Removal of total phenols from olive-mill wastewater using an agricultural by-product, olive pomace

Athanasios S. Stasinakis *, Irene Elia, Anastasios V. Petalas, Constantinos P. Halvadakis

Department of Environment, University of the Aegean, University Hill, Mytilene 81 100, Greece

ARTICLE INFO

ABSTRACT

The purpose of this study was to investigate the sorption of total phenols, which are contained in olive-mill wastewater (OMWW), on solid by-products of olive pomace processing mills. Preliminary batch experiments were conducted using three different types of olive pomace, dried olive pomace (OP-1), dried and solvent extracted olive pomace (OP-2) and dried, solvent extracted and incompletely combusted olive pomace (OP-3). According to the results, OP-3 showed high performance for total phenols sorption and stability. For sorbent concentration of $10\,g\,L^{-1}$ and sorbate concentration of $50\,mg\,L^{-1}$, more than 40% of initial total phenols concentration was removed. Sorption kinetics was well described by the pseudo-second order rate model ($R^2 > 0.99$). Total phenols removal efficiency was improved by increasing sorbent concentration and solution's pH or decreasing particle size of the sorbent material. The Langmuir and Freundlich isotherms sufficiently described OP-3 sorption capacity for the concentration range studied ($50–500\,mg\,L^{-1}$). Fixed bed sorption experiments showed that lower flow rates and smaller particle size of sorbent resulted in longer column exhaustion time and higher initial removal efficiency. Experiments with thermally or chemically regenerated OP-3 showed that sorption capacity deteriorated after regeneration.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Olive-mill wastewater (OMWW) is a characteristic by-product of olive-oil production and a major environmental problem in the Mediterranean area because of its high and toxic organic load and its low pH. The maximum BOD and COD concentrations of OMWW can reach values up to 110 and $170\,g\,L^{-1}$, respectively [1], while the presence of phenolic compounds at concentrations ranging between 1.5 and $10.2\,g\,L^{-1}$ [2,3] increases the toxic load, causing OMWW unsuitable for further use. The large produced volume of OMWW and the brief olive-producing period aggravate these characteristics. In particular, the annual OMWW production in Mediterranean olive growing countries is ranged between 7 and over 30 million m³ and occurs between November and March [1].

Due to the fact that most of the produced OMWW is discharged untreated into the environment; there is a strong requirement for OMWW management. Various physico-chemical treatment methods such as flotation, sedimentation, use of selected membranes, oxidation by O_3 and Fenton reagent have already been used [1,4,5]. However, these methods are too expensive to find a

wide application. Additionally to the above, the use of biological methods – based on anaerobic or aerobic processes – has also been investigated [6–8]. High total phenols concentrations in OMWW have limited the effectiveness of these methods due to their antibacterial activity [1,9,10].

It is evident that the adaptation of a cheap and convenient pretreatment method for total phenols removal could make easier biological treatment. So far, few studies have been carried out using sorbent materials for the removal of polyphenolic compounds contained in OMWW. Al Malah et al. [11] used activated clay and reported that sorption of phenols was reversible and mainly due to hydrophobic interactions. Activated carbon obtained from treated olive pomace has also been used for polyphenols sorption, succeeding efficient phenol removal [2]. Treated olive pomace is a by-product of olive pomace processing mills which is produced in great amounts in Mediterranean countries. According to a previous study, 0.3 million tonnes of treated olive pomace are estimated to be produced annually in Greece [12], while its price is ranged between 0.02 and 0.03 Euro per Kg. However, its transformation to activated carbon demands the use of several chemical or physical activation methods [2,13], preventing its wide use. So far, treated olive pomace has been used without previous activation for the removal of heavy metals [14] and methylene blue [15]. However, there are no data for its direct use as sorbent material on total phenols removal that are contained in OMWW.

The purpose of the present study was to investigate the use of several solid by-products of olive pomace processing mills (dried

---

Nomenclature

b	Langmuir constant related to the enthalpy of the process ($L\,mg^{-1}$)
C_e	concentration of the sorbate in the solution at equilibrium time ($mg\,L^{-1}$)
C_t	concentration of the sorbate in the solution at time t ($mg\,L^{-1}$)
C_0	initial concentration of the sorbate in the solution ($mg\,L^{-1}$)
k_1	first order equilibrium rate constant (min^{-1})
k_2	second order rate constant of sorption ($g\,mg^{-1}\,min^{-1}$)
K_F	Freundlich constant related to the sorption capacity ($mg\,g^{-1}$) $(L\,mg^{-1})^{1/n}$
n	Freundlich parameter related to the intensity of sorption
N	number of observations
P	normalized percent deviation
q_e	amount of substrate sorbed per specified amount of sorbent at equilibrium time ($mg\,g^{-1}$)
q_t	amount of substrate sorbed per specified amount of sorbent at time t ($mg\,g^{-1}$)
Q	Langmuir constant related to the sorption capacity ($mg\,g^{-1}$)

---

olive pomace, OP-1, dried and solvent extracted olive pomace, OP-2, and dried, solvent extracted and incompletely combusted olive pomace, OP-3) on total phenols removal. Initially, the equilibrium time was investigated and afterwards, the effects of sorbent mass concentration ($1–50\,g\,L^{-1}$), solution's pH (4–10), sorbent particle size (<1.4 mm, 1.4–2 mm, >2 mm) and initial sorbate concentration ($50–500\,mg\,L^{-1}$) on total phenols uptake were studied in batch experiments. Chemical and thermal regeneration experiments were also performed to investigate whether treated olive pomace could be reused after regeneration. Finally, a glass column was fully loaded with sorbent material of different particle size and wastewater was poured over the column at different flow rates ($1–9\,mL\,min^{-1}$) to assess the practical utility of the sorbent.

2. Materials and methods

2.1. Collection of OMWW and sorbent materials

OMWW samples were collected during the oil-harvesting season from nine olive mills located in the island of Lesvos (Greece). Samples were collected in plastic vessels, transported to the laboratory immediately after sampling and stored at 4 °C. The concentrations of COD, total suspended solids and total phenols were 44297 ± 15933, 19372 ± 6106 and $2287 \pm 1235\,mg\,L^{-1}$, respectively, while pH values were ranged from 4.6 to 5.2.

Three types of olive pomace (OP-1, OP-2 and OP-3) were collected from an olive pomace processing mill in the island of Lesvos (Greece) and they were sieved to desired particle size such as <1.4 mm, 1.4–2 mm and >2 mm. Regarding the production of different types of this material in olive pomace processing mills, OP-1 is produced after drying of olive cake, while OP-2 is produced after extraction of OP-1 using hexane and vapor. This type of olive pomace is either rejected to the environment or it is incompletely combusted in boilers of olive pomace processing mills and other industries. The solid product of this combustion (OP-3) can be further used as fuel with low calorific value.

2.2. Sorption batch experiments

Preliminary batch experiments were performed to investigate the effect of different types of treated olive pomace (OP-1, OP-2 and OP-3) on total phenols removal and to calculate the sorption equilibrium time. For this reason, 2 g of olive pomace samples were introduced into three 250-mL conical flasks. The flasks were put on a shaker and appropriate volumes of filtered OMWW and distilled water were added to provide a final volume of 200 mL and a concentration of total phenols equal to $50\,mg\,L^{-1}$. Homogenous samples were taken at predetermined different time intervals (0–24 h), filtered using glass-fiber filters (GF/F, pore size 0.7 μm, Whatman, England) and the filtrates were analyzed for residual total phenols concentration. To quantify any potential release of polyphenolic compounds by the sorbents, three additional batch flasks were operated with no addition of sorbate solution and samples were collected at the start and at the end of the experiment (0, 24 h). Moreover, to quantify any losses of polyphenolic compounds due to sorption on the conical flasks, an additional batch reactor was operated containing only sorbate solution with known total phenols concentration [16]. During the experiments, all flasks were sealed with Parafilm to prevent the loss of phenols by volatilisation [17].

To investigate the effect of olive pomace concentration on total phenols removal, similar experiments were repeated using different OP-3 concentrations ($1–50\,g\,L^{-1}$). Moreover, sorption experiments were conducted at different solution's pH (4–10) and using different sorbent's particle size (<1.4 mm, 1.4–2 mm, >2 mm). The effect of initial concentration of sorbate on the removal efficiency was investigated by using different concentrations of total phenols (50, 100, 200, 300, 400 and $500\,mg\,L^{-1}$). All the experiments were performed at a temperature of 20 ± 2 °C. After equilibrium time, the samples were filtered and analyzed for total phenols.

2.3. Regeneration experiments

To investigate the effect of thermal regeneration on total phenols removal, batch experiments were initially performed in the presence of $100\,mg\,L^{-1}$ total phenols. After termination of these experiments, OP-3 samples were thermally regenerated in air atmosphere at 100, 150, 200 and 250 °C for 2 h in a Thermolyne 30400 oven and sorption experiments were repeated using regenerated OP-3. To investigate the effect of chemical regeneration on total phenols removal, a similar experimental procedure was followed. To achieve chemical regeneration, OP-3 samples were stirred for 2 h in the presence of an organic solvent (acetone 20% (v/v) or methanol 20% (v/v)). After organic solvent removal, washing of OP-3 with distilled water and drying at 50 °C for 1 h, sorption experiments were performed in the presence of $100\,mg\,L^{-1}$ total phenols.

2.4. Fixed bed sorption experiments

In fixed bed experiments, a glass column (0.7 cm i.d. and 15 cm length) was filled with 30 g of OP-3 on glass wool support. Before starting the experiments, distilled water was pumped in an upflow mode to remove any trapped air from the bed. Afterwards, diluted OMWW containing $500\,mg\,L^{-1}$ total phenols was delivered up flow to the column using a peristaltic pump (Masterflex L/S) at three different flow rates (1, 3 and $9\,mL\,min^{-1}$). To obtain breakthrough curves, samples were periodically collected from the top of the column and analyzed for residual concentration of total phenols. To investigate the effect of particle size on total phenols removal, similar experiments were performed using different sorbent's particle size (<1.4 mm, 1.4–2 mm, >2 mm).
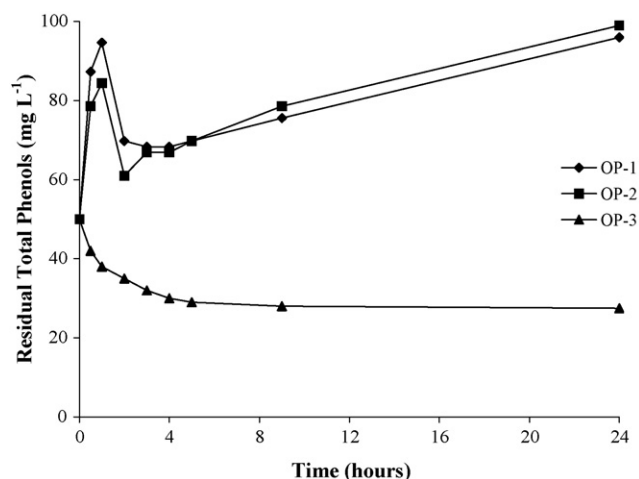
Fig. 1. Residual total phenols concentration in batch experiments with different types of olive pomace (initial sorbate concentration: 50 mg L^{-1}; sorbent mass: 2 g; sorbent size: <2 mm).

2.5. Analytical methods

Total phenols were determined on filtered samples using the spectrophotometric method associated with the Folin-Ciocalteau phenol reagent [18]. Specifically, a 10 mL diluted sample or phenolic standard was mixed with 0.5 mL of the Folin-Ciocalteu reagent and 1.5 mL of a sodium carbonate solution (200 g L^{-1}). The final solution was left in the dark for 1 h (20 °C) and afterwards the absorbance of the solution was measured at 750 nm (Hach spectrophotometer, model DR/2400). A similar procedure was followed using a distilled water reagent blank. For the instrumental calibration, standard phenol's solutions of 0, 0.1, 0.3, 0.5, 0.8 and 1 mg L^{-1} were used. The repeatability/reproducibility of the analytical method was sufficient (R.S.D. < 10%). Samples' pH was measured using a digital calibrated pH-meter (Hach, model Sension 2). Concentrations of COD and total suspended solids were determined according to *Standard Methods* [19].

3. Results and discussion

3.1. Effect of olive pomace type and sorption kinetics

No sorption of total phenols on the conical flasks walls was observed in experiments conducted in the absence of sorbent. In batch reactors using OP-1 and OP-2 as sorbents, residual total phenols concentrations were changed with time according to Fig. 1. On the whole duration of the experiment, residual total phenols concentrations were higher than the initial concentration of 50 mg L^{-1} and almost doubled 24 h after the start of the experiment. This behavior was probably due to the release of polyphenolic compounds contained in these sorbents. This hypothesis was further proved by determining total phenols concentration in similar batch reactors operating in the absence of OMWW. Specifically, in batch reactors using OP-1 and OP-2 as sorbents, residual total phenols concentrations of 50.8 and 30.3 mg L^{-1} were determined respectively, at the end of the experiment (24 h).

On the contrary, in the presence of OP-3, total phenols removal was high during the first hour of the experiment, while it was gradually reduced until the attainment of equilibrium (∼5 h) (Fig. 1). This behavior has also been noticed for other toxic compounds and the existence of a two-step reaction model for toxic compounds sorption has been reported [20,21]. The first step is a rapid uptake phase in which the sorbate is sorbed in external surfaces and relative large pores, while the second one is a slow phase where the sorbate slow enters into small micropores due to the diffusion effect [16]. Determination of solution's pH showed that after sorbent addition, pH value was directly increased from 4 to 10 and remained constant on the whole duration of the experiment. This increase of solution's pH in the presence of treated olive pomace is probably due to the basic character of this sorbent.

To investigate possible release of polyphenolic compounds contained in OP-3, a batch reactor operating in the absence of OMWW was also used. At the end of the experiment, no total phenols were detected in the dissolved phase, indicating OP-3 stability as sorbent material. The above results revealed that OP-1 and OP-2 could not be used as sorbents for the treatment of OMWW due to their trend to desorb polyphenolic compounds. On the other hand, OP-3 showed significant sorption capacity and stability. As a result, the following batch and column experiments were conducted using OP-3 as sorbent.

The kinetics data of total phenols onto OP-3 were analyzed using pseudo-first order (Eq. (1)) and pseudo-second order models (Eq. (2)) [22]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{2}$$

where q_t (mg g^{-1}) is the amount of substrate sorbed per specified amount of sorbent at time t (min), q_e is the amount sorbed per specified amount of sorbent at equilibrium time (mg g^{-1}), k_1 is the first order equilibrium rate constant (min^{-1}) and k_2 is the second order rate constant of sorption (g mg^{-1} min^{-1}).

The experimental and model predicted data are shown in Table 1. Comparison of R^2 values indicated that sorption of total phenols onto OP-3 followed second order kinetics. Moreover, the calculated q_e value obtained from Eq. (2) was in agreement with experimental q_e value (Table 1).

3.2. Effect of olive pomace concentration

The effect of OP-3 concentration on total phenols removal is illustrated in Fig. 2. In these experiments, initial total phenols concentration was equal to 56 mg L^{-1}. According to the experimental results, total phenols removal on equilibrium time was increased with increasing sorbent concentration from 1 to 50 g L^{-1} (Fig. 2). As a result, in the presence of 1 g L^{-1} OP-3, almost 17% of total phenols were removed, while total phenols removal exceeded 90% when 50 g L^{-1} of OP-3 was used. A similar effect of sorbent concentration on toxic compounds removal has often been reported in the literature [15,20,23].

The results obtained in the aforementioned experiments are promising comparing to other treatment methods that have already been applied in OMWW for total phenols removal. Saez et
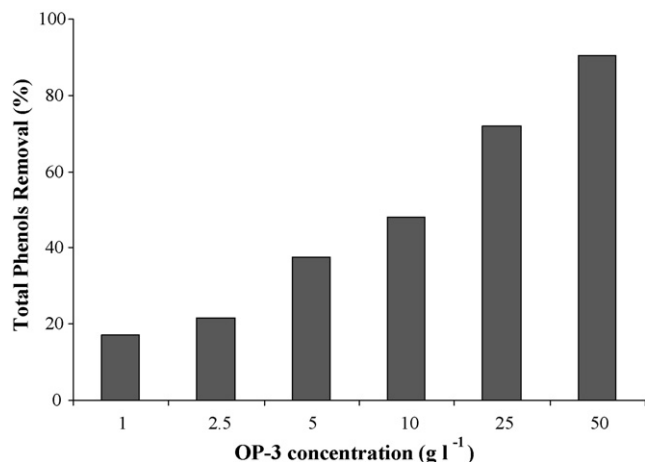
Table 1
Determination of sorption kinetic rate constants in experiments using OP-3 as sorbent material

C_0 (mg L^{-1})	q_e (exp) (mg g^{-1})	Pseudo-first order			Pseudo-second order		
		$k_1 \times 10^{-3}$ (min^{-1})	q_e (cal) (mg g^{-1})	R^2	$k_2 \times 10^{-3}$ (g mg^{-1} min^{-1})	q_e (cal) (mg g^{-1})	R^2
50	2.10	0.70	2.54	0.9442	5.24	2.59	0.9947

Fig. 2. Effect of sorbent (OP-3) concentration on percentage removal of total phenols (initial total phenols concentration: 56 mg L^{-1}; sorbent size: <2 mm).

Fig. 3. Effect of pH on percentage removal of total phenols sorbed on OP-3 (initial sorbate concentration: 70 mg L^{-1}; sorbent mass: 2 g; sorbent size: <2 mm).

al. [24] reported 43% reduction in phenols after 90 days residence in evaporation ponds. In that study, the initial phenolic content was equal to 1470 mg L^{-1}. Israilides et al. [25], using OMWW that contained initial total phenols concentration of 11410 mg L^{-1}, observed phenols reduction equal to 50% and 99% after 1 and 10 h of electrolysis, respectively. Al-Malah et al. [11] reported that almost 80% of total phenols removed when activated clay was used as sorbent material (sorbent concentration equal to 21 g L^{-1}, initial phenol concentration equal to 1190 mg L^{-1}). Galiatsatou et al. [2] reported that total phenols removal ranged from 13 to 73% using different types of activated carbon originated from olive stone and solvent extracted olive pomace (sorbent concentration equal to 4 g L^{-1}, initial phenol concentration equal to 205 mg L^{-1}).

3.3. Effect of solution's pH

To investigate the effect of solution's pH on total phenols removal, a series of flasks were prepared, containing OP-3 (sorbent concentration, 10 g l^{-1}, x < 2 mm) and diluted OMWW (initial total phenols concentration, 70 mg l^{-1}) at various pH values ranging from 4 to 10. Solution pH was adjusted with 0.5 M, HCl and NaOH solutions.

According to the results, total phenols removal increased with increase of solution's pH and the higher sorption rates were observed at pH 10 (Fig. 3). So far, the effect of pH on total phenols removal by treated olive pomace has not been investigated. However, in a previous study where basic character activated carbon was prepared from olive stone and olive pulp, significant total phenols removal was also observed [2]. The adsorption capacity of phenolic compounds onto activated carbon and similar adsorbent materials depends on several factors such as the physical nature of the adsorbent, the nature of the adsorbate and the solution's conditions [26]. Regarding the role of solution's pH, it is widely known that at solution's pH lower than the pK_a, phenols remain undissociated, while at pH values higher than pK_a, phenolic compounds dissociate into anionic forms, leaving negligible amount of neutral molecules [27]. In this study, due to the use of real wastewater containing a great number of different polyphenolic compounds (with different pK_a value for each compound), a clear conclusion cannot be derived for the existence of ionic or neutral forms of phenolic compounds in solution. However, based on the fact that the pK_a value of phenol is equal to 9.89 [26], then it is possible that for the pH range used in this study, both polyphenolic compounds and surface groups coexisted in their protonated and deprotonated forms. As a result, all three different types of surface-phenol interactions could occur
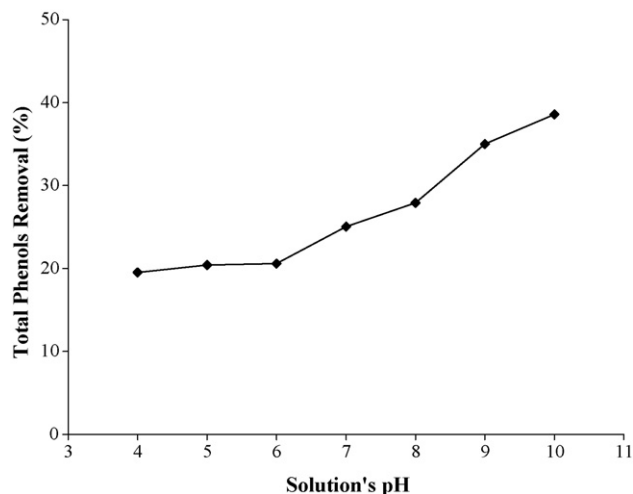
simultaneously. Specifically (a) electron donor–acceptor interactions between the aromatic phenolic ring and the basic surface oxygen groups; (b) dispersion effect between the aromatic phenolic ring and the π electrons in carbons; (c) electrostatic attraction and repulsion when ions are present [28].

3.4. Effect of particle size and initial total phenols concentration

The effect of OP-3 particle size on total phenols removal can be seen in Fig. 4. Experiments were performed in triplicate using initial total phenols concentrations ranging between 50 and 500 mg L^{-1}. The sorption capacity of total phenols was significantly higher (at 95% confidence interval, using one-way ANOVA) in experiments where OP-3 with particle size lower that 1.4 mm was used. On the other hand, no significant difference was observed when OP-3 with particle size ranging between 1.4 and 2 mm and higher than 2 mm was used (Fig. 4). In previous studies where clay [29] and unburned carbon [30] were used as sorption materials for phenols removal, the particle size had a similar effect on target compounds sorption. This behavior is probably due to the fact that sorption is a surface phenomenon. As a result, the smaller particle size offers comparatively larger surface area per unit weight of the sorbent and hence higher phenol removal at equilibrium time.

Regarding the effect of initial total phenols concentration on their removal, the amount of phenols sorbed per unit mass of OP-
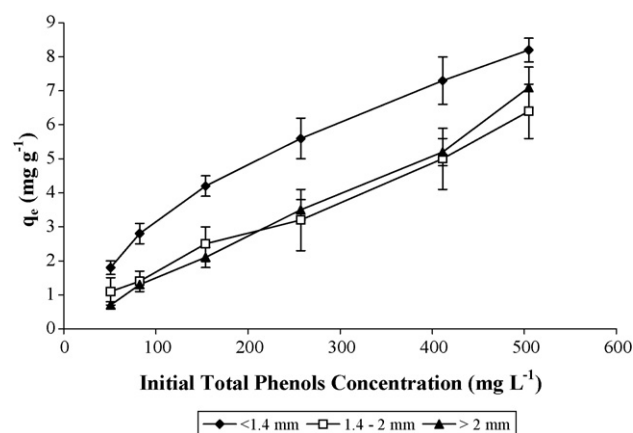

Fig. 4. Effect of particle size on equilibrium sorption capacities of total phenols on OP-3 (initial sorbate concentration: 50–500 mg L^{-1}; sorbent mass: 2 g; pH: 10).

Table 2
Langmuir and Freundlich parameters for total phenols sorption onto OP-3, regression coefficient squares (R^2) and normalized percent deviations (P) values (initial sorbate concentration: 50–500 mg L^{-1}; sorbent mass: 2 g; sorbent size: <1.4 mm)

Sorption isotherms							
Langmuir				Freundlich			
Q (mg g^{-1})	b (L mg^{-1})	R^2	P	K_F	$1/n$	R^2	P
11.40	5.5×10^{-3}	0.989	4.20	0.267	0.57	0.990	4.57

3 increased with increase of initial total phenols concentration (Fig. 4), possibly due to the higher availability of the sorbate in the solution. Moreover, higher initial total phenols concentration increased driving force to overcome mass transfer resistance of phenols molecules between the aqueous and solid phases resulting in higher probability of collision between total phenols and sorbent [23].

The data obtained in experiments using OP-3 with particle size lower that 1.4 mm were fitted to the Langmuir (Eq. (3)) and Freundlich (Eq. (4)) sorption isotherms [30].

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

where C_e is the equilibrium concentration of the sorbate in the solution (mg L^{-1}), q_e is the amount sorbed at equilibrium time (mg g^{-1}), Q (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the sorption capacity and enthalpy of the process, respectively, K_F is the Freundlich constant related to the sorption capacity (mg g^{-1}) (L mg^{-1})$^{1/n}$ and n is the empirical Freundlich parameter related to the intensity of sorption.

To check the adequate fit of experimental data to Langmuir and Freundlich equations, values of regression coefficients squares (R^2) were compared. Additionally, values of normalized percent deviation (P) were calculated using Eq. (5) [31].

$$P = \frac{100}{N} \sum \frac{(|q_{e(exp)} - q_{e(cal)}|)}{q_{e(exp)}} \qquad (5)$$

where $q_{e(exp)}$ is the experimental value of q_e obtained at any value of C_e, $q_{e(cal)}$ is the calculated value of q_e according to the corresponding equation and N is the number of observations. It is generally accepted that when the P-value is less than 5, the fit is considered to be adequate [31].

The calculated Langmuir and Freundlich parameters are presented in Table 2. Comparison of R^2 values as well as P values indicated that both Langmuir and Freundlich isotherms described sufficiently OP-3 sorption capacity (Table 2). According to the results, when applying the Langmuir model, the maximum phenol sorption capacity Q was equal to 11.40 mg g^{-1}. When fitted to the Freundlich equation, the value of K_F was 0.267 (mg g^{-1}) (L mg^{-1})$^{1/n}$, while the value of $1/n$ was less than 1, indicating favorable sorption of total phenols onto OP-3 [17].

3.5. Effect of regeneration

As it has already been reported in Section 2.3, sorption experiments were performed in the presence of 100 mg L^{-1} total phenols using regenerated OP-3 to investigate the possibility of its reuse. According to the results, the sorption capacity of OP-3 was significantly decreased (at 95% confidence interval, using one-way ANOVA) after thermal or chemical regeneration (Fig. 5). The highest removal efficiencies were observed for thermally regenerated OP-3 at 250 °C ($\cong$14%) and chemically regenerated OP-3 using acetone
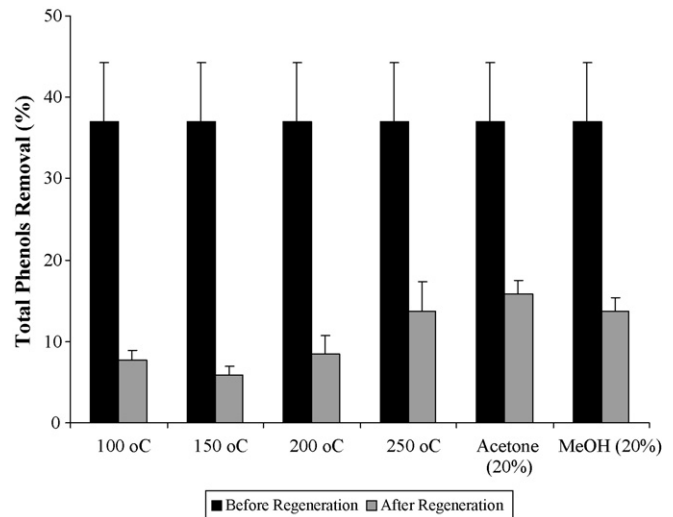
Fig. 5. Effect of thermal and chemical regeneration on total phenols removal efficiency (initial sorbate concentration: 100 mg L^{-1}; sorbent mass: 2 g; sorbent size: <2 mm, pH: 10).

20% ($\cong$16%). It is possible that if higher regeneration temperature had been applied, greater total phenols removal efficiency could be achieved. For instance, Roostaei and Tezel [16] reported that when zeolite HiSiv 1000 was regenerated at 360 °C for 15 min, the adsorption capacity of this sorbent on reagent grade phenol did not change. However, due to the low price of the sorbent used in the present study (OP-3), the loss in properties when regeneration is carried out and the energy cost of heating, the future tendency could be the disposal or incineration of this sorbent after its exhaustion.

3.6. Fixed bed sorption experiments

The breakthrough curve results of OP-3 were investigated at different flow rates (1–9 mL min^{-1}), using diluted OMWW (initial concentration 500 mg L^{-1}). As it was expected, in all column experiments OMWW effluent pH was increased to almost 10 due to the properties of the sorbent material. The effect of flow rate on total phenols breakthrough curve is shown in Fig. 6. Higher flow rates resulted in shorter column saturation/exhaustion time probably due to the fact that increased flow rate resulted in lower residence time in the bed and consequently lower bed
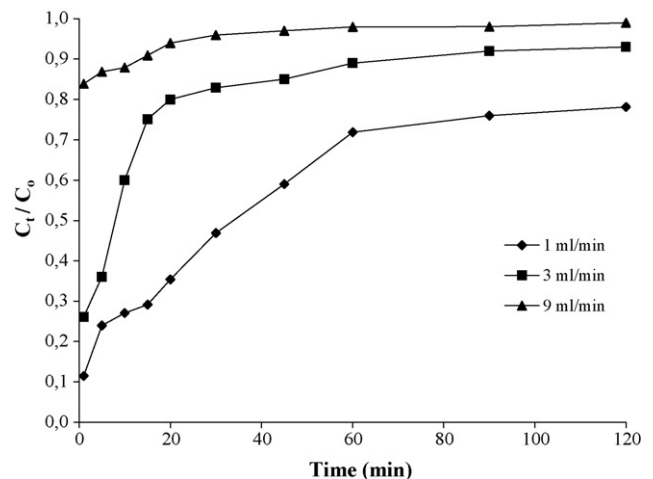
Fig. 6. Effect of different flow rates on total phenols breakthrough curve (initial sorbate concentration: 500 mg L^{-1}, particle size: >2 mm).
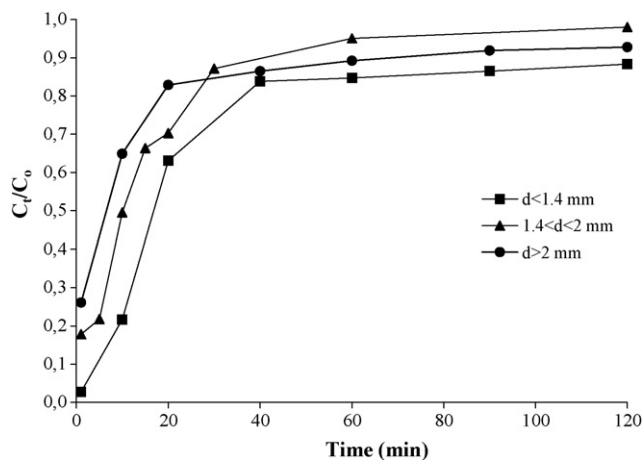
Fig. 7. Effect of different particle size on total phenols breakthrough curve (initial sorbate concentration: 500 mg L^{-1}, flow rate: 3 mL min^{-1}).

utilization. This phenomenon could also be attributed to diffusion limitations of the solute into the pores of the sorbent [32]. In the experiment performed with flow rate 1 mL min^{-1}, complete exhaustion ($C_t/C_o = 1$) was never reached and at the end of the experiment total phenols concentration in effluent wastewater remained significantly lower than concentration in the influents. It was also noted that lower flow rate yielded better initial removal efficiency (1 mL min^{-1}, 90% initial removal efficiency) than higher flow rate (9 mL min^{-1}, 17% initial removal efficiency) (Fig. 6).

In experiments performed using OP-3 of different particle size, exhaustion time increased and better initial removal efficiency was observed when particles smaller than 1.4 mm were used (Fig. 7). A similar behavior was also noticed for COD decrease (data not shown). Apart from phenolic compounds removal, this reduction of COD could be possibly due to the sorption of other high molecular weight organic molecules onto the filtering media.

4. Conclusions

The objective of this study was to investigate total phenols removal efficiency by several types of treated olive pomace. OP-1 and OP-2 could not be used as sorbent materials due to their trend to release polyphenolic compounds. On the contrary, OP-3 presented stability and significant sorption capacity which was affected by the concentration and the particle size of the sorbent as well as the solution's pH. Total phenols sorption on OP-3 followed the pseudo-second order rate equation and described sufficiently by Langmuir and Freundlich sorption isotherms. Column studies showed that decrease of influent flow rate and particle size enhanced OP-3 sorption capacity. According to the results, OP-3 could be used as a pretreatment method for total phenols removal containing in OMWW. The use of this material as sorbent provides a two-fold solution to environmental problems; the decrease of solid waste volume as well as the treatment of industrial wastewater at a reasonable cost.

References

[1] M. Niaounakis, C.P. Halvadakis, Olive Processing Waste Management-Literature Review and Patent Survey, second ed., Elsevier, Amsterdam, 2006.
[2] P. Galiatsatou, M. Metaxas, D. Arapoglou, V. Kasselouri-Rigopoulou, Treatment of olive mill waste water with activated carbons from agricultural by-products, Waste Manage. 22 (2002) 803–812.
[3] M.S. Fountoulakis, S.N. Dokianakis, M.E. Kornaros, G.G. Aggelis, G. Lyberatos, Removal of phenolics in olive mill wastewaters using the white-rot fungus *Pleurotus ostreatus*, Water Res. 36 (2002) 4735–4744.
[4] J. Gonzalez-Lopez, E. Bellilo, C. Benitez, Reduction of total polyphenols in olive mill wastewater by physico-chemical purification, J. Environ. Sci. Health Part A 29 (1994) 851–865.
[5] A.J. Beltran-Heredia, A.J. Torregrosa, J.F. Garcia-Araya, J.R. Dominguez-Vargas, J.C. Tierno, Degradation of olive mill wastewater by the combination of Fenton's reagent and ozonation with an aerobic biological treatment, Water Sci. Technol. 44 (2001) 103–108.
[6] N. Assas, L. Ayed, L. Marouani, M. Hamdi, Decolorization of fresh and stored-black olive mill wastewaters by Geotrichum candidum, Process Biochem. 38 (2002) 361–365.
[7] B. Zenjari, H. El Hajjouji, G. Ait Baddi, J.R. Bailly, J.C. Revel, A. Nejmeddine, M. Hafidi, Reduction of toxic compounds during the composting of olive mill waste water-straw mixture, J. Hazard. Mater. A 138 (2006) 433–437.
[8] H. El Hajjouji, J.R. Bailly, P. Winterton, G. Merlina, J.C. Revel, M. Hafidi, Chemical and spectroscopic analysis of olive mill waste water during a biological treatment, Bioresour. Technol. 99 (2008) 4958–4965.
[9] R. Borja, A. Martin, R. Maestro, J. Alba, J.A. Fiestas, Enhancement of the anaerobic digestion of oil mill waste waters by removal of phenolic inhibitors, Process Biochem. 27 (1992) 231–237.
[10] M. Hamdi, Toxicity and biodegradability of olive oil wastewaters in anaerobic digestion, Appl. Environ. Biotechnol. 37 (1992) 155–163.
[11] K. Al-Malah, M.O.J. Azzam, N.I. Abu-Lail, Olive mills effluent (OME) wastewater post treatment using activated clay, Sep. Purif. Technol. 20 (2000) 225–234.
[12] C.J. Israilides, Utilization of solid organic agro industrial wastes, in: Proceedings of Meeting on Management of Organic Wastes and Residuals, Athens, 2001, p. 123.
[13] P. Galiatsatou, M. Metaxas, V. Kasselouri-Rigopoulou, Mesoporous activated carbon from agricultural by-products, Microchim. Acta 136 (2001) 147–152.
[14] S.H. Gharaibeh, W.Y. Abu-el-sha'r, M.M. Al-Kofahi, Removal of selected heavy metals from aqueous solutions using processed solid residue of olive mill products, Water Res. 32 (1998) 498–502.
[15] F. Banat, S. Al-Ashen, R. Al-Ahmad, F. Bni-Khalid, Bench-scale and packed bed sorption of methylene blue using treated olive pomace and charcoal, Bioresour. Technol. 98 (2007) 3017–3025.
[16] N. Roostaei, H. Tezel, Removal of phenol from aqueous solutions by adsorption, J. Environ. Manage. 70 (2004) 157–164.
[17] I. Vazquez, J. Rodriguez-Iglesias, E. Maranon, L. Castrillon, M. Alvarez, Removal of residual phenols from coke wastewater by adsorption, J. Hazard. Mater. 147 (2007) 395–400.
[18] J.D. Box, Investigation of the Folin-Ciocalteu phenol reagent for the determination of polyphenolic substances in natural waters, Water Res. 17 (1983) 511–525.
[19] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Port City Press, Baltimore, Maryland, 1998.
[20] A.S. Stasinakis, N.S. Thomaidis, D. Mamais, M. Karivali, T.D. Lekkas, Chromium species behaviour in the activated sludge process, Chemosphere 52 (2003) 1059–1067.
[21] K.K. Singh, A.K. Singh, S.H. Hasan, Low cost bio-sorbent 'wheat bran' for the removal of cadmium from wastewater: kinetic and equilibrium studies, Bioresour. Technol. 97 (2006) 994–1001.
[22] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium(VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon, J. Hazard. Mater. B124 (2005) 192–199.
[23] E. Malkoc, Y. Nuhoglu, M. Dundar, Adsorption of chromium(VI) on pomace—An olive oil industry waste: batch and column studies, J. Hazard. Mater. B138 (2006) 142–151.
[24] L. Saez, J. Perez, J. Martinez, Low molecular weight phenolics attenuation during simulated treatment of wastewaters from olive oil mills in evaporation ponds, Water Res. 26 (1992) 1261–1266.
[25] C.J. Israilides, A.G. Vlyssides, V.N. Mourafeti, G. Karvouni, Olive oil wastewater treatment with the use of an electrolysis system, Bioresour. Technol. 61 (1997) 163–170.
[26] A. Dabrowski, P. Podkoscienlny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon—a critical review, Chemosphere 58 (2005) 1049–1070.
[27] M. Ahmaruzzaman, D.K. Sharma, Adsorption of phenols from wastewater, J. Colloid Interface Sci. 287 (2005) 14–24.
[28] K. Laszlo, P. Podkoscielny, A. Dabrowski, Heterogeneity of polymer-based active carbons in adsorption of aqueous solutions of phenol and 2,3,4-trichlorophenol, Langmuir 19 (2003) 5287–5294.
[29] P.S. Nayak, B.K. Singh, Removal of phenol from aqueous solution on low cost clay, Desalination 207 (2007) 71–79.
[30] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.
[31] E. Ayranci, O. Duman, Adsorption behaviors of some phenolic compounds onto high specific area activated carbon cloth, J. Hazard. Mater. 124 (2005) 125–132.
[32] F. Gode, E. Moral, Column study on the adsorption of Cr(III) and Cr(VI) using Pumice, Yarikkaya brown coal Chelex-100 and Lewatit MP 62, Bioresour. Technol. 99 (2008) 1981–1991.