Olive mill wastewater phenolic compounds adsorption onto active olive stones: equilibrium isotherms and kinetics study

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Abstract: Phenol, being the major wastewater pollutant has adverse effects on the human health. Various biological and non-biological methods are used for removal of the phenol from wastewater such as adsorption, photodecomposition, volatilisation and others. The present study is focused on studying the environmental state of art of olive mills operating in the southern areas of Tunisia. It also investigates the feasibility of transforming olives solid residue into an effective, high capacity and low cost adsorbent for total phenol removal from olive mill wastewater (OMWW). Results indicated that the used activated olive stones, with 368.3 m^2/g *BET* surface area, exhibit high total phenol adsorption capacity. Adsorption equilibrium is represented by Langmuir isotherm model ($Q_0 = 333.3$ mg/g). Total phenol adsorption kinetics is best modelled by pseudo-second order reaction rate and Dumwald-Wagner (intra-particle) diffusion model. Reduction of the total phenol content in OMWW is achieved in mini column test of activated olive stones fixed bed adsorption.

Keywords: polyphenols; OMWW; olive mill wastewater; activated olive stones; adsorption isotherms; adsorption kinetics.

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1 Introduction

In the Mediterranean countries, the olive oil industry is an important activity. These countries take approximately 95% of the world olive oil production. Due to the promotion of olive oil health benefits, the world demand is increasing and therefore the production is steadily growing to meet the needs of consumers. However, two sub products of the olive oil industry, pomace and vegetation water also called olive mill wastewater (OMWW), create environmental challenges (Dimitris et al., 2015). The solid residue is reused in agriculture and industry, while vegetable water is discharged into sewers or land applied in soils.

In general, for each ton of olives processed, 1.3 m^3 of black waters are produced. These effluents are considered toxic wastewater. Their release into nature without any prior treatment is a major environmental problem especially for the Mediterranean countries. The toxicity of the OMWW is attributed to the presence of high biological oxygen demand (105 g/L), chemical oxygen demand (180 g/L), total solids content (102 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. Therefore, the treatment of this OMWW is necessary (Marianna et al., 2016). Physical, chemical and/or biological treatment methods have been developed to address this problem (Abaynesh et al., 2016). Most of these alternatives have the problem of high cost and low efficiency and generation of toxic by-products especially for high phenol concentration in wastewater.

This work focuses on the removal of polyphenols from OMWW by a physicochemical method that is adsorption on activated olive stones. There are many advantages of adsorption, among them are the low space requirements for batch and continuous fixed bed units, simplicity of design and ease of operation, non-pollutant to water, no odour emissions and low-cost of the adsorbent. One of the most widely used adsorbents is activated carbon. It has been estimated that between 60-80% of organic constituents from OMWW can be absorbed by activated carbon (Khaled et al., 2011). This study is dedicated to investigate the adsorption process of total phenol in OMWW onto activated olive stones. Different indicators are used to evaluate the total phenol adsorption efficiency. Equilibrium studies provide important information about the maximum adsorption capacity. They also test the applicability of Freundlich and Langmuir equilibrium isotherms.

This study highlights the main factors affecting adsorption systems i.e., temperature, pH, solubility of adsorbate, and characteristics of the adsorbent.

2 Literature review

2.1 Phenolic content of OMWW

Olives are rich in simple and complex phenolic compounds. During the olive oil extraction process, due to the chemical characteristics of polyphenols that are water-soluble, the partition between water and oil is different and the major proportion of these compounds goes from the olive pulp to the aqueous phase, that is the OMWW (i.e., <1% in the olive oil vs. 18% in olives). OMWW phenolic content shows great variability both from the qualitative and quantitative point of view, depending on several factors, such as type of olive, stage of maturity, and most importantly type of production process. The extraction system does not seem to qualitatively alter the phenolic composition of olive oil, but it affects its concentration, with the two-phase decanter OMWW being the richest in quantity

More than 30 different phenolic compounds have been detected in OMWW and reported by several authors (Theodora et al., 2011).

2.2 Adsorption of phenol and activated olive stones

Many researches are dedicated to study the removal of phenol and its substituents from aqueous solutions onto different conventional and non-conventional adsorbents. (Valderrama et al., 2010) concluded that adsorption of phenol onto carbonaceous activated carbon is faster compared to polymeric resin. (Hank et al., 2014) proved in their kinetics study that activated clay has a higher adsorption capacity of phenol than commercial grade activated carbon. Gassan et al. (2013) achieved high phenol adsorption capacity onto local activated phosphate rock.

In Mediterranean countries, olive stones, are very abundant agricultural by-product, and could be a very adequate raw material to obtain good adsorbent. Activated carbon prepared chemically from olive stones proved to be an excellent decontaminant of polluted water with heavy metals and organic compounds like phenols (Spahis et al., 2008). Nour et al. (2016) showed that high surface area activated carbon, 1339 m^2/g, 1271 m^2/g, respectively, can be produced from olive husk. The adsorption capacity of phenolic compounds onto activated carbon produced from olive stones has been investigated by many researchers. Marques et al. (2017) obtained high phenol adsorption capacity (158.7 g/g) using chemically activated ($ZnCl_2$) olive stones. Chun et al. (2016) showed that the capacity of phenol adsorption onto activated olive husk is higher than that on commercial activated carbon.

2.3 Factors affecting adsorption equilibrium

The characteristics of the adsorbent including surface area, pore size distribution, adsorbent dose and surface chemistry play an important role in the adsorption process and affect the adsorption equilibrium. On the other hand, the solubility of the adsorbate is a key factor affecting the adsorption capacity. In general, the adsorption increases with the decrease of adsorbate solubility (El Boujaady et al., 2014). The affinity of weak organic acids or bases for activated carbon is a function of pH. In general, the adsorption of molecule is preferred in neutral form as its affinity to water increases when it is ionised, and therefore reducing the adsorption capacity (Runliang et al., 2014). The competitive adsorption of multi-solute system may affect the adsorption of a certain constituent from liquid phase.

The average OMWW pH value in the study area is 4.8. Moreover, *pH* is kept unchanged during the batch and continuous treatment experiments. In general, phenolic compounds are weak acids, which are slightly soluble in water with $pK_a = 9.89$. In addition at high pH (7–11), as reported by Gassan et al. (2013), the surface of activated olive stones is also negatively charged; so, there is an increase in the electrostatic repulsion between phenolic anions and the surface of the activated carbon. Therefore, the natural pH of OMWW is considered the optimum value to be maintained during treatment.

Several researchers showed that the adsorption of phenol decreases with temperature increase above 30°C. The temperature augmentation reduces the attractive forces between phenol and the adsorbent and an increase the adsorbent thermal energy is also observed. It also leads to conclude that physical adsorption has an important role besides chemisorption in phenol attachment onto the adsorbent (Ekpete and Horsfall, 2011).

Dynamic equilibrium is mainly used to describe the equilibrium state in adsorption system. When the adsorbent surface is exposed to gas or liquid, the liquid/gas molecules strike on the surface of the solid where some of these molecules get adsorbed and the others rebound. The rate of adsorption at the beginning is high as the adsorption sites on the surface of the solid are all available. The rate of adsorption decreases by time as the surface gets covered by adsorbate molecules. On the other hand, the rate of desorption increases since more molecules rebound until equilibrium is reached between the rate of adsorption and the rate of desorption (Marcilloa et al., 2017).

2.4 Adsorption equilibrium models

Adsorption equilibrium equations are a good tool to describe the adsorption systems. They provide useful information about the adsorbate and adsorbent surface properties and the adsorbability of a certain compound. There are several equilibrium isotherm models including Freundlich, Langmuir, Redlich-Peterson, Tempkin and many other models developed to fit adsorption systems with various conditions. However, the most important and used isotherms in the field of adsorption for environmental clean-up are Langmuir and Freundlich isotherms (Muthanna and Samar, 2012).

The linear form of Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \tag{1}$$

The linear form of Freundlich equation is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

2.5 Adsorption kinetics

Studying adsorption kinetics is important since they give insight about how well the adsorption system behaves and the rate at which specific constituent is removed onto the adsorbent. Adsorption kinetics clear out whether the adsorption process is chemical or physical and which specifically is the rate limiting step. Several models are used to describe the adsorption process. These models are classified into adsorption reaction and adsorption diffusion models.

The adsorption reaction models are:

- The pseudo-first order kinetic model is considered the earliest models developed to describe the kinetic process of adsorption (Yeon and JinHyun, 2017). This model is based on adsorption capacity and described as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

- The pseudo-second order kinetic model. Based on this model, the rate of adsorption is dependent upon the amount adsorbate on the surface of the adsorbent at time *t* and that at equilibrium (Idil et al., 2017). This model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{1}{q_e} t \tag{4}$$

$$V_0 = k_2 q_e^{\,2} \tag{5}$$

- The second order kinetic model is described as follows in solution systems (Jianxin and Muqing, 2014):

$$\frac{t}{C_t} = k_2^* t + \frac{1}{C_0} \tag{6}$$

The adsorption diffusion models are:

- *Liquid-film diffusion model*: The linear film diffusion mass transfer rate (2017) as follows:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -R' t \tag{7}$$

$$R' = \frac{3D_e}{r_0 \Delta r_0 k'} \tag{8}$$

- *Weber-Morris model*: Aljeboree et al. (2017) found that in many adsorption cases as the adsorption of phenolic compounds, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time *t*.

$$q_t = k_{int} t^{0.5} \tag{9}$$

Equation (9) is applied if the intra-particle diffusion model is the rate limiting step, which is not always the case as film diffusion and intra-particle models may apply simultaneously (Stoeckli and Hugi-Cleary, 2001).

- *Dumwald-Wagner model*: This model is based on intra-particle diffusion concept which fits in modelling different adsorption processes like *p*-toluidine adsorption on polymeric adsorbents (Wang et al., 2004) according to equation (10):

$$\log\left(1 - \frac{q_t}{q_e}\right) = -\frac{K}{2.303} t \tag{10}$$

- *Double exponential model*: Edidiong et al. (2017) suggested an adsorption model under the assumption that adsorption is controlled by external and internal diffusion and a slow intra-particle diffusion step according to the Eq. (11) under the assumption that the rapid diffusion step is negligible:

$$\ln(q_e - q_t) = \ln\left(\frac{D_2}{m_a}\right) - k_2 t \tag{11}$$

3 Materials and methods

3.1 Effect of adsorbent dose

Different weights (0.03–1.4 g) of activated olive stone were added to 25 mL of Sfax OMWW mixture with initial total phenol concentration (C_i) of 4017.9 mg/L. The mixture was agitated at 150 rpm and 25°C in water bath shaker for 48 h. The equilibrium total phenol concentration C_e of each sample was analysed using Gas Chromatography Mass Spectrometry (Shimadzu, QP2010SE). The chemical products were purchased from Thermo Fisher Scientific.

3.2 Adsorption equilibrium study

Four 100 mL Erlenmeyer flasks were filled out with 50 mL of OMWW with 100%, 75%, 50%, 25% and 10% of initial total phenol concentration (C_i) of Sfax OMWW mixture (4017.9 mg/L). In addition, 0.35 g of activated olive stones was added to each flask. The mixture was agitated at 150 rpm and 25°C in water bath shaker for 48 h. The equilibrium total phenol concentration C_e of each sample was analysed using GC-MS quantitative method.

3.3 Adsorption kinetics study

One 100 mL Erlenmeyer flask was filled out with 50 mL of Sfax OMWW mixture of initial total phenol concentration (C_i) of 4017.9 mg/L. An amount of 0.6 g of activated olive stones is added to the flask. The mixture was agitated at 150 rpm and 25°C in water bath shaker for 48 h. During this period, regular sampling was carried out at equal intervals of 40 min. Total phenol concentration C_e of each sample was analysed using GC-MS.

4 Results and discussion

4.1 Effect of adsorbent dose

According to Figure 1, significant increase in total phenol removal is observed when the adsorbent dose is increased from 0 g/25 mL to 0.3 g/25 mL of OMWW. Beyond this dose, the total phenol removal is almost constant.

This result can be explained by the fact that increasing the amount of adsorbent will increase the total surface area available for adsorption. For higher adsorbent dose, more adsorption sites are available which lowers the driving force for intra-particle adsorption at each adsorption site. Therefore, there is less utilisation of the adsorption capacity of the adsorbent. This leads to conclude that 12 g/L is considered to be the optimum activated olive stones dose for efficient batch treatment.

4.2 Total phenol adsorption equilibrium modelling

The relationship between the initial total phenol concentration in OMWW (C_i) and adsorption capacity (q_e) is depicted in Figure 2. It is observed that the increase in C_i

augments phenol uptake as well as q_e. This is due to the enhanced mass driving force toward the activated olive stones with significant increase observed when C_i is in the range (500–2000) mg/L. In the study area, most of OMWW samples have initial total phenol concentration above 2000 mg/L, indicating that the equilibrium adsorption capacity is almost the same. The adsorption isotherm shown in Figure 3 is concave downward indicating strongly favourable isotherm that leads to higher adsorption capacity as depicted in the values of Langmuir constants. A strongly favourable isotherm would also lead to shorten the mass transfer zone in the fixed bed adsorption column.

Figure 1 Effect of activated olive stones dose on total phenol removal efficiency (see online version for colours)

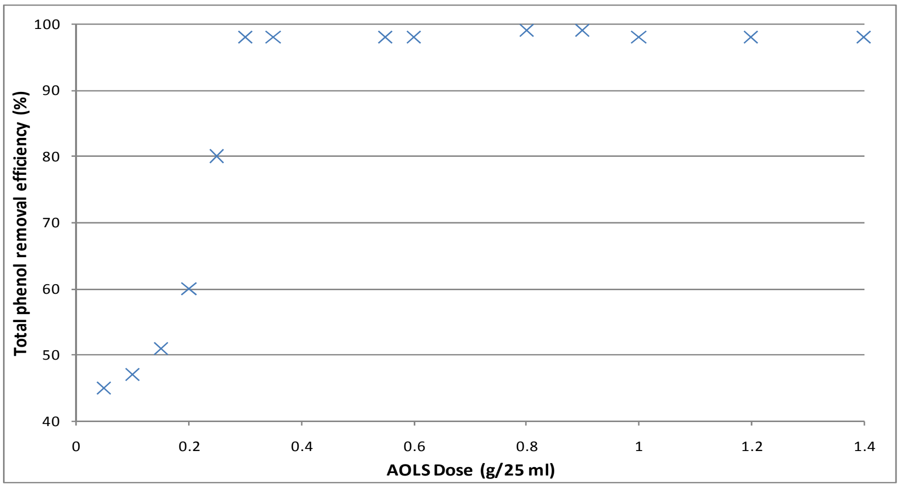


Figure 2 Effect of initial total phenol concentration on adsorption onto activated olive stones (see online version for colours)

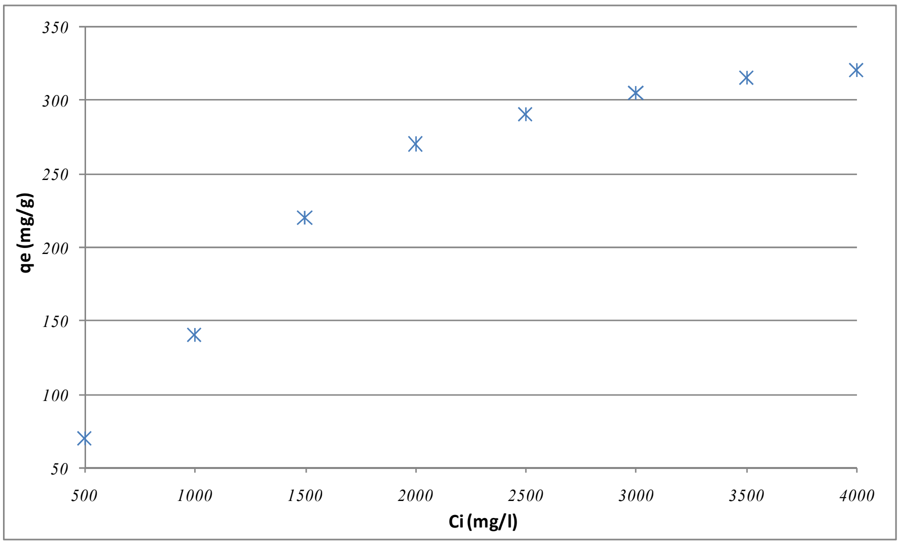
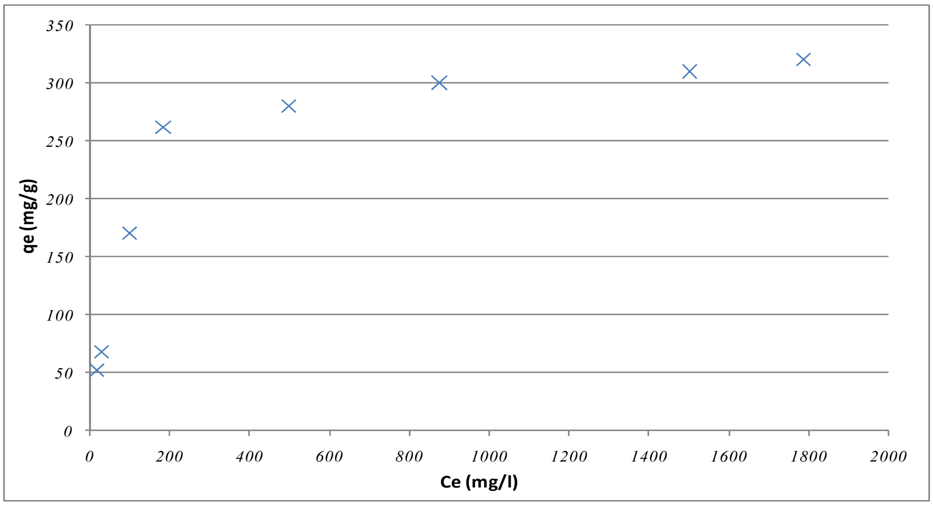


Figure 3 Equilibrium adsorption isotherm of total phenol onto activated olive stones (see online version for colours)



As indicated in Figures 4 and 5, the Langmuir isotherm model gives better representation of the isotherm results. This is an expected result as the Langmuir isotherm is more flexible in modelling adsorption from highly concentrated aqueous solutions compared to Freundlich isotherm. Good Langmuir isotherm fit is also reported in literature for phenol adsorption onto other adsorbents, i.e., olive stones and commercial activated carbon (Marques et al., 2017).

Figure 4 Freundlich adsorption isotherm of total phenol onto activated olive stones (see online version for colours)

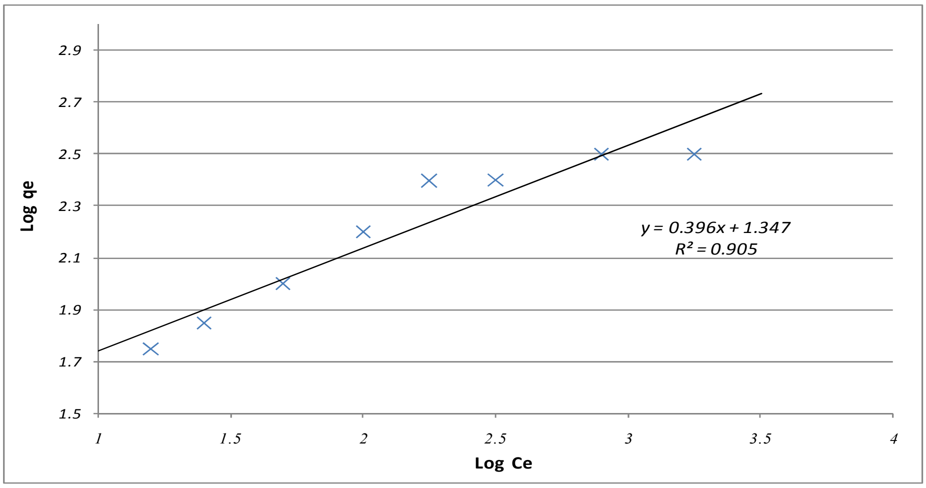
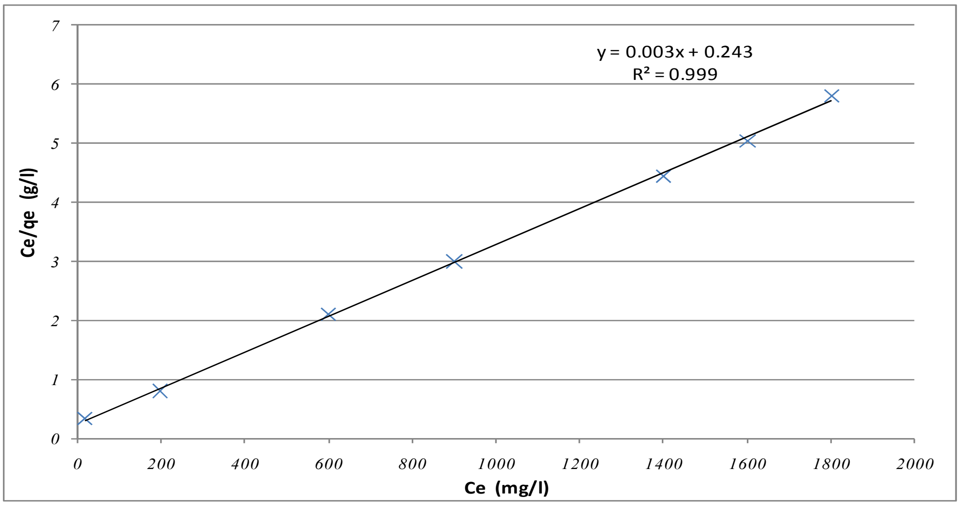


Figure 5 Langmuir adsorption isotherm of total phenol onto activated olive stones (see online version for colours)



As shown in Table 1, the correlation coefficient R^2 gives privilege for Langmuir isotherm over Freundlich. The maximum Langmuir capacity Q_0 is reasonable and simulating the equilibrium adsorption capacity (318.9 mg/g) for initial total phenol concentration (C_i) of 4017.9 mg/L. On the contrary, Freundlich *n* parameter does not give a good fit (*as* $n > 1$) and K_F constant is considered low and unreasonable with reference to high experimental adsorption capacity results.

Table 1 Isotherms constants for total phenol adsorption onto activated olive stones

Coefficients of Freundlich adsorption isotherm		
N	K_F	R^2
2.5	20.7	0.906
Coefficients of Langmuir adsorption isotherm		
Q_0	K_L	R^2
333.3	0.012	0.999

4.3 Adsorption kinetics of total phenol onto activated olive stones

The total phenol removal efficiency onto activated olive stones as function of time is depicted in Figure 6. Steep increase in the removal efficiency is observed up to 200 min of batch contact with activated olive stones. After 24 h, an insignificant increase is observed as shown in the flat portion of the curve. This indicates that most of total phenol removal is achieved in the first 7 h of contact time in batch treatment.

The reaction modelling of total phenol adsorption presented in Figures 7–9 indicate that chemisorption plays an important role in phenol adsorption on activated olive stones, taking into consideration that the correlation coefficients (R^2) of the three reaction models presented in Table 2 are close to 1. Better representation of pseudo-second order kinetic is observed over pseudo-first and second order models.

Figure 6 Effect of contact time on total phenol removal efficiency (see online version for colours)

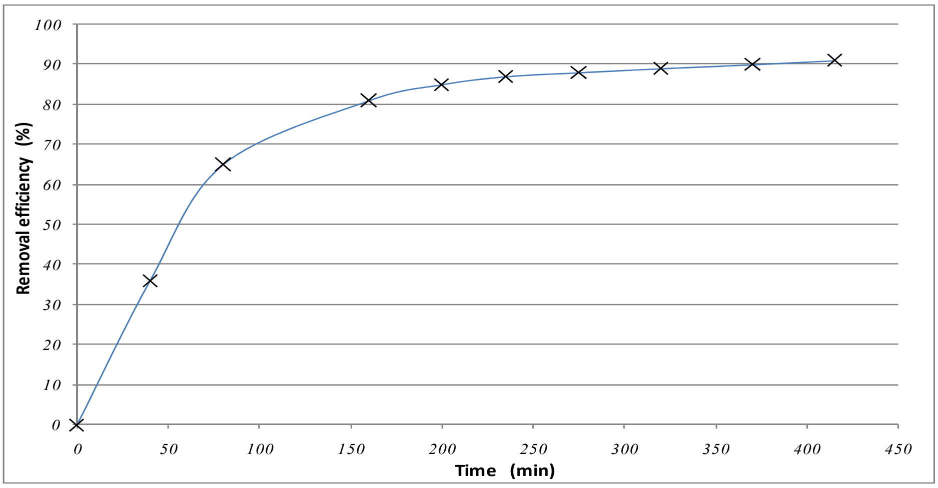


Table 2 Reaction models parameters of total phenol adsorption onto activated olive stones

	Parameter	*Unit*	*Value*
Pseudo-first order	k_1	min^{-1}	0.009
	$q_{\text{e (cal)}}$	mg/g	226.8
	R^2	/	0.983
	RSD (q_e)	mg/g	0.21
Pseudo-second order	k_2 (10^5)	g/(mg.min)	4.5
	$q_{e\text{ (cal)}}$	mg/g	357.1
	R^2	/	0.996
	RSD (q_e)	mg/g	0.1
Second order	$K_2^*(10^6)$	L/(mg.min)	6.1
	$C_{0\text{ (cal)}}$	mg/L	4761.9
	R^2	/	0.995
	RSD (C_0)	mg/L	0.12

The calculated equilibrium adsorption capacity of pseudo-second order reaction simulates experimental equilibrium capacity with reference to the small relative standard deviation (*RSD*) given in Table 2. The *RSD* between experimental and calculated values from fitting, q_e (exp) = 309.2 mg/g and C_0 (exp) = 4017.9 mg/L.

Similar results are obtained for phenol adsorption onto other adsorbents reported in literature (Ekpete and Horsfall, 2011; Tseng et al., 2010) and the values of $k_2 \times q_e$ (more than 0.046 min^{-1}) are higher than the value obtained in this work (0.016 min^{-1}). It is worth to mention that all the k_2 values in literature correspond to adsorption from pure phenol solutions, which is faster when compared with total phenol adsorption from OMWW. The presence of interfering and adsorption competing constituents in OMWW decreases the rate of phenolic compounds, i.e., magnesium and phosphate ions. In addition, the initial concentration, temperature, pH of the solution, adsorbent dose and agitation speed affect the adsorption kinetics.

Figure 7 Pseudo-first order kinetic modelling of total phenol adsorption onto activated olive stones (see online version for colours)

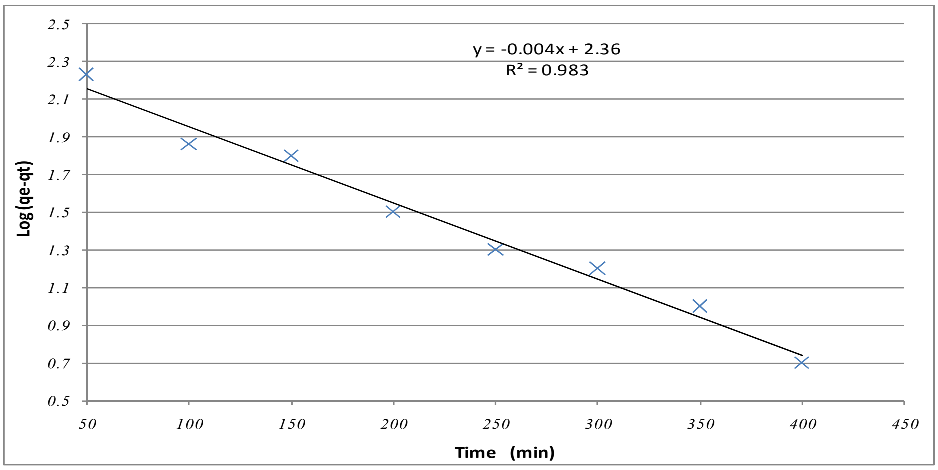
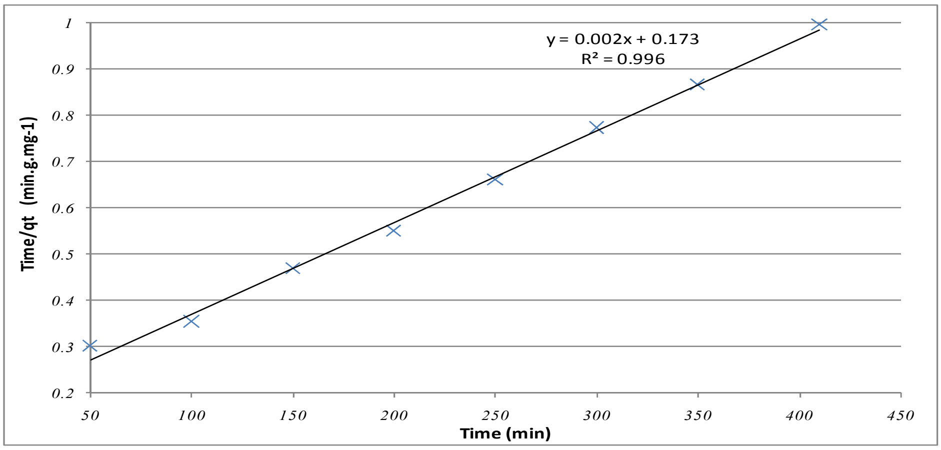


Figure 8 Pseudo-second order kinetics modelling of total phenol adsorption onto activated olive stones (see online version for colours)



The diffusion modelling of total phenol adsorption onto activated olive stones is presented in Figures 10–13. The high correlation coefficient (R^2) of the intra-particle diffusion model indicates that intra-particle diffusion is the rate limiting step. Still film diffusion is present but considered a faster step. This result is in agreement with double exponential modelling with high R^2 (0.983). Similar finding is reported in literature for phenol adsorption onto various adsorbents (Imran et al., 2012).

Figure 9 Second order kinetic modelling of total phenol adsorption onto activated olive stones (see online version for colours)

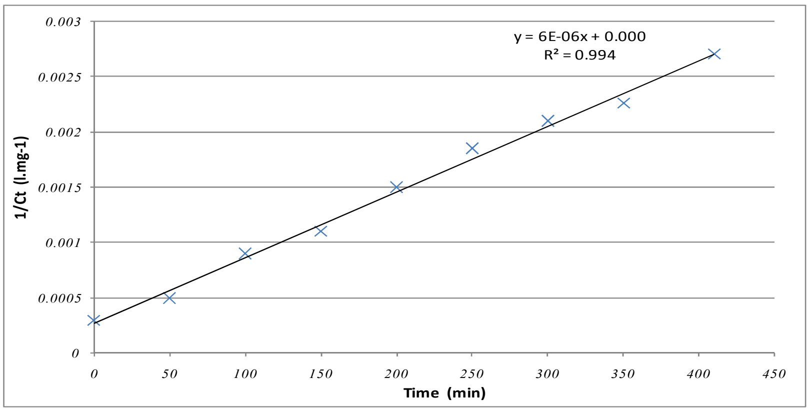


Figure 10 Liquid film diffusion modelling of total phenol adsorption onto activated olive stones (see online version for colours)

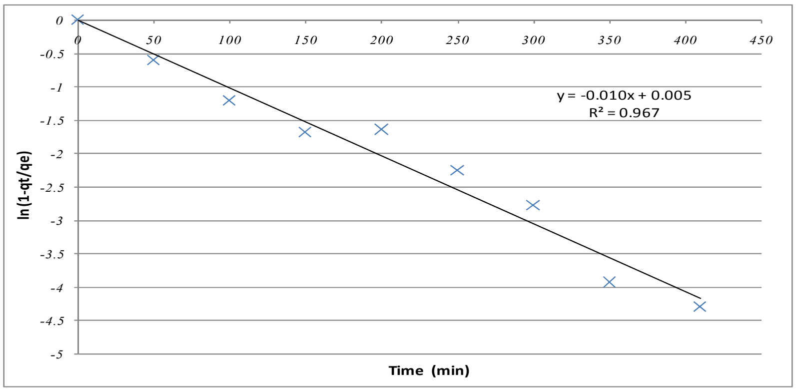


Figure 11 Intra-particle diffusion (Weber-Morris) modelling of total phenol adsorption (see online version for colours)

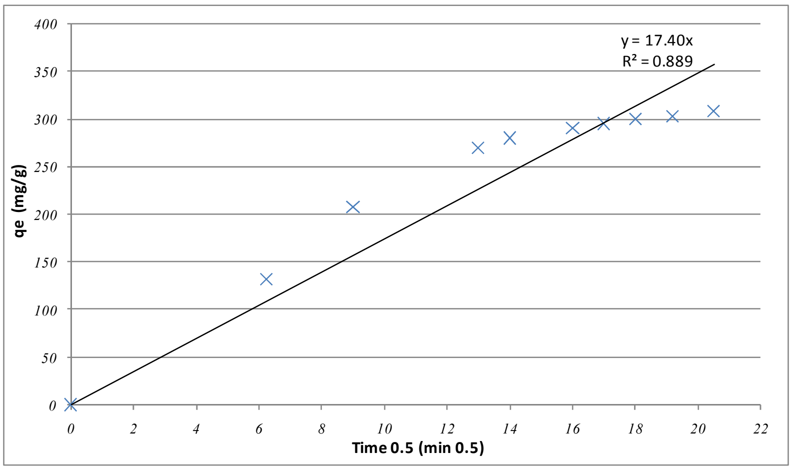


Figure 12 Intra-particle diffusion (Dumwald-Wagner) modelling of total phenol adsorption onto activated olive stones (see online version for colours)

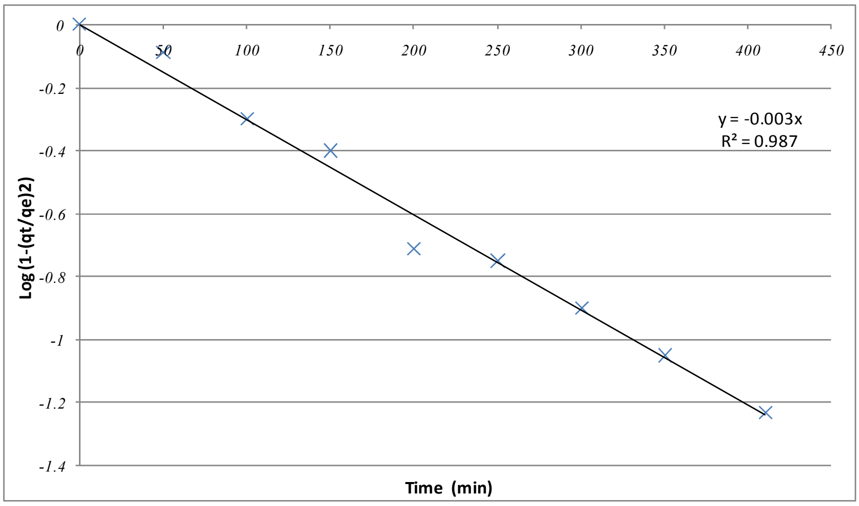
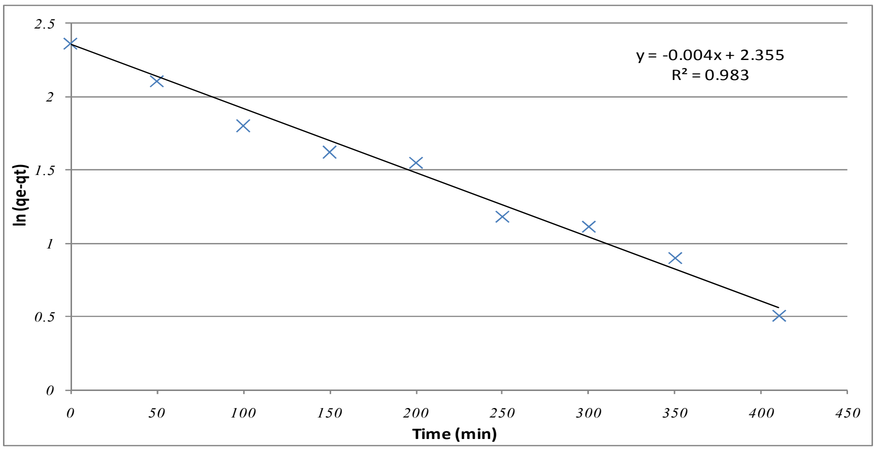


Figure 13 Double exponential diffusion modelling of total phenol adsorption onto activated olive stones (see online version for colours)



5 Conclusions

The batch adsorption experiments proved that activated olive stones are a promising abundant, low-cost and high capacity adsorbent for the removal of total phenol from OMWW due to the following reasons:

- Relatively low dose of activated olive stones achieves high percentage of total phenol removal from highly concentrated OMWW (92.4% in 24 h).
- High adsorption capacity of total phenol onto activated olive stones is observed and the adsorption capacity is exponentially increased with initial total phenol concentration in OMWW.

- Equilibrium studies signify favourable adsorption isotherm for total phenol adsorption onto activated olive stones and the Langmuir isotherm represent better the equilibrium system than Freundlich isotherm.
- The adsorption process is considered to be of medium speed at low agitation speed and the equilibrium is almost achieved after 7 h of OMWW contact with activated olive stones.
- Kinetic modelling indicates that total phenol adsorption is best represented by pseudo-second order rate and Dumwald-Wagner intra-particle diffusion models and proves that both physical adsorption and chemisorption are cooperative in total phenol removal mechanism with dominance for physical diffusion with reference to rate constants.
- Finally, it can be conducted that the treatment process studied in this work, gives a very acceptable removal efficiency of polyphenols. These results would be improved by studying the effect of operational experimental conditions such as temperature, mixing velocity to get the most of this natural waste.

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List of symbols

BET	Brunauer, Emmett and Teller
GC-MS	Gas Chromatography Mass Spectrometry
pH	Potential of Hydrogen
n	Freundlich equation constant
OMWW	Olive mill wastewater
RSD	Relative standard deviation
t	Time (min)
C_e	Equilibrium concentration of the adsorbate (mg/L)
C_t	Concentrations of solute at time t (mg/L)
C_0	Concentrations of solute at time $t = 0$ (mg/L)
D_e	Effective liquid film diffusion coefficient (cm^2/min)
D_2	Adsorption rate parameters of the slow step (mg/L)
K_L	Langmuir constant related to the energy of adsorption (L/mg)
K_F	Freundlich relative adsorption capacity constant $[(mg/g)(L/mg)^{1/n}]$
k_1	Pseudo-first-order rate constant (min^{-1})
k_2	Rate constant [g/(mg.min)]
K_2	Diffusion parameters of the slow step (min^{-1})
k_2*	Rate constant [L/(mg.min)]
k'	Equilibrium constant of adsorption
m_a	Weight of adsorbent (g)
Q_0	Maximum adsorption capacity (mg/g)
q_e	Equilibrium adsorption capacity (mg/g)
q_t	Adsorption capacity at time t (mg/g)
R'	Liquid film diffusion constant (min^{-1})
r_0	Radius of adsorbent beads (cm)
V_0	Initial adsorption rate [mg/(g.min)]
Greek symbols	
Δr_0	Thickness of liquid film (cm)