

EQUILIBRIUM, THERMODYNAMIC AND KINETIC MODELING FOR THE ADSORPTION OF TEXTILE DYE (BEMACID BLUE) ONTO ACTIVATED CARBON SYNTHESIZED FROM OLIVE CORES

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Abstract: The present study focuses on the valorization of an agricultural waste, olive cores that have been chemically activated by an oxidizing agent (H_3PO_4) in order to improve its adsorptive capacities. For a better orientation of its uses a range of physicochemical tests has been carried out: the ash content (1.87 %), the moisture content (1.089 %), the iodine value ($317.26 \text{ mg} \cdot \text{g}^{-1}$) and the isoelectric point ($\text{pH}_{\text{PZC}} = 3.2$). In order to test the performance of our activated carbon, we chose the Bemacid Blue (BB) dye as a pollutant. The adsorption of this dye was monitored by UV-Visible spectrophotometer. Several parameters have been studied, including contact time, temperature, initial concentration, adsorbent dosage. The kinetics and thermodynamics of adsorption of Bemacid Blue by activated olive cores were studied. The adsorption kinetics have been well described by the pseudo second order model. The adsorption kinetics seem to satisfy the Langmuir isotherm model ($R^2 = 0.9931$) with respect to the Freundlich and Temkin isotherms. This study demonstrated that chemically activated olive cores can be used as a new adsorbent for the treatment of water contaminated by textile dyes.

Keywords: *activated carbon (AC), adsorption, agricultural residues valorization, Bemacid Blue (BB), olive cores*

INTRODUCTION

Water is the major constituent of living matter. In most living organisms, the water content is about 70 % or more. Water is a vital element whose importance on a planetary level is constantly recalled. Its pollution by industrial and agricultural activities is a major concern of our developed societies, hence a vast subject of studies to reduce this pollution at the source if possible or in the effluents if necessary with appropriate curative treatments.

Among the industries consuming water in large quantities, one finds at the top of the list, the textile industry which constitutes a great source of water pollution [1]. The water discharged from the textile mills is highly concentrated in coloring matter which is sometimes not degradable or poorly degradable, making biological treatments difficult to apply. So it is necessary to find techniques of high efficiency and with a not very high cost. Many adsorbents have been tested to reduce dye concentrations from aqueous solutions. Activated carbon is regarded as an effective but expensive adsorbent due to its high costs of manufacturing and regeneration [2]. In addition to activated carbon, other adsorbents including peat [3], chitin [4], chitosan [5], silica [6], perlite [7], natural phosphate [8], hydroxyapatite [9], Titania [10], and some agricultural wastes [11 - 14] have also been reported. However, the adsorption capacities of the above mentioned adsorbents are not very high. In order to improve the efficiency of the adsorption processes, it is necessary to develop cheaper and easily available adsorbents with high adsorption capacities. For this purpose, we studied the decolorization of an aqueous solution of Bemacid Blue as an organic pollutant model by adsorption using as adsorbent activated carbon synthesized from agricultural residues (olive cores) by chemical pathways (using acid H_3PO_4) [15]. The activated carbon obtained was characterized by a range of physicochemical tests. For the present study, a batch-contact-time method was used, and the equilibrium of BB adsorption on to AC was investigated with attempts to fit the data to Langmuir, Freundlich, and Temkin equations. The adsorption of BB on AC was examined as a function of temperature, initial dye concentration, mass adsorbent particle, and contact time. Kinetic and thermodynamic studies were conducted to evaluate the adsorption capacity of AC.

MATERIALS AND METHODS

Preparation of active carbon

The nuclei were collected from Elnekhil Labiodh Medjadja region in Chlef, Algeria. The precursor used in the manufacture of activated carbon (AC), such as olive cores, is first washed several times with distilled water until the odor disappears and clear rinse water is obtained. The cores were dried for 24 hours at 110 °C in an oven (Gallankaurp, model 82000, Germany). The cores were then crushed and sieved through a sieve ($d < 0.630$ mm) in order to obtain a powder which will constitute the raw material. The powder obtained is then washed several times with distilled water to remove the impurities (dust and water-soluble substances) and then dried at 110 °C for 24 hours before being activated.

Among the acids, phosphoric acid has been widely used for the activation of coals [16]. To this end, 20 g of the raw sample were mixed with 40 g of the H_3PO_4 solution (40 %

by weight) and stirred for 10 h. The mixture is placed in an oven for 24 hours at 110 °C. The product was placed in a calcination furnace (LV3 11 NABERTHERM IMLAB, France), with a heating rate of 1 °C·min⁻¹ and maintained at a temperature of 450 °C for one hour (1 hour). The product obtained was washed with distilled water several times until the pH of the filtered water is between 6 and 7. Finally, this sample must be dried at 110 °C for 24 h [17].

Dye solution preparation

Bemacid Blue ($\lambda_{\text{maximum}} = 604 \text{ nm}$) is an industrial synthetic dye for dyeing polyamide textile chemical nature that was provided by the Soitex Tlemcen-Algeria. The dye used in this research belongs to the group E which is distinguished by a high level of light fastness, good migration power, good coverage streaking kinetic origin, good combinability, quick exhaustion even low temperature and rapid fixation with the saturated steam. Dye solutions (1000 mg·L⁻¹) were prepared by dissolving 1 g of dye in 1 L of double distilled water. Experimental solutions of the desired concentration were obtained by further dilution.

Adsorption Studies

Adsorption studies for the evaluation of activated carbon for the removal of Bemacid Blue dye from aqueous solutions were carried out by using the batch contact adsorption. For these experiments, fixed amount of adsorbents 1 g were placed in a 500 mL glass Erlenmeyer flasks containing 300 mL of dye solutions (50, 100, and 200 mg·L⁻¹), which were stirred at 350 rpm at temperatures between 298 K and 328 K at pH 5.31.

Subsequently, in order to separate the adsorbent from the aqueous solutions, the flasks were centrifuged (Modèle 800, Ref.: SOC-YLE10004 (Socimed), France) at 400 rpm for 10 min, and aliquots of 2 mL of the supernatant were properly diluted with water. The final concentrations of the dye remaining in the solutions were determined by UV / visible (S6) spectrophotometry (Unicam 8625, Labexchange the world's N.1, France). Absorbance measurements were made at the maximum wavelength of Bemacid Blue which was 604 nm. The amount of the dye uptake of the removal of dye by the adsorbents was calculated by applying (Equation 1):

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

where q_t is the amount of dye taken up by the adsorbent (mg·g⁻¹); C_0 is the initial Bemacid Blue concentration put in contact with the adsorbent (mg·L⁻¹), C_t is the dye concentration (mg·L⁻¹) after the batch adsorption procedure, V is the volume of dye solution (L) put in contact with the adsorbent, and m is the mass (g) of the adsorbent.

Characterization

Fourier Transform Infrared Spectroscopy, FT-IR (IR Prestige-21, Shimadzu, Japan) was used to identify the different chemical functional groups present in the AC. The analysis was carried out using KBr and the spectral range varying from 4000 to 400 cm. The FT-

IR spectra of the free unloaded AC were compared with those obtained for AC loaded with BB.

Iodine Index

In a 100 mL beaker, approximately $m = 0.2$ g of activated carbon previously steamed at 110 °C for 24 hours is weighed. 20 mL of 0.02 N iodine solution are added and stirred for 4 to 5 min. The mixture is filtered and 10 mL of the filtrate is taken and placed in an Erlenmeyer flask. From the burette, sodium thiosulfate is poured into the Erlenmeyer flask containing the filtrate until the solution is completely discolored.

Point of zero charge pH_{pzc}

The determination of the pH_{pzc} of the used activated carbon was as follows: a series of 50 mL of 0.1 M NaCl solutions were poured in closed conical flasks, the pH was adjusted in the range of 2–12. Then, in each solution, 50 mg of adsorbent was soaked under agitation at room temperature and the final pH was measured after 24 h. The pH_{pzc} is defined as the point where the curve $pH_{initial}$ versus pH_{final} crosses the line $pH_{initial} = pH_{final}$.

Error functions

Within recent decades, linear regression has been one of the most viable tool defining the best-fitting relationship quantifying the distribution of adsorbates, mathematically analyzing the adsorption systems and verifying the consistency and theoretical assumptions of an isotherm model. The degree to which the theoretical models fit the experimental results was determined based on several mathematically rigorous error functions (Root Mean Square error (RMSE) Equation 2) for the calculation of the error deviation [18].

$$RMSE = \sqrt{\left(\frac{1}{N-2}\right) \sum (q_{e,exp} - q_{e,cal})^2} \quad (2)$$

where: $q_{e(exp)}$ ($mg \cdot g^{-1}$) is the experimental value of uptake, $q_{e(cal)}$ the calculated value of uptake using a model ($mg \cdot g^{-1}$), and N the number of observations in the experiment (the number of data points). The small the $RMSE$ values, the better the curve fitting.

The Sum of Error Squares ($SSE \%$) is one method which has been used in the literature to test the validity of each model that has been used. The SSE is given by Equation 3:

$$SSE = \frac{1}{N} \sqrt{\sum (q_{e,exp} - q_{e,cal})^2} \quad (3)$$

Low value indicates a better SSE smoothing.

Distribution functions such as Chi-square (χ^2), if data from the model are similar to the experimental data χ^2 will be a small number, if they are different, χ^2 will be a large number (Equation 4).

$$\chi^2 = \sum \frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}} \quad (4)$$

Adsorption isotherms

Equilibrium data commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. These data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. Langmuir, Freundlich and Temkin isotherms were used to describe the equilibrium characteristics of adsorption. An accurate isotherm is important for design purposes. Linear regression is commonly used to determine the best fit model, and the method of least squares has been widely used for obtaining the isotherm constants [19 - 22]. The Langmuir model is based on the assumption that the biosorption occurs on specific homogeneous sites of the biosorbent and the monolayer biosorption onto a surface containing a finite number of uniform sites with no transmigration of adsorbate in the plane of the surface [23]; the isotherm is expressed by Equation 5.

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (5)$$

where: C_e is the equilibrium dye concentration ($\text{mg} \cdot \text{L}^{-1}$), q_e the amount of biosorbed dye ($\text{mg} \cdot \text{g}^{-1}$), q_m the amount for a complete biosorption monolayer ($\text{mg} \cdot \text{g}^{-1}$), and K_L the constant related to the affinity of the binding sites and energy of biosorption ($\text{L} \cdot \text{mg}^{-1}$). The linear form of the Langmuir isotherm equation is given as Equation 6:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (6)$$

A dimensionless constant separation factor (R_L) of the Langmuir isotherm was used to determine the favorability of the biosorption process. R_L is defined using equation 7; its value indicates the type of isotherm: irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) (Equation 7) [23].

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

The Freundlich expression is an empirical equation based on the biosorption onto a heterogeneous surface. The equation generates an exponential shaped theoretical equilibrium curve [24] and is represented as follows (Equations 8 and 9):

$$q_e = k_F C_e^{\frac{1}{n}} \quad (8)$$

$$\text{Log}(q_e) = \text{Log}(k_F) + \frac{1}{n_F} \text{Log}(C_e) \quad (9)$$

where: K_F is the Freundlich constant and ($1/n_F$) the heterogeneity factor, related to the capacity and the biosorption intensity.

Temkin's model rests on the assumption that during the adsorption gas phase, the heat of adsorption due to interactions with the adsorbate decreases linearly with the recovery

rate θ . From q_e plotted as a function of $\ln C_e$, B_T , and K_T values can be determined (Equation 10) [25]:

$$q_e = \frac{RT}{B_T} \ln(K_T \cdot C_e) \quad (10)$$

where: R is the perfect gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the absolute temperature (K), B_T is the variation in energy of adsorption ($\text{J} \cdot \text{mol}^{-1}$), and K_T is the constant of Temkin ($\text{L} \cdot \text{mg}^{-1}$).

Adsorption kinetics

The kinetic is important for understanding the treatment of aqueous solutions because it provides valuable information about the mechanism of biosorption processes and potential rate-controlling steps, such as the mass transport [26].

Experimental data of BB biosorption using activate carbon were evaluated by the pseudo-first and pseudo-second order kinetics models to understand the mechanisms of the biosorption process.

The pseudo-first-order rate expression of [27] is generally described by the following Equation 11 [28]:

$$\text{Log}(q_e - q_t) = \text{Log} q_e - \frac{k_1}{2.303} t \quad (11)$$

where: q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t ($\text{mg} \cdot \text{g}^{-1}$), respectively, and k_1 the pseudo-first-order rate constant (min^{-1}), k_1 is obtained from the slope of the linear plot of $\log(q_e - q_t)$ against t .

The pseudo-second-order kinetic model is expressed as (Equation 12) [29]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

where: k_2 is the rate constant of second-order biosorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). If the second-order kinetic is applicable, the plot of t/q_t against t of equation 12 should give a linear plot. The initial biosorption rate " h " ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) is expressed as [30]:

$$h = k_2 q_e^2 \quad (13)$$

Adsorption thermodynamics

The temperature presents a notable effect on the biosorption and the thermodynamic parameters such as change in the standard free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) are determined (Equations 14 and 15) [30]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

$$\ln k_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} = -\frac{\Delta G^\circ}{RT} \quad (15)$$

The plot of $\ln K_L$ as a function of $1/T$ should give a linear relationship with a $\Delta H^\circ/R$ slope and an ordinate at the origin of $\Delta S^\circ/R$.

RESULTS AND DISCUSSION

Physico-chemical analysis of active carbon

From the results in Table 1, it can be seen that the ash content of the prepared CA represents a low content of mineral matter (ash), it is within the standard (<10 %) therefore a low ash content indicates a good adsorbent. In addition to a low humidity, this observation shows a low conservation of the water content by the activated carbon, it is in the standard (<5 %) The similar results are also observed by Abbas [23], for activated carbon based on coconut shell (% C = 1.68 % and % H = 1.48 %).

Table 1. The moisture values, ash content and iodine value of the active carbon studied

	Humidity [%]	The ash rate [%]	The iodine value [mg·g ⁻¹]	pH _{PZC}
Activated carbon	1.089	1.87	317.26	3.2

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR technique was used to examine the particular vibration of the surface groups and bonds responsible for dye adsorption.

To explore the characteristics of the biosorbent FT-IR analysis of AC were performed at the range of 4000 - 400 cm⁻¹ as shown in Figure 1. The FT-IR spectrum presented a broad band located around 3550 cm⁻¹ which is assigned to O–H stretching vibrations of hydrogen bonded hydroxyl groups. The peak at about 2750 cm⁻¹ was attributed to the asymmetric and symmetric stretching vibrations of CH₂ and CH₃. The band around 1600 cm⁻¹ was associated with C=C and C=O stretching in the aromatic ring. The peak at 1200 cm⁻¹ may be due to C–O stretching vibrations. Also it is important to notice that the band intensities decreased in the FT-IR spectrum of BB loaded AC because the functional groups of the AC surface have been occupied with BB. This study demonstrated that BB was adsorbed and penetrated into the interlayer space of the AC.

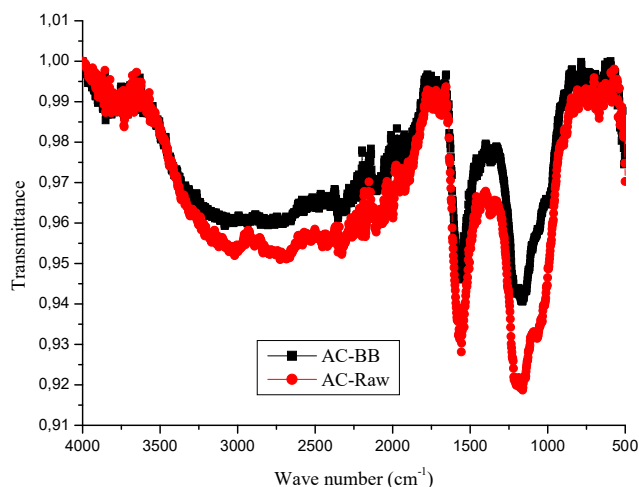


Figure 1. FT-IR spectra of AC and AC loaded BB sample

Optimization of adsorption parameters

The optimization of different adsorption parameters such as the solution pH , contact time, initial concentration, adsorbent dose and temperature at different time intervals was carried out for Bemacid Blue onto activated olive cores.

Contact time effect

Figure 2 illustrates the variations in the adsorbed amount of Bemacid Blue as a function of time. Note that the equilibrium time is independent of the initial concentration and that the adsorbed quantity of Bemacid blue increases with the contact time, following two slopes: The first part consists of a rapid adsorption after 5 minutes. This phase corresponds to a transfer of the adsorbate from the liquid phase to the surface of the material. This phenomenon observed during the first minutes of the reaction can be interpreted by the fact that, at the beginning of the adsorption, the number of active sites available on the surface of the adsorbent material is much greater than that of the sites remaining after a certain time. The second part is slower. This area corresponds to equilibrium after 45 minutes. This phenomenon was also observed by Abbas [31] during the adsorption of toxic dye Direct red 28 on the AC.

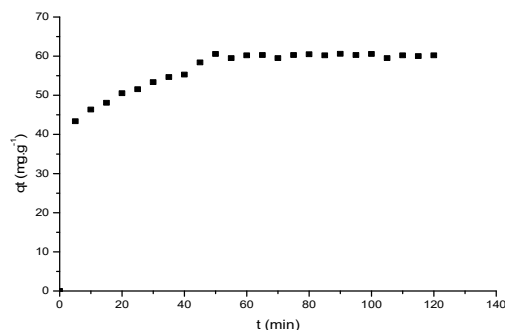


Figure 2. Effect of contact time on the quantity adsorbed by the AC:
 $V = 300\text{mL}$, $C_0 = 200\text{ mg}\cdot\text{L}^{-1}$, $m = 1\text{ g}$, $T = 328\text{K}$ and $\text{pH} = 5.31$

Effect of adsorbent dose

The potential of adsorbent to remove Bemacid Blue from its solution is determined by the initial concentration [32]. The removal efficiency (%) and adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$) as a function of biosorbent dose are shown in the Figures 3 and 4, respectively. They reveal that on increasing adsorbent dose from (0.25, 0.5, 1 and 1.5 g) the percent removal increases and adsorption capacity decreases. With increasing adsorbent dose, more surface area and active sites are available for adsorption [33] and therefore the percent removal increases. However, adsorption capacity decreases as biosorbent dose increases. This could be explained by: - number of adsorption sites remain unbounded during the biosorption process, - the external surface area is reduced by the agglomeration of biomass particles at higher doses, - desorption of BB could occur at high adsorbent doses because of particles interaction [34]. A conclusion, with higher dosage of adsorbent there would be greater availability of exchangeable sites from Bemacid Blue.

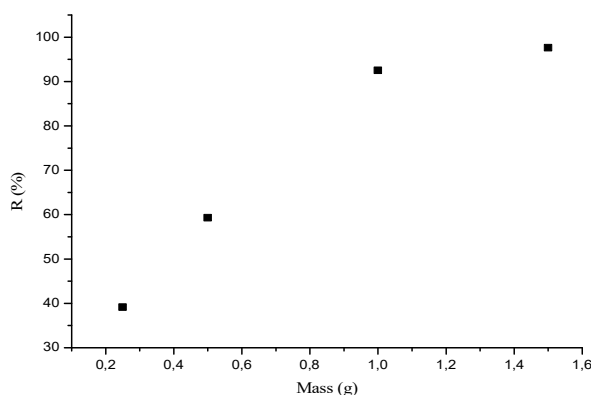


Figure 3. Effect of biosorbent dose on biosorption efficiency of Bemacid Blue by AC: $V = 150\text{ mL}$, $C_0 = 200\text{ mg}\cdot\text{L}^{-1}$, $T = 328\text{ K}$ and $\text{pH} = 5.31$

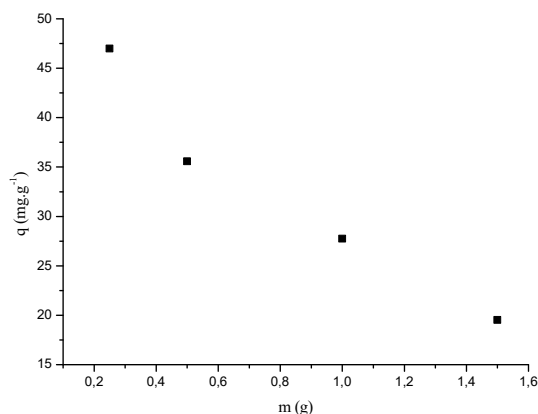


Figure 4. Effect of biosorbent dose on biosorption capacity of *Bemacid*
 Blue by AC: $V = 150 \text{ mL}$, $C_0 = 200 \text{ mg}\cdot\text{L}^{-1}$, $T = 328 \text{ K}$ and $\text{pH} = 5.31$

Effect of pH

The pH of the solution is a crucial controlling parameter in the biosorption [35, 36]. The pH of the dye solution is one of the most important parameter as the protonation of functional groups on adsorbent surface and the chemistry of dye molecules are strongly affected by pH of the solution. The influence of pH solution on BB adsorption onto AC is shown in Figure 5. It shows that the adsorption capacity of tested dye on AC decreases slightly with increasing pH . The adsorption of BB (anionic) can be envisaged by an electrostatic interaction between the sulfonic group of the dye (negative) and the positive charge of the carbon which is perhaps reinforced by the polarity of the dye molecule. This interaction decreases when the pH increases while tending towards the pH_{PZC} of the coal, because the surface charge of the coal gradually becomes zero, then changes sign for $\text{pH} > \text{pH}_{\text{PZC}}$. In this case, the decrease in adsorption is explained by the electrostatic repulsion between the dye molecule (negative) and the surface of the carbon which becomes more and more negative when the pH becomes basic. These results mentioned above are mainly used in the biosorption of Direct red 28 dye on Apricot stones [31].

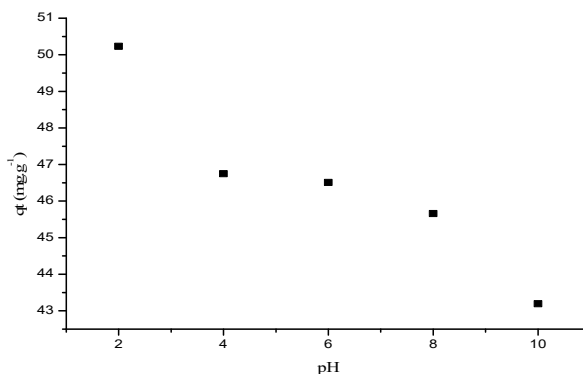


Figure 5. Effect of pH on the quantity adsorbed by the CA:
 $V = 300 \text{ mL}$, $C_0 = 200 \text{ mg}\cdot\text{L}^{-1}$, $m = 1 \text{ g}$ and $T = 328 \text{ K}$

Effect of initial concentration

In order to study the influence of the initial concentration of the dye on the AC, tests were carried out with concentrations of 50, 100 and 200 mg·L⁻¹. The other parameters are kept constant. Figure 6 shows the effect of the initial dye concentration on the adsorbed amount at the same contact time. For the three concentrations used, the adsorbed amount increases with increasing reaction time by following two different slopes. The first is fast, while the second is slow and could express the balance between the dye fractions retained and those that remain free. We note that the adsorbed amount of the dye is better for the high concentration 200 mg·L⁻¹. The maximum adsorbed amounts at equilibrium for the three concentrations (50, 100 and 200 mg·L⁻¹) with respective values of 12.6, 26.4 and 53.2 mg·g⁻¹. The biosorption process is very rapid and reaches equilibrium at about 10 min for a low concentration. For an initial concentration of 100 mg·L⁻¹ reached 25 min and 45 min respectively for 200 mg·L⁻¹.

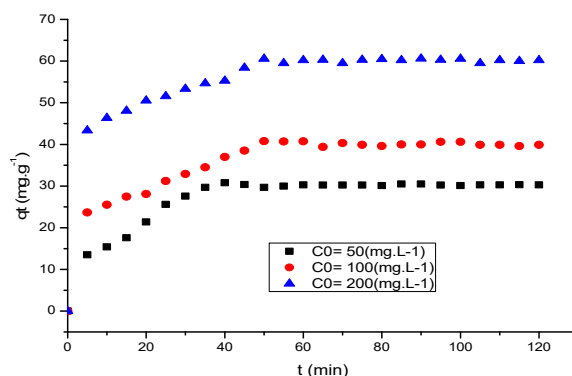


Figure 6. Effect of the dye concentration on the amount adsorbed by the AC: $V = 300 \text{ mL}$, $m = 1 \text{ g}$, $T = 328 \text{ K}$ and $\text{pH} = 5.31$

Effect of temperature

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles as a result of the reduced viscosity of the solution. In addition, changing the temperature alters the equilibrium capacity of the adsorbent for a particular adsorbate. A study of the temperature dependence of the adsorption processes therefore gives valuable information about the enthalpy and entropy changes accompanying adsorption.

In order to determine the optimum temperature which allows the best adsorption, studies have been carried out, using a water bath, allowing the temperature to be maintained at the desired value (between 25 °C and 55 °C). The experiments were carried out by adding 1 g of the AC to the solution of Bemacid Blue (200 mg·L⁻¹, initial pH) and a contact time of 45 min.

From Figure 7, it can be seen that the adsorbed amount is proportional to the temperature. As the temperature increases, so does the mobility of the dye in solution and the decrease in attraction forces or diffusion of the dye on the surface of AC.

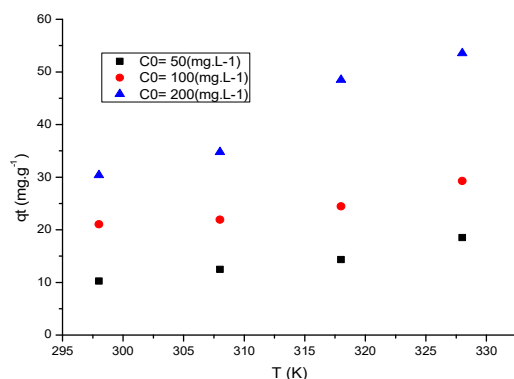


Figure 7. Effect of temperature on the adsorbed amount of Bemacid Blue by AC:
 $V = 300 \text{ mL}$, $m = 1 \text{ g}$ and $\text{pH} = 5.31$

Application of equilibrium models

The theoretical parameters of adsorption isotherms along with the regression coefficients, RMSE, χ^2 and SSE are listed in Table 2. The equilibrium data are accommodated well by the Langmuir model, with high correlation coefficients (R^2 0.9931). Such coefficients are indicative of monolayer coverage of the BB at the outer surface of the AC particles, and with maximum adsorption capacity (Table 2).

Table 2. Results of the parameters of the different adsorption models on the BB /AC

Parameters of the model	System	System MB / AC (apricot kernel) [37]	This study BB / AC			
	C_0 [mg·L ⁻¹]	100	200			
	T[K]	323	298	308	318	328
Freundlich	K_F	19	1.124	3.001	1.704	1.138
	$1/n_F$	0.876	0.65	0.525	0.615	0.743
	R^2	0.96	0.884	0.901	0.965	0.934
	RMSE [%]		6.7122			
	χ^2 [%]		2.8233			
Langmuir	q_m [mg·g ⁻¹]	94.60	77.513	88.495	93.458	185.185
	K_L [L·mg ⁻¹]	0.26	$4.03 \cdot 10^{-3}$	$5.93 \cdot 10^{-3}$	$4.39 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$
	R^2	0.996	0.893	0.914	0.969	0.947
	RMSE [%]		6.968			
	χ^2 [%]		2.9815			
Temkin	B_t [kJ·g ⁻¹ ·mol ⁻¹ ·mg ⁻¹]	5.4001	59.213	56.323	48.466	34.178
	R^2	0.96	0.858	0.915	0.960	0.934
	RMSE [%]		70.6035			
	χ^2 [%]		99.203			
	SSE [%]		24.962			

The results of Table 2 also show that an increase in temperature from 298 to 328 K promoted an increase in the adsorption capacity. The Freundlich isothermal model presents RMSE and SSE values that are roughly similar to those of Langmuir. Similar results were found for the adsorption of methyl blue (MB) onto AC (apricot kernel) [37]. According to the R_L (0.001, 0.554, 0.694, 0.457) values, all the systems correspond to favorable adsorption processes while the Langmuir model suggests that the adsorption of molecules takes place on a homogeneous monolayer surface without interaction between the adsorbed molecules. The values tended toward zero, representing the ideal irreversible case, rather than toward unity, representing the completely reversible case [38].

A comparative evaluation of the adsorbent capacities of various types of adsorbents for the adsorption of dyes is listed in Table 3. Compared with some data in the literature, Table 3 shows that the activated carbon studied in this work has very large adsorption capacity.

Table 3. Comparison of the maximum monolayer adsorption of some dyes on various adsorbents

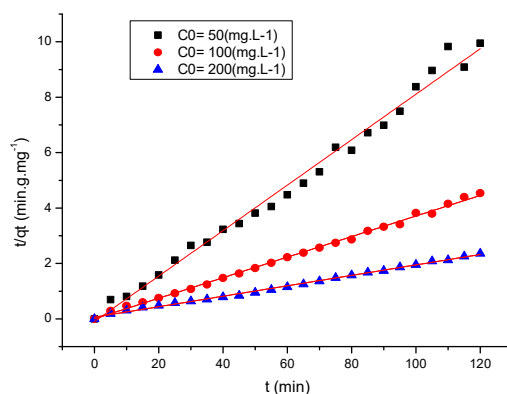
Dyes	Adsorbent	Maximum adsorption capacity [$\text{mg}\cdot\text{g}^{-1}$]	Reference
Bemacid blue	Olive cores based activated carbon	53.26	Present work
Direct red 28	Modified Apricot Stone	32.85	[31]
Congo red	Coir pith-based activated carbon	6.72	[11]
Direct red 89	Chemviron GW activated carbon	8.40	[39]
Direct red 89	Sludge-based activated carbon	49.20	[39]
Methylene blue	Corn cob powder calcined	46.28	[40]

Application of kinetics models

The kinetic parameters for the biosorption of Bemacid blue onto AC are calculated and summarized in Table 4 and Figure 8. We can observe that the pseudo-first-order model is not applicable in the present case, as high RMSE, SSE and χ^2 values were observed. It is clear from the results that the R^2 value is very high (0.9963), and low RMSE and χ^2 were obtained. This indicates that biosorption of Bemacid Blue follows pseudo-second-order more than pseudo-first-order model. Biosorption capacity of the biosorbent determined from the fitted pseudo-second-order kinetic model was comparable to the biosorption capacity determined from the experimental. The conformity between experimental data and the model predicted values was expressed by the R^2 , RMSE, χ^2 and SSE. A relatively high R^2 value (close or equal to one) and low values of RMSE and χ^2 indicates that the model successfully describes the kinetics of adsorption. Similar results have been observed in the adsorption of organic pollutants onto MB/AC (apricot kernel) [37].

Table 4. Results of application of the adsorption models of Bemacid Bleu on system studied at 328K

Pseudo-1	System	System MB / AC (apricot kernel) [37]	System BB / AC		
	T(K)	298	328		
	C ₀ [mg·L ⁻¹]	74.7	50	100	200
	q _{e, exp} [mg·g ⁻¹]	/	12.361	12.657	53.268
	q _{e, cal} [mg·g ⁻¹]	0.899	1.592	3.081	11.934
	K ₁ [min ⁻¹]	0.046	0.00667	0.01289	0.0209
	q _{e, cal} /K ₁	19.54	238.68	239.02	571.00
	R ²	0.899	0.0722	0.2213	0.4431
	SSE [%]		3.589	3.192	13.778
	χ ² [%]		245.772		
	RMSE [%]		43.8314		
Pseudo-2	q _{e, exp} [mg·g ⁻¹]	/	13.083	27.454	53.269
	q _{e, cal} [mg·g ⁻¹]	7.463	12.195	26.954	53.191
	K ₂ [g·mg ⁻¹ ·min ⁻¹]	0.078	0.071	0.353	0.0056
	q _{e, cal} /K ₂	95.68	171.76	76.378	9498.39
	R ²	0.999	0.9895	0.9976	0.9963
	SSE [%]		0.296	0.1666	0.026
	χ ² [%]		0.0740		
	RMSE [%]		1.022		

**Figure 8.** Application of the pseudo-second order model for the adsorption of the system Bemacid Blue /AC; $m = 1$ g, $V = 300$ mL and $T = 328$ K

Thermodynamic studies

As a result, the thermodynamic parameters such as (ΔG^0), (ΔH^0) and (ΔS^0) for the adsorption of Bemacid Blue on AC are determined from Figure 9, are grouped in Table 5. The negative values of (ΔG^0) confirm the feasibility of the process and the spontaneous nature of the adsorption with a high preference for the dye on the material studied. The values of (ΔH^0) are negative in the temperature range 298-328 K, indicating that the adsorption reaction is exothermic for the material (AC). Positive values of (ΔS^0) reflect the affinity of the materials tested to the Bemacid Bleu molecules during adsorption. Moreover, the negative ΔS^0 value ($-0.11922 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) suggests a decrease in the randomness at the Solid/solution interface during adsorption of BB on to AC.

Table 5. Results of the thermodynamic parameters of the system (Bemacid blue /AC)

T [K]	ΔG^0 [kJ·mol ⁻¹]	ΔH^0 [kJ·mol ⁻¹]	ΔS^0 [kJ·mol ⁻¹ ·K ⁻¹]
298	-38.7064	-41.4536	- 0.11922
308	-4.73384		
328	-2.34944		

Generally, the free energy variation (ΔG^0) for physisorption is lower than that for chemisorption. The first is between -20 and $0 \text{ kJ}\cdot\text{mol}^{-1}$ and that of the second varies between -80 and $-400 \text{ kJ}\cdot\text{mol}^{-1}$ [6]. This news indicated that physisorption could dominate the adsorption of Bemacid Bleu on material (AC).

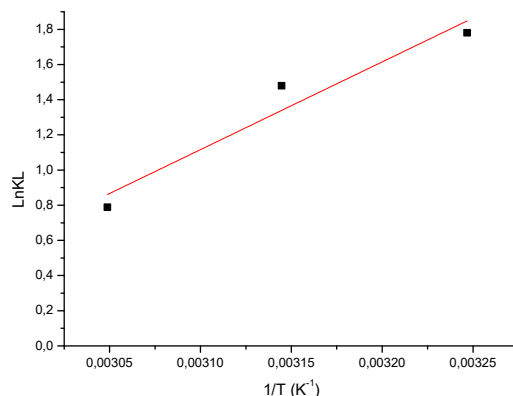


Figure 9. Application of the Van't Hoff equation to determine enthalpy, adsorption of the system Bemacid Blue /AC: $V = 300 \text{ mL}$, $m = 1 \text{ g}$ and $T = 328 \text{ K}$

CONCLUSION

The present study has shown that activated carbon prepared from olive cores can be employed as effective and low cost adsorbent for the removal of Bemacid Blue from

aqueous solution. Increased the initial concentration led to an increase of the adsorption capacity of AC. The Langmuir model provides a better fit of the equilibrium adsorption data than the Freundlich one. The maximum adsorption capacity calculated from the Langmuir model is found to be $185.185 \text{ mg}\cdot\text{g}^{-1}$. The adsorption of BB onto AC follows the pseudo-second-order kinetic model. The negative values of the three thermodynamic parameters characterized the reaction as an exothermic and spontaneous physisorption, during which the order of distribution of the molecules of the dye on AC increases compared to that in the solution.

The results of the present investigation showed that:

- AC is a potentially useful adsorbent for the adsorption of dyes, an issue of environmental concern.
- The advantage of using agricultural by-products as raw materials for manufacturing-activated carbon is that these raw materials are renewable and potentially less expensive to manufacture.
- The natural abundance of this food waste can provide a new adsorption medium that can contribute to the treatment of wastewater.
- The comparison of the adsorption capacity of the prepared adsorbent with other adsorbents shows its industrial and economic interests.
- This study in tiny batch gave rise to encouraging results, and we wish to achieve the adsorption tests in column mode under the conditions applicable to the treatment of industrial effluents.

NOMENCLATURES

BB	Bemacid Blue
AC	Activated Carbon
SEE	Sum of squared errors
RMSE	Root Mean Square <i>Error</i>

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