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Decontamination of olive mill wastewater with tow natural materials: Sand and starch

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ABSTRACT

This paper evaluated the removal of poly-phenols from olive mill wastewater in a batch reactor as monitored by adsorption using tow natural materials, namely sand and commercial starch. It was found that for the same experimental conditions (similar OMW, stirring rate, contact time and initial pH), starch is more suitable for this treatment. This physicochemical process effectively allowed the removal of more than 70% of phenolic components present in the OMW solution while the treatment with sand lowered their concentration by only 45%. The effect of pH and adsorbent concentration was also studied and similar important results were attained with the adsorbents at specific pH. Furthermore, kinetic models and adsorption isotherms were determined for each adsorbent.

Key words: Adsorption; Batch; Olive mill wastewater; Sand; Starch

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INTRODUCTION

The olive oil industry generates liquid effluents in large quantities and the main waste is the olive mill wastewater (OMW). In the Mediterranean Basin, the annual production of OMW can exceed 30 million m^3 [1]. Knowing that an inhabitant rejects annually an average of about 20 Kg of BOD, the OMW produced in the world can match the waste of 21 million people. Various quantities and compositions of effluent are obtained depending on the olives being pressed, the climatic conditions and the extraction mechanism [2]. The OMW ranges from black to dark-red reflecting the presence of phenolic compounds. Its pH is generally between 4 and 5. The high level of toxicity of this effluent is due essentially to polyphenols content, organic matters, COD of 100-150 g/L, BOD of 200 g/L, total suspended solids (TSS) and total dissolved solids (TDS). Adsorption using low-cost adsorbents becomes an effective and economic method for wastewaters treatment [3].

Many studies have been proposed for treating OMW, such as evaporation ponds [4], composting [5], thermal treatment [6], and physicochemical process [7]. But, at the best of our knowledge, few among them directed the attention to the treatment by natural adsorbents (starch and sand) which were applied to urban wastewater [8; 9].
Starch is an energy storage material for living plants that is composed of two poly-glucans: amylopectin and amylase and a single type of carbohydrate: glucose. It is inexpensive and very abundant in the world as a mixture of natural polymers. That is why; there is an increasing interest in its efficiency as a renewable raw material for non-food industrial applications. Starches are characterized by several properties such as hydrophilic, poly-functional, biodegradable, high chemical reactivity, and adsorption capacities [10].

Recently, Crini invented a new cross-linking starch ion-exchanger material, namely starch-enriched flour (provided by a flour mill situated in Patornay, Sauvin SA, France). The use of sand in the decontamination of OMW is considered as a biological treatment by bacterial cultures that are economic, available and not toxic.

The purpose of this work is to investigate the efficiency of these adsorbents and to study the effects of adsorbent concentration; contact time and pH. The mechanism of adsorption was described through various tests like the equilibrium isotherms analyzed according to the Langmuir and Freundlich models.

EXPERIMENTAL SECTION

2. 1. Experimental set up

The materials used for our experiments were the commercial starch obtained from corn grains and the sand collected from the beach of Kelibia, North Tunisia. The OMW were obtained from a three phase continuous extraction factory in Sfax, South Tunisia. It was filtered and conserved to prepare a stock solution for kinetics and equilibrium tests. Sodium carbonate anhydrous Na_2CO_3, Methanol solvent and Folin Ciocalteu's phenol reagent were bought from Fluka and UV-VIS spectrophotometer (Aquarious CECIL CE 7400) with high accuracy was used for absorbance measurements in all experiments.

The adsorption capacities of the material were monitored with the spectrophotometer by converting absorbance data into concentration data to be plotted as a function of the different parameters in each experiment. Phenolic compounds were quantified by means of the Folin-Ciocalteu calorimetric method using a calibration curve with the Gallic acid as standard [11].

2.2. Experimental Method

The experiments were conducted in a batch reactor without any further chemical treatment to ensure an economic and non toxic procedure and to promote the adsorption phenomenon at the solid/liquid interface. We have studied the efficiency of sand and commercial starch in the removal of pollutant from the OMW and the input/output liquid was analyzed for total polyphenols.

Adsorption isotherms [10] were performed using standard procedure that consists in mixing a fixed volume of OMW solution with a known amount of adsorbent in controlled conditions of contact time, agitation rate, temperature and pH. This process is favored for small and medium size applications since it is cheap, simple to operate and provides easily interpretable results.

In each experiment, 20 mL of OMW solution, containing an amount of 8, 82 g/L of polyphenols, were mixed with a determined weigh of material at the desired concentration in a tightly closed flask. The solution was stirred on a thermostatic shaker at a medium agitation rate. Then, it was filtered to remove any adsorbent particles, and the filtrate was analyzed using the Folin Ciocalteu reagent. Absorbance was measured by a UV/vis spectrophotometer at the maximum absorption wavelength (λ_{max} = 750 nm). The concentration was estimated quantitatively with the use of a linear regression equation obtained by plotting a calibration curve of the Gallic acid over a range of concentrations.

The amount of polyphenols adsorbed by the material at time t (q_t) was calculated from the mass balance equation given by (1). At the equilibrium time ($C_t = C_e$, $q_t = q_e$), we used (2) to determine the amount of polyphenols adsorbed q_e. We also determined the percentage of polyphenols removal (R in %) by using (3) [10].

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

$$q_e = V(C_0 - C_e)/m \qquad (2)$$

$$R = 100(C_0 - C_t)/C_0 \qquad (3)$$

Where: - C_0 and C_t are the initial and final polyphenols concentrations (mg/L),
- V is the volume of OMW solution (L)
- m is the mass of adsorbent used (g)
- C_e is the concentration at equilibrium (mg/L).

Effect of adsorbent concentration: Different solutions were prepared with a fixed volume of OMW and various concentrations of materials (15, 50, 75, 100 and 150g/L). The experiments were conducted for 20 h at 25°C and at natural pH which is low (4,7) owing to the presence of phenolic acids and fatty acids;

Effect of initial pH: In this experiment, the concentration of 15g/L was chosen for starch and 100g/L for sand since they lead to the elimination of about 50% of polyphenols with a moderate amount of material. The solutions were studied at different pH (from 2 to 10) for a constant contact time, 20h; the initial pH was adjusted using either HCl or NaOH. The pH value modification after contact with the material did not affect the determination of the final polyphenols concentrations. This study allows the determination of the optimum pH at which maximum removal could be achieved.

Effect of temperature: Different tests on sand and starch showed that adsorption capacity of the material is affected negatively with the temperature variation. For this reason, this study was found to be useless for the optimization of the adsorbent efficiency. Generally, the adsorption of organic pollutants onto a material is defined as an exothermic mechanism. Therefore, the temperature increase will weaken the physical and chemical bonds between these compounds and the active sites of the material [12].

Kinetic experiments: Polyphenols adsorption onto material was conducted for various time intervals to determine when adsorption was reached and the maximum abatement was obtained.

RESULTS AND DISCUSSION

3.1. Effect of the adsorbent concentration

We varied the concentration of the material with a contact time of 20 hours for each experiment to reach the adsorption limits. The figures (1) and (2) show the variations of polyphenols concentrations in OMW (mg/L) versus adsorbent amount for respectively starch and sand.

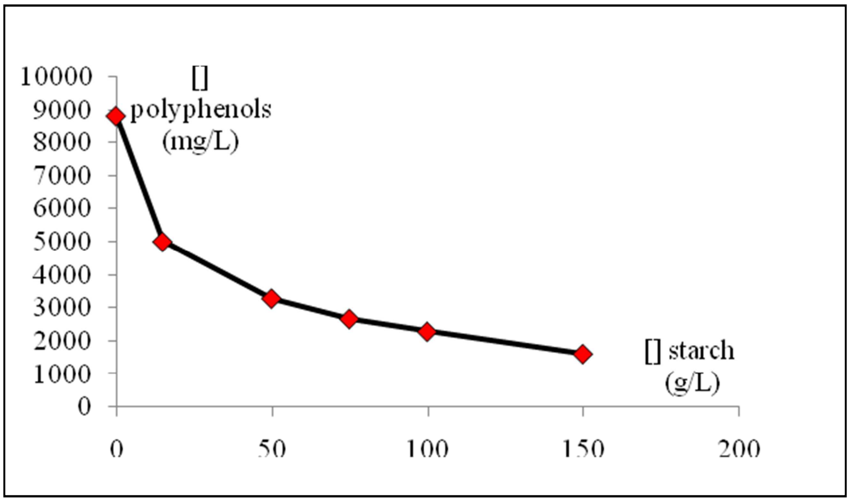

Fig. 1. Effect of starch amount on polyphenols concentration. (The concentration of starch ranges from 0 to 150 g/L)

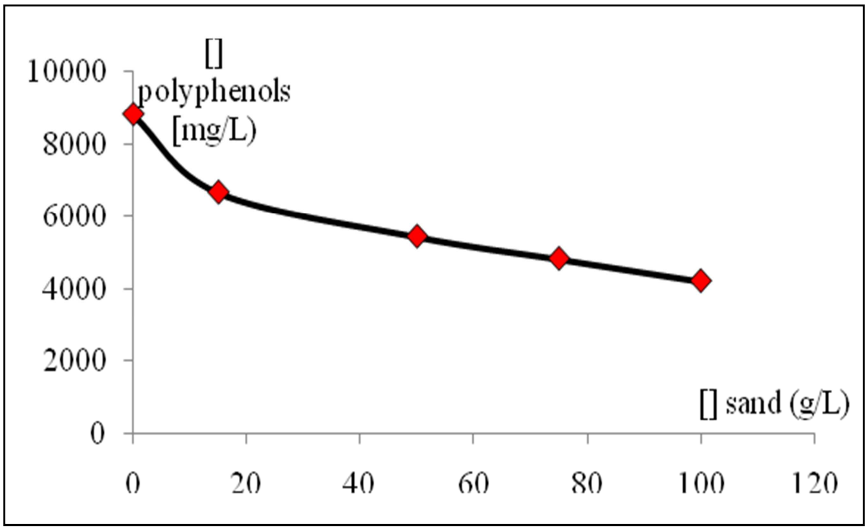

Fig. 2. Effect of sand amount on polyphenols concentration. (The concentration of starch ranges from 0 to 100 g/L)

Analysis of the graphic (Fig.3) indicate that starch is more efficient than sand in decreasing the organic load in the effluent. The polyphenols concentration fell by 52%, 62%, 69%, 73% and 86% for different adsorbent concentrations respectively 15g/L, 50g/L, 75g/L, 100g/L et 150g/L. Polyphenols concentration decreased significantly with 15g/L of starch from 8,82 g/L to 4,22 g/L. The adsorption rate of polyphenols molecules increased proportionally with the addition of starch and became almost unchanged at 100 g/L with a concentration of nearly 2.31 g/L.

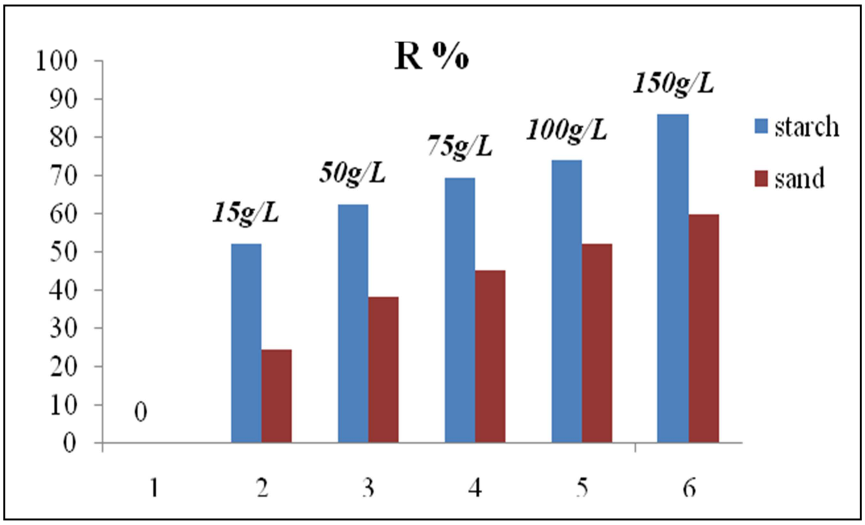

Fig. 3. Adsorption rate of polyphenols. (Comparison of starch and sand adsorption capacities for a range of concentration from 0 to 150 g/L)

In the case of sand, the removal of polyphenols is less important for the same concentrations of material. For 15 g/L, the amount of polyphenols decreased to 6,67 g/L and reached only 50% at a concentration of 100 g/L, which is huge and not economic.

It is understood that when the adsorbent dosage was higher, the number of active sites increases leading to the increase in the amount of adsorbed components. Then, the adsorption process was carried more efficiently and rapidly.

3.2. Effect of the initial pH

The contact time for each experiment is 20 hours at the optimal adsorbents concentrations (15g/L for starch and 100g/L for sand).

The pH of the solution is the most important parameter influencing the adsorption capacity. It affects the adsorption mechanism and the physicochemical interactions between the polyphenols and the adsorptive sites of adsorbents.

The results (Fig. 4) show that starch adsorption capacity is favored in an acidic medium with a maximum adsorption rate of 70% at pH = 5,5 while in a basic medium, its efficiency decreased dramatically and reached a percentage of 40% at pH = 9. We can admit that this material acts in the wide pH range of the solution which is generally equal to 4,7. At this pH, the surface of starch becomes positively charged and polyphenols molecules negatively charged which contributes to higher adsorption capacities. From a practical point of view, this will be very interesting since it will not require very accurate adjustment of the solution pH. When pH exceeds 6, low adsorption is observed indicating a possible development of negative charge on the material which creates repulsive forces and inhibits the adsorption process [13].

These results are in agreement with Thawornchaisit and Pakulanon [14] studies of phenols' adsorption on dried sludge which reported a decrease of adsorption at higher pH due to electrostatic repulsion between the negative sites and the phenolate ions.

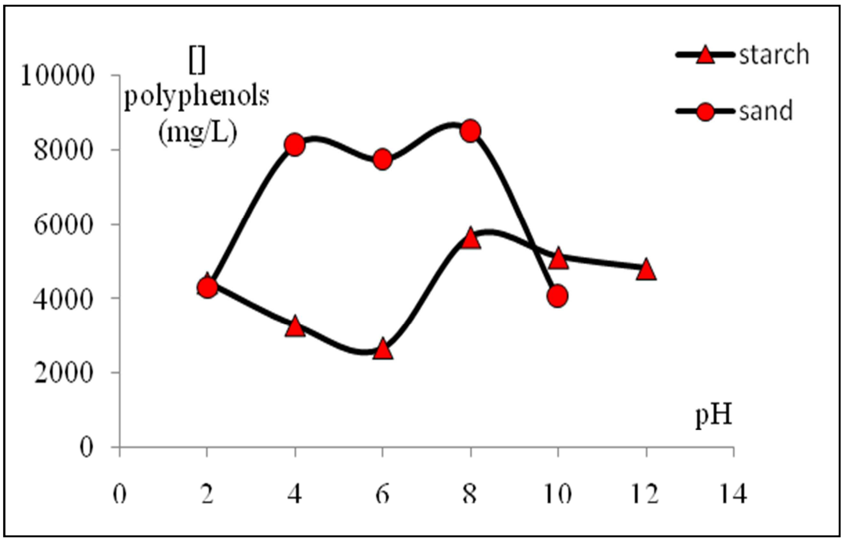

Fig. 4 - Effect of the initial pH on adsorption capacity. (pH ranges from 2 to 12 for starch and from 2 to 10 for sand)

Sand doesn't have a clear behavior in both mediums. Indeed, in a strongly acidic solution (pH=2), it allowed the removal of 50% of polyphenols. But, this ability decreased with the increase of pH and became very low (3%-12%) at pH between 4 and 8. Then, the sand efficiency rose to 54 % at pH = 10. This behavior demonstrated that an increase of the pH to high-alkalinity (pH > 8) resulted in an increase in the polyphenols adsorption capacity.

The effect of pH on adsorption cannot be limited to a surface charge modification or as a result of electric interactions. Many other factors such as weak forces interactions, ionic strength and irreversible bindings can lead to adsorption of molecules on adsorbent surfaces especially in the case of bio-adsorbents.

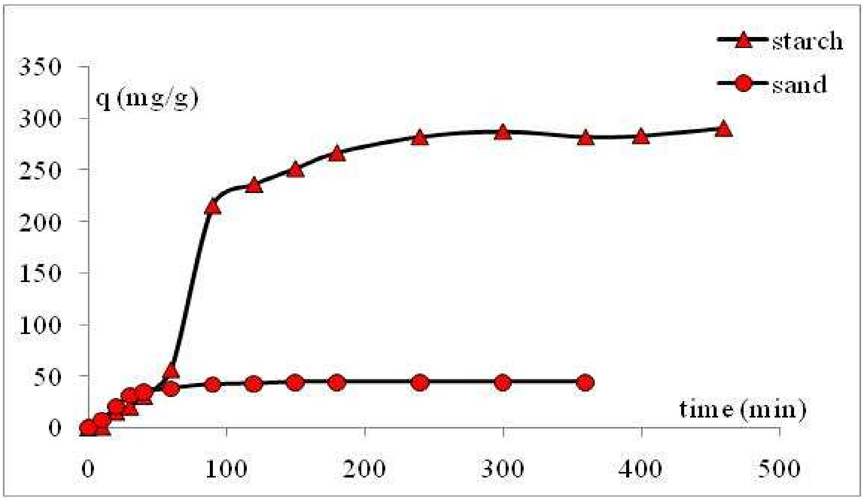

Fig. 5 - Adsorption kinetic of polyphenols

3.3. Kinetic experiments

A good pollutant adsorbent in wastewater decontamination is characterized by a high adsorption capacity and also a fast rate. Therefore, adsorption kinetic is very important for the selection of materials since it describes the chemical reaction rate. This process is mainly governed by the mass transfer of pollutants at the interface solid/liquid. The experimental data (Fig. 5) for the adsorption kinetic of polyphenols were recorded for 8h at a concentration of 15g/L for starch and 100g/L for sand in order to have clear appearances of the variations. The obtained plots show that q_t values increased with time until reaching a constant value indicating that no more polyphenols were removed from the solution. This result indicates that, at this time, the adsorbed amount of pollutant was in a state of dynamic equilibrium with that being desorbed from the adsorbent. This equilibrium was established after 240 min for starch and 150 min for sand and there is no significant improvement for a further contact time. Adsorption rate of phenolic compounds on starch and sand can be considered much faster than those reported for some other adsorbents. For example, the sorption equilibrium of phenol on dried sewage sludge [14] and adsorption of bromophenols onto carbonaceous adsorbents [15] was reached within 20h and 8h respectively.

We noticed that the curves have different appearance since starch reacts faster than sand. The initial adsorbed amount increased rapidly with time since there were many accessible sites. This result suggests strong interactions between polyphenols molecules and the materials particles. After reaching the maximum of adsorption, the quantity of adsorbed pollutant remained almost constant. This is due to the decline of vacant active sites at the end of the process or to the formation of repulsive forces between the pollutant on the adsorbent surface and the bulk phase [16]. Thus, the phenolic compounds must struggle to get into the pores [17].

In order to investigate the mechanism of adsorption which can be: adsorption surface, diffusion mechanisms and/or chemical reaction, the verification of the appropriate kinetic model for each adsorbent was studied by plotting the most common models: first-order, pseudo-second order, Elovich and intra-particle diffusion models.

- Pseudo first order:

The pseudo-first order model (Fig.6) is expressed by the equation: $\ln(q_e - q_t) = \ln(q_e) - kt$ where k (h^{-1}) is the constant of equilibrium rate ; q_e and q_t represent the amount of adsorbed phenolic compounds (mg/g) at equilibrium and at any time, t (h) [18].

The pseudo-first-order parameters: k, correlation coefficient, theoretical and experimental q_e values are given in Table 1.

Table 1 - Pseudo-first order parameters

parameter	q(e, exp) (mg/g)	q(e, cal) (mg/g)	R^2	k (h^{-1})
Starch	29	32,346	0.9809	0.8562
Sand	44.54	39,01	0.9694	1.7621

As shown in the table, the correlation coefficient (R_1^2, $R_2^2 > 0,84$) and the constant k (k_1, $k_2 > 0,5$) are important and the theoretical values of q_e are very close to the experimental values for both adsorbents. These results confirm that the pseudo-first order is appropriate to study the adsorption kinetic of polyphenols on starch and sand.

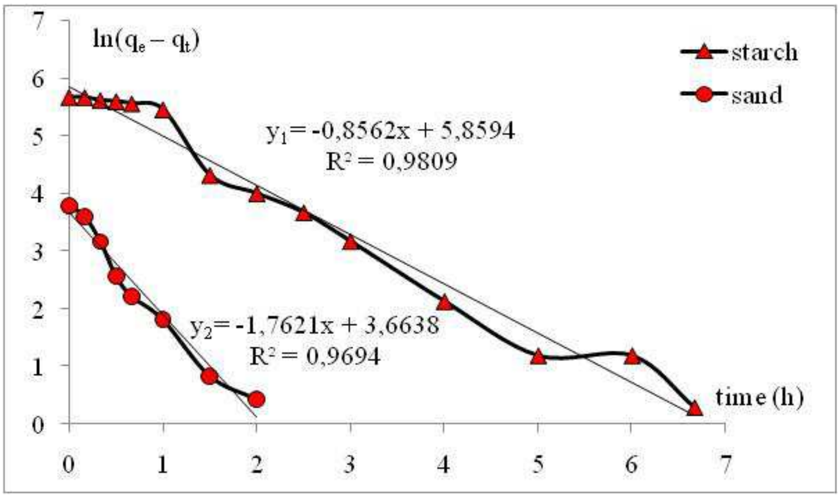

Fig. 6 - Pseudo-first order kinetic model. (Ln $(q_e - q_t) = f(t)$ and the corresponding equation (y_1 for starch and y_2 for sand)

- Pseudo second order

The pseudo-second order is examined by plotting the curve t/q_t based on time, according to the equation: $t/q_t = 1/(kq_{max}^2) + (1/q_{max})t$ where k is a kinetic constant of the pseudo-second order [19].

The figure (7) indicates that this model doesn't correlate with the experimental results of starch (R^2_1 = 0, 0489) while it absolutely describes the behavior of sand over time (R^2_2 = 0, 9892). The results are gathered in Table 2.

Table 2 - Pseudo-second-order parameters

parameter	q(e, exp) (mg/g)	q(e, cal) (mg/g)	R^2	k ($mg^{-1}g\ min^{-1}$)
Starch	29	100	0.0489	0.0049
Sand	44.54	47.62	0.9892	0.021

We noted that sand adsorption kinetic can be expressed with both pseudo-first and second order equations but the pseudo-second order gives a better description since the correlation coefficient is higher and the q(e,cal) is closer to q(e,exp).

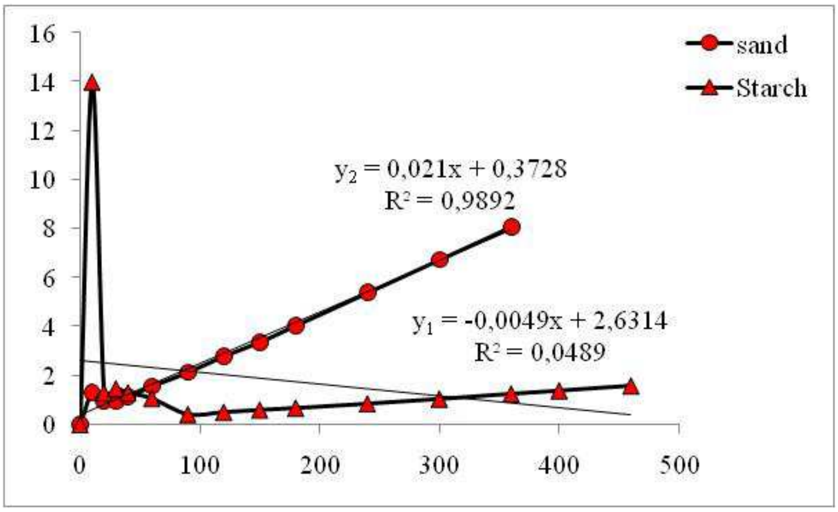

Fig. 7 - Pseudo-second order kinetic model. ($t/q_t = f(t)$)

-Elovich model

This model (Fig. 8) can be described as: $q_t = 1/b\ Ln(ab) + 1/b\ Ln(t)$ where the constant a is the initial adsorption rate and b is related to the activation energy and the adsorption heat [20].

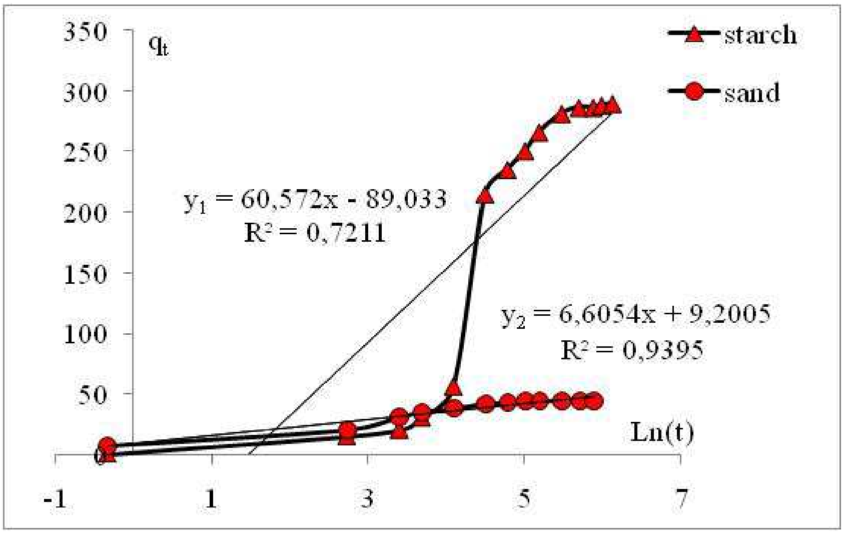

Fig. 8 - Plotting of the Elovich equation. ($q_t = f(Ln(t))$)

We noted that the adsorption kinetic of starch can't be represented with the Elovich model (R^2= 0.7211) while we can adopt it in the case of sand (R^2= 0.9395).

- Model of intra-particle diffusion

The intra-particle diffusion model (Fig. 9) underlines the heterogeneity of the particles of the material. In this model, the adsorption is first described by an external mass transfer followed by an intra-particle diffusion, by means of the equation of Weber-Morris:

$q_t = k_{id,i}\, t^{1/2} + C_i$ [21 ; 22].

Where $k_{id,i}$ (mg $g^{-1}s^{-1/2}$) is the constant of step i, C_i is a constant describing the thickness of the diffusion limit layer.

If the curve $q_t = f(t^{1/2})$ is linear, we conclude that the intra-particle diffusion is produced, and if the curve passes by the origin, than the process is limited only by diffusion. If not, then there is another limiting factor than diffusion [23; 24].

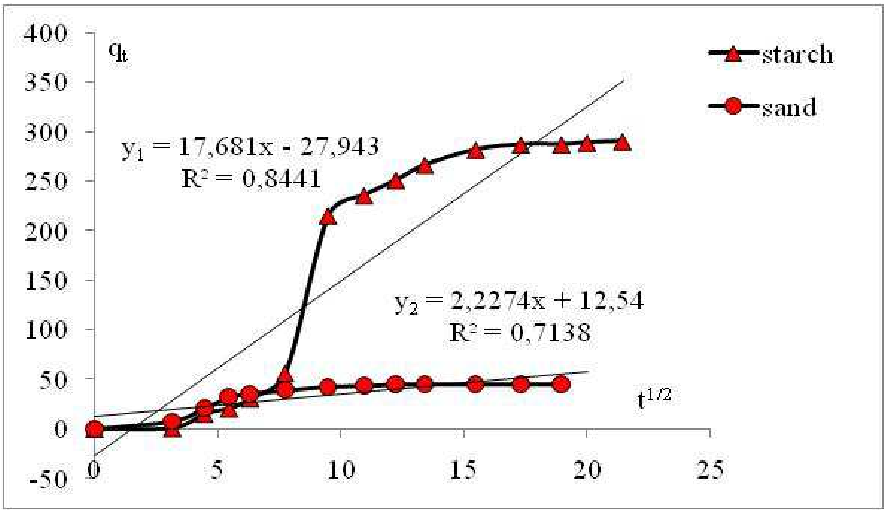

Fig. 9 - The intra-particle diffusion model for the starch adsorption. ($q_t = f(t^{1/2})$)

The Figure (9) shows that the intra-particle diffusion model doesn't fit the adsorption kinetic of polyphenols on starch ($R^2 = 0.8441$) and sand ($R^2 = 0.7138$) since the R^2 values are much lower than those of the pseudo-first order and the pseudo-second order.

3.4. Isotherms studies

The equilibrium relationship between adsorbent and adsorbate is described as the polyphenols distribution between the solid and the liquid medium at this point. This phenomenon is converted into adsorption isotherms using the available mathematical models [25].

Adsorption isotherms are very useful since they provide information about the adsorbent efficiency and adsorption isotherm constants which reveal the surface properties, the adsorbent affinity and the adsorbed layer structure.

The shape of an isotherm gives a prediction of its favoritism and also an idea about the solute-surface interaction [26]. The variation of the amount of adsorbed polyphenols at equilibrium Q_e (mg/g) based on the polyphenols concentration in solution C_e (mg/L) is determined. The curve $Q_e = f(C_e)$ represents the adsorption isotherm. These experimental data are then correlated with mathematical models among which, Langmuir and Freundlich isotherms are the commonly used in the determination of the maximum adsorption capacity of the material and the adsorption constant K_{ads} which characterizes adsorbent-adsorbate interactions. For this, the curve $1/Q_e = f(1/C_e)$ was plotted (Figure 10) to study the Langmuir model whose equation is valid for a monolayer adsorption on a surface with a limited number of identical sites:

$1/Q_e = 1/ Q_{max} + (1/ Q_{max}. K_L).1/C_e$

Where K_L is the equilibrium Langmuir constant that shows the affinity of binding sites.

This model is mainly used for a pollutant removal from a liquid solution. It is based on the concept that the adsorbed energy is uniform during the adsorption process and suggests that polyphenols occupies specific homogeneous sites within the adsorbent. Only one molecule can be adsorbed at each site [27]. The main characteristic of the Langmuir isotherm can be defined by the constant called the equilibrium parameter $R_L = 1/(1+bC_0)$, which indicates the type of isotherm:

($R_L = 0$): irreversible
($0 < R_L < 1$): favorable

(R_L = 1): linear
(R_L >1): unfavorable [28].

The obtained results (Table 3) confirm that the adsorption of phenolic compounds on starch and sand is favorable and has R_L values between 0 and 1.

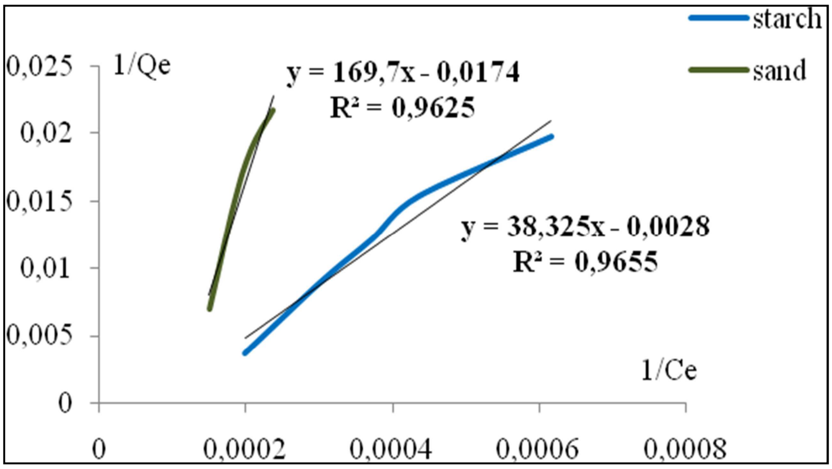

Fig. 10 - Langmuir adsorption isotherm. (Isotherms allowed the determination of the layer category for the adsorbed molecules, $1/Q_e$ = f ($1/C_e$)

While the curve ln (Q_e) = f (ln (C_e)) is designed to study the Freundlich model (Figure 11) which the equation is: Ln Q_e = Ln(K_F) + (1/n).Ln(C_e) with K_F is the Freundlich constant related to the adsorption capacity of the adsorbent and n is a constant indicating greatness of adsorbate-adsorbent relationship.

This model is mostly used in the case of heterogeneous sites with various fixation energies and especially in the case of a possible formation of more than one adsorption monolayer. The equation suggests that adsorption energy exponentially declines on completion of the available sites of the adsorbent. We concluded that the adsorption of phenolic compounds on starch and sand is favorable and has an n value between 0 and 1 (Table 3).

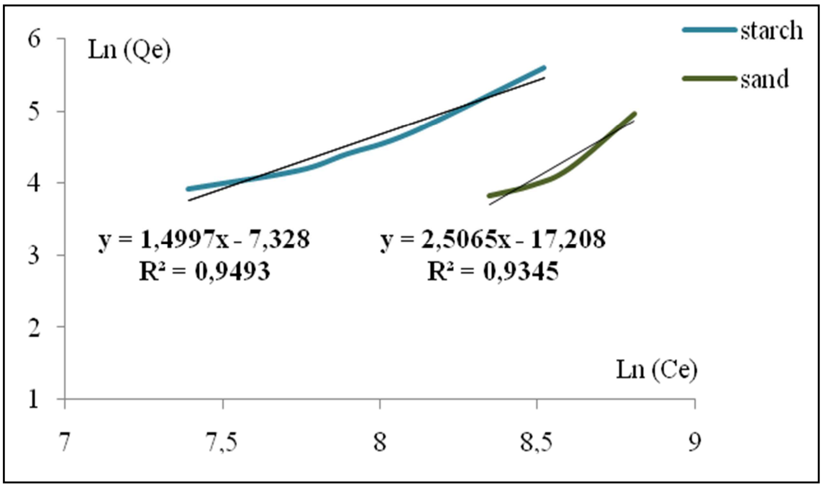

Fig. 11 - Freundlich adsorption isotherm. Ln (Q_e) = f (Ln (C_e))

The correlation coefficients show that the phenolic compounds adsorption in this study can be fitted with both Langmuir and Freundlich models. This result suggests a formation of mono and hetero-layer phenolic compounds on the adsorbent surface. This phenomenon can be explained by the chemical nature of the surface of the material.

The adsorption capacity may be affected by the non-uniform energy levels resulting from the various intensities and distributions of the active functional groups. In fact, monolayer coverage is induced by active centers with lower energy level while the hetero-layer is formed by those with higher energy level due to their strong chemical bonds [29].

Table 3 - Adsorption isotherms parameters

	Starch	Sand
Langmuir	Q_{max} = 357.14 K_L = $7,30.10^{-5}$ R_L = 0.608 R² = 0,9655	Q_{max} =57.47 K_L = 10^{-4} R_L = 0.525 R² = 0,9625
Freundlich	n = 0.6668 K_F = $6,56.10^{-4}$ R² = 0,9493	n = 0.399 K_F = $3,36.10^{-8}$ R² = 0,9345

Table 4 - Adsorption capacity of phenolic compounds by various adsorbents reported in literature

Adsorbent	Q_{max}	Reference
Activated coal	1.84	[30]
Resin AP-246	0.071	[31]
Coconut shell	205.84	[32]
Banana peel	688.9	[33]

The adsorption capacity of low-cost adsorbents tested for the removal of phenolic compounds is presented in the table 4. It is clear that sand has a medium adsorption capacity (Q_{max} = 57.47) compared to the other adsorbents while starch is considered with a high capacity (Q_{max} = 357.14).

CONCLUSION

Natural adsorbents used in this study have proven their efficiency in the removal of phenolic compounds from olive mill wastewater. The main characteristics of the adsorption process on sand and starch can be summarized as follow:

- The tow materials allow the removal of pollutant from the OMW but starch has a better and faster adsorption rate than sand with the same adsorbent concentrations, revealing that starch could be employed as a promising adsorbent for phenolic compounds elimination.

- The pH played an obvious effect on the phenolic compounds adsorption capacity. The variation of pH shows that the adsorption rate of starch is maximum 70% at a pH = 6 with a concentration of 15g/L while sand acts with a concentration of 100g/L to reach only 52% at a higher pH =10.

- Both Langmuir and Freundlich isotherms are appropriate to describe the adsorption of phenolic compounds onto starch and sand.
- The adsorption capacity increased with time and reached a determined limit q_{max} in 4 h of contact with starch and 1h.30min with sand.
- Adsorption kinetics followed mostly the pseudo-first order model with starch and the pseudo-second order with sand.
- All the results showed that the starch and sand materials were efficient low-cost adsorbents for the removal of polyphenols from OMW.

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