Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.819166

52 (2014) 2875–2885
March

Taylor & Francis
Taylor & Francis Group

Removal of phenolic compounds from olive mill wastewater by adsorption onto wheat bran

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Received 25 January 2012; Accepted 27 May 2013

ABSTRACT

The use of wheat bran for the removal of phenolic compounds from olive mill wastewater (OMW) at different adsorbent doses (10–60 g/L), pH (3–11), and contact time (0.25–24 h) was investigated. Our findings demonstrate that wheat bran, an inexpensive and easily available biomaterial, can be an alternative for the more costly adsorbents used for the removal of phenolic compounds from OMW. Increase in the wheat bran dosage from 10 to 50 g/L significantly increased the phenolic compounds adsorption rate from 45 to 67%. Increase in pH to high alkalinity resulted in an increase in the phenolic compounds' adsorption capacity. The adsorption process was found to be relatively fast, and it reached equilibrium in 4 h of contact time. The Freundlich and Langmuir adsorption models were used for the mathematical description of the adsorption equilibrium and it was found that the experimental data fitted very well in the Freundlich model. Batch adsorption models based on the assumption of the pseudo-first-order, pseudo-second-order, and intraparticle diffusion mechanism were applied to examine the kinetics of the adsorption. The results showed that kinetic data followed more closely the pseudo-second-order model, than the pseudo-first-order and intraparticle diffusion. Desorption studies showed that at low pH value, the desorption of phenolic compounds was efficient.

Keywords: Wheat bran; Adsorption; Phenolic compounds; Olive mill wastewaters; Desorption

1. Introduction

Adsorption is one of the most effective processes of advanced wastewater treatment, which industries employ to reduce hazardous organic and inorganic wastes in effluents. It is also used to remove toxic inorganic and organic compounds from contaminated ground water. Phenolic compounds are considered to be hazardous wastes, which are released into the aquatic environment by various industrial activities: chemical, petrochemical, paper, wood, metallurgy,

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Presented at Water and Environment International Conference (WATEIC 2011), Marrakech, Morocco, 26–29 October 2011

and coking plants. Phenolic compounds are also found in the wastewaters of agro-industrial processes like olive oil mills, tomato processing, and wine distilleries [1,2]. The olive oil mill wastewater (OMW) contains very high amounts of organic matter (up to 15% by weight), which resists degradation and constitutes an important environmental problem due to the phenolic compounds, which are known to have antimicrobial and phytotoxic properties.

The phenolic compounds that have been identified in OMW are: caffeic acid, p-coumeric acid, vanillic acid, protocatechuic acid, syringic acid, p-hydroxybenzoic acid, p-hydroxyphenylacetic acid, veratric acid, 3,4,5-triméthoxybenzoic acid, 4-hydroxyphenyl alcohol, 3,4-dihydroxyphenyl ethanol, oleuropeine, L-cafeylglucose, tyrosol, hydroxytyrosol, apeginine, and lutolin-7-glycosid acid [3–9]. The phenolic compounds' concentration depends on the sort of oil extraction technology, and on the cultivar and ripeness stage of the olives.

Several methods were reported for the removal of pollutants from OMW (Table 1). These technologies can be divided into three categories: biological, chemical, and physical. All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods have not been widely applied at large scale in the olive oil mills.

Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many low-cost adsorbents, including natural materials, biosorbents, and waste materials from industries and Agrulture, have been proposed by several workers. These materials could be used as adsorbents for the removal of phenolic compounds from solutions. Some of the reported sorbents include activated charcoal [10], coal [11], dried activated sludge and fly ash [12], palm pith carbon [13], and beet pulp [14]. Despite the numerous studies reported in the literature, the attention remained mainly focused upon simple phenols, chlorophenols, and nitrophenols. Natural phenolic compounds with a more complicated structure and/or other functions have received little attention. Garcia–Araya et al. [15] investigated the adsorption of some phenolic acids on activated carbon. Razmkhar et al. [16] studied the adsorption of phenolic compounds; among them, tyrosol, catechol, and vanillic acid on yeast in order to remove these compounds were suspected to be involved in the browning of white wines. The adsorption of caffeic acid on imprinted monoliths has been studied by Li et al. [17] by frontal chromatography.

The purpose of this work is to investigate the efficiency of wheat bran as a biosorbent for the removal of natural phenolic compounds from OMW. The effects of various operating parameters on biosorption, such as sorbent dosage, initial pH, and contact time, were monitored and optimal experimental conditions were determined. Equilibrium isotherm data were fitted to Freundlich equations, and constants of isotherm equation were determined. Adsorption kinetics of phenolic compounds onto wheat bran were also analyzed by using pseudo-first-order kinetics, pseudo-second-order kinetics, and intraparticle diffusion models.

2. Experimental

2.1. OMW and sorbent materials

OMW samples were collected during the oil-harvesting season from a three-phase continuous extraction unit located in Marrakech region, southern Morocco. Samples were collected in plastic cans (120 L-capacity) and kept at room temperature.

Wheat bran was obtained from local wheat flour mills. The collected material was then washed several times with distilled water to remove all flour and dirt particles. The washed materials were then dried in a hot oven at 50 °C for 12 h. The dried material was then ground using a steel mill. The adsorbent was sieved through 1 mm sieve and used as such, without any treatment. Characteristics of the used wheat bran were determined and the results are summarized in Table 2. Rates of volatile matter, ash, and moisture were determined according to Rodier methods [18].

2.2. Analytical methods

The pH, electrical conductivity (EC), total suspended solid (TSS), biochemical oxygen demand (BOD_5), total Kjeldhal nitrogen (TKN), ammonia nitrogen (NH_4^+), nitrite (NO_2^-), orthophosphates (PO_4^{3-}), total phosphorus (PT), and chloride (Cl^-) were determined by AFNOR methods [19]. Nitrate (NO_3^-) was analyzed as nitrites after their reduction through a cadmium–copper column according to Rodier [18]. The total and dissolved chemical oxygen demands (COD) were determined by a spectrophotometer method of APHA [20]. Reducing sugars were determined by colorimetric method according to Dubois et al. [21]. Density was determined by weighing an exactly measured volume of sample. Phenolic compounds were quantified by means of the Folin–Ciocalteu calorimetric method [22] using caffeic acid as standard. Chromatographic separations of phenolic substances were carried out on C-18 column (5 mm, 4.6 × 250 mm) using H_3PO_4 (0.1%)-water-Acetonitrile/water (7/3) mobile phase system. Detection was performed at 280 nm and an isocratic elution rate was 0.8 mL/min. K^+, Na^+, and Ca^{2+} were analyzed with the flame photometry method.

Table 1
Principal existing and emerging processes for OMW removal

	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicy acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent great, capacity, produce a high-quality treated effluent	The regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints,
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification Non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

Table 2
Chemical properties of wheat bran used in the experiments

Parameters	Data
Moisture content (%)	8.40
Volatile matter (%)	70.9
Ash (%)	3.20
pH	7.03
Particle size (mm)	<1

2.3. Experimental procedure

Preliminary batch experiments were performed to investigate the effect of wheat bran on phenolic compounds removal and to calculate the sorption equilibrium time. For this reason, different doses (1–6 g) at various pHs (3–11) were introduced into a 250 mL shaking flask containing 100 mL of OMW with a known concentration of total phenols (13.45 g/L). pH studies were conducted to determine the optimum pH for maximum phenolic compounds removal. The pH of the suspension was adjusted by 0.1 N HCl or NaOH solutions. The flasks were put on a rotary shaker (rotatest 74,581) at 200 rpm at 30 ± 2˚C. Homogenous samples were taken at predetermined different time intervals (0.25, 0.5, 1, 1.5, 2, 3, 4, 5, 10, 24 h), filtered using a 0.6 mesh stainless steel sieve, and centrifuged for 20 min at 5,100 rpm. The filtrates were analyzed for residual phenolic compounds concentration. Experiments were conducted in duplicate and the negative controls (without adsorbent) were simultaneously carried out.

The amount of adsorption at equilibrium, q_{eq} (g/g), and the percent adsorption (%) was computed as follows:

$$q_{eq} = \left[(C_0 - C_{eq})V\right]/X \quad (1)$$

$$\text{Percent adsorption}(\%) = (C_0 - C) \times 100\,/C_0 \quad (2)$$

where C_0 and C_{eq} are the initial and equilibrium concentrations of phenolic compounds (g/L), V is the volume of solution (L), X is the weight of wheat bran (g) and C is the phenolic concentration at the end of adsorption.

In the desorption studies, the adsorbent (5 g) used for the adsorption experiments of OMW at pH = 7 was separated from the solution by centrifugation and washed gently with water to remove any unabsorbed phenolic compounds. Then the spent adsorbent (1 g)

was agitated at 200 rpm for 12 h with 100 mL of distilled water and adjusted to different pH value (pH: 12 and 1.2).

3. Results and discussion

3.1. OMW characterization

Table 3 shows that the pH of the raw OMW is relatively low (5.06) owing to the presence of compounds such as phenolic and organic acids. The EC was very low (6.85 mS/cm) compared to that usually reported for OMW in Marrakech which according to Zenjari et al. [23] varies between 25.3 and 36.6 mS/cm which is attributed to salting practices for the conservation of the olives before they are triturated.

OMW contains high concentration of total suspended solids (TSS 2.07 g/L), and high organic matter content (70.22 g O_2/L of total COD, 48.69 g O_2/L of dissolved COD). Such a large organic loading makes biological purification very difficult to perform. Toxicity, in this type of effluent can arise from the high levels of phenolic compounds (13.45 g/L).

HPLC chromatograms depicted in Fig. 1 show Hydroxytyrosol (0.275 g/L) and tyrosol (0.062 g/L) as the two major monomer phenolic compounds encountered in our samples. Such composition is almost similar to that reported by other researchers [24]. As determined by the HPLC analysis the phenolic compounds content is found to be less than that obtained by the Folin–Ciocalteu determination. The Folin–Ciocalteu method is known to be not specific to phenolic compounds; other molecules can react with this reagent leading to an over estimation of the phenolic content.

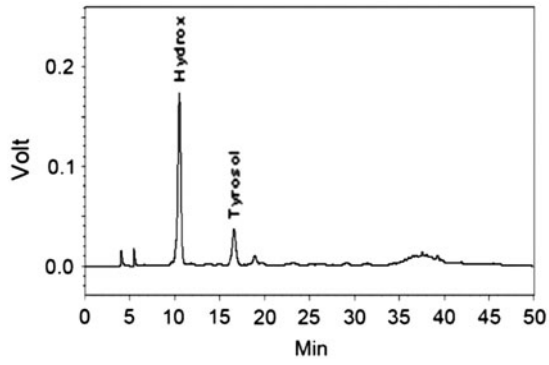

Fig. 1. HPLC chromatograms of the phenolic compounds from raw olive mill effluent.

The OMW contained also a high level of TKN (1.96 g/L), the total P (0.42 g/L) and high concentrations of sodium (0.46 g/L) and chloride (1.4 g/L) were probably due to salting of the olives.

Table 3
Physical-chemical determination of the raw OMW (mean values of three separate analysis ± standard deviation)

Parameters	Data
pH (25°C)	5.06
EC (mS/cm) à 20°C	6.85
Total suspend solid (TSS) (g/L)	2.07 ± 0.02
TKN (g/L)	1.96 ± 0.01
NH_4^+ (mg/L)	0.64 ± 0.04
NO_3^- (mg/L)	0.4 0 ± 0.07
NO_2^- (mg/L)	4.00 ± 0.03
Total phenols (g/L)	13.45 ± 0.01
Total COD (gO_2/L)	70.22 ± 1.22
Dissolved COD (g O_2/L)	48.69 ± 3.18
BOD_5 (g O_2/L)	16.74 ± 0.19
PO_4^- (g/L)	0.36 ± 1.43
Total P (g/L)	0.42 ± 0.003
Cl^- (g/L)	1.42 ± 0.001
K^+ (g/L)	2.11 ± 0.00
Ca^{2+} (g/L)	0.06 ± 0.00
Na^+ (g/L)	0.46 ± 0.00
Reducing sugar (g/L)	0.12 ± 0.008
Density (g/L)	1.10 ± 0.02

3.2. Preliminary adsorption tests

Before running experiments, to determine the adsorption isotherms, some preliminary experiments were carried out in order to test the effect of wheat bran on removal of phenolic compounds from OMW. The tests were carried out with two concentrations of adsorbents (1 and 5%) at room temperature, under agitation, and one-day contact time. Table 4 shows that with 1% of wheat bran, we can obtain an elimination of 12, 9, and 11% of phenolic compounds, COD, and color intensity, respectively. The increase of this amount of adsorbent to 5% improved the elimination of the phenolic compounds (63%), COD (53%), and color intensity (63%).

The HPLC analysis of the residual phenolic compounds of the OMW, after the adsorption on the wheat bran at a concentration of 1% (Fig. 2(a)) shows an elimination of 21% of the hydroxytyrosol and 13% of the tyrosol. With 5% of the bioadsorbent, the treatment allowed a complete elimination of monomeric compounds, 100% of hydroxytyrosol, and 100% of tyrosol (Fig. 2(b)).

Table 4
Efficiency of reducing pollutant charges in OMW using wheat bran as bioadsorbant

Wheat bran (%)	Polyphenol (%)	COD (%)	Coloration
1	12	9	11
5	63	53	63

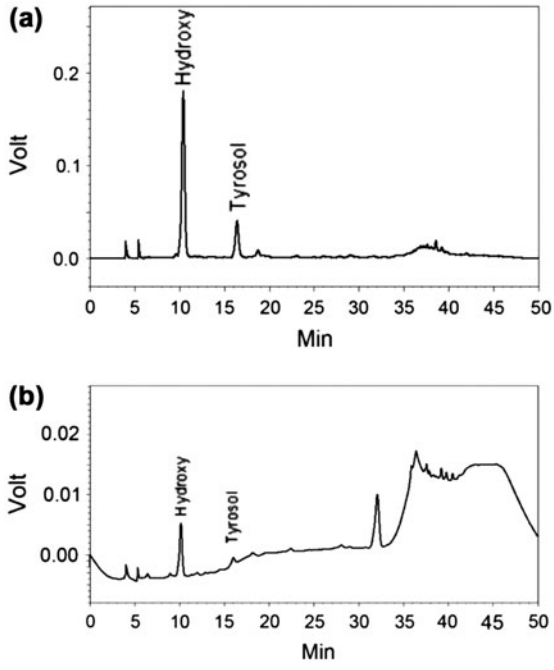

Fig. 2. HPLC analysis of the phenols from OMW after treatment with 1% (a) and 5% (b) of wheat bran.

3.3. Effect of adsorbent rates

The influence of adsorbent dosage and equilibrium uptake is depicted in Fig. 3. The adsorption of phenolic compounds on wheat bran was determined with 100 mL of OMW containing 13.45 g/L of total phenolic compounds. The system was agitated for 24 h (200 rpm) at a constant temperature (30 ± 2°C) at the origin, pH 5. The increase in adsorbent dosage from 10 to 50 g/L resulted in a decrease from 13.45 to 4.62 g/L (66% of phenolic compounds removal). A further increase in adsorbent dosage (>50 g/L) did not lead to significant improvements in adsorption. This seems to be due to the binding of almost all phenolic compounds to the sorbent, and the establishment of equilibrium between the phenolic compounds bound to the sorbent and those remaining unadsorbed in the solution. Thus, all our subsequent experiments are performed at an adsorbent dosage of 50 g/L.

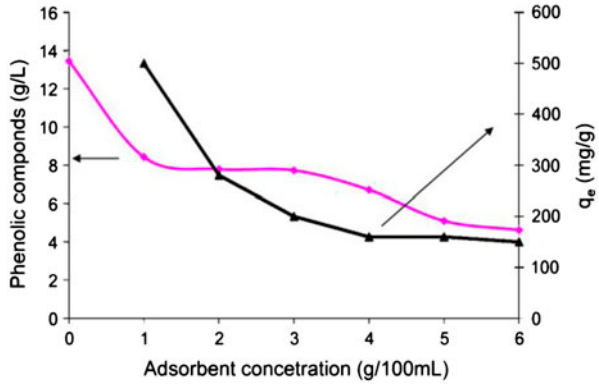

Fig. 3. Influence of adsorbent concentration on adsorption rates of phenolic compounds and the equilibrium uptake (Conditions: 100 mL of OMW, temperature: 30°C, contact time: 24 h, and initial pH 5).

With increasing adsorbent dosage from 10 to 60 g/L, the adsorption of phenolic compounds per unit weight of adsorbent decreased from 500 to 150 mg/g. Many factors can contribute to this adsorbent concentration effect. The first and most important factor is that adsorption sites remain unsaturated during the adsorption reaction. This is due to the fact that as the dosage of adsorbent is increased, there is less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the adsorbent. The second cause may be the aggregation/agglomeration of sorbent particles at higher concentrations, which would lead to a decrease in the surface area and an increase in the diffusional path length. Similar phenomena were also observed for phenolic compounds adsorption onto banana peel [25] and phenol onto hydroxyapatite nanopowders [26]. As a result, the removal of a given amount of solute can be accomplished with greater economy of adsorbent, if the solution is treated with separate small batches of adsorbent rather than in a single batch with filtration between each stage [27].

3.4. Effect of pH on phenolic compounds biosorption

pH is one of the most important factors affecting the adsorption process, particularly on the adsorption capacity. Fig. 4 shows the effect of pH on the adsorption of phenolic compounds onto wheat bran on 100 mL OMW. Agitation was maintained for 24 h (200 rpm) at (30 ± 2°C) at the predetermined optimal adsorbent dosage (50 g/L). The phenolic compounds adsorption was found to increase with the increasing pH, and it increased from 14 to 94% for an increase

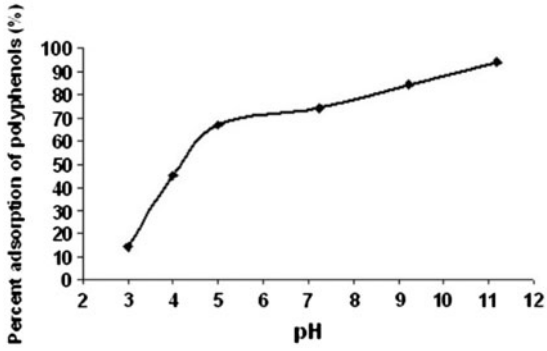

Fig. 4. Effect of pH on adsorption of phenolic compounds by wheat bran. (Conditions: 100 mL of OMW, temperature: 30 °C, contact time: 24 h, and sorbent dose: 50 g/L).

in pH from 3 to 11. At neutral pH, the elimination of total phenols is very important (74%). The adsorption capacity of phenolic compounds onto wheat bran 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 [28].

Regarding the role of pH, it is widely known that at pH lower than the pKa, phenols remain undissociated, while at pH values higher than pKa, phenolic compounds dissociate into anionic forms leaving negligible amount of neutral molecules [29]. In this study, due to the use of natural wastewater containing a great number of different organic acids, two monomer phenolic compounds and polyphenolic compounds (hydroxytyrosol, tyrosol), with different pKa value for each monomer, a clear conclusion cannot be derived for the existence of ionic or neutral forms of phenolic compounds in solution. However, taking into account that the pKa value of phenol is equal to 9.89 [28], it is possible that in pH range studied, both polyphenolic compounds and surface groups coexist in their protonated and deprotonated forms. In a study where several solid byproducts of olive pomace processing mills [30] were used as sorption materials for total phenols removal from OMW; the total phenols removal increased with the increase of the solution's pH and the highest sorption rates were observed at pH 10.

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 electrons in carbons; and (c) electrostatic attraction and repulsion when ions are present [31].

3.5. Effect of contact time

The adsorption of phenolic compounds onto wheat bran was studied as a function of contact time, in order to determine the required equilibrium time. Rapid uptake and quick establishment of equilibrium time demonstrates a good efficiency of the particular adsorbent for its use in wastewater treatment. A series of contact time experiments has been carried out with 100 mL of OMW; agitation was maintained for 24 h (200 rpm) at 30 ± 2 °C and at the predetermined optimal adsorbent dosage (50 g/L).

The effect of contact time on the sorption of phenolic compounds by wheat bran is shown in Fig. 5. As can be seen in this figure, the contact time necessary to reach equilibrium is about 4 h and the amount of phenolic compounds sorbed by wheat bran increases with time and then reaches a constant value beyond which no more is removed from solution. The time required to attain this state of equilibrium reflects the sorption capacity of the sorbent under the operating conditions. A similar contact time was observed by Xiaoli and Youcai [32], on the adsorption of phenolic compounds by aged refuse. However, adsorption rate of phenolic compounds on wheat bran was found to be relatively much faster than those reported for some other normal adsorbents. Thawornchaisit and Pakulanon [33] determined that the sorption equilibrium of phenol on dried sewage sludge was reached within 20 h. Adsorption of bromophenols onto carbonaceous adsorbents derived from fertilizer solid waste was performed by Bhatnagar [34] and the equilibrium time was about 8 h.

The HPLC analysis of the residual phenolic compounds of the OMW after adsorption on the wheat bran at a concentration of 50 g/L and pH 7 after 4 h shows an elimination of 98% of the hydroxytyrosol and 100% of the tyrosol.

3.6. Isotherm studies

The equilibrium adsorption isotherm is of importance in the design of adsorption systems [35]. In general, the adsorption isotherm describes how adsorbates interact with adsorbents and thus is critical in optimizing the use of adsorbents. Several isotherm equations are available and two important isotherms were selected for this study: the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm is based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface. These binding sites have the same affinity for adsorption of

a single molecular layer and there is no interaction between adsorbed molecules.

The linearized Langmuir equation is represented as follows [36]:

$$C_{eq}/q_{eq} = 1/bQ_m + C_{eq}/Q_m \quad (3)$$

where b is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L/g), and Q_m represents a partical limiting adsorption capacity when the surface is fully covered with phenolic compounds that assists in the comparison of adsorption performance. Q_m and b were calculated from the slope and intercept of the straight lines of the plot C_{eq}/q_{eq} vs. C_{eq}. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L), which is defined by the following relationship [37]:

$$R_L = 1/(1 + bC_0) \quad (4)$$

According to the value of R_L, the isotherm shape may be interpreted as follows: $R_L > 1.0$ unfavorable, $R_L = 1.0$ linear, $0 < R_L < 1$ favorable or $R_L = 0$ irreversible.

The results given in Table 5 show that the adsorption of phenolic compounds onto wheat bran is favorable and has an R_L value between 0 and 1.

The Freundlich isotherm is the earliest known relationship describing the sorption equation [38]. The Freundlich isotherm model is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. Theoretically, using this expression, an infinite amount of adsorption can occur [38]:

$$\ln q_{eq} = \ln K_F + 1/n \ln C_{eq} \quad (5)$$

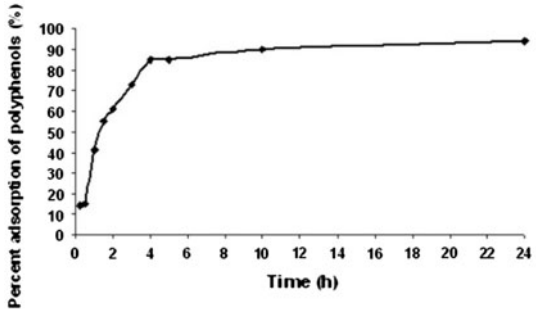

Fig. 5. Effect of contact time on adsorption of phenolic compounds by wheat bran. (Conditions: 100 mL of OMW, temperature: 30°C, sorbent dose: 50 g/L, and pH 7).

where K_F is a Freundlich constant that shows adsorption capacity of adsorbent, n is a constant which shows greatness of relationship between adsorbate and adsorbent. k_F and $(1/n)$ can be determined from the linear plot of ln q_{eq} vs. ln C_{eq}. It is generally stated that the values of n in the range of 1 to 10 represent good adsorption. In the present work, the exponent was $1 < n < 10$ indicating favorable adsorption (Table 5).

The equilibrium isotherm for the adsorption of phenolic compounds on wheat bran was determined with 100 mL of OMW with a known concentration of phenolic compounds (13.45 g/L). The system was agitated for 24 h (200 rpm) in a constant temperature (30°C) at initial pH 5. Fig. 3 shows the adsorption isotherms of phenolic compounds (q_e vs. C_e) using wheat bran. The Q_m, b, R_L, R_1^2 (correlation coefficient for Langmuir isotherm), K_F, n, and R_2^2 (correlation coefficient for Freundlich isotherm) are given in Table 5.

On the basis of the analysis of adsorption data of Langmuir model and Freundlich model, the correlations of adsorption data of the two models are investigated. The results demonstrated that the Freundlich isotherm fitted the experimental data better than the Langmuir isotherm. The fit of the data to the Freundlich equation may indicate the heterogeneity of the adsorbent surface. This observation is not rare, as similar findings have been reported before [14,26,32]. As seen in Table 5, the magnitude of K_F and n of the Freundlich isotherm constants showed the tendency of phenolic compounds uptake from the adsorption medium with high capacity of the wheat bran; the maximum adsorption capacity for phenolic compounds onto wheat bran was found to be 487.3 mg/g. On a comparison of the maximum capacity, Q_m, of different type of low-cost adsorbents used for removal of phenols and phenolic compounds (Table 6), the adsorption capacity of wheat bran was relatively high when compared with other adsorbents. Difference of phenolic compounds uptake are due to the properties of each adsorbent such as structure, functional groups, and surface area.

3.7. Kinetics of the adsorption process

Knowledge of the adsorption kinetic constitutes the first step in the investigation of the possibility of using an adsorbent for a particular separation task. In this study, the first-order kinetic model, pseudo-second-order kinetic model, and an intraparticle diffusion kinetic model were used to elucidate the adsorption mechanism.

Table 5
Isotherm constants and the correlation coefficients of Langmuir and Freundlich isotherms

Langmuir isotherm					Freundlich isotherm		
Effluent	Q_m (mg/g)	b (L/g)	R_1^2	R_L	K_F	n	R_2^2
OMW	487.3	0.13	0.73	0.33	0.08	1.83	0.86

Table 6
Langmuir and Freundlich constants for phenol and phenolic compounds adsorption by various adsorbents reported in literature

Adsorbent	Adsorbate	Qm (mg/g)	References
Activated coal	Phenol	1.84	[39]
Resin AP-246		0.071	
Resin OC-1074		0.043	
Coconut shell	Phenol	205.84	[40]
Palm pith carbon	2,4-Dichlorophenol	19.16	[41]
Paper mill sludge	2,4- Dichloro-phenol	4.49	[42]
Banana peel	Phenolic compounds	688.9	[25]
Active carbon	Phenol	236	[43]
	4-Nitrophenol	227	
	4-Catechol	144	
Active charcoal	Catechol	320	[44]
	Tyrosol	399	
Wheat bran	Phenolic compound	487,3	This study

The first-order kinetic model [45,46] is given as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (6)$$

where q_e and q_t refer to the amount of phenolic compounds adsorbed (mg/g) at equilibrium and at any time, t (h), respectively, and k_1 (h^{-1}) is the equilibrium rate constant of pseudo-first-order sorption. Values of k_1 are calculated from the slope of the plots of ln ($q_e - q_t$) vs. t.

The pseudo-second-order kinetic model [45,46] is expressed as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

where k_2 is the rate constant for pseudo-second-order kinetics (g/g h). Values of k_2 and q_e were calculated from the plot of t/q_t against t.

Since neither the first-order nor the pseudo-second-order kinetic model can identify the diffusion mechanism, the intraparticle diffusion model [26] was also used to analyze and elucidate the diffusion mechanism. The intraparticle diffusion model is expressed as:

$$q_t = k_p t^{1/2} + C \quad (8)$$

where q_t is the amount of phenolic compounds adsorbed at equilibrium (mg/g) at time t, C is the intercept, and k_p is the intraparticale diffusion rate constant (g/g $h^{1/2}$). Values of k_p and C were calculated from the plot of q_t against $t^{1/2}$.

The adsorption kinetic parameters of phenolic compounds under the experimental conditions were calculated from the plots and are shown in Table 7. The correlation coefficient values (R^2) range between zero and one. R^2 of one show that 100% of the variation of experimental data is explained by the regression equation. The R^2 was applied to determine the relationship between the experimental data and the kinetics in most studies. The R^2 for the first-order kinetic model, pseudo-second-order kinetic model, and the intraparticle diffusion kinetic model were 0.96, 0.98, and 0.85, respectively. It is clear to see that the R^2 value for the pseudo second-order kinetic model is higher than those for the first-order kinetic and intraparticle diffusion kinetic models. Therefore, this section suggested that the pseudo-second-order model was the best choice among the three kinetic models to describe the adsorption behavior of phenolic compounds onto

Table 7
Kinetics constants and the correlation coefficients for different kinetic models

	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
$q_{(e,exp)}$ (g/g)	$q_{(e,cal)}$(g/g)	k_1 (h^{-1})	R_1^2	$q_{(e,cl)}$(g/g)	k_2 (g/g h)	R_2^2	k_p(g/g $h^{1/2}$)	C(g/g)	R_3^2
0.48	0.26	0.56	0.96	0.38	1.25	0.98	0.096	0.019	0.85

wheat bran suggesting that the pseudo-second-order adsorption mechanism is predominant and the overall rate of the adsorption process appears to be controlled by the chemical reaction.

The theoretical $q_{(e,cal)}$ values were much close to the experimental $q_{(e,exp)}$ values in Table 7. In view of these results, it can be said that the pseudo-second-order kinetic model in contrast to the pseudo-first-order model provided a good correlation for the adsorption of phenolic compounds onto wheat bran.

3.8. Desorption studies

Desorption studies will help to elucidate the nature of adsorption process and to recover the precious phenols. Moreover, it also will help to regenerate the sorbents, so that it can be used again to develop the successful sorption process. The desorption experiments were carried out at different values of pH.

The results showed that the desorbed amounts of phenolic compounds at neutral pH of water (pH 7.0), acetic acid (pH 1.2), and alkaline water (pH 12) are 0.35; 1.05, and 0.5 g/g, respectively. The adsorption of phenolic compounds increased in an alkaline medium and decreased in an acidic medium. According to Namasivayam and Yamuna [47,48], this behavior indicates that the adsorption of phenolic compounds on wheat bran is done by the adsorbent through chemisorption.

The number of positively charged sites increases with the decrease of pH. A positively charged surface site on the adsorbent favors the desorption of phenolic compounds due to electrostatic repulsion. At acidic pH, a significantly high electrostatic repulsion exists between the positively charged surface of the adsorbent and phenolic compounds.

4. Conclusion

The present work explores a new cheaper, economical, and selective adsorbent as an alternative to costly adsorbents for the removal of phenolic compounds from OMW. The main characteristics of the adsorption process can be summarized as follows:

- The amount of phenolic compounds adsorbed was found to vary with adsorbent dosage, pH, and contact time.
- The adsorption of phenolic compounds per unit weight of wheat bran decreased as the percent adsorption increased with increasing the adsorbent dosage.
- The equilibrium solid-phase concentrations of phenolic compounds q_e (487.3 mg/g) decreased with the increasing adsorbent concentrations, due to a lower fraction of occupied binding sites on wheat bran surfaces at high wheat bran concentrations.
- The pH played an obvious effect on the phenolic compounds adsorption capacity onto wheat bran. Increase in pH to high alkalinity resulted in the increase in the phenolic compounds adsorption capacity.
- The adsorption process was very fast, and it reached equilibrium in 4 h of contact, which is much faster than that of some other normal adsorbents for the removal of phenolic compounds.
- The Langmuir and Freundlich adsorption models were used to represent the experimental data and equilibrium data, which fitted very well to the Freundlich isotherm model. The monolayer adsorption capacity (Q_m) was obtained as 487.3 mg g^{-1} at optimum pH (7.0) and temperature (30°C). The adsorption capacity of wheat bran was relatively high when compared with some other adsorbents reported in literature.
- The kinetic data fitting results showed that the adsorption of phenolic compounds onto wheat bran followed the pseudo-second-order kinetic model.
- Desorption experiments showed almost chemiosorption interactions between the natural phenolic compounds and the adsorption sites on the wheat bran.
- The results showed that the wheat bran might be a new potential, biocompatible, and good adsorbent for the removal of phenolic compounds from OMW.

Acknowledgments

This work was supported by:

*The pole of competences of Water and Environment (PC2E).

*PROTARS II contract N˚ 34 2005 – 2010.

*European project, FP7 SOWAEUMED (Network in Solid Waste and Water Treatment between Europe and Mediterranean Countries, Contract N˚ 245843).

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