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REMOVAL OF POLYPHENOLS FROM OLIVE MILL WASTEWATER BY ADSORPTION ON ACTIVATED CARBON PREPARED FROM PEACH STONES

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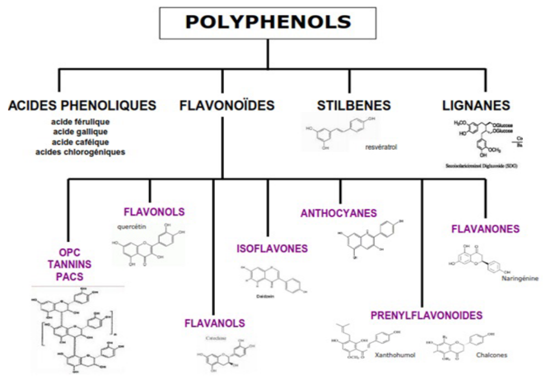
The characterization of the olive mill wastewater by physicochemical analysis of some parameters showed significant pollution load, expressed particularly by a high content of turbidity, chemical oxygen demand and polyphenols.
The objective of this study is the removal of phenolic compounds from olive mill wastewater by adsorption on activated carbon, prepared from a lino-cellulosic waste "peach stones" thermally treated. This processing technique is chosen because of its efficiency and ease of implementation.
The chronological steps for obtaining active carbon are as follows: cleaning, drying, crushing and finally its carbonization at 900 °C. The characterization of the carbon material showed properties comparable to those of many coals manufactured industrially.
Adsorption tests on the obtained material results in about 83% removal rate of polyphenols (at 20 °C, 2 g of activated carbon and 1 hour of contact time).
The study of the influence of pH and temperature shows that at acidic pH and ambient temperature (T = 20°C), the optimal adsorption of polyphenols is reached (91%) and follows quite well the Freundlich model. The adsorption kinetics is rapid and it is pseudosecond order type.



INTRODUCTION

The olive oil industry is an important activity, concentrated mainly in the Mediterranean countries. These take approximately 95% of world production.[1] Due to the promotion of beneficial olive oil health benefits, world demand is increasing and therefore the production is steadily growing to meet the needs of consumers.[2] However this production creates a disadvantage that the generation of two sub products, for the olive oil industry, which are the pomace and vegetation water also called olive mill wastewater. The solid residue is reused in agriculture and industry, while vegetable water is discharged into sewers or land applied in soils.

The olive mill wastewater is characterized by an intensive dark brown to black colour, it is

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generated in large quantities by the olive industry due to the extensive use of water for olive oil extraction. In general, for each ton of olives processed, 1.3 m^3 of black waters are produced.[3] These effluents are considered toxic wastewater. Their release into nature, without any prior treatment, is a major environmental problem especially for Mediterranean countries.

The toxicity of the olive mill wastewater is attributed to the presence of high biological oxygen demand (BOD: 1260 g/L), chemical oxygen demand (COD: in the range of 80200 g/L), total solids content (40150 g/L), acidic pH (about 5) and high concentration of recalcitrant compounds, difficult to degrade, such as polyphenols (up to 10 g/L), which are responsible for phytotoxic effects and cause serious environmental concerns.[4,5]

The treatment of this olive wastewater is therefore necessary. Many treatment methods have been developed to address this problem:physical, chemical and/or biological.[6-8] Most of these alternatives have the problem of high cost and low efficiency and generation of toxic products especially for high phenol concentration in wastewater.

This work focuses on the removal of polyphenols from olive mill wastewater by a physicochemical method that is adsorption on activated carbon prepared from a lino-cellulosic waste. Adsorption, using activated carbon, is the most widely used technique for the removal of organic compounds given its efficiency and ease of implementation.[9] Many researchers have overcome the problem of activated carbon high cost through developing low cost high capacity alternative adsorbents from conventional and non-conventional wastes.[10] In this study investigates transforming local wastes into activated carbon. The raw material "peach stones" thermally treated at 900 °C is used; this type of treatment has already been successfully applied in order to improve the texture parameters (exchange surface area and porous volume) of several materials.[11,12]

EXPERIMENTAL

Physicochemical characterization of olive mill wastewater

After pretreatment of olive mill wastewater, to remove solids suspension, it is kept in closed containers at low temperature and away from light until use.

All parameters that may be altered are analyzed in the laboratory in the shortest possible time in accordance with conservation rules and normalized analysis method. The pH was analyzed using a pH meter (WTW inoLab pH 720), the turbidity by a turbidimeter (HACH 2100AN Turbidimeter), the conductivity by a conductivity meter (WTW inolabcond 720), the analysis of the COD is carried out according to the experimental protocol of the French standard,[13] and polyphenols are analyzed by the colorimetric Gutfinger method[14] using a UV visible spectrophotometer (Shimadzu UV-1800).

Preparation of activated carbon from peach stones

The peach stones taken as raw material do not have a carbon structure or a texture (specific surface area, surface functions, porosity, etc.) that make them capable of adsorbing any pollutant. The thermal and / or chemical activation changes in an irreversible manner the surface of the raw material to permit retention by adsorption of organic and inorganic substances. For a pollutant and a material, several activation variations can be made: thermal (choice of steam or carbon dioxide as an oxidant) and / or chemical (in the presence of inorganic acids and metal oxide).[15,16] In this study, the peach stones grains retained after grinding, sieving (0.5 to 2 mm) are thermally activated by direct pyrolysis at 900 °C in a tubular oven (Cyol), under a nitrogen stream, for a period of three hours of contact time to obtain a dry residue free resins or other non-carbon compounds.

Any residual carbonization is removed by extensive washing with hydrochloric acid (10%) and distilled water under reflux until a neutral pH measured in the rinsing water. The protocol used by Anundo Polania[17] helped to clean the micro-porosity of an activated carbon made from coconut. Before undertaking its use in adsorption of polyphenols testing, the treated coal is dried in an oven at 105 °C to constant weight, for at least 8 hours.

Physicochemical characterization of the obtained adsorbent

The physicochemical characterization of the prepared activated carbon required the use of several analytical methods. The surface area is determined by the BET method, using the Micromeritics ASAP 2010 type apparatus.The porous volume (Vp) is deduced from the adsorption isotherm of nitrogen in the capillary condensation zone. Zeta potential or potential of hydrodynamic shear, defining free water and bound water in the particle is measured using a Malvern 3000 HS zetameter; the measurements are performed on samples of 200 mg of powdered activated carbon in 50 mL of distilled water at 25 °C. Elemental analysis of carbon, hydrogen, nitrogen and sulfur is performed by photoemission spectroscopy induced X-ray (XPS). The dosage of the acidic and basic sites surface of coal was performed by the titrimetric acid-base method proposed by Boehm.[18] For acid sites: carboxylic acids, lactones, phenols and quinones, they are determined successively by mixing 1 g of carbon in a volume of 50 mL of each of the bases: $NaHCO_3$, Na_2CO_3, NaOH and $NaOC_2H_5$ at concentration of 0.1N. These four solutions were stirred simultaneously for 24 hours at 20°C; after filtration of each mixture, the acid sites are dosed back by HCl 0.1 N. Similarly, the basic surfaces were assayed by contacting 1 g of carbon with 50 mL of HCI 0.1 N. After 24 hours of steering at 20 °C, 10 mL of filtrate are dosed with NaOH 0.1 N. In order to detect differences in morphology in the production of coal, the photos are taken using an electronic microscope JEOL JEM-100B, with a scanning accessory (ASID) and EDAX analyzer (Energy DispersiveX-Ray Analysis).

Table 1

Physicochemical characteristics of the studied olive mill wastewater

Analyses parameters	Values	Algerian standard discharge of industrial liquid effluent
pH	4.82	6.5-8.5
Conductivity (mS/cm)	4	/
Color	black	/
Odor	Disagreeable	/
Turbidity (NTU)	8727	/
COD (mg d'O_2/L)	7417	120
polyphenols (mg/L)	5614	0.3

Adsorption tests of polyphenols from olive mill wastewater

For practical reasons and in order to increase adsorption capacity, the fine fraction of coal to 1 mm is chosen for adsorption tests. Indeed, the use of activated carbon powder is advocated by many authors.[19] The determination of removal efficiency of polyphenols on used coal necessitates previous optimization of two key parameters: the contact time and the mass of the adsorbent.

To do this, various masses of coal (0.5, 1, 1.5 and 2 g), previously dried at 105 °C for at least 1 hour until a constant weight, are mixed with 100 mL of olive mill waste water solution in a series of Erlenmeyer flasks with a capacity of 250 mL. After stirring at variables contact times, maintained at a constant temperature in a water bath (Memmert), the samples are filtered and then the residual concentration of polyphenols is measured by UV spectrophotometry in visible range. The calculation of polyphenols removal rate, expressed as a percentage, is based on the following formula:

$$T(\%) = \frac{C_I - C_F}{C_I} 100 \quad (1)$$

T(%): Removal rate of polyphenols

C_I : initial concentration of polyphenols (g/L)

C_F : final concentration of polyphenols (g/L)

The effect of the temperature (20, 30, 40 and 55°C with 2 g of carbon), of pH (2, 4.84, 7, 10 and 2 g of coal) and the initial concentration of polyphenols (2 hours of contact time, and 2g of coal) has been studied.

The examination of Langmuir[20] and Freundlich[21] isotherms permit to verify whether the adsorption is attainted or not. The modeling adsorption equation of Langmuir (2) and Freundlich (3), under the linear form, are:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m Ce} \quad (2)$$

$$\ln Q_e = \ln K_f + \frac{1}{n} Ce \quad (3)$$

Qe: adsorption capacity, at equilibrium, of solute per gramme of adsorbent (mg/g);

Ce: concentration of solute at equilibrium (mg/L);

Qm: maximum adsorption capacity of Langmuir (mg/g);

b: Langmuir constant (L/mg);

Kf and n: empirical constants of Freundlich (the capacity and the intensity of adsorption).

RESULTS AND DISCUSSION

Physicochemical characterization of olive mill wastewater

The physicochemical analysis of the studied olive mill wastewater (Table 1) shows that the polyphenol content is 5614 mg/L, this concentration greatly exceeds the Algerian standards of discharge of industrial liquid effluent. These compounds can disrupt the ecosystem by their inhibitive effect of natural biodegradation.

Physico-chemical characterization of activated carbon

Knowledge of the physico-chemical characteristics of activated carbon, is necessary for the understanding of many phenomena such as adsorption, desorption, ion exchange and others.[22] Table 2 shows the main physicochemical characteristics of coal prepared from peach stones. The results show that the coal is mainly composed of carbon and oxygen; other hetero-elements like nitrogen and sulfur can coexist according to the used raw material.[19]

The pH of the prepared coal is almost neutral (6.93). For the moisture content and the textural parameters, on which is based the industrial firstly, namely the surface area and porosity, are suitable for an industrial operation. For example the value of the specific surface area (623 m^2/g) is comparable to those found by some authors. Duranoglu *et al.*[23] showed that an activated carbon (made from peach stones thermally treated at 850°C) has a specific surface of 608 m^2/g.

Moreover, it is noted that the value of the zeta potential is negative; this is related to the phenomenon of compression of the double layer of the particles and the zeta potential reduction or cancellation. The zeta potential of the activated carbon particles thus enables an estimate of the surface charge carried by this and therefore can lead to an interpretation of the results obtained during the adsorption of pollutant.

Analysis of the coal surface showed more basic surface oxides than acid due to the pyrolysis at 900 °C. Remember that this surface effect has long been known.[15] The observed low concentrations of carboxylic acid are probably due to the coal pyrolysis temperature. Julien[24] found that these surfaces are virtually eliminated with an activated carbon prepared from coconut for pyrolysis at 600 °C.

The observations of coal by scanning electron microscope **(Fig. 1)** show a well developed porosity over the entire surface of the activated carbon with some heterogeneity. In addition, there may be also the presence of a multitude of fine particles attached to the activated carbon. These particles can be attributed to both a reminiscence of vegetable origin of coal and impurities formed during its preparation.

Table 2

Main physicochemical characteristics of the prepared coal

Parameters	Values
C (%)	83.1
H (%)	6.7
O (%)	28.0
N (%)	3.2
S (%)	1.5
pH	6.93
Specific Surface (m^2/g)	623
Porous volume (cm^3/g)	0.63
Zeta potential (mV)	-21.96
Total of acid functions (meq/g)	1.80
- Carboxylic function	0.15
- Lactones function	0.32
- Phenol function	0.50
- Quinone function	0.83
Total basic functions (meq/g)	2.43

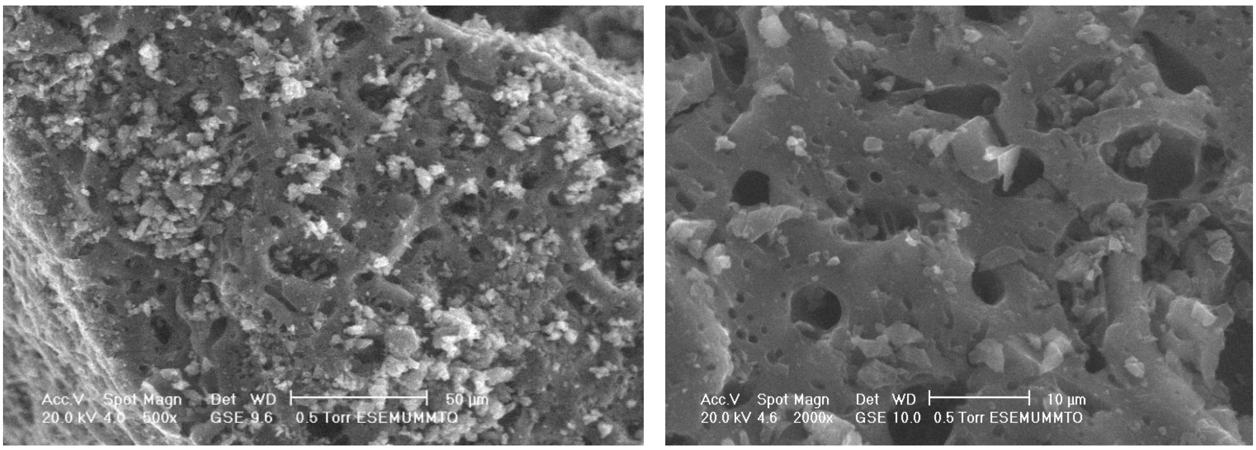

Fig. 1 – Observation of prepared coal by scanning electron microscope.

Result of the adsorption kinetics of polyphenols

Influence of the mass of the adsorbent and adsorption kinetics

In general, the search for the adsorption kinetics, depending on the mass of the adsorbent, is a prerequisite for the determination of the contact time or equilibrium between the solute and the adsorbent, in view optimization of adsorption.[19,25] According to the results reported in Fig. 2, it is noted that the performance of the adsorption of polyphenols increases with the mass of activated carbon. For the masses of 0.5, 1, 1.5 and 2g of adsorbent result in adsorption efficiencies of 57, 61, 79 and 83%, the observed increase is 26%.

For kinetics adsorption of polyphenols by activated carbon, Fig. 2 shows that the pseudo equilibrium is reached after 60 minutes of contact for all adsorbent masses. The shape of the kinetic curve possesses two parts. The first shows the exponential adsorption after 60 minutes, while the second part is stationary platen with slower adsorption to saturation of coal.

Rocha[26] found an adsorption equilibrium time for polyphenols on a polymeric resin of 180 minutes.

Determination of kinetic model

The adsorption kinetics is studied by the equation of pseudo first order (Eq 4)[27] and pseudo second order (Eq 5).[28]

$$\ln(q_e - q) = -K_{Lag}t + \ln q_e \tag{4}$$

$$\frac{t}{q} = \frac{1}{K_b q_e^2} + \frac{t}{q_e} \tag{5}$$

qe and q: quantities of polyphenols adsorbed by the active carbon respectively in equilibrium time and at time t.

K_{lag} and k_b: adsorption constants

According to Fig. 3 and 4, the two models have a linearity of the equation with a correlation coefficient $R^2 \geq 0.99$. However, according to Table 3 below, The model which has the value of the maximum equilibrium adsorption capacity, theoretically determined, approximately equal to that calculated experimentally is the pseudo second order. So, the adsorption kinetics of polyphenols on the activated carbon is pseudo second order type. These findings are in accordance with those obtained by Aliakbarian *et al.*[29] . Consequently, the adsorption reaction may be seen as diffusion controlled. In this context, it is extra-particular transfer material (transfer of material from the liquid phase towards the outer surface of the particles, step may be neglected due to the stirring of the sample), the intraparticle transfer under the influence of a concentration gradient of the material from the outer surface of the particles to the active sites and pores, and finally the adsorption reaction itself.[30]

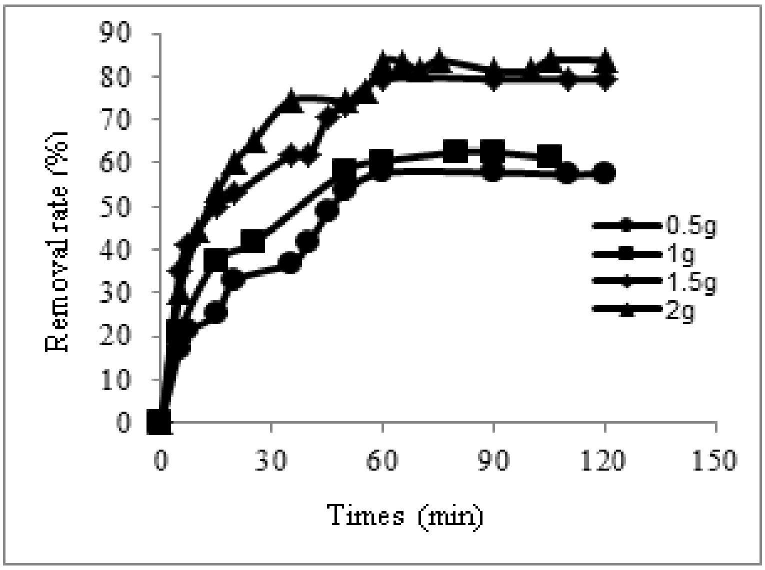

Fig. 2 – Influence of the adsorbent masse on adsorption rate of polyphenols as function of contact time.

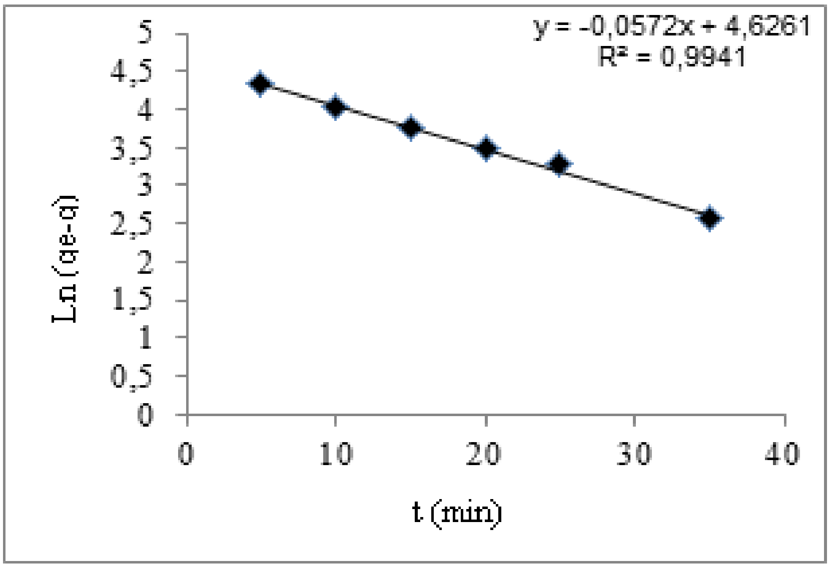

Fig. 3 – Linearisation as pseudo first order model.

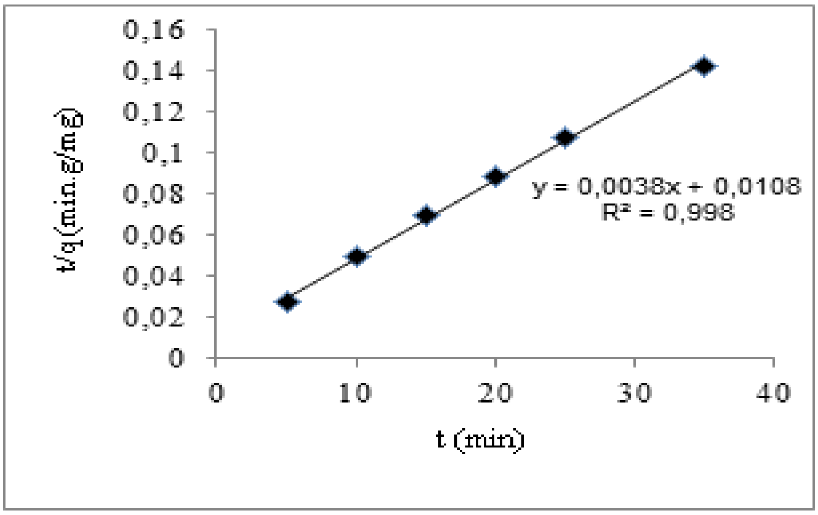

Fig. 4 – Linearisation as pseudo second order model.

Table 3

Values of characteristics constants for two models of adsorption kinetic

Pseudo first order			Pseudo second order		
Qe_{theo} (mg/g)	Qe_{exp} (mg/g)	k_{Lag} (min^{-1})	Qe_{theo} (mg/g)	Qe_{exp} (mg/g)	k_b (g/mg/min)
257.7	102.11	0.0572	257.7	263.15	1.33×10^{-3}

Influence of pH

The pH is an important parameter to be taken into account because it influences the solubility and the charge of the surface of the adsorbent. The results of Fig. 5 show that the decrease in the pH results in high removal rate of polyphenols. The yield reaches its maximum (91%) in an acidic medium (pH = 2), and then falls to 65% as it passes to a basic medium (pH = 10).These findings are consistent with those obtained by Banat *et al.*[31] in studying the adsorption of phenol on bentonite, where they showed that the efficiency of adsorption of phenols increases when the pH value of the solution is low. Morena-Castilla *et al.*[32] found similar results when the adsorption of phenol on activated carbon at different pH.

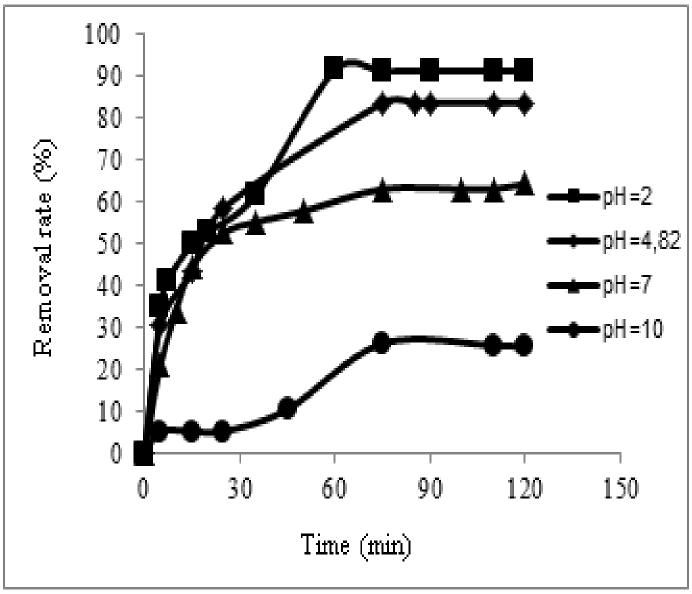

Fig. 5 – Influence of pH on the removal rate of polyphenols.

Effect of temperature

Measurements of the performance of polyphenols removing at different temperatures (20, 30, 40 and 55 °C) yields the results illustrated in Fig. 6. At 20 °C, the reduction rate of the concentration of the polyphenols on the prepared coal is 83.72%. The increase in sample temperature at 30, 40 and 55 °C reduces the effectiveness of treatment. At 55 °C, the removal rate was reduced by about 50% compared with the test at 20 °C. Thus, the increase in temperature reduces considerably the stability of bonds between the active sites of coal and phenolic compounds.

Modeling of the adsorption equilibrium

The change in the amount of phenolic compounds adsorbed on the activated carbon depending on the initial concentration of olive mill wastewater under the following conditions: mass of activated carbon equal to 2 g, contact time: 1 hour and the temperature: 20 °C is shown in Fig. 7. The figure indicates that the adsorption capacity of the phenolic compounds is not significant at low concentrations. As the concentration increases, the adsorbed amount increases greatly.

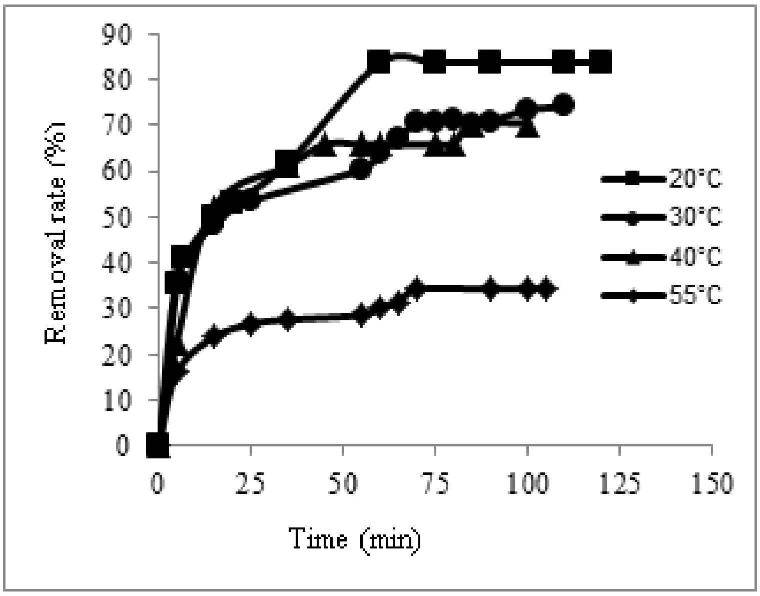

Fig. 6 – Influence of temperature on removal of polyphenols.

Referring to the classification of Giles *et al.*[33] this corresponds to the isotherm type Langmuir. In this type of adsorption isotherm, the initial part informs about the availability of active sites for the adsorbate and the bearing means forming a monolayer. The curve indicates that a large amount of polyphenols adsorbed at low concentrations when active sites are available. When the concentration increases, it becomes increasingly difficult to polyphenols to find vacant sites to set which promotes forming a monolayer.

The obtained isotherms, described by the two linear models Langmuir and Freundlich (Fig. 8 and 9), show that the linear coefficient of determination of the Freundlich model is closer to 1, so the adsorption equilibrium is described better by this model. This may be explained by the continuous distribution of adsorption sites and also by the presence of unsaturated sites. The different characteristic constants of Langmuir and Freundlich isotherms are grouped in Table 4.

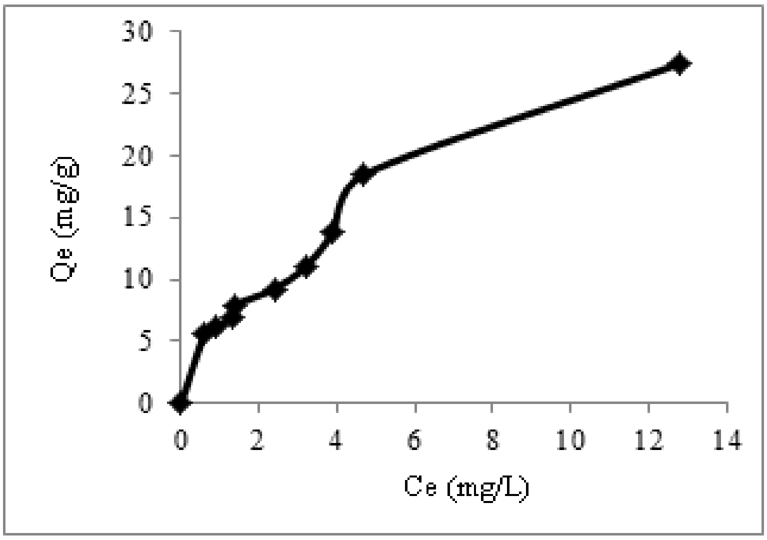

Fig. 7 – Adsorption isothermes of polyphenols on coal.

Table 4

Values of characteristics constant of the two adsorption models

Langmuir Model			**Freundlich Model**		
Qm (mg/g)	b (L/mg)	R^2	kf	n	R^2
16.4	0.75	0.870	6.5	1.88	0.974

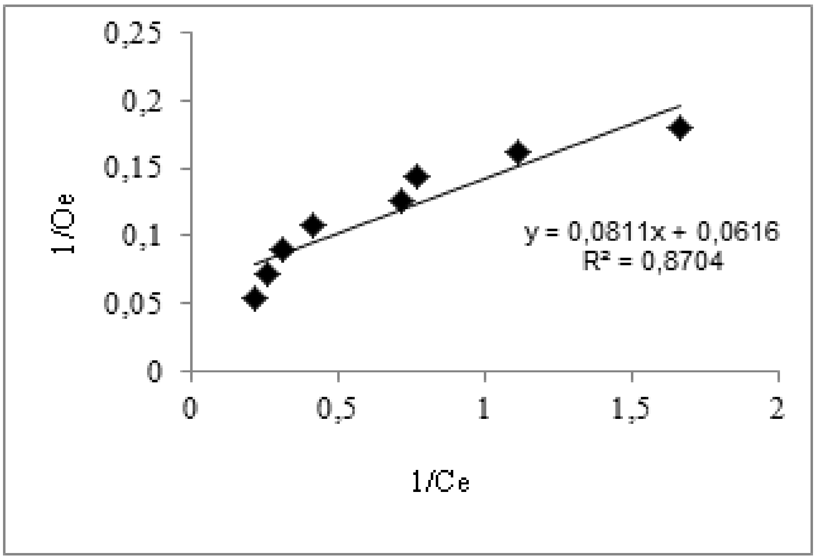

Fig. 8 – Isotherm adsorption modeling of polyphenols on activated carbon according to Langmuir equation.

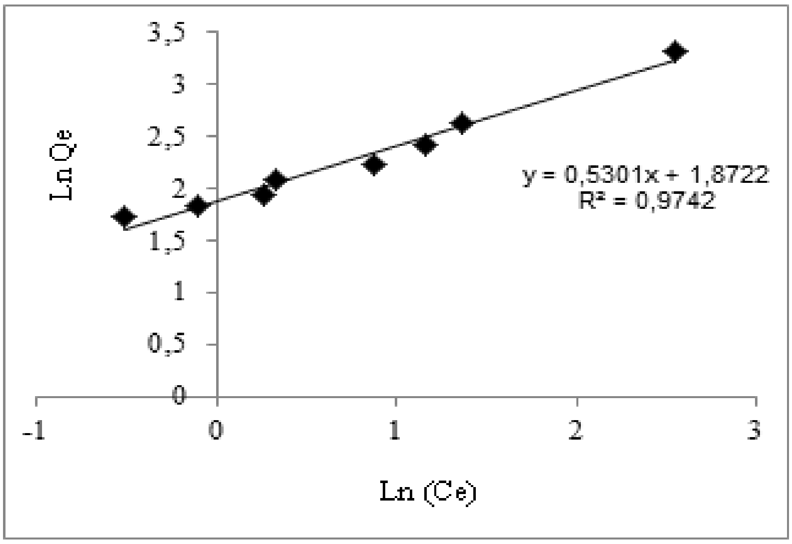

Fig. 9 – Isotherm adsorption modeling of polyphenols on activated carbon according to Freundlich equation.

CONCLUSIONS

The physicochemical analysis of the studied olive mill wastewater indicates that Algerian standards defining the limits of discharges of industrial liquid effluents are often exceeded for many parameters (organic matter: COD and polyphenols) so treatment of these waters is imposed.

The objective of our work is to reduce the concentration of polyphenols by the adsorption process on activated carbon made from peach stones.

The characterization of the prepared activated carbon showed properties comparable to those of many industrially produced coals.

The study of polyphenols adsorption on activated carbon allows us to achieve the following results:

The equilibrium time is reached after 60 minutes. The best removal efficiency is estimated at 91% in specific experimental conditions (acidic medium: pH=2, ambient temperature: 20°C and the adsorbent mass equal to 2 g). The adsorption follows the model of Freundlich and the adsorption kinetics is rapid and it is pseudo second order type.

The increase of the medium temperature causes a decrease in the efficiency of the removal of polyphenols.

Finally, we can say that the treatment process selected in this work, gives a very acceptable removal efficiency of polyphenols. The improved results obtained by the use of other conditions, is possible to get the most of this natural waste.

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