



Chemically modified olive stone: A low-cost sorbent for heavy metals and basic dyes removal from aqueous solutions

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ABSTRACT

In the present work, we have investigated the sorption efficiency of treated olive stones (TOS) towards cadmium and safranine removal from their respective aqueous solutions. TOS material was prepared by treatment of olive stones with concentrated sulfuric acid at room temperature followed up by a subsequent neutralization with 0.1 M NaOH aqueous solution. The resulting material has been thoroughly characterized by SEM, energy-dispersive X-ray (EDX), MAS ¹³C NMR, FTIR and physicochemical parameters were calculated. The sorption study of TOS at the solid–liquid interface was investigated using kinetics, sorption isotherms, pH effect and thermodynamic parameters. The preliminary results indicate that TOS exhibit a better efficiency in terms of sorption capacities toward the two pollutants (128.2 and 526.3 mg/g for cadmium and safranine, respectively) than those reported so far in the literature. Moreover, the sorption process is ascertained to occur fast enough so that the equilibrium is reached in less than 15 min of contact time. The results found in the course of this study suggest that ion exchange mechanism is the most appropriate mechanism involved in cadmium and safranine removal. Finally, the sorption efficiency of TOS is compared to those of other low-cost sorbents materials yet described in the literature.

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1. Introduction

Nowadays, the various industrial activities are ceaselessly increasing and they produce liquid effluents which are often contaminated with harmful/poisonous substances. Water pollution with toxic compounds is of major concern for human health as well as for the environmental quality. Among these compounds, heavy metals and textile dyes are the most dangerous for the environment. The heavy metals are known to be highly toxic at very low concentration in water whereas the dyes have a great influence on the photosynthetic activity in aquatic biota and exhibit a low biodegradability. Numerous studies were devoted to their elimination, and have mainly concentrated on the development of an efficient and cost-effective removal process. Heavy metals removal methods cited in the literature generally involve adsorption processes on activated carbon [1,2], ion exchange mechanism [3–5], or complexation by natural and synthetic reagents [6–8], whereas the sorption on activated carbon was applied to dyes removal [9].

The removal process by means of activated carbon is however costly. From this standpoint, numerous investigations were conducted by scientists in this growing and important field of research for the exploration of alternative methods using less expensive natural materials. Among these materials, agricultural waste byproducts have attracted a great deal of consideration owing to their low cost, abundance, and readiness to use as adsorbent whether in their raw or carbonized form. The frequently reported carbonization method in the literature is that of sulfuric acid treatment of agricultural waste byproducts such as jackfruit peel [10], corn stalk [11], apricot stone [12] and corncobs [13]. As yet, the latter method was not applied to olive stones, hence never reported in the literature to the best of our knowledge.

Olive stones are an agricultural waste predominantly produced in the Mediterranean countries. The materials resulting from their carbonization have been successfully used as sorbents for a wide variety of pollutants in aqueous solutions. Excellent papers are available and provide further insight into this field of research. For instance, Cimino et al. [14] have reported the use of an olive cake carbon, prepared by heat treatment at 700 °C, in the removal of cadmium from aqueous solution. On the other hand, Kula et al. [15] have studied the cadmium removal from aqueous solutions by olive stones, initially impregnated with ZnCl₂ and carbonized

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at 650 °C under nitrogen atmosphere. Galiatsatou et al. [2] have also investigated the zinc sorption efficiency of a carbon obtained from carbonized olive stones at 850 °C and activated under steam at 800 °C. The starting premise of this work was the aim of developing an efficient material based on raw olive stone for the removal of heavy metals and basic dyes by performing a cheaper and simple modification method under “mild” operating conditions. Besides, no prior work was devoted to dyes removal from aqueous solutions by olive stones.

In this study, the preparation of TOS was carried out by impregnation of olive stones with concentrated sulfuric acid followed up with neutralization. The resulting material was used to remove cadmium and a basic dye (safranin) from aqueous solutions. The sorption parameters (kinetics, isotherms, pH and temperature) were investigated. The sorption mechanism is discussed from the sorption data and the physicochemical analyses (SEM, energy-dispersive X-ray (EDX), FTIR and MAS ¹³C NMR).

2. Experimental

2.1. Starting materials

Olive stones were provided by ENCG factory from Sig (Algeria). The preparation of TOS material was performed according to a modified procedure reported elsewhere for jackfruit peel [10] and for an olive cake [14].

In a typical experiment, olive stone (200 g) were washed several times with distilled water, dried at 105 °C overnight, crushed, and 250 μm sieved. The resulting material, noted raw olive stones (ROS) was mixed with concentrated sulfuric acid (acid/olive stone ratio: 8:1, w/w) and the resulting suspension was left to rest at room temperature for 24 h. The obtained dark solid was filtered off and washed repeatedly with distilled water until neutral pH. The filtered material was then suspended in a 0.1 M NaOH aqueous solution and refluxed for 1 h. After cooling, the suspension was filtered and the solid material was washed repeatedly with distilled water until neutral pH and finally dried at 105 °C overnight. This material was noted treated olive stones (TOS).

2.2. Characterization of materials

2.2.1. Iodine number

The iodine number of TOS was determined according to the procedure described by Namane et al. [16]. In a dry 250 cm³ Erlenmeyer flask, 0.1 g of TOS was placed and fully wetted with 10 cm³ of diluted HCl (5% by weight). Then, a 0.1 M iodine solution (100 cm³) was poured into the flask and the mixture was vigorously shaken for 30 s. After filtration, 50 cm³ were titrated with 0.01 M sodium thiosulfate solution.

2.2.2. Determination of the zero point charge pH (pH_{ZPC})

The pH corresponding to the point of zero charge, ZPC for the carbon was determined by the pH drift method reported by Khan and Wahab [13]. TOS was soaked in HCl for 24 h in order to convert any remaining sodium salt of the acid functional groups into their acidic form. After filtration, the residual material was washed several times with distilled water till neutrality (AgNO₃ negative test) and dried at 105 °C. The pH drift was measured on 0.005 M NaCl solutions (20 mL) placed in jacketed titration vessels, thermostated at 298 K. Nitrogen was bubbled through the solutions to stabilize the pH. The pH was then adjusted to successive initial values between 2 and 10 by adding HCl or NaOH and TOS (0.06 g) was added to the solution. The final pH was reached after 48 h.

The surface of the material is neutral when pH = pH_{ZPC}.

The surface is negatively charged at pH values greater than pH_{ZPC}, and positively charged at pH values lower than pH_{ZPC} [17].

2.2.3. FTIR characterization

The IR spectrum of the sample was recorded using a Model FOURIER MATTSON genesis series Fourier transform infrared spectrometer operating in the range 4000–400 cm⁻¹.

2.2.4. SEM analysis

The morphological analysis was carried out by means of Philips SEM 505 equipped with EDX analyser.

2.2.5. MAS NMR characterization

The MAS NMR spectrum of TOS was recorded using a Bruker Digital NMR AVANCE 300.

2.3. Study of cadmium and safranin removal with treated olive stone

2.3.1. Kinetic study

The kinetic study was accomplished with suspensions of TOS (25 mg) in 50 mL of cadmium nitrate solutions (25 mg/L). The mixtures were stirred during different time intervals, ranging from 5 to 180 min and then centrifuged. The cadmium concentration in supernatants was determined using a Pye Unicam SP9 atomic absorption spectrophotometer with an air/acetylene flame at 228.8 nm wavelength.

The same procedure was used for the kinetic sorption study of safranin; in this case the initial safranin concentration was 150 mg/L and the solid/solution ratio was 50 mg of TOS in 50 mL of solution.

The safranin concentration in supernatants was determined with a HACH DR4000U UV-visible spectrophotometer at 516 nm.

The sorbed amounts were determined from the difference between the initial and final concentrations.

2.3.2. pH effect on cadmium and safranin removal

The pH effect was studied on suspensions of TOS (25 mg) in 50 mL of cadmium solutions (25 mg/L) and on suspensions of TOS (50 mg) in safranin solutions (200 mg/L). The pH was adjusted in the range 3–6 and 4–10 for cadmium and safranin solutions, respectively. The resulting mixtures were stirred for 1 h and then centrifuged. The cadmium and safranin concentrations in the supernatants were determined as mentioned above.

2.3.3. Sorption isotherms

The sorption isotherms were established using TOS suspensions in cadmium and safranin solution at pH 4 and 6.8, respectively. The solid/solution ratio was 0.5 g/L for cadmium solutions and 1 g/L for safranin ones. The concentrations in the aliquots were ranging from 25 to 150 mg/L and from 25 to 600 mg/L for cadmium and safranin, respectively. The suspensions were stirred for 1 h and subsequently centrifuged. The equilibrium concentrations of cadmium and safranin in the supernatants were analyzed as mentioned above in Section 2.3.1.

2.3.4. Temperature effect

The influence of temperature on the removal process was studied at three different temperature values (25, 35 and 45 °C) on TOS suspensions in cadmium and safranin solutions at concentrations of 50 and 300 mg/L, respectively. The solid/solution ratios for cadmium and safranin solutions were 0.5 and 1 g/L, respectively. The suspensions were stirred during 1 h, then centrifuged and the

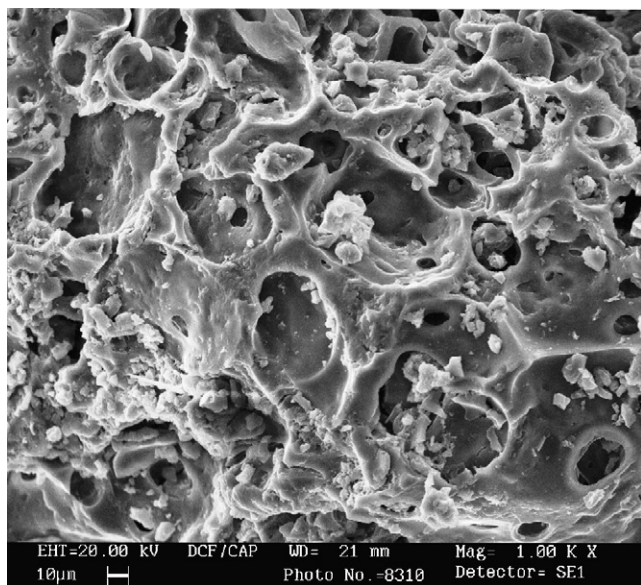


Fig. 1. SEM image of the treated olive stone surface.

supernatants were analyzed by the same techniques as mentioned in the previous sections.

3. Results and discussion

3.1. Characterization of the treated olive stones

The SEM image (Fig. 1) shows a highly porous morphology of the treated material with pores of different sizes and shapes. The image also reveals that the external surface is full of cavities which suggest that TOS material exhibits a high surface area. Similar morphology was already seen for a treated olive cake with sulfuric acid [14] and a cornelian cherry treated with sulfuric acid at 200 °C [18]. On the other hand, the high surface area of the material is also confirmed by the iodine number value (760 mg/g). For activated carbon adsorbents, the iodine number is often considered as a measure

Table 1
Physicochemical characteristics of sulfuric acid treated olive stone

Parameter	
Moisture (%)	0.73
Bulk density (g/ml)	0.57
Weight loss after treatment (%)	25
Ash content (%)	14.3
Volatile matter (%)	53.5
Iodine number (mg/g)	760
pH _{ZPC}	2.62
pH of an 1% (w/w) aqueous suspension (acidic form)	3.3
pH of an 1% (w/w) aqueous suspension (sodic form)	7.3
Sulfonic and carboxylic groups (mequiv./g)	1.16

of its adsorption ability for low-molar-mass solutes. This number gives information about the internal area of an activated carbon. Correlation between the BET surface area and the iodine number is established and well documented [2,12,16].

The EDX analysis (Fig. 2) shows that the treatment of olive stones with sulfuric acid led to a material with a high sulfur contents. This can be argued by the well-known sulfonation of lignocellulosic constituents of the olive stone leading to the formation of sulfonic acid functional groups. The observed sodium content is the result of NaOH treatment which led to the conversion of the acid groups into their sodic form. The sulfonic and carboxylic acid groups may confer to the treated material ion exchange properties in the elimination process. The sulfur and sodium contents led to high ash contents (14.3%) as seen in Table 1.

The presence of strong sulfonic acid groups is also suggested by the value of the pH_{ZPC} obtained from Fig. 3. This value (2.6) and those of the acidic and the sodic forms of TOS suspensions (3.3 and 7.3, respectively) confirm the strong acid character of the acid form and the neutral character of the sodic form (Table 1). Khan and Wahab have reported similar values of pH_{ZPC} (2.7) and pH value of 3.3 relative to the acid form of slurry obtained from a treated corncob with sulfuric acid [13].

The existence of carboxylic acid functional groups in TOS is indubitably revealed in the solid-state ¹³C NMR spectrum shown in Fig. 4. This spectrum shows a signal at 175 ppm which is characteristic of C=OOH and C=OOR carbonyl groups [19]. Moreover, the FTIR spectrum of TOS (Fig. 5) shows a large OH band around

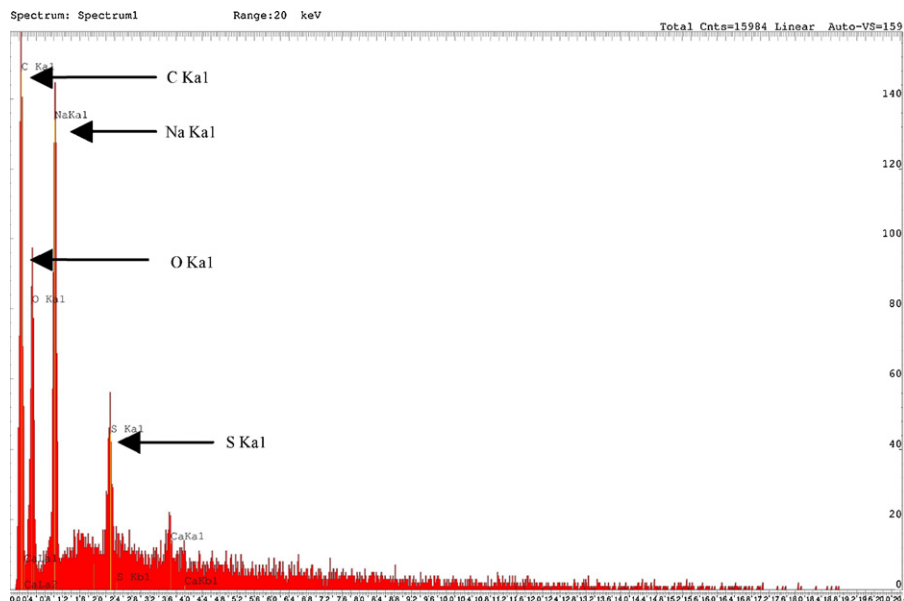


Fig. 2. EDX microanalysis of the treated olive stone.

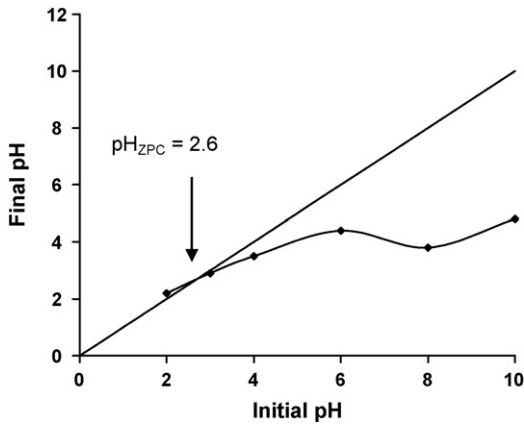


Fig. 3. pH drift Plot of treated olive stone suspensions.

3400 cm^{-1} , two weak alkyl C–H stretching absorption bands at 2916 and 2888 cm^{-1} and the C=O characteristic bands at 1704 cm^{-1} (carboxylic acid) and 1608 cm^{-1} (carboxylate functional groups).

Similar values were reported by Khan and Wahab for a treated corncob with sulfuric acid [13] and by Shin and Rowell for a sulfonated juniper wood [20]. The sulfonate S=O bands appear usually in the fingerprint region where the assignments are difficult to attribute as the superimposed vibration bands take place within this region.

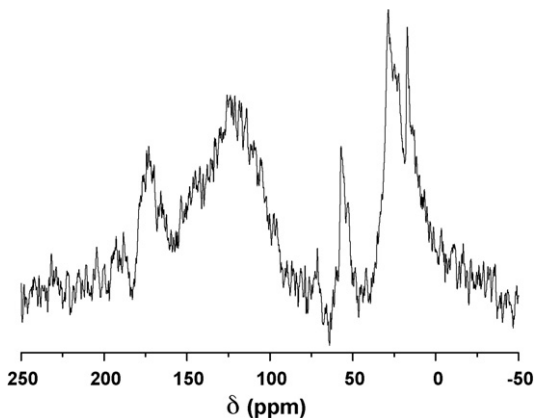


Fig. 4. MAS ^{13}C NMR spectrum of treated olive stone.

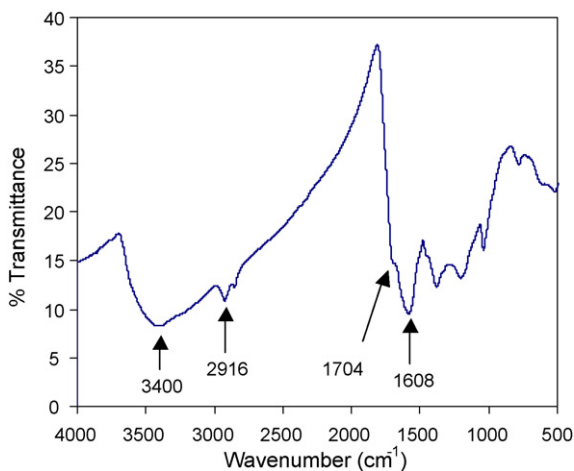


Fig. 5. FTIR spectrum of treated olive stone.

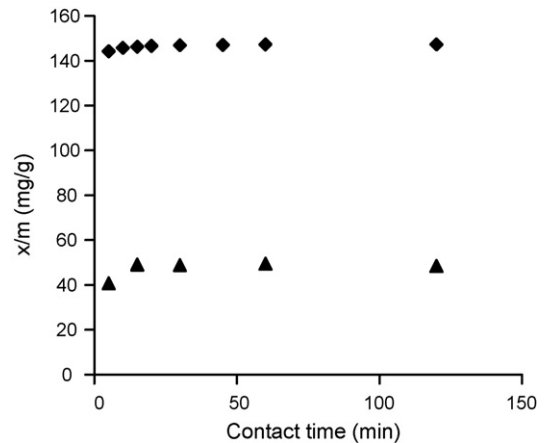


Fig. 6. Effect of contact time on safranin (◆) and cadmium (▲) removal by TOS.

3.2. Kinetic study of safranin and cadmium removal with treated olive stone

3.2.1. Contact time effect

The plots of Fig. 6 show that the cadmium and safranin sorption equilibria are reached in less than 15 min of contact time. Moreover the plots did not reveal any intraparticle diffusion step which should give rise to a slope decrease between the fast initial step and the equilibrium plateau.

3.2.2. Kinetic modelling

The sorption kinetics is an important aspect in the control of pollutants removal process. The Lagergren's first-order kinetic model and the Ho's pseudo-second-order model are the most frequently used in the literature to predict the mechanism involved in the sorption process [21].

The Lagergren's first order model [21] is expressed by the equation:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_t and q_e (mg/g^{-1}) are respectively the amounts of sorbed dye at time t and at equilibrium and k_1 (min^{-1}) is the first order rate constant. Integration of the Eq. (1) gives:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Eq. (2) shows a linear relationship between $\log(q_e - q_t)$ and t . Linear regression calculations allow obtaining the values of the rate constant k_1 and the equilibrium removal capacity q_e . Our results did not fit this model.

Due to its good correlation with the experimental results, the more recent pseudo-second-order model has been extensively used by several researchers in the same field [21]. This model is expressed by the following equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

The integration of Eq. (3) and its linearization gives the expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

The plots of t/q_t versus t (Fig. 7) are straight lines where slopes and intercepts are respectively $1/q_e$ and $1/k_2 q_e^2$. The rate constant k_2 and the equilibrium sorption capacity q_e values are calculated from

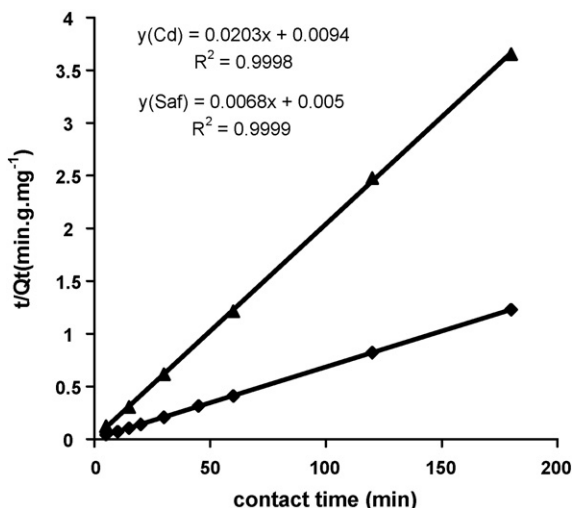


Fig. 7. Pseudo-second-order plot for safranin (♦) and cadmium (▲) removal from aqueous solutions with TOS.

Table 2
Comparison of experimental and calculated values for the second-order sorption rate constants

Pollutant	q_e experimental (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	q_{eq} .calculated (mg g ⁻¹)	R^2
Safranin	147.3	0.00925	147.0	0.999
Cadmium	49.4	0.0438	49.3	0.999

these parameters. The calculated k_2 and q_e values and the corresponding linear regression determination coefficient R^2 values are reported in Table 2. Good correlation is observed between experimental data and the pseudo-second-order kinetic model with determination coefficient values higher than 0.99. Values of the rate constant k_2 are of the same order of magnitude than those reported in the literature for cadmium removal by activated olive stones with ZnCl₂ [15] and for basic dyes removal by activated sludge [22].

For both pollutants, the differences between the experimental and calculated values of the equilibrium removal capacity were lower than 1%.

3.3. pH effect on cadmium and dye removal

Fig. 8 shows the plots of TOS sorption capacity versus pH ranging from 3 to 6 for cadmium and from 4 to 10 for safranin. It was

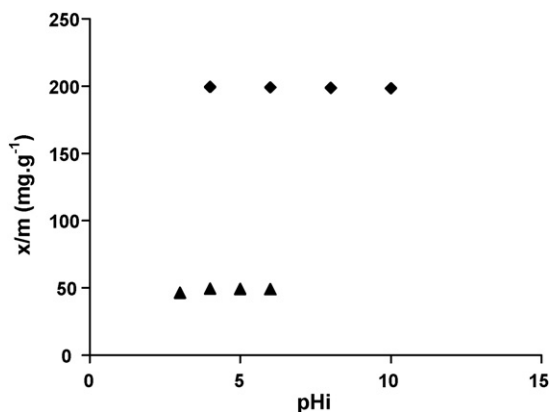


Fig. 8. Effect of initial solution pH on safranin (♦) and cadmium (▲) removal by TOS.

observed that the sorption capacity is practically constant in these pH domains because of the low value of pH_{ZPC} (2.6) which indicates that the surface charge on the material is negative in the investigated pH range. This result suggests that the removal mechanism could be an ion exchange process. A similar observation was reported by Waranusantigul et al. in the study of a basic dye (methylene blue) removal from aqueous solution by a spirodela polyrrhiza biomass [23].

3.4. Sorption isotherms

The equilibrium sorption experimental data obtained in this study were analyzed using the commonly used Freundlich and Langmuir isotherm models.

The empirical Freundlich model which is known to be satisfactory for low concentrations is expressed by the equation:

$$q_e = K_F \times C_e^{1/n} \tag{5}$$

where q_e is the equilibrium sorption concentration of solute per gram of adsorbent (mg/g); C_e is the equilibrium aqueous concentration of the solute (mg/L); K_F and n are Freundlich constants which are related to the adsorption capacity and the intensity of adsorption.

Eq. (5) can be linearized in its logarithmic form which enables the determination of Freundlich constants as below:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{6}$$

The Langmuir isotherms model is described by the following equation:

$$q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e} \tag{7}$$

where q_e (mg/g) is the amount of dye removed per gram of sorbent, Q_{max} (mg/g) is the maximum sorption capacity, C_e (mg/L) is the dye concentration in the equilibrium solution, and K_L (L/mg) is the Langmuir constant related to the adsorption energy.

For the convenience of plotting and determining the Langmuir constants, the Langmuir Eq. (7) can be rearranged to linear form as below:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max}K_L} \tag{8}$$

Figs. 9 and 10 show Freundlich and Langmuir isotherms for the safranin and cadmium sorption on TOS. Fig. 9 shows a correct fit of the Freundlich model but nevertheless the Langmuir model (Fig. 10) fits better the experimental results. The determination

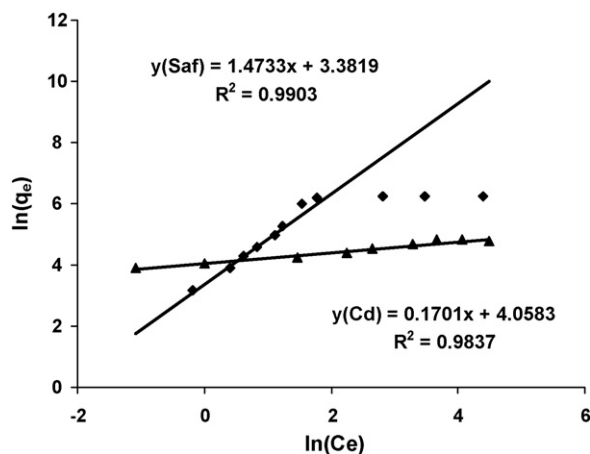


Fig. 9. Freundlich isotherms of safranin (♦) and cadmium (▲) removal by TOS.

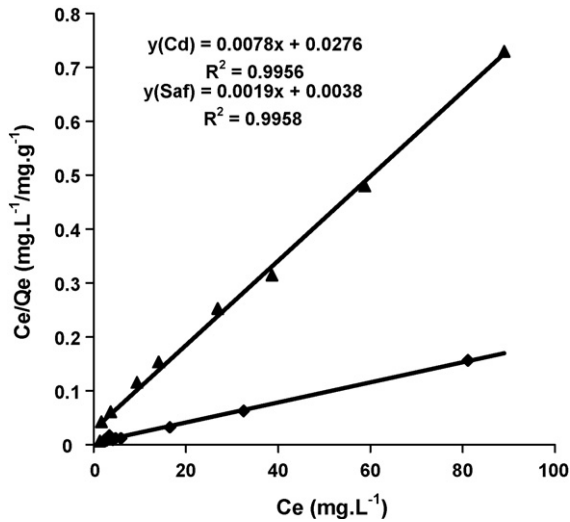


Fig. 10. Langmuir isotherms of safranine (♦) and cadmium (▲) removal by TOS.

Table 3

Langmuir and Freundlich constants for safranine and cadmium adsorption on treated olive stone

Pollutant	Langmuir constants			Freundlich constants ^a		
	Q_{\max} (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
Safranine	526.3	0.500	0.9958	29.4	0.679	0.990
Cadmium	128.2	0.283	0.9956	57.9	5.88	0.984

^a Results obtained for low concentrations.

coefficient values for this model were higher than those of Freundlich model (0.9958 and 0.9956 for the Langmuir model in contrast to Freundlich model which gives values of 0.9903 and 0.9837 for safranine and cadmium, respectively). The calculated parameters of Freundlich and Langmuir are reported in Table 3. The maximum sorption capacities expressed in mmol/g are 1.49 and 1.14 for safranine and cadmium, respectively. These results also suggest an ion exchange process which will be discussed in a following section.

These capacities are better than those of many materials reported in the literature (Table 4).

3.5. Temperature effect

The study of the temperature effect on safranine and cadmium removal by TOS enabled us to determine the thermodynamic parameters (ΔG° , ΔH° and ΔS°) of these reactions by using the

Table 4

Comparison of activated carbons and other low-cost sorbents for cadmium and safranine removal

Sorbents (treatment)	Pollutant	Sorption capacity (mg/g)			Reference
		298 K	308 K	318 K	
Bagasse pith (200 °C and 400 °C under steam with SO ₂ and H ₂ S)	Cadmium	149.9			[26]
Jackfruit peel (H ₂ SO ₄ at 160 °C)	Cadmium	52			[10]
Corn stalk (H ₂ SO ₄ + ZnCl ₂ at 200 °C)	Cadmium	36.4			[11]
Apricot stone (H ₂ SO ₄ at 200 °C)	Cadmium	33.57			[12]
Olive stone (raw)	Cadmium	7.73			[27]
Olive stone (raw)	Cadmium	9.72			[28]
Olive stone (raw)	Cadmium	0.9			[29]
Olive cake carbon (700 °C)	Cadmium	13.5			[14]
Olive stone (H ₂ SO ₄ , room temperature + refluxing in 0.1N NaOH for 1 h)	Cadmium	128.2			This work
Rice husk carbon	Safranine	294.1			[30]
Spent bleaching earth (impregnation with NaOH and heating at 100 °C)	Safranine	555.6			[31]
Olive stone (H ₂ SO ₄ , room temperature. + refluxing in NaOH 0.1N for 1 h)	Safranine	526.3			This work

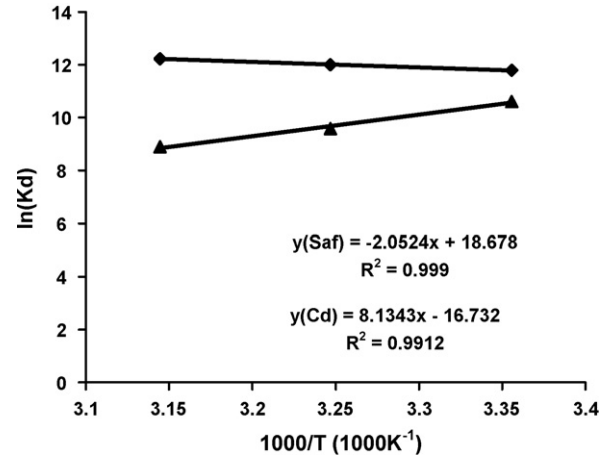


Fig. 11. Plots of $\ln K_d$ vs. $1000/T$ for safranine (♦) and cadmium (▲) removal by TOS.

following equation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

R , ideal gas constant; T , temperature (K); K_d , distribution coefficient (amounts of removed safranine and cadmium per gram of material divided by its concentration in the liquid phase).

The plot of $\ln(K_d)$ versus $1000/T$ gives a straight line, the slope and the intercept correspond to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively.

The plots of $\ln(K_d)$ versus $1000/T$ for safranine and cadmium removal with TOS (Fig. 11) show a positive slope for cadmium and a negative one for safranine.

The thermodynamic parameters calculated from the values of the slopes and the intercepts are reported in Table 5. A negative ΔG° value indicates that the removal process is spontaneous for both pollutants (safranine and cadmium). Furthermore, the values of ΔG° decrease when the temperature rises thus showing the increase in the feasibility of the adsorption process at higher temperatures. ΔS° can be used to describe the randomness at the solid-solution interface during the removal process. As shown in Table 5, the ΔH° and ΔS° values for cadmium are negative. Similar results were reported by Kula et al. [15]. The results obtained for

Table 5

Values of thermodynamic parameters for safranine and cadmium removal with treated olive stone

Pollutant	ΔS° (J mol ⁻¹ K ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)		
			298 K	308 K	318 K
Safranine	155.3	17.1	-29.2	-30.8	-32.3
Cadmium	-139.1	-67.6	-26.2	-24.8	-23.4

safranin were quite different. The positive values of ΔH° and ΔS° could be explained by the bulk and the organic nature of the dye and also by a possible structural deformation occurring during the sorption process. Positive values of the same order of magnitude were reported for the sorption of a basic dye on unburned carbon [24].

3.6. Sorption mechanism

The obtained results suggest an ion exchange mechanism to describe the safranin and cadmium removal by TOS material. The main observations which confirm this mechanism are as follows:

Preliminary tests revealed that TOS did not remove anionic dyes from aqueous solutions.

SEM micrograph and the iodine number indicated that the sulfuric acid treatment of the olive stone led to material having a high porosity.

The spectroscopic data (EDX, FTIR and MAS ^{13}C NMR) suggest the presence of the sodium salt form of acid functional groups on the material surface.

The sorption rate is very fast in such a way that the equilibrium is reached in less than 15 min.

The sorbed amounts of safranin and cadmium expressed in mmol/g (1.49 and 1.14, respectively) were practically equal (the cadmium species present in aqueous solution at pH4 were Cd^{2+} , $\text{Cd}(\text{OH})^+$ and $\text{Cd}(\text{HCO}_3)^+$ [25]; the excess of sorbed safranin amount is probably due to an additional sorption by an hydrophobic interaction process between the carbon surface and the organic dye molecules.

The pH_{ZPC} of TOS (Table 1) indicates that the surface of the material is negatively charged at pH values greater than pH_{ZPC} . Therefore, the sorption of cadmium and safranin was not affected by the pH in the range investigated. Moreover, the very low pH value of ZPC and of the 1% acid form TOS suspension (2.6 and 3.3, respectively) is an indication of the presence of strong acid functional groups on the TOS surface. Furthermore, the strong acidic character is confirmed by the neutral pH value of the TOS sodic form (7.3).

In addition to these qualitative evidences, the contents of sulfonic and carboxylic groups reported in Table 1 (1.16 mequiv./g) corresponds to the cadmium and the safranin removal capacity of TOS.

4. Conclusion

In this study, raw olive stones were treated with concentrated sulfuric acid without heating or using any special atmosphere environment, leading to a low-cost sorbent with a good affinity for positively charged species. The obtained material was characterized and used for basic dye and heavy metal removal from aqueous solutions. The kinetic and sorption data fitted well the second-order kinetic model and the Langmuir model, respectively, with good values of the determination coefficient.

The sorption process was found to be pH independent. The proposed ion exchange sorption mechanism is discussed on the basis of SEM, MAS ^{13}C NMR, EDX, FTIR and mass balance results. The obtained sorption capacities toward safranin and cadmium were better than many low-cost materials yet reported in the literature.

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