Chemical treatment of olive pomace: Effect on acid-basic properties and metal biosorption capacity

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Abstract

In this study, olive pomace, an agricultural waste that is very abundant in Mediterranean area, was modified by two chemical treatments in order to improve its biosorption capacity. Potentiometric titrations and IR analyses were used to characterise untreated olive pomace (OP), olive pomace treated by phosphoric acid (PAOP) and treated by hydrogen peroxide (HPOP). Acid–base properties of all investigated biosorbents were characterised by two main kinds of active sites, whose nature and concentration were determined by a mechanistic model assuming continuous distribution for the proton affinity constants. Titration modelling denoted that all investigated biosorbents (OP, PAOP and HPOP) were characterised by the same kinds of active sites (carboxylic and phenolic), but with different total concentrations with PAOP richer than OP and HPOP. Single metal equilibrium studies in batch reactors were carried out to determine the capacity of these sorbents for copper and cadmium ions at constant pH. Experimental data were analysed and compared using the Langmuir isotherm. The order of maximum uptake capacity of copper and cadmium ions on different biosorbents was PAOP > HPOP > OP. The maximum adsorption capacity of copper and cadmium, was obtained as 0.48 and 0.10 mmol/g, respectively, for PAOP. Metal biosorption tests in presence of Na^+ in solution were also carried out in order to evaluate the effect of chemical treatment on biomass selectivity. These data showed that PAOP is more selective for cadmium than the other sorbents, while similar selectivity was observed for copper.
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1. Introduction

Heavy metals in wastewaters are hazardous to the environment. Due to their toxicity, their presence in aquatic ecosystems poses human health risks and causes harmful effects to living organisms in water and also to the consumers of them [1,2]. Toxic heavy metals are released into the environment from a number of industries such as mining, plating, dyeing, automobile manufacturing and metal processing.

Several processes have been used and developed over the years to remove these metals dissolved in industrial wastewaters: chemical precipitation, ion exchange, membrane filtration or adsorption. However, these conventional technologies are often neither effective nor economical especially when metals are presented at relatively low concentrations [3]. Development of more cost-effective remediation systems that reduce heavy metal concentrations to environmentally acceptable levels at affordable cost is required.

Biosorption is a process that has been studied by several researchers as an alternative technique to conventional methods for heavy metal removal from wastewater. It makes use of biomaterials as adsorbents, those that are generally available at low cost and abundant in nature.

In previous studies, metal removing abilities of live and dead cells of various species of bacteria, algae, fungi and yeasts were investigated and mechanisms of metal–micro-organism interactions [4–10] and many biologically based processes were patented [11,12]. Also several agricultural wastes were already tested to remove heavy metals such as apple residues [13], coffee wastes [14], grape stalks [15], olive mill solid residues [16–18], olive stones [19,20], pine barks [21], plant root tissues [22], rice

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bran [23], sunflower stalks [24], tea leaves [25,26], tree ferns [27], and so on.

Biosorption can be explained by considering different kinds of chemical and physical interactions among the functional groups present on the biosorbent and the heavy metals in solution. Biosorption involves different processes such as complexation, coordination, electrostatic attraction, or micro-precipitation [28]. The identification of these mechanisms and the characterisation of the active sites of the biomass are fundamental steps for the optimisation of the operating conditions in product development and process design.

For adsorption of heavy metals, surface chemistry of the biosorbent plays a key role since adsorption is favoured by the presence of oxygen-containing functional groups which can be very different according to the nature of the biosorbent: carboxylic, phosphate, sulphate, amino, amide and hydroxyl groups are the most commonly found [29,30]. These specific functional groups are essential for the adsorption of heavy metals due their chelating attributes. In particular, acidic groups (such as carboxylic and phenolic ones) for pH values greater than pK_a are mainly in dissociated form and can exchange H^+ with metal in solution. At pH lower than pK_a values, complexation phenomenon can also occur, especially for the carboxylic groups [31]. The reaction can occur due to ion exchange reaction of the metal cation with the hydrogen ion previously attached:

$$M^{n+} + n(-COOH) \Leftrightarrow (-COO)_nM + nH^+ \quad (1)$$

The concentration of such acidic groups can be increased by chemical treatment involving oxidation. Depending on the chemical activation method, partial oxidation takes place and the biomass surface becomes rich in a variety of functional groups whose nature and concentration depend on the method of activation, chemicals used, and temperature of preparation. The determination of type and concentration of active sites generated by chemical treatment is of great importance for the optimisation of the biosorbent adsorptive behaviour.

Among agro-industrial wastes olive pomace is one of the most abundant in the Mediterranean Basin. Olive pomace consists of fibre (as cellulose), lignin and uronic acids along with oily wastes and polyphenolic compounds [32]. This complex matrix contains numerous fixed polyvalent functional groups (such as carboxylic, hydroxylic and methoxy groups) and a high amount of fixed anionic and cationic functional groups. Olive production across the Mediterranean area has a long and prestigious past, which today is firmly rooted in the economic, social and cultural life of its inhabitants. Around the region, around eight million hectares are dedicated to olive cultivation producing, all told, some 1,800,000 tonnes of oil.

Table 1 summarises previous results of chemical treatment of different activated carbons from olive oil production wastes used for some compounds adsorption. All the papers about olive pomace (except [17]) use this waste as precursor for activated carbon preparation. In the present work olive pomace was treated for improving its biosorption capacity without producing activated carbon. The possible effects of chemical treatments onto native olive pomace were discussed on the basis of Fourier trans-

Table 1
Summary table of literature researches using olive pomace as biosorbent material or precursor for activated carbon production

Material	Chemical activation conditions	Characterisation tests	Effect	Reference
Olives stones	Carbonisation (N_2, 850 °C). Steam activation. Chemical activation by $(NH_4)_2S_2O_8$ or H_2O_2.	X-ray diffractometer. FT-IR. Nitrogen BET surface area. SEM. Partial Boehm titrations. Methylene blue adsorption.	Good adsorptive properties towards MB. Basic nature of the sample surfaces (good tendency towards reaction with H^+).	[33]
Olive pulp and olive, peach and apricot stone	Carbonisation (N_2, 850 °C). Steam/nitrogen mixture. Activation oxidation by $(NH_4)_2S_2O_8$ in 1 M H_2SO_4.	Zinc adsorption. Nitrogen BET surface area. Boehm titration.	Oxidation with $(NH_4)_2S_2O_8$ increased the total acidic surface oxygen groups and zinc uptake. Treatment with H_2SO_4 origins activated carbons with lower surface basicity, higher oxygen content and much lower zinc uptake.	[34]
Olive oil mill wastes	Carbonisation (steam, 600, 700 and 800 °C). Chemical activation by H_2SO_4 (10%, 24 h) or steam-pyrolysed (800 °C, 2 h).	Thermogravimetric analysis. Nitrogen BET surface area.	Development in the texture parameters depends on treatment temperature and duration of reaction. Pyrolysis/carbonisation is suggested to enhance removal of low molecular volatiles.	[35]
Olive seeds	Chemical activation by H_3PO_4 (85%), 2 days. Carbonisation (400, 600 and 800 °C).	Methylene blue adsorption.	Higher adsorption capacities.	[36]
Olive stones	Extraction with ethanol/benzene. Treated with H_2SO_4 (72%) (20 °C, 2 h). Treated with H_2SO_4 (3%) (boiling, 4 h).	Thermogravimetric analysis.	H_2SO_4 treatment removes the hemicellulose and cellulose is only slightly removed.	[37]
Olive mill solid residue	Chemical activation by HCl (5 M) (60 °C, 1 h). Carbonisation (N_2, 800 °C). Activation (CO_2, air or steam; 800, 850, 900 and 950 °C; 0.5 to 2 h).	Nitrogen BET surface area. Phenol adsorption.	Optimum activation temperature 850 °C. Optimal activation time of 2 h. Steam the most efficient activator as compared with air and CO_2.	[38]
Olive-waste cakes	Hexane extraction. Carbonisation (N_2, 400 °C). Activation (steam; 750 and 850 °C; 0.5 and 1 h).	N_2 and CO_2 adsorption tests. Isotherms of methylene blue. Mercury porosimetry.	Activation time and activation temperature are the most influential factors. Optimum activation temperature 1095 K. Optimal activation time of 68 min.	[39]
Olive pomace	Hexane extraction NaOH 2 M (under argon pressure to avoid oxidation of phenols).	Cu, Cd and Pb adsorption. Potentiometric titrations.	These treatments decrease total sites concentration. NaOH treatment causes a lower reduction of the total sites concentration than n-hexane treatment.	[17]

form infrared spectroscopic analyses, potentiometric titrations and biosorption tests of copper and cadmium.

2. Materials and methods

2.1. Olive pomace

Olive pomace was supplied by an Italian olive oil production plant as pressed and sunny dried disks. Solid samples were ground by an electric mixer and particle size distribution was determined by using an automatic sieve [40].

2.2. Chemical treatment of olive pomace by H_3PO_4 (PAOP)

50 g of olive pomace were added to 250 mL of phosphoric acid (50%) and mixed thoroughly for 1 day to establish complete contact between phosphoric acid and biomass at room temperature. Then the sample was filtered and washed several times to remove phosphoric acid residues until the pH of rising water remained constant. After that, the sample was dried in an oven at 105 °C for 24 h. Hereafter abbreviated as PAOP.

2.3. Chemical treatment of olive pomace by H_2O_2 (HPOP)

50 g of olive pomace were added to 250 mL of hydrogen peroxide (1 M) and mixed thoroughly for 3 h to establish complete contact between hydrogen peroxide and biomass at room temperature. The pH was controlled and maintained at 8. Then the sample was filtered and washed several times to remove hydrogen peroxide residues until the pH of rising water remained constant. After that, the sample was dried in an oven at 60 °C for 24 h. Hereafter abbreviated as HPOP.

2.4. Potentiometric titrations

Pomace suspensions (2 g of olive pomace in 40 mL of deionised water) were titrated by standard solutions of NaOH 0.1 N (basic branch) and HCl 0.1 N (acid branch). The pH of the suspension was measured after each addition of titrant (0.05 mL) by a pH-meter when a stability had been obtained (2 min).

2.5. IR analyses

IR spectra were performed by using KBr as transparent component for the dilution of solid biosorbents. Biosorbent-bearing disks of KBr were prepared by two successive dilutions: 0.002 g samples of each solid were mixed with 0.3 g of KBr; 0.03 g of this mixture were diluted again with other 0.3 g of KBr. 0.15 g samples of this second mixture were pressed and used for disk preparation. The signals of CO_2 and aqueous vapour in the air and possible impurities of KBr were subtracted from all the spectra by collecting a background spectrum. Eight scansions between 400 and 4000 cm^{-1} were performed for each spectrum. IR spectra were performed by using olive pomace, olive pomace treated by hydrogen peroxide (HPOP) and by phosphoric acid (PAOP).

2.6. Equilibrium isotherms of copper and cadmium

All biosorption tests were performed by the batch technique using the three different biosorbents (OP, PAOP, HPOP).

Batch sorption experiments for single-component were carried out preparing heavy metal solutions of $Cu(NO_3)_2$ and $Cd(NO_3)_2$ in distilled water. Equilibrium biosorption was determined by using 10 g/L olive pomace suspensions in 40 mL of metal nitrate solution with initial concentrations ranging from 10 to 200 mg/L. Samples were kept under magnetic stirring at room temperature for 90 min according to kinetic tests (experimental data not reported here). During biosorption tests pH was maintained constant at 5 by additions of 0.1 M HCl or 0.1 M NaOH. Solid–liquid separation was performed by centrifugation and the liquid equilibrium concentration was determined by an Inductively Coupled Plasma (ICP) Spectrophotometer.

2.7. Batch biosorption tests in presence of sodium ions

A set of Erlenmeyer flasks containing 40 mL of 0.1M $NaNO_3$ solution with 40 or 80 mg/L of copper, or 30 or 50 mg/L of cadmium was used in the experiments. OP, PAOP and HPOP (0.4 g) were contacted with the ionic buffered metal solutions for 90 min on a rotary shaker at room temperature and constant pH 5. The contents of the flasks were filtered and the filtrates were analysed for residual metal concentration using the ICP.

3. Results and discussion

3.1. Preliminary biosorption tests of olive pomace treatment

For choosing the better conditions for chemical treatment of olive pomace, this sorbent was modified by oxidation using either H_2O_2 or H_3PO_4 at different conditions (data not reported here) and then a copper biosorption test was carried out (initial copper concentration = 50 mg/L, pH 5, room temperature). These activating agents and conditions for the chemical treatment were chosen considering previous results with activated carbons (Table 1).

The evaluation of the metal specific uptake at the equilibrium q_e (mmol/g of biosorbent) was obtained using mass balances of metallic ion and biomass in the system,

$$q_e = \frac{C_i V_i - C_e V_e}{m} \quad (2)$$

where C_i is the initial copper concentration (mM), C_e is equilibrium copper concentration (mM), V_i and V_e are the initial and final volume in the reactor (L), and m is the weight of solid used for biosorption test (g).

Higher copper uptakes were obtained for the treatments chosen for olive pomace in this study. The value of q_e for untreated olive pomace in this biosorption test was 0.043 mmol/g, however when olive pomace was treated by H_2O_2 the value was obtained $q_e = 0.056$ mmol/g and when was treated by H_3PO_4 a value of

0.090 mmol/g was obtained. Preliminary tests using larger concentrations of H_2O_2 or H_3PO_4 or longer activation time did not determine an improvement of copper biosorption at pH 5.

3.2. Potentiometric titration

The applications of titration techniques become a powerful tool for the characterisation of heterogeneous materials involved in biosorption processes [41]. Potentiometric titration was used as a physico-chemical method to study the acid properties of selected biosorbent materials in order to quantify the functional acidic groups for sorption and to determine their affinities by considering their partial or total ionisation equilibrium reactions. The acid–base properties of the active groups on the adsorbent can predict the removal capacity at different equilibrium pH and can also be used to investigate ionic interactions in solution [42–44].

Potentiometric titrations of untreated olive pomace were already performed and modelled as reported Pagnanelli et al. [17]. Untreated samples used in this work were specifically addressed again in order to isolate the effects of treatment from those of variability of natural samples.

Potentiometric titration curves obtained for untreated olive pomace and treated olive pomace are rather flat testifying the heterogeneity of the matrix and the impossibility of distinguishing separated groups as distinct flexes (Fig. 1). The sorbents impart significant buffering capacity to the suspensions between pH 2 and 11. The comparison among the experimental data evidenced that the main differences occurring are related to the change of the total concentration of the active sites.
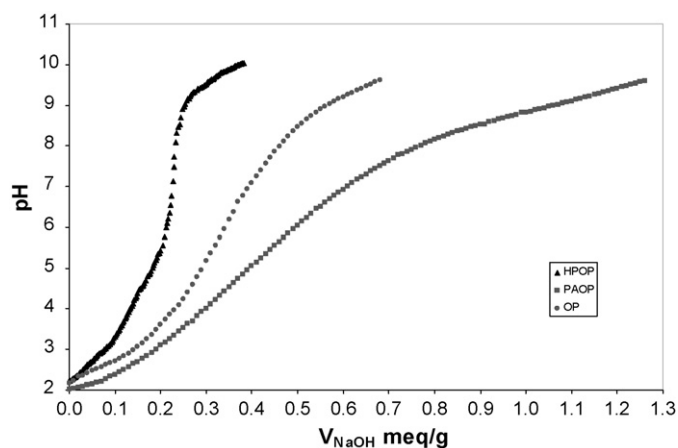

Fig. 1. Potentiometric titration of native olive pomace (OP) and olive pomace treated by H_2O_2 (HPOP) and H_3PO_4 (PAOP).

A quantitative evaluation of the total concentration of acidic sites was obtained by the graphic method of Gran [45] (Table 2). Comparing the values obtained for the different biosorbents (OP, PAOP, HPOP), it can be evidenced that PAOP is richer in active sites than OP and HPOP. This can be due to the oxidation that increases acid sites concentration. On the other side, treatment by hydrogen peroxide decreases acid site concentration in comparison with untreated olive pomace, perhaps due to partial degradation of the vegetal matrix. This hypothesis is supported by the fact that using larger concentration of hydrogen peroxide in the treatment of olive pomace was obtained a lower Cu sorption (preliminary biosorption tests not reported here).

Table 2
Adjustable parameters for discrete and continuous models of native olive pomace, olive pomace treated by phosphoric acid and olive pomace treated by hydrogen peroxide titration curves and active site concentrations estimated by Gran's method with their corresponding standard deviations (Δ)

Solid sample	Q_{max}	Δ_{Qmax}	$Q_{max\ discrete}$	$Q_{max\ continuous}$
Gran's method				
OP	0.00054	9×10^{-5}	0.00069	0.00090
PAOP	0.00110	5×10^{-5}	0.00115	0.00130
HPOP	0.00022	2×10^{-5}	0.00032	0.00030

Solid sample	$Q_{max,1}$	$\Delta_{Q_{max,1}}$	$Q_{max,2}$	$\Delta_{Q_{max,2}}$	$\log K_{H,1}$	$\Delta \log K_{H,1}$	$\log K_{H,2}$	$\Delta \log K_{H,2}$	SS_R (mmol^2/g^2)	R^2
Discrete model										
OP	0.00035	1×10^{-5}	0.00034	1×10^{-5}	3.31	0.04	8.60	0.06	1.0×10^{-6}	0.983
PAOP	0.00044	1×10^{-5}	0.00071	2×10^{-5}	4.39	0.06	8.53	0.04	3.54×10^{-7}	0.994
HPOP	0.00017	1×10^{-5}	0.00015	1×10^{-5}	3.88	0.04	8.88	0.07	1.31×10^{-7}	0.989

Solid sample	$Q_{max,1}$	$\Delta_{Q_{max,1}}$	$Q_{max,2}$	$\Delta_{Q_{max,2}}$	$\log K_{H,1}$	$\Delta \log K_{H,1}$	$\log K_{H,2}$	$\Delta \log K_{H,2}$	m_1	Δm_1	m_2	Δm_2	SS_R (mmol^2/g^2)	R^2
Continuous model														
OP	0.00041	7×10^{-5}	0.0005	2×10^{-4}	3.6	0.6	9.5	0.5	0.24	0.04	0.4	0.1	2.44×10^{-7}	0.996
PAOP	0.00052	2×10^{-5}	0.00078	4×10^{-5}	5.0	0.1	8.77	0.02	0.31	0.01	0.61	0.03	7.89×10^{-9}	0.999
HPOP	0.00015	1×10^{-5}	0.00015	3×10^{-5}	4.19	0.08	9.5	0.2	0.44	0.02	0.9	0.2	5.51×10^{-8}	0.995

Solid sample	$F_{cal} = \dfrac{S_{Rd}^2}{S_{Rc}^2}$	$F_{0.05}$
F-test		
OP	4.36	1.27
PAOP	44.23	1.29
HPOP	2.37	1.34

In the following the titration curve data were transformed into an adsorption isotherm, Q versus pH, with Q equal to the total negative charge concentration in the solid (mmol/g) calculated by the charge balance for each titration point:

$$[Na^+]_{added} + [H^+] = \sum_{j=1}^{N}[B_j^-] + [OH^-] + [Cl^-]_{added} \quad (3)$$

where the term $\sum_{j=1}^{N}[B_j^-]$ (equal to Q) represents the sum of the concentrations of all the types (possible n) of acidic ionised groups.

Considering that the concentration of Na$^+$ added is equal to $V_b C_b / V_T$ and the concentration of Cl$^-$ is equal to $V_a C_a / V_T$, the following can be obtained

$$Q = \frac{(V_b \cdot C_b - V_a \cdot C_a)/V_T + [H^+] - K_w/[H^+]}{m} \quad (4)$$

where V_b (mL) and V_a (mL) are the base and acid volumes, C_b (mM) and C_a (mM) are the base and acid concentrations, V_T is the total volume (mL) of the suspension and m is the solid amount (g).

The main kinds of functional groups can be denoted by the first derivative of smoothed titration data (Mathcad), which depicts the distribution of acidic sites in terms of their $\log K_H$ values (Fig. 2).

Potentiometric titrations of the different biosorbents have been modelled by developing a mechanistic approach. A mechanistic approach aims to describe the effect of pH on acid–base properties of the biomass suspension by the hypothesis of a specific set of reactions which include the chemical mechanism determining the variation of negative charge on the biosorbent. In particular, the chemical mechanism used here assumes that there are two different kinds of weakly acidic sites able to bind proton
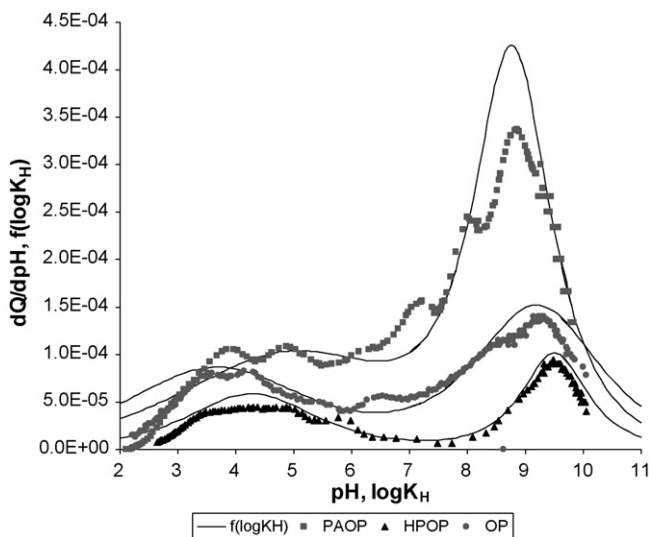
$$B_i^- + H^+ \overset{K_{H,i}}{\longleftrightarrow} B_i H \quad (5)$$

Fig. 2. First derivative (dQ/dpH) and proton affinity distribution functions ($f(\log K_H)$) for olive pomace (OP) and olive pomace treated by H$_2$O$_2$ (HPOP) and H$_3$PO$_4$ (PAOP).

Combining then charge and mass balances, acidic constants and concentrations of the active sites can be estimated as adjustable parameters by a non-linear regression method [29,43,46].

$$Q_H = \sum_{i=1}^{n} \frac{Q_{max,i}}{1 + K_{H,i}[H^+]} \quad (6)$$

For titration curves without distinct flex points the continuous approach can be used by introducing a quasi-Gaussian distribution of Sips for the logarithm of the protonation equilibrium constant of the active site [44,47–49].

$$Q_H = \frac{Q_{max,1}}{1 + (\tilde{K}_{H,1}[H^+])^{m1}} + \frac{Q_{max,2}}{1 + (\tilde{K}_{H,2}[H^+])^{m2}} \quad (7)$$

More details about mechanistic approaches used in this paper were reported by Pagnanelli et al. [17–18,44].

In Fig. 2 was represented the first derivate of smoothed experimental data and the quasi-Gaussian distribution function (Eq. (8)). All biosorbents were characterised by two main regions of buffering capacity denoting acid–base reactions occurring in the zones of pH 3–5 and 8–10, which the literature lists for carboxylic and phenolic groups. The buffering capacity denoted by the first derivative were adequately characterised by the quasi-Gaussian distribution function.

$$f(\log K_H) = \frac{\ln(10)\sin(m\pi)}{\pi[(K_H/\tilde{K}_H)^{-m} + 2\cos(m\pi) + (K_H/\tilde{K}_H)^m]} \quad (8)$$

where $\tilde{K}_H$ is the median value of the distribution and m ($0 < m < 1$) is a parameter related to the shape of the distribution [49].

In Fig. 3 the comparison among experimental data of potentiometric titrations (reported as negative charge excess versus pH) and model predictions by discrete and continuous approaches were represented assuming that two main types of weakly monoprotic acidic sites (B$_1^-$ and B$_2^-$) are present on solid. In Table 2 each adjustable parameter is given along with the standard deviation (Δ) evaluated during non-linear regression by computer software (scientist).

The performances of the two models were also compared by using an F-test evaluated considering that the continuous model has $g = 6$ parameters and the discrete model has $k = 4$ parameters:

$$F_{cal} = \frac{S_{Rd}^2/(n - k)}{S_{Rc}^2/(n - g)} \quad (9)$$

where S_{Rd}^2 is the residual sum of squares of discrete model, S_{Rc}^2 is the residual sum of squares of continuous model, and n is the total number of experimental data.

For all biosorbents $F_{cal} > F_{\alpha,n-k,n-g}$ that is the model corresponding to the denominator (continuous) is statistically better than the other (discrete), providing a better fit, according to the chosen level of significance ($1 - \alpha = 0.05$).

The total capacity estimated by Gran's method was in agreement with that predicted by these models. Moreover, the acidic constants determined in the modelling phase are realistic, considering that the structure of olive pomace is characterised by different weakly acidic groups. The buffering capacity denoted
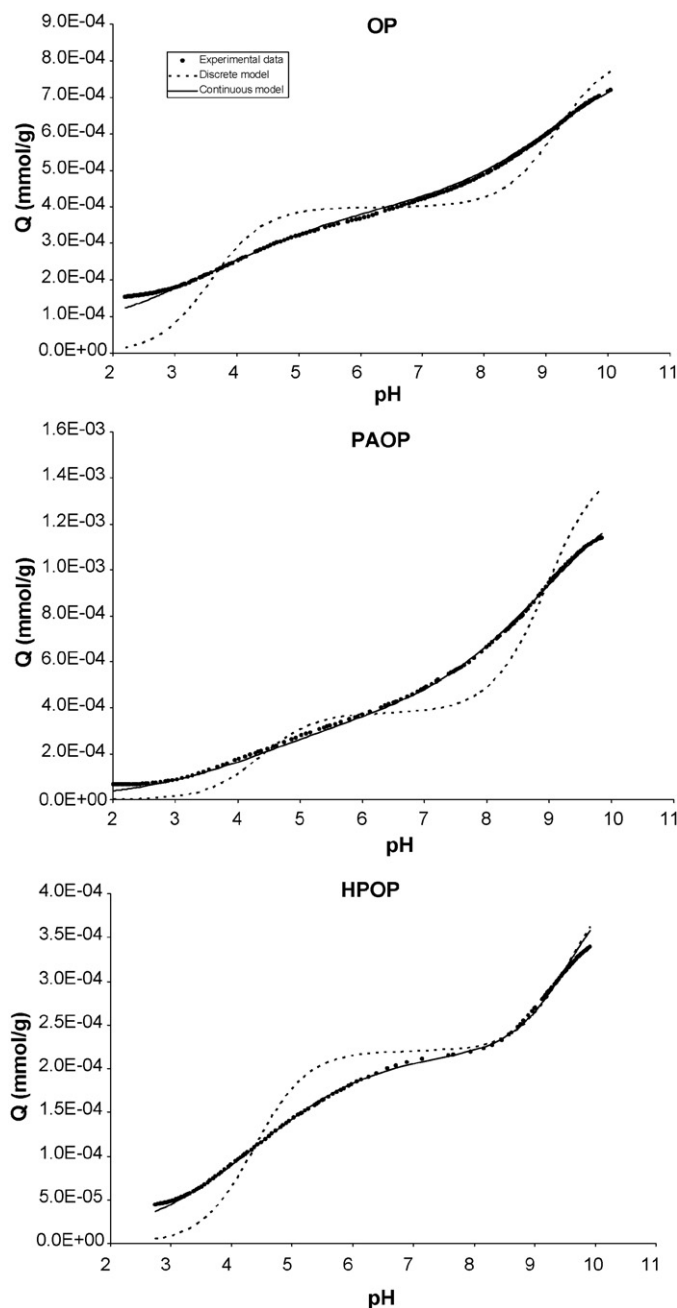
Fig. 3. Comparison among experimental data of potentiometric titrations and discrete and continuous model predictions for native olive pomace (OP) and olive pomace treated by H$_2$O$_2$ (HPOP) and H$_3$PO$_4$ (PAOP).

by the first derivative were adequately characterised by the quasi-Gaussian distribution function. Similarities were observed when comparing the pK_a values obtained in the present work for OP, PAOP and HPOP. The buffering capacity of the native and treated pomace suspension is concentrated in the pH range that is typical of carboxylic dissociation (3–5) and in the pH range (8–12) of phenolic dissociation. The pK_a of 3 corresponds to a carboxylic moiety linked to an aromatic group. The pK_a of 5 is attributed to a carboxylic moiety linked to an aliphatic chain. The proximity of another carboxylic group could be responsible for a higher ionisation and lower pK_a values. The pK_a values obtained in

the present work (Table 2) indicated that the carboxylic acidic groups in the PAOP were linked to aliphatic chains rather than to aromatic groups, however values obtained for OP indicated carboxylic moiety linked to an aromatic group. The phenolic acidic groups have ionisation constants between 8 and 12 depending on the different substitutions of the phenolic groups.

3.3. IR spectral analysis

In order to confirm the groups responsible for the metal adsorption and changes in composition IR spectrum on solid phase for OP, APOP and HPOP was carried out. Fig. 4 shows the IR spectra.

As for OP, the broad peak at 3410 cm^{-1} can be attributed to the O–H stretching vibrations. The peaks at 2918 and 2848 cm^{-1} are due to C–H stretching vibrations of CH, CH$_2$ and CH$_3$ groups. The peak at 1707 cm^{-1} can be assigned to C=O stretching vibration of carboxylic groups. Two peaks at 1621 and 1418 cm^{-1} were attributed to asymmetric and symmetric stretching of carboxylate, respectively. The intense peak at 1061 cm^{-1} along with the weak peak at 1212 cm^{-1} and the shoulder at 1136 cm^{-1} are C–O stretching vibrations of ethers and alcohols.

IR spectrum of olive pomace chemically treated by hydrogen peroxide (HPOP) denoted only a partial modification of functional properties. Main peaks and wavenumbers observed for olive pomace are preserved, even though there are significant changes in the relative intensities of these peaks. In particular, the increase of the relative intensity of C=O peak (1726 cm^{-1}) with respect to C–O stretching vibrations of ethers and alcohols (1032 cm^{-1}) confirmed the partial oxidation of such functional groups.

IR spectrum of PAOP denoted only few identifiable peaks meaning that PA treatment determined a significant chemical modification with respect to native olive pomace. Main differences are the increase of the relative intensity of the peak at 1707 cm^{-1} characteristics of esters and carboxylic acids [50] and the disappearance of the band at 1061 cm^{-1} that in OP was due to C–O of ethers and alcohols. These changes
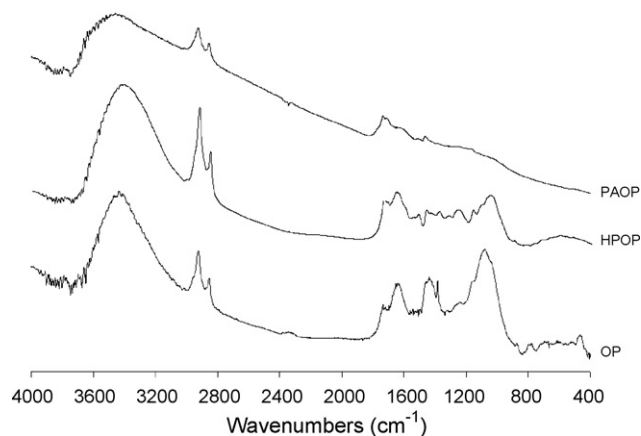

Fig. 4. IR spectra of native olive pomace (OP) and olive pomace treated by H$_2$O$_2$ (HPOP) and H$_3$PO$_4$ (PAOP).

of functional properties are specifically due to the effects of phosphoric acid In fact literature data showed that PA impregnation of lignin structures can cause particles swelling and dissolution to the botanical structure leading to formation a new poly-biopolymer by cleavage of the aryl–ether bonds, the formation of ketone groups, condensation and dehydration [50–52].

3.4. Analysis of isotherm data

Isotherm studies were performed for single component systems (copper and cadmium ions) at pH 5 and at room temperature with the different biosorbents.

The sorption process considered in this work involves a biosorbent (OP, PAOP or HPOP) as the solid phase and an aqueous phase containing dissolved species to be sorbed (Cu and Cd ions). Due to the higher affinity of the sorbent for the ionic species, they are attracted and bound to the solid by different mechanisms. This process takes place until equilibrium between the amount of solid-bound ions and their concentration in solution is reached. Langmuir sorption model [53] was used to describe equilibrium between adsorbed species on the solid (q_e) and in solution (C_e), at a constant temperature (room temperature)

$$q_e = \frac{b \cdot q_m \cdot C_e}{1 + b \cdot C_e} \qquad (10)$$

where q_e is the amount (mmol/g) of metal adsorbed per gram of biomass weight at the equilibrium, C_e is the residual (equilibrium) metal concentration left in solution after binding (mmol/L), q_m is the maximum possible amount of metallic ion adsorbed per unit of weight of adsorbent and b is a constant related to the affinity of the binding sites for the metals (L/mmol).

Model parameters (q_m and b) for three single component systems in copper and in cadmium were obtained by non-linear regression and presented in Table 3.

The plots in Figs. 5 and 6 demonstrate that the Langmuir equation provided a reasonable description of the experimental data with correlation coefficients greater than 0.97, as shown in Table 3.

The sorbents can be then compared by their respective q_m values which were calculated from fitting the Langmuir isotherm model to the experimental data. Biosorbent "goodness" can be measured by its maximum sorbent capacity (q_m) and metal affinity (b).
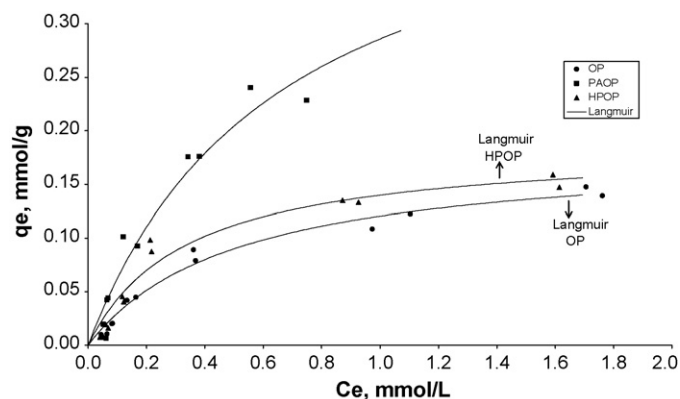

Fig. 5. Copper removal from aqueous solutions using native olive pomace (OP) and olive pomace treated by H_2O_2 (HPOP) and H_3PO_4 (PAOP) (10 g/L biosorbent suspension, pH = 5).
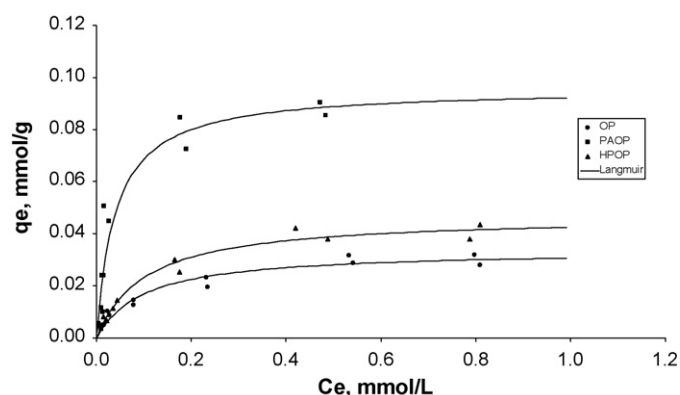

Fig. 6. Cadmium removal from aqueous solutions using native olive pomace (OP) and olive pomace treated by H_2O_2 (HPOP) and H_3PO_4 (PAOP) (10 g/L biosorbent suspension, pH = 5).

Chemical treatments produce improvements in olive pomace sorbing capacity towards copper and cadmium (Table 3), with PAOP exhibiting the highest sorption for either metal. Regarding metal selectivity chemical treatment by phosphoric acid determines a substantial improvement (b goes from 9.97 L/mmol for OP to 25.31 L/mmol for PAOP), while no significant change was observed for copper.

Comparing the results for the two heavy metals, sorption for copper at the same equilibrium pH, is higher than cadmium for the three biosorbents (for OP copper sorption is more than five times the sorption of cadmium, for PAOP is almost five times and for HPOP is more than four times). Cadmium and

Table 3
The corresponding parameters with their standard deviations of Langmuir isotherm estimated for metal binding by the three biosorbents at pH 5 and room temperature

Metal	Solid sample	q_m (mmol/g)	Δq_m (mmol/g)	b (L/mmol)	Δb (L/mmol)	SS_R (mmol^2/g^2)	R^2
Langmuir isotherm							
Cu	OP	0.18	0.01	2.0	0.3	6×10^{-4}	0.99
	PAOP	0.5	0.1	1.5	0.6	4×10^{-3}	0.98
	HPOP	0.19	0.01	3.0	0.6	2×10^{-3}	0.98
Cd	OP	0.03	0.01	10	2	6×10^{-5}	0.99
	PAOP	0.10	0.01	25	7	1×10^{-3}	0.97
	HPOP	0.05	0.01	10	2	7×10^{-5}	0.99

copper ions have the same charge but cadmium is about two times heavier than copper. As a consequence, at charge parity, cadmium presents a larger sterical impediment than copper. This can be an explanation of the smaller cadmium maximum specific uptake. Nevertheless, further studies are necessary to elucidate the biosorption mechanism. Also, a comparison of biosorption capacities (q_m) of OP, HPOP, PAOP and some other biosorbents reported in literature are listed in Table 4.

3.5. Effect of the presence of NaNO₃

Wastewaters usually contain more ions than single metal. The presence of other ions in wastewater is expected to cause interference and competition phenomena for adsorption sites and lead to more complex mathematical formulations. Heavy metal-bearing solutions were then modified into binary systems of one primary-target metal (copper or cadmium) and one ubiquitous ionic competitor (sodium). Different initial concentrations were chosen for copper and cadmium tests in order to work in the range of concentration presenting linear dependence between metal concentration in the solid and liquid phase.

The results showed that the uptakes of the two metals studied were reduced in all the cases (Fig. 7). The ratios between q_e without NaNO₃ and q_e with the presence of 0.1 M NaNO₃ were also reported. These ratios showed that the decrease in metal uptake in the presence of sodium was higher at increasing metal concentrations, for example, in cadmium uptake by HPOP the ratio

Table 4
Maximum adsorptive capacity from copper and cadmium (mmol/g) on different agriculture by-products

Metal	Biosorbent	q_m	Ref.
Copper	Carrot residue	0.515	[54]
	Olive pomace treated by H₃PO₄	0.500	This study
	Sugar beet pulp	0.330	[55]
	Tree fern	0.184	[56]
	Olive pomace	0.180	This study
	Olive pomace treated by H₂O₂	0.190	This study
	Apple residues	0.170	[13]
	Banana peel	0.075	[57]
Cadmium	Grape bagasse	0.479	[58]
	Vermicompost	0.294	[59]
	Olive pomace treated by H₃PO₄	0.190	This study
	Apple residues	0.158	[13]
	Olive pomace treated by H₂O₂	0.100	This study
	Olive stone	0.040	[20]
	Olive pomace	0.030	This study
	Fly bagasse ash from sugar	0.018	[60]

increase of 1.58–1.89. The order of decrease in copper uptake for the presence of sodium was PAOP > HPOP > OP, while for cadmium the order was HPOP > OP > PAOP. In the case of cadmium 47% sorption decrease was observed for HPOP when cadmium initial concentration was 50 mg/L (ratio = 1.89). For OP and PAOP this decrease is lower, 39% and 18%, respectively
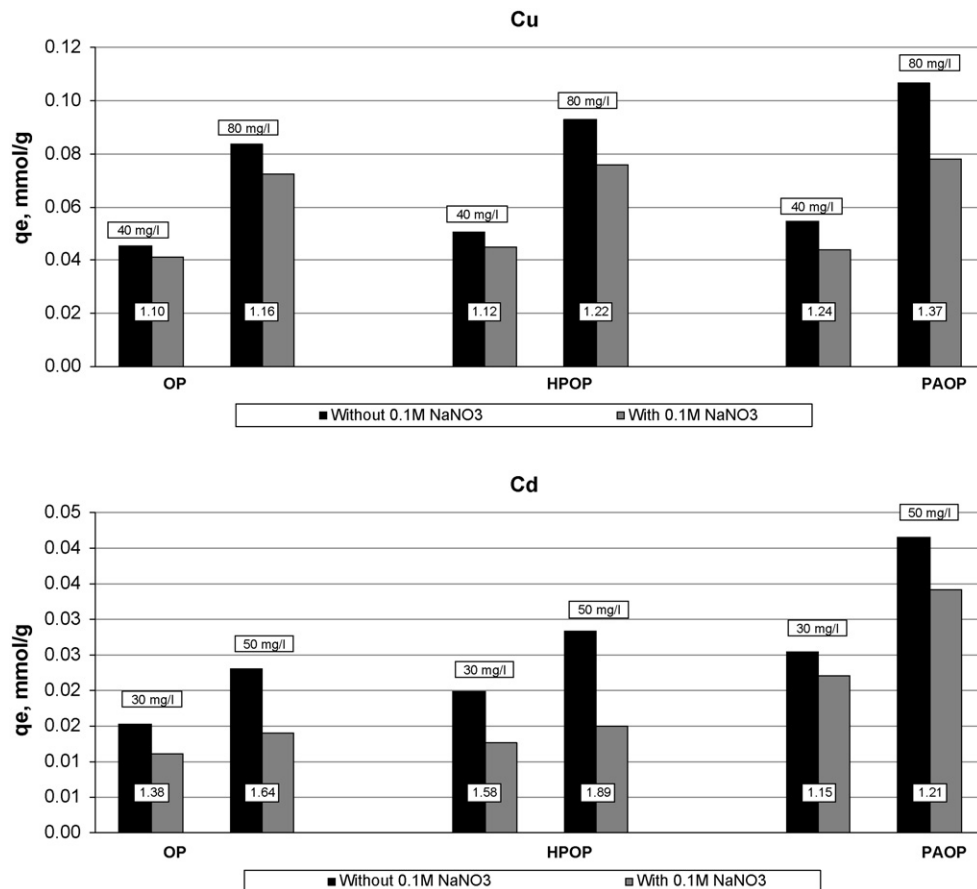

Fig. 7. Effect of sodium ions on copper and cadmium biosorption at pH 5.

(ratios = 1.64 and 1.21). This is in agreement with the constant b values of Langmuir isotherm representing the affinity between the sorbent and the metal ion. Comparing both metal ions, the effect of the $NaNO_3$ on the copper uptake was less significant than that observed for the cadmium uptake. Consequently, the effect of an ubiquitous competitor can vary depending upon both type of the heavy metal and/or sorbent.

4. Conclusions

Biosorption can be an alternative to conventional systems for the removal of toxic metals from industrial effluents. Olive pomace, an agricultural waste, has been identified as a potentially cheap and efficient material to treat water contaminated with selected heavy metals. This study centres in the chemical activation of olive pomace by H_2O_2 and H_3PO_4. Untreated olive pomace (OP), olive pomace treated by phosphoric acid (PAOP) and treated by hydrogen peroxide (HPOP) were compared with particular attention to the surface chemistry. The chemical modification of olive pomace may be justified by improving metal sorption properties (increase of sorption capacities or enhancement of sorption selectivity). In particular, the main conclusions emerging from adsorbent characterisation and mechanistic modelling regard the identification of carboxylic and phenolic groups and have confirmed that the surfaces of these solids are heterogeneous. Weakly acidic surface functional groups may be identified by applying a proton affinity distribution function. Treatment by phosphoric acid produced an increase of acid group concentration, however treatment by hydrogen peroxide produced a decrease of titrable acid groups perhaps because the treatment with this oxidant destroys or produces the combustion of cellular walls.

Langmuir isotherm was used for a preliminary comparison of sorption capacity and affinity onto these biosorbents. There is observed an increase in biosorption capacity when olive pomace is treated by oxidants like hydrogen peroxide and phosphoric acid. The sequence of uptake per unit weight was: PAOP > HPOP > OP. Copper loading capacity of untreated (OP) and treated olive pomace (PAOP and HPOP) has been estimated as 0.18, 0.48 and 0.19 mmol/g, respectively, while cadmium loading capacity were 0.03, 0.10 and 0.05 mmol/g for cadmium.

The presence of sodium ion inhibited uptake of individual metals being HPOP the sorbent more affected.

In summary, this study indicates that a positive potential exists for the improvement of its biosorption capacity using chemical agents. The results presented in this paper show that copper and cadmium biosorption is dependent on surface chemistry and the porosity of the sorbents. Olive pomace activated with phosphoric acid, PAOP, may be regarded as prospective biosorbent for the removal of heavy metals from water solutions presenting both increased biosorption capacity and improved selectivity for target metals.

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