm in an isothermal shaker (IKA KS 4000 IC) for 24 h until the dye removal reached equilibrium. All the experiments were carried-out in duplicates and at the natural pH of the solution (pH = 5.6).The factors affecting dye adsorption efficiency were investigated: initial dye concentration, sorbent amount, pH, temperature and contact time.
The effect of pH on the color removal efficiency was analyzed over the pH range of 4 to 10. The pH study was carried out using Britton–Robinson buffer solution.

2.3. Analysis methods

The solution containing different dye concentrations was determined spectrophotometrically at the maximum absorption wavelength. Red No. 3 shows an intense absorption peak in the visible region at 524 nm which corresponds to the maximum absorption peak of the Red No. 3 monomer.

The pH solution was measured using a Hanna pH meter provided with a combined glass electrode (Model Hanna HI1053B).

The amount of dye uptake per unit mass of sorbent at time t, (q_t, mg g^{-1}) and at equilibrium (q_e, mg g^{-1}) was calculated using Eqs. (1) and (2). The sorption efficiency was calculated applying Eq. (3):

$$q_t = \frac{C_i - C_t}{m} * V \qquad (1)$$

$$q_e = \frac{Ci - Ce}{m} * V \qquad (2)$$

$$R\,(\%) = \frac{Ci - Ce}{Ce} * 100 \qquad (3)$$

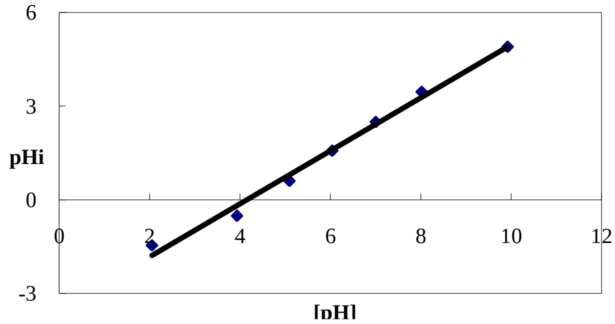
where: C_i is the initial dye concentration (mg L^{-1}); C_t and Ce, the concentration of dye at time t and at equilibrium (mg L^{-1}); *m*, the amount of dried sorbent used (g); *V*, the volume of the solution (L).

3. Study on the factors influencing the Red No. 3 sorption process

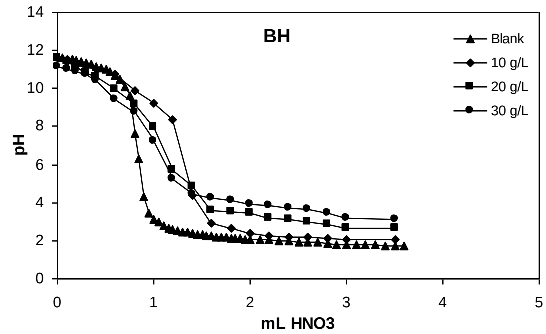
3.1. Determination of point of zero charge (pH_{pzc})

The data obtained using immersion techniques (IT) for pH_{pzc} determination are plotted in the fig.1 a. The experimental curves corresponding to potentiometric mass titrations method (PMT) technique are presented in the Fig. 1b.

The results obtained by applying IT and PMT are in concordance. The point zero charge determines the surface charge of the sorbent at a given pH and its knowledge offers information's about the possible electrostatic interactions between sorbent and various chemical species [21]. The pH_{pzc} determined value for BH was 4.6. The obtained data indicated that the BH surface is mostly acidic and this could be a favorable property for Red No. 3 adsorption at pH<6 when the sorbent is positively charged.



a)



b)

Fig. 1. Point of zero charge of BH determined using a) immersion techniques and b) potentiometric mass titrations method

3.2. Effect of pH on dye uptake

To analyze the effect of pH on the sorption capacity of BH on the amount of dye removal, the experiments were carried out at different initial solution pH values varying from 4 to 10 (Fig. 2). For a pH less than 5, Red No. 3 in contact with sorbent reacts with the buffer solution and the absorbance of the solution decreased very much due to the strong acidity of the medium that conducts to dye precipitation [22].

The effect of pH on the amount of dye sorbed and process efficiency, respectively can be observed in the fig.2. The minimum amount of Red No. 3 sorption was achieved at pH 10, value that increased at 0.72 mg g^{-1}, with the decrease of pH until 5.

As in the case of PSH, in the study conducted by Apostol *et al*. [13] the removal of Red No. 3 using BH occurs mainly by ion-exchange reaction because at pH values coresponding to acid domain the surface of the adsorbent is positively charged (high H^+ concentration), so the electrostatic attraction between the adsorbent and the adsorbate (which is an anionic dye) is enhanced.

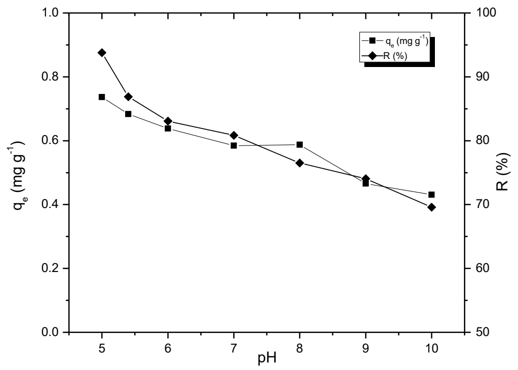


Fig. 2. Effect of pH on the Red No. 3 uptake onto BH (C_i=20 mg L^{-1}; $C_{sorbent}$=20 g L^{-1})

3.3. Effect of sorbents concentration on sorption efficiency

The influence of BH concentration on Red No. 3 adsorption was conducted at an initial dye concentration of 20 mg L^{-1}. In solution, the concentration of BH varied between 5 and 50 g L^{-1}. Fig. 3 shows the results of Red No. 3 sorption, at the equilibrium for various sorbent dosages. The percentage of dye removed starting with 20 g L^{-1} of BH concentration become almost constant, the curve approaching plateau (Fig. 3).

The increase in the sorption efficiency of Red No. 3 with the BH dosage can be explained by a high surface area and the availability of more adsorption sites [23, 24]. At sorbent dosage higher than 20g L^{-1} the Red No. 3 concentration in the two phases (BH surface and the solution) come to equilibrium with each other [25].

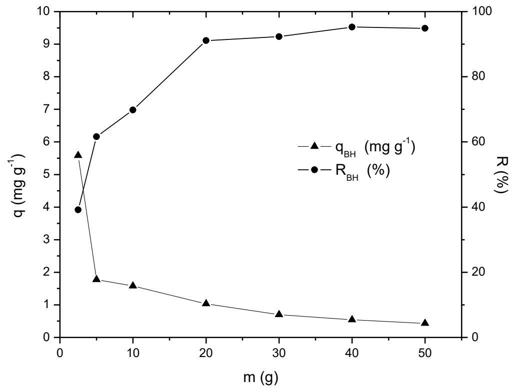


Fig. 3. Effect of amount of sorbents on Red No. 3 removal (C_i = 20 mg L^{-1}; pH = 5.6)

3.4. Effect of initial dye concentration on uptake capacity of the sorbent

The contact time influence on the sorption of Red No. 3 on BH was investigated at the ambiental temperature using initial concentrations between 10 and 30 mg L^{-1}.

For 50 and 100 mg L^{-1} Red No. 3 uptakes were evaluated at various temperature (20, 30 40 and 50°C).

The results show that the amount of Red No. 3 adsorbed increased with contact time for the concentrations tested at ambiental temperature in the shaker. The apparent equilibrium is achieved at around 5h after experiment started. The increasing of initial Red No. 3 concentration raises the q value from 0.4 to 1.2 mg g^{-1} (Fig. 4).

Figs. 5a and 5b present the results obtained for the assay with 50 mg L^{-1} and 100 mg L^{-1} Red No. 3 at different temperatures. It can be observed that, when a solution of 50 mg L^{-1} Red No. 3 was used at different temperature the dye uptake at equilibrium shows differences as compared to the assay conducted with 100 mg L^{-1}. Using 50 mg L^{-1} Red No. 3 initial concentration, at 20°C the dye uptake is around 1.3 mg g^{-1}, while at 50°C the dye uptake is around 1.7 mg g^{-1}.

In the case of 100 mg L^{-1} initial dye concentration at 20°C the dye uptake is around 1.7 mg g^{-1}, while at 50°C dye uptake is around 2.2 mg g^{-1}.

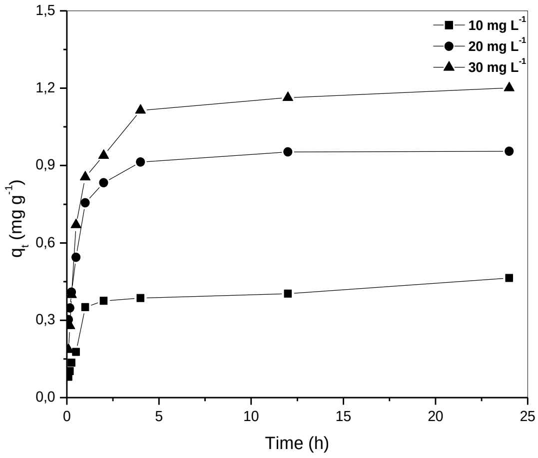


Fig. 4. Effect of contact time for different initial concentration of Red No. 3

3.5. Thermodynamic parameters

Thermodynamic parameters obtained from the slope and intercept (Fig. 6) of Van't Hoff plots are shown in the Table 2. The negative values of ΔG° demonstrate that Red No. 3 sorption is spontaneous for the temperature range evaluated.

The positive values of enthalpy's change (ΔH°) shows that the sorption process is endothermic, increased temperature leads to a higher Red No. 3 amount uptake at equilibrium. The positive values of ΔS° achieved in this case is in concordance with the study conducted using pumpkins seeds hulls as sorbent by Apostol *et al.* [13] and reveals the affinity of Red No. 3 for its uptake by BH.

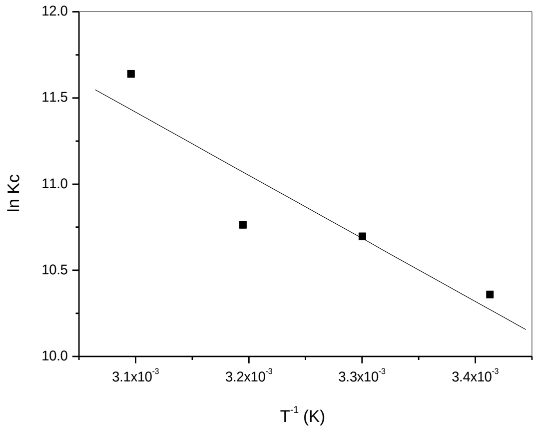
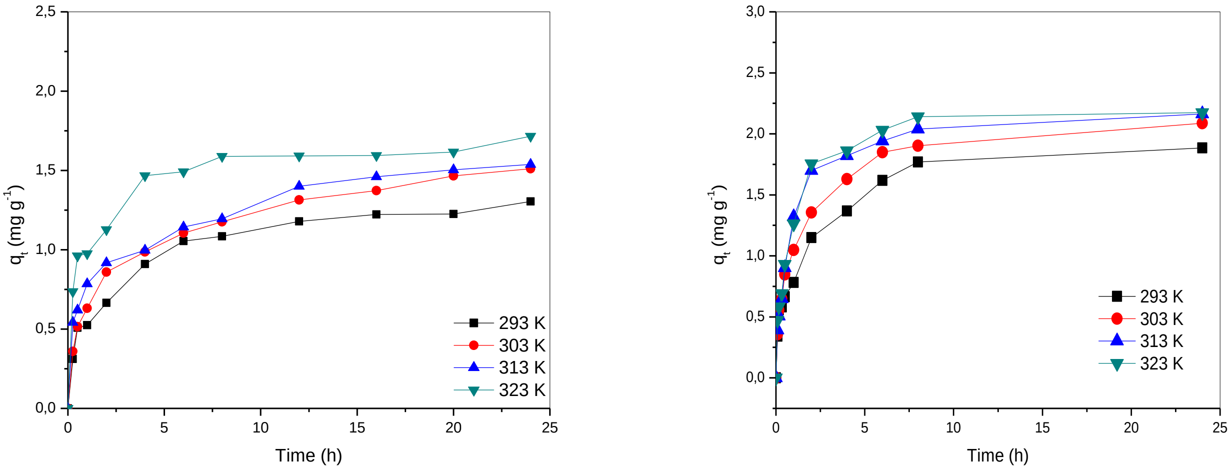


Fig. 6. Plot of ln K_L vs.T^{-1} for the removal of Red No. 3 by BH



a) b)

Fig. 5. Effect of contact time for (a) 50 mg L^{-1} and (b) 100 mg L^{-1} Red No. 3 at different temperature

Table 2.

Thermodynamic parameters for the sorption of Red No. 3 on BH

Temperature (K)	K_L (L mmol^{-1})	Thermodynamic parameter		
		ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
293	0.04068	-22.97	30.44	182.3
303	0.05705	-24.79		
313	0.06103	-26.61		
323	0.1465	-28.44		

4. Conclusions

The analyses made in this study indicated that Red No. 3 can be attached by beans hulls molecules. The amount of dye sorbed was found to vary with the initial dye concentration and contact time besides the main parameters influencing the process: low acid pH (5) value and at 20 g L^{-1} sorbent dosage.

Thermodynamic parameters obtained from the slope and intercept of Van't Hoff plots showed negative values of $\Delta G°$ and demonstrate that adsorption is highly favorable and spontaneous; the positive values of enthalpy change (ΔH°) stand for the endothermic nature of the processes. The positive values of $\Delta S°$ obtained for Red No. 3 - BH system reveal the affinity of the dye for the adsorbent.

In these conditions BH is effective for Red No. 3 sequestration from aqueous solutions since a wide range of concentrations may be applied in batch system (5-400 mg L^{-1}).

5. Acknowledgments

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