

BATCH COMPARATIVE STUDY OF SORPTIVE PROPERTIES OF TWO VARIETIES OF ALMOND PEELS FOR BEZANYL RED (ACID DYE) FROM SYNTHETIC AQUEOUS SOLUTIONS

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ABSTRACT

The ability of two varieties (hard and soft) of almond peels, as inexpensive sorbents for the removal of bezanyl red (acid dye) from synthetic aqueous solutions has been studied. After their characterization by different techniques, (elemental analysis, biochemical analysis, IR spectroscopy, thermogravimetric analysis, scanning electron microscopy and mercury porosimetry), the dye sorption kinetics and equilibrium isotherm have been investigated in batch conditions. The influence of some parameters such as: contact time, initial dye concentration and sorbent variety on dye sorption kinetics, has been studied. Dye uptake was time contact, initial dye concentration and sorbent variety dependent. Two simplified kinetic models including a first-order and a pseudo second-order rate equation were selected to describe the sorption kinetics. Bezanyl red sorption process followed a pseudo second – order rate kinetics. The experimental sorption equilibrium data at natural pH of solution have been analyzed using linearized forms of Langmuir and Freundlich models. The Freundlich model was found to provide an acceptable fit to the experimental data than the Langmuir model whatever the variety of almond peels tested. Low and different maximum dye sorption capacities were obtained about: 8.14 and 14.60 mg/g with soft and hard almond peels respectively under the experimental conditions tested here.

Keywords: Removal, Sorption, Bezanyl red, Almond peels.

1. INTRODUCTION

Synthetic dyes are extensively used for dyeing and printing in industries. Their presence in watercourses is aesthetically unacceptable and may be visible at concentration as low as 1 ppm (Rafatullah et al. [1]). Moreover, they may also affect photosynthetic activity in aquatic systems by reducing light penetration (Bielska and

Szymanowski [2]). Among the various types of dyes, various acidic dyes are used to color nylon, wool, sole in textile industries, paper and leather. This class of dyes is the most problematic, because they tend to pass through conventional treatment systems unaffected (Garg et al. [3], Kapdan et al. [4], Robinson et al. [5]). Although different physical and / or chemical treatment methods are efficient in treating a dye wastewater, they are quite expensive and have operational problems (Aksu [6], Wang et al. [7]) . As a result, there is a search for low-cost, naturally occurring, abundant sorbent materials that can serve as viable alternatives to activated carbon used in adsorption process.

This work studies the possibility of using two varieties (hard and soft) of a agricultural waste namely: almond peels as inexpensive sorbents for the removal of bezanyl red (acid dye), as a model of acid dyes, from synthetic aqueous solutions. This material is abundantly available in Algeria, hence cost effective sorbent. After characterization of the sorbents using using different analysis methods, sorption equilibrium and kinetics tests were performed in batch conditions. The influence of some parameters such as: contact time, initial dye concentration and sorbent variety on dye sorption kinetics, has been studied. Two simplified kinetic models including a pseudo first-order and pseudo second-order models were selected to analyse the dye sorption kinetics. The sorption equilibrium data were obtained at natural pH of solutions. In order to describe the dye sorption isotherms mathematically and to obtain information about the maximum dye sorption capacity of each sorbent variety tested, these equilibrium data were analysed using Langmuir and Freundlich models. These fundamental data could be useful for further developments in the treatment of practical waste or process effluents.

2. MATERIALS AND METHODS

2.1 Sorbents and dye

Two varieties of almond peel (soft and hard) used as sorbents are cheap and highly available lignocellulosic wastes in Algeria. These wastes were collected from the region of Bensekrane (Tlemcen-Algeria-) at different periods: summer 2005 (soft almond peel and summer 2006 (hard almond peel) in the form of large flakes. These wastes were sun/air dried at ambient temperature during many days, crushed with a Moulinex Easy power R68 mill and sieved with an Automatic Sieve Shaker D403 device (Controlab) to keep only the size range 1.25-2 mm. These materials obtained were used as sorbent materials after the following treatment chosen arbitrary: 10 g of each waste were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of $25\pm 1^\circ\text{C}$ during 4 h, filtered, washed thoroughly with distilled water to remove all the adhering dirt

particles until constant pH and no colour observed, then oven-dried at 85 ± 5 °C for 24 h.

Bezanyl red (E-3BS), as a commercial salt with unknown structure, was kindly donated by SOITEX Company located in the City of Tlemcen-Algeria. It was used as received without further purification, in single component aqueous solutions. 1000 mg/L stock solutions of this dye were prepared in distilled water. All working solutions of the desired concentration were prepared by successive dilutions. OK

2.2 Characterization of sorbents

The sorbents were characterized using elemental analysis (an elementary analyzer THERMOFINNIGAN Flash EA 1112 fitted with an automatic sampler and a chromatographic column PORAPAK), biochemical analysis (the accelerated extracting system ASE 200[®] of Dionex Company), Fourier transform infrared spectroscopy (a spectrophotometer PERKIN ELMER Spectrum 2000), thermogravimetric analysis (a thermobalance SETARAM Setsys TG 12), scanning electron microscopy (a HITACHI S 4800 model microscope) and mercury porosimetry (mercury porosimeters PASCAL 140).

2.3 Sorption experiments

2.3.1 Uptake kinetics

In each sorption experiment, 1L of dye solution of known concentration in the range of 50-500 mg/L was added to 1g of sorbent in a beaker agitated vigorously by a magnetic stirrer at 400 rpm using a water bath maintained at a constant temperature 25 °C. In all cases, the working pH was that of the original solution and was not adjusted. Samples from the clear supernatant, at appropriate time intervals, were pipeted from the beaker by the aid of the very thin point pipette, which prevented the transition of sorbent samples to solution. Their dye concentrations were determined using UV-visible spectrophotometer (Beckman 24, USA) at λ_{\max} 512 nm. The dye uptake q_t (mg dye/g sorbent) was determined as follows:

$$q_t = (C_0 - C_t).V/m \quad (1)$$

where: C_0 and C_t are the initial and time dye concentration (mg/L), respectively, V is the volume of solution (mL), and m is the sorbent weight (g) in dry form.

Blank runs, with only the sorbent in distilled water, were conducted simultaneously at similar conditions to account for any colour leached by the sorbent and sorbed by the

glass container. Blanks were also run simultaneously, without any sorbent to determine the impact of pH change on the dye solutions. Preliminary experiments had shown that dye sorption losses to the container walls were negligible.

2.3.2. Uptake equilibrium

The dye equilibrium isotherms were determined by contacting a constant mass 0.25 g of each sorbent material with a range of different concentrations of dye solutions: 50-1000 mg/L. The mixture obtained was agitated in a series of 250 ml conical flasks with equal volumes of solution 250 ml for a period of 8 h at a constant temperature 25 ± 1 °C. The contact time (≤ 1 h depending on the type of sorbent tested) was previously determined, but, in order to avoid sorption error i.e. a pseudo-equilibrium, 8 h was chosen to study sorption equilibrium. The mixture pH was not controlled after the initiation of experiments. At equilibrium, the final pH was measured. The equilibrium concentration of unbound dye was determined with a UV-visible spectrophotometer. The equilibrium dye uptake q_e (mg dye/g. sorbent) was determined by difference between concentrations: initial and at equilibrium, respectively.

Duplicate tests showed that the maximum standard deviation of the results was ± 5 %.

3. RESULTS AND DISCUSSION

3.1. Characterization of sorbents

As results (not all are presented here) obtained, as examples, Tables 1 and 2 present the results of elemental analysis and the porosity of the two varieties of almond peel used.

Table 1: Elemental and biochemical analysis of the different sorbents tested

Sorbent	%C	%H	%N	%O	Extractives %	Lignin %	Holocellulose %
Hard almond peel	45.50	5.85	0.81	45.69	5.40	42	51
Soft almond peel	46.21	5.72	0.95	42.77	4.39	44	50

Table 2: Porosity characterisation of sorbents

Sample	Hard almond peel	Soft almond peel
Total cumulative volume (mm ³ /g)	474.55	241.52
Total specific surface area (m ² /g)	35.23	13.84
Average pore diameter (μ)	3.96	5.88
Total porosity (%)	29.67	30.03

All the both substrates present high carbon and oxygen contents. From biochemical analysis, we can notice that both varieties of almond peels contain approximately similar amounts of cellulose and hemicelluloses. Regarding the size distribution of particles and porosity of substrates used, clear differences can be observed (see Table 2).

3.2 Kinetics studies

3.2.1 Effect of contact time

A preliminary experiment was performed to determine the equilibrium time. According to Fig. 1 obtained for an initial bezanyl red concentration 100 mg/L, the kinetics of dye sorption by the two varieties of almond peel presents a shape characterized by a strong increase of the amount of dye sorbed during the first minutes of contact solution – almond peel, follow-up of a slow increase until to reach a state of equilibrium. The necessary times to reach this equilibrium are about: 0.5 and 1h

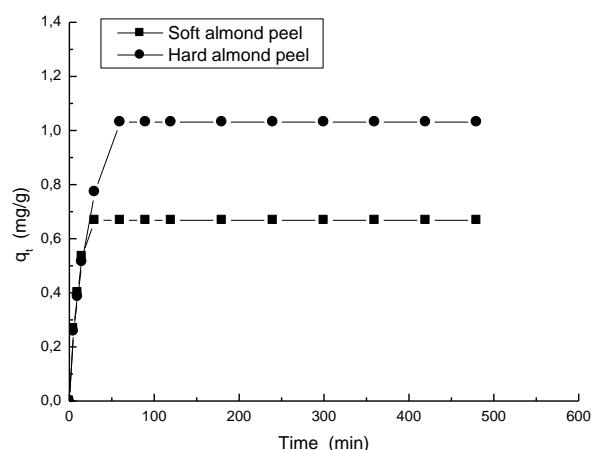
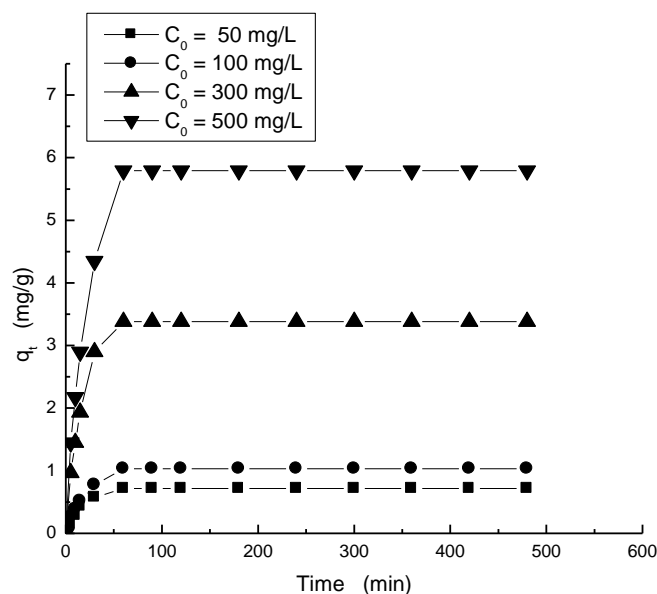


Fig. 1 Kinetic of bezanyl red from aqueous solution by two varieties of almond peel.. (Experimental conditions: $C_0= 100$ mg/L, sorbent dose= 1g/L, particle size= 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, $T= 25$ °C)

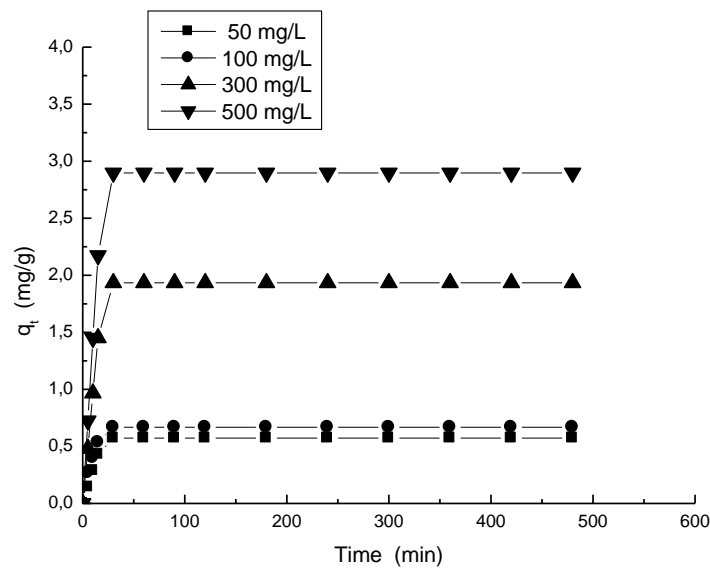
respectively for soft and hard almond peel, and, an increase of removal time to 8 h doesn't show notable effects. At equilibrium, about 0.64 % and 1.05 % of initial dye solution were removed by soft ($q_e = 0.67$ mg/g) and hard ($q_e = 1.03$ mg/g) almond peels, respectively under these experimental conditions. During the course of dye sorption by each variety of almond peel tested, a decrease in the initial pH value of the solution between the initial and equilibrium time was observed (Fig. no shown here). This suggests that dye binding to almond peels tested is associated with the fixation of OH^- ions from solution by the sorbent surface or a release of H_3O^+ ions from the sorbent surface into the solution. At this stage, further investigations are required to understand the mechanisms involved in dye sorption by this type of complex natural materials.

3.2.2 Effect of initial dye concentration

Several sorption experiments were also undertaken to study the effect of the initial dye concentration (50 – 500 mg/L), on the bezanyl red sorption kinetics from synthetic aqueous solution by each variety of almond peel tested here. Initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence, a higher initial concentration of dye will enhance the sorption process (Gulnaz et al. (8)). According to Fig. 2, for all dye concentrations studied, the obtained curves present the same shape characterized by a strong increase of the amount of dye sorbed during the first minutes of contact solution – sorbent, follow-up of a slow increase until to reach a state of equilibrium.



(A)



(B)

Fig. 2 Effect of initial bezanyl red concentration on dye sorption kinetics by hard (A) and soft (B) almond peels. (Experimental conditions: sorbent dose = 1g/L, particle size: 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, T= 25 °C)

Under these experimental conditions, from the results obtained at equilibrium, the necessary time to reach equilibrium is about: 0.5 and 1 h respectively for soft and hard almond peel, independent on initial dye concentration, and an increase of dye removal time to 8 h did not show notable effects. The amount of bezanyl red sorbed at the equilibrium increases with the initial dye concentration: about 0.57 mg/g ($C_0 = 50$ mg/L) and 2.90 mg/g ($C_0 = 500$ mg/L) with soft almond peel, and, 0.72 mg/g ($C_0 = 50$ mg/L) and 5.79 mg/g ($C_0 = 500$ mg/L) with hard almond peel. During the course of dye sorption by each variety of almond peel tested (Fig. no shown here), a slight increase in the initial pH value of the solution followed by some equilibrium state was observed.

3.2.3 Modelling

To analyze the kinetic data of bezanyl red sorption by each variety of almond peel under the experimental conditions tested, two common models from the literature, namely: the first-order rate model of Lagergren (Lagergren [9]) and the pseudo second-order rate model (Ho and McKay [10,11]) were chosen and shown below as Eqs. (2) and (3) in their linear forms:

$$\log (q_e - q_t) = \log q_e - k_L t / 2.3 \quad (2)$$

$$t/q_t = 1/k \cdot q_e^2 + t/q_e \quad (3)$$

where: k_L is the Lagergren rate constant of sorption (min^{-1}) and k the pseudo second-order rate constant of sorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$); q_e and q_t are the amounts of dye sorbed ($\text{mg} \cdot \text{g}^{-1}$) at equilibrium and at time t , respectively. For all initial dye concentrations, the different values of constants from the slope and intercept of linear plots of $\log(q_e - q_t)$ vs. t and t/q_t vs. t (see Fig.3 as a typical example) are summarized in the Table 3.

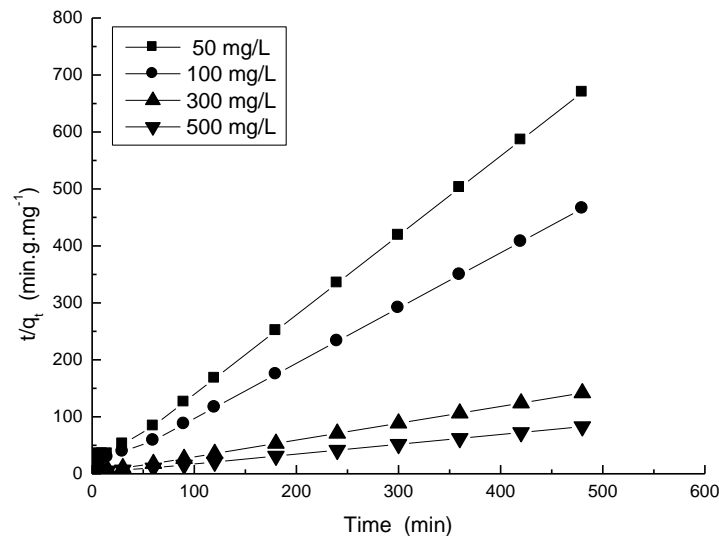


Fig.3 Pseudo-second order model for bezanyl red sorption kinetics by hard almond peels. (Experimental conditions: sorbent dose = 1g/L, particle size: 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, T= 25 °C)

The results obtained and presented in Table 4 confirm that the kinetic data obtained follow the pseudo second-order kinetic model. Compared to the first-order rate model ($0.9608 < R^2 < 0.9981$), the pseudo second-order rate model adequately described the kinetics of dye sorption with good correlation coefficients ($0.9989 < R^2 > 0.9998$). The equilibrium dye sorption capacity, q_e , increases with the increase in the initial dye concentration. The values of q_e obtained from the fitting to the pseudo second-order rate model are very similar to the experimental values obtained from the sorption kinetics at equilibrium. In this model, all the steps of sorption such as: external diffusion, internal diffusion, and sorption are lumped together and it is assumed that the difference between the average solid phase concentration and the equilibrium concentration is the driving force for sorption, and that the overall sorption rate is proportional to the square of the driving force [40].

Table 3 Models rate constants for bezanyl red sorption kinetics by two varieties of almond peel tested: effect of initial dye concentration.

		First-order kinetics model				Pseudo second order kinetics model		
C_0 (mg/L)		$q_{e,exp.}$ (mg/g)	$q_{e,cal.}$ (mg/g)	$k_L \cdot 10^2$ (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	$k \cdot 10^2$ ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	R^2
		Hard almond peel						
50	0.72	0.72	5.50	0.9918	0.74	15.28	0.9989	
100	1.03	1.01	4.53	0.9980	1.06	9.82	0.9990	
300	3.38	3.50	6.43	0.9930	3.46	4.08	0.9994	
500	5.79	5.67	4.54	0.9981	5.96	1.75	0.9990	
		Soft almond peel						
50	0.57	0.63	9.14	0.9610	0.58	33.75	0.9994	
100	0.67	0.69	10.48	0.9880	0.67	49.35	0.9998	
300	1.93	2.12	9.12	0.9605	1.96	9.98	0.9994	
500	2.90	3.18	9.12	0.9608	2.94	6.68	0.9994	

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3.3 Equilibrium study

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3.3.1 Sorption isotherms

Equilibrium data, commonly known as sorption isotherms, are basic requirements for the design of sorption systems. These data provide information on the capacity of the sorbent or the amount required to remove a unit mass of pollutant under the system conditions (Özacar [13,14]). Fig. 4 shows the bezanyl red sorption isotherms, (q_e vs. C_e), by the two varieties of almond peels tested here at natural pH of solutions which are of L type according to the classification of Giles et al. [15] for liquid-solid adsorption. From the plot of these isotherms, the maximum capacities of dye sorbed by these sorbents tested are about: 4.2 mg/g (soft almond peel) and 6.60 mg/g (hard almond peel) under these experimental conditions.

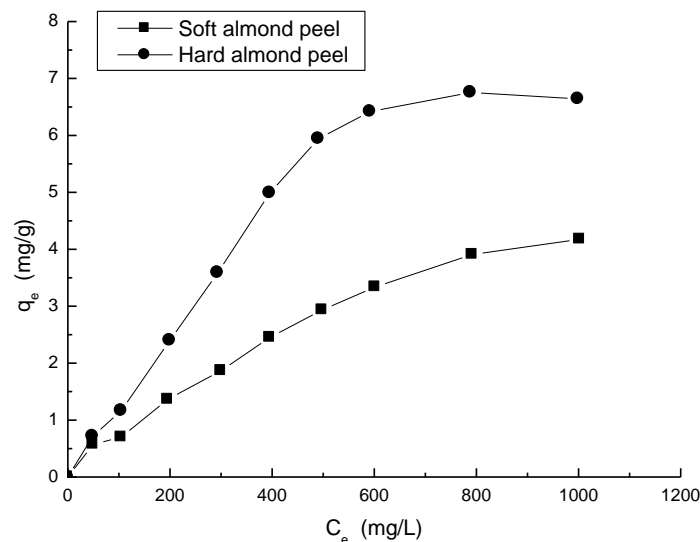


Fig. 4 Isotherms of bezanyl red sorption by two varieties of almond peel at 25 °C

From these results and by comparison between these two varieties of almond peel, in spite the little difference observed in their low performances, hard almond peel appears to be more effective to remove bezanyl red from synthetic aqueous solution under the experimental conditions tested here. The difference in dye sorption capacities obtained by these two varieties of almond peel could be attributed to possible differences in their chemical and/or physical characteristics (i.e. porosity, specific areas, etc...).

During the experiments of dye sorption equilibrium by each variety of almond peels tested, for all initial dye concentration used, a decrease in the initial pH value of the solution between the initial and equilibrium time was also observed, and, the pH value at equilibrium increased with the initial dye concentration.

3.3.2 Modeling

In order to optimise the design of a sorption system to remove pollutant from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations have been tested in the present study, namely, Langmuir [16] and Freundlich [17]. This modelling permits us to determine the maximal capacity of sorption. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression; i.e. the isotherm giving an R^2 value closest to unity is deemed to provide the best fit.

a) The linearised Langmuir model has the following form:

$$C_e/q_e = 1/K_L \cdot q_m + C_e/q_m \quad (4)$$

with: q_e : amount of dye sorbed at equilibrium per g of sorbent (mg/g), q_m : maximal dye sorption capacity of sorbent material (mg/g), C_e : equilibrium dye concentration in the solution (mg/L) and K_L : constant of equilibrium (L/mg) depending on temperature and the applied conditions. If the model of Langmuir is valid to describe the experimental results, it must verify the linearised shape of the basis equation, in system of coordinates $C_e/q_e = f(C_e)$, that will permit to obtain the constants q_m and K_L from the intercepts and slopes.

b) The linearised Freundlich model has the following form:

$$\ln q_e = \ln K_F + n \ln C_e \quad (5)$$

where: q_e and C_e are as described before, K_F and n : positive constants depending on the nature of system solute- sorbent and temperature, $n < 1$. If this equation is verified with data of sorption equilibrium, we must obtain a straight line in the system of coordinates $\ln q_e = f(\ln C_e)$, the slope and the intercept to the origin give the values of constants n and K_F respectively.

Table 4 Parameters of Langmuir and Freundlich models for bezanyl red sorption isotherms by two varieties of almond peel tested.

Sorbent	Langmuir model			Freundlich model		
	q_{\max} (mg/g)	$K_L \cdot 10^3$ (L/mg)	R^2	K_F	n	R^2
Hard almond peel	14.60	1.069	0.7552	0.030	0.82	0.9614
Soft almond peel	8.14	1.095	0.8668	0.029	0.73	0.9802

From results obtained (Figs. not shown here) and the model parameters determined by least squares fit of the experimental sorption data presented in Table 4, it appears that the Freundlich model acceptably fits the experimental results over the experimental dye concentration range with acceptable coefficients of regression ($R^2 = 0.9614-0.9802$). According to coefficients of correlation ($R^2 = 0.7552-0.8668$) obtained, the model of Langmuir is not adequate for modelling the isotherm of dye sorption by each sorbent tested in all the domain of studied concentrations. The applicability of these models should be considered as a mathematical representation of the dye sorption equilibrium over a given dye concentration range. The mechanistic conclusions from the good fit of the models alone should be avoided. In spite of these limitations, these models can provide information on dye-uptake capacities for any performance comparison between various sorbent materials (Kapoor and Viraraghavan [18]). For comparison, the dye sorption capacities obtained by these two varieties of almond peel tested are lower than those of some other agricultural solid wastes reported in the literature and commercial activated carbons mainly because their high specific areas, although this direct comparison is difficult due to the varying experimental conditions used in these studies.

CONCLUSIONS

The present study shows that the two varieties of almond tested tested can be acceptably used as sorbents for the removal of bezanyl red from synthetic aqueous solutions. For each variety tested, the quantity of dye sorbed at equilibrium depends on contact time, initial dye concentration and increases with an increase of these two parameters. The kinetics of bezanyl red sorption was well described by a pseudo-second order rate model. An acceptable fitting of dye sorption equilibrium data was obtained with Freundlich model in all the range of concentrations studied. Under the investigated experimental conditions, the maximum dye sorption capacities obtained by these sorbents tested were different and low, and, followed the order: hard almond peel > soft almond peel. The results obtained stimulate the prosecution of this research because there are still several very important aspects to clarify.

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