Comparative study of isotherm parameters of lead biosorption by two wastes of olive-oil production

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ABSTRACT

Batch isotherm studies were carried out on a laboratory scale: (i) to investigate the effectiveness to remove lead of two wastes (olive stone (OS) and olive tree pruning (OTP)), untreated and chemically treated; and (ii) to examine the applicability of various adsorption isotherms to fit the experimental data. Results from tests were analyzed using seven equilibrium isotherm correlations (Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Redlich–Peterson, Sips, and Toth equations). The sum of the squares of the errors was determined for each isotherm and the Langmuir equation provided the best fit. Chemical treatments increased the biosorption properties of these materials. The maximum biosorption capacities were: 6.33, 49.13, 14.83, and 38.93 mg g^{-1} for untreated OS, HNO$_3$-OS, H$_2$SO$_4$-OS, and NaOH-OS, respectively, and 26.72, 86.40, 72.78, and 123.80 mg g^{-1} for untreated OTP, HNO$_3$-OTP, H$_2$SO$_4$-OTP, and NaOH-OTP, respectively. Finally, the loss of mass for each waste (13.9, 14.3, and 36.8% for HNO$_3$-OS, H$_2$SO$_4$-OS, and NaOH-OS and 35.1, 27.5, and 46.7% for HNO$_3$-OTP, H$_2$SO$_4$-OTP, and NaOH-OTP, respectively) was taken into account and an effectiveness coefficient was determined for each adsorbent material.

Key words | agricultural waste, biosorption, chemical treatment, lead, olive stone, olive tree pruning

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INTRODUCTION

The contamination of the environment from different activities has become an increasingly serious problem in recent years. Heavy metals are one class of toxic pollutants released into the surface water and groundwater as a result of various activities such as industry, mining, and agriculture. Lead is a hazardous heavy metal because it does not take part in biological processes and it tends to accumulate in ecosystems. As well, it may enter the body via inhalation, ingestion, and skin adsorption, having effects on children and adults, even at low concentrations (Gundogdua *et al.* 2009; Lourie *et al.* 2010; Tawfik *et al.* 2013). The high use of this metal in industry has caused a higher level in wastewaters. The United States Environmental Protection Agency (USEPA) requires lead in drinking water not to exceed 0.015 mg L^{-1}. For that, all industrial effluents containing lead ions should be treated to reduce Pb(II) to an acceptable level (Bernardo *et al.* 2013; Calero *et al.* 2013b).

Biosorption is an emerging method with several advantages over conventional methods including ease of operation, high efficiency and no formation of any residual chemical sludge. However, the major advantage of biosorption is that it can be used *in situ*, and with proper design, it may not need any industrial process operations and can be integrated with many systems (Zhou *et al.* 2004; Martín-Lara *et al.* 2013).

To follow the path to sustainable development and resource renewability, an important point is searching for new uses of waste products. Lignocellulosic biomass is drawing attention as an economical and renewable source of energy. Spain is the world's leading producer of olive oil; just in Andalusia an average annual amount of 900,000 tons are produced, which generates a high amount of waste (mainly, olive pruning and olive stone). Olive stone (OS) is a waste from the separation process of the olive cake and olive tree pruning (OTP) is a waste from the olive pruning process. Considering the large amount of these residues generated yearly, a low-cost alternative to their disposal is necessary (AAE 2011; Feria *et al.* 2011). Andalusia produces per year an average of more than 2 million tons of OTP (assuming that 1 hectare of OTP generates 3 tons of olive oil) and more than 10,000 tons of OS (assuming that 11.5% of olive production is OS waste) (AAE 2011). Therefore, the

obtained biomass from olive trees can be an abundant and renewable material to exploit, considering there are as yet no industrial applications for it.

Although there are several studies using these wastes as biosorbents (Martín-Lara *et al.* 2009; Ronda *et al.* 2013), there are few that study their behavior when they are chemically treated, that is, the comparison between them. Thus, the main novelty of this work is the study of the use of the two abundant wastes as biosorbent of lead and the effect of chemical treatments on them, as well as applying a high number of models to fit experimental data.

For all of the above, the proposed aims of this work are: the performance of batch isotherm studies on laboratory scale to investigate the effectiveness of untreated and chemically treated OS and OTP in the removal of lead and the analysis of the applicability of seven equilibrium isotherm correlations to fit experimental data.

MATERIALS AND METHODS

Biomass

Two biosorbents (OS and OTP) were obtained from olive farms in the province of Jaén (Spain). Solids were milled with an analytical mill (IKA MF-10) and the fraction <1.000 mm was chosen for the study.

Olive stone

The OS is a waste from the separation process of the olive cake that takes place during the months November–March.

Olive tree pruning

OTP is a waste from the olive pruning process. It is performed between the months of February and March.

Modification by chemical treatment of the raw biomass

The chemical modification of biomass was performed using three chemical solutions: nitric acid (HNO_3), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH). A previous study was performed with several acid and basic solutions (HNO_3, H_2SO_4, H_3PO_4, HCl, NaOH, and KOH). Chemical solutions with better results (HNO_3, H_2SO_4, and NaOH) were chosen in this work to study more deeply the biosorption process and to compare their results. The solutions for treatment were prepared at different concentrations (0.1, 1,

and 2 M). One liter of these solutions was used to treat 10 g of biomass in a flask at constant temperature (50 °C). Biomass and chemical solution were mixed for 24 h to establish complete contact. Then, the biomass was repeatedly washed with distilled water until the pH of rinsing water remained constant. The treated biosorbents were dried in an oven at 40 °C for 24 h and afterwards stored for later use.

Preparation of lead solutions

A stock solution of 2,000 mg L^{-1} Pb(II) was prepared to dissolve the desired amount of $Pb(NO_3)_2$ (lead(II) nitrate) in 500 mL of distilled water. Solutions of different concentrations were prepared by appropriate dilution of the above stock Pb(II) solution.

Characterization of untreated and chemically treated biosorbents

Untreated and chemically treated biosorbents were characterized in previous published works (Calero *et al.* 2013a; Martín-Lara *et al.* 2013). A summary of results obtained for both are shown in Supplementary Table S1 (available online at http://www.iwaponline.com/wst/072/153.pdf).

Experimental procedure

To study the biosorption equilibrium of Pb(II) with OS and OTP as sorbent solids (untreated and chemically treated) different experimental tests were performed. The operational conditions were chosen according to previous studies (Calero *et al.* 2013b) and were as follows: pH = 5, concentration of biosorbent = 10 g L^{-1}, concentration of chemical agent = 2.0 M (for OS) and 1.0 M (for OTP), and temperature = 25 °C (constant during all the experiment). Experiments were carried out at different initial lead concentrations: 40, 50, 80, 150, 200, 250, 400, 800, 1,600, and 2,400 mg L^{-1}. The total contact time was 120 min and samples were taken at initial and final times. The pH was initially adjusted to the desired value and it was kept constant with 0.1 N HCl and 0.1 N NaOH solutions. After 120 minutes the final lead concentrations were measured by an absorption spectrophotometer (Perkin Elmer, model A Analyst 200).

Theoretical background

Biosorption capacity is the one of the most important characteristics of a biosorbent. It is the amount of sorbate taken up by the biosorbent, per unit mass of the biosorbent.

Biosorption capacity is of paramount importance to the capital cost because it dictates the amount of biosorbent required, which also fixes the volume of the adsorbed vessels. The biosorption capacity of Pb(II) at equilibrium q_e (mg g^{-1}) was calculated according to the following mass balance equation for the metal ion concentration:

$$q_{\mathrm{e}} = \frac{C_{\mathrm{i}} - C_{\mathrm{e}}}{m} V \tag{1}$$

where q_{e} (mg g^{-1}) is the amount biosorbed at equilibrium, C_{i} (mg L^{-1}) and C_{e} (mg L^{-1}) are the initial and the equilibrium metal concentrations, respectively, m (g) is the mass of biosorbent and V (L) is the volume of solution.

Isotherms were obtained by equilibrating metal ion solutions of different initial Pb(II) concentrations. The equilibrium can be described using adsorption isotherm models (Aksu & Tezer 2005). There are numerous isotherm models, which are usually based on different theoretical assumptions and that have a different number of parameters (degrees of freedom). Supplementary Table S2 (available online at http://www.iwaponline.com/wst/072/153.pdf) shows the main models from the literature with number of parameters and degrees of freedom.

In this work, four models of two parameters (Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin) and three models of three parameters (Redlich–Peterson, Sips, and Toth) were selected. These models are described below.

Langmuir isotherm

The Langmuir isotherm assumes that biosorption takes place at specific homogeneous sites on the surface of the adsorbent, meaning once a lead molecule occupies a binding site, no further biosorption can occur at that site (Langmuir 1918). The Langmuir isotherm model can be presented by Equation (2):

$$q_{\mathrm{e}} = \frac{b \cdot q_{\mathrm{m}} \cdot C_{\mathrm{e}}}{1 + b \cdot C_{\mathrm{e}}} \tag{2}$$

where C_{e} is the equilibrium lead concentration in the solution (mg L^{-1}), q_{e} is the equilibrium lead uptake on the biosorbent (mg g^{-1}), q_{m} is the maximum biosorption capacity (mg g^{-1}), and b is the Langmuir constant that is related to the affinity of binding sites and is related to the energy of sorption (L mg^{-1}).

Freundlich isotherm

The Freundlich isotherm model describes a multilayer adsorption with the assumption of a heterogeneous surface in which the energy, a term in the Langmuir equation, varies as a function of the surface coverage (Freundlich 1906). The model can be presented as:

$$q_{\mathrm{e}} = K_{\mathrm{F}} \cdot C_{\mathrm{e}}^{1/n} \tag{3}$$

where K_{F} (L g^{-1}) and n (dimensionless) are characteristic constants that indicate the extent of the biosorption and the degree of non-linearity between solution concentration and biosorption, respectively.

Dubinin–Radushkevich isotherm

Another isotherm usually used in biosorption study is that proposed by Dubinin & Radushkevich (1947). Those authors indicated that solid characteristics are related to the porous structure of the solid. The isotherm can be represented by Equation (4):

$$q_{\mathrm{e}} = q_{\mathrm{m}} \cdot \mathrm{e}^{(-B \cdot \varepsilon^2)} \tag{4}$$

where q_{m} (mol g^{-1}) is the maximum biosorption capacity in the equilibrium (it can be also represented as mg g^{-1}), B is a model constant (mol^2 kJ^{-2}), and ε is the Polanyi potential and is represented by:

$$\varepsilon = R \cdot T \cdot \ln\left(1 + \frac{1}{C_{\mathrm{e}}}\right) \tag{5}$$

where R is the universal gas constant (kJ mol^{-1} K^{-1}), T is the temperature (K). The constant B is the activity coefficient related to the mean free adsorption energy.

$$E = \frac{1}{\sqrt{2B}} \tag{6}$$

where E is the average value of sorption energy (kJ mol^{-1}). This value gives information about the biosorption mechanism, either physical or chemical (Hany *et al.* 2014). If the E-value lies between 8 and 16 kJ mol^{-1}, the biosorption process occurs chemically and if $E < 8$ kJ mol^{-1}, the biosorption process takes place physically (Lodeiro *et al.* 2006; Sari & Tuzen 2008; Amjad *et al.* 2013).

Temkin isotherm

The Temkin isotherm (Temkin & Pyhev 1940) takes into account the adsorbent–adsorbate interactions on the adsorbent surface. The Temkin isotherm assumes that sorption

energy of all molecules in the layer decreases linearly with the coverage due to adsorbent–adsorbate interactions. Hamdaoui & Naffrechoux (2007) proposed Equation (7):

$$\theta = \frac{R \cdot T}{\Delta Q} \ln K_0 \cdot C_e \tag{7}$$

where θ is the fraction cover (q_e/q_m), ΔQ is the energy change sorption (kJ mol^{-1}) and K_0 is the Temkin equilibrium constant (L mg^{-1}).

Redlich–Peterson isotherm

The Redlich–Peterson isotherm (Redlich & Peterson 1959) contains three parameters and it is an empirical equation that may be used to represent adsorption equilibrium over a wide concentration range. The mechanism of adsorption is a hybrid model featuring both Langmuir and Freundlich isotherms and it does not follow ideal monolayer adsorption (Prasad & Srivastava 2009). The Redlich–Peterson isotherm is given by Equation (8) (Ho *et al.* 2002):

$$q_e = \frac{A \cdot C_e}{1 + B \cdot C_e^g} \tag{8}$$

where A and B are two constants (L g^{-1} and (L mg^{-1})^g, respectively) and g is an exponent that describes the system heterogeneity (between 0 and 1). When $g = 1$, Equation (8) can be simplified to the Langmuir isotherm and when $g = 0$, Equation (8) can be simplified to the Henry law. From Equation (8) and by non-linear regression, model parameters can be obtained.

Sips isotherm

The Sips isotherm is a combination of the Langmuir and Freundlich models and it is mainly used to describe heterogeneous surfaces. When sorbate concentration is low, it is reduced to the Freundlich isotherm, while when sorbate concentration is high, it predicts a biosorption capacity in monolayer which is characteristic of the Langmuir isotherm (Günay *et al.* 2007). The Sips isotherm is given by Equation (9):

$$q_e = \frac{b \cdot q_m \cdot C_e^{1/n}}{1 + b \cdot C_e^{1/n}} \tag{9}$$

where all parameters have the same meaning as in the Langmuir and Freundlich isotherms.

Toth isotherm

The Toth isotherm (Toth 1962), derived from potential theory, has been used to describe the adsorption process in heterogeneous systems. This isotherm assumes an asymmetric quasi-Gaussian power distribution and it considers that most of the binding sites have sorption energy less than the mean value. The Toth isotherm is given by Equation (10):

$$q_e = \frac{q_m \cdot C_e}{\left((1/K_1) + C_e^{1/n} \right)^n} \tag{10}$$

where q_m is the Toth maximum biosorption capacity (mg g^{-1}), K_1 is the Toth equilibrium constant (L mg^{-1}), and n the Toth exponent (it is the same n as for the Freundlich equation). When $n = 1$, Equation (10) is reduced to the Langmuir equation.

RESULTS AND DISCUSSION

Characterization of biosorbents

A summary of physicochemical properties of both biosorbents and the main changes produced during chemical treatments is shown in Supplementary Table S1 (online at http://www.iwaponline.com/wst/072/153.pdf). The physicochemical characterization of biosorbent is vital to understand the metal binding mechanism onto biomass. Thus, most treatments improve properties of biosorbent in order to increase its biosorption capacity. Some changes are produced on the biosorbent surface (such as increasing the surface area or increasing the average pore volume and the pore diameter) and other changes are produced on functional groups of biosorbent (adding of new functional groups or changing percentages of lignin and holocellulose compounds). These changes have been comprehensively studied in previous works (Calero *et al.* 2013a; Martín-Lara *et al.* 2013), but a summary table helps to understand better the results of this paper.

Equilibrium biosorption

The study of equilibrium biosorption provides fundamental physicochemical data to evaluate the applicability of the biosorption process to real scale. This equilibrium biosorption is usually described by equations (isotherms), whose

parameters are related to superficial properties of biosorbents, their biosorption capacity, and the affinity of sorbent and the sorbate at constant temperature and pH. The obtained isotherms for untreated and chemically treated OS and OTP at respective operational conditions are shown in Figures 1 and 2.

It is observed for both biosorbents that maximum biosorption capacity of lead increased significantly when biosorbents were chemically treated. This is related to modifications of the superficial properties of the biosorbents (facilitating the binding of ions with their surfaces) and to modifications in mechanisms of binding implicated in the biosorption process. Thus, the maximum biosorption capacity of untreated OS was 6.3 mg g^{-1} while for chemically treated OS with HNO_3, H_2SO_4, and NaOH this value was 49.1 mg g^{-1}, 14.8 mg g^{-1}, and 38.9 mg g^{-1},
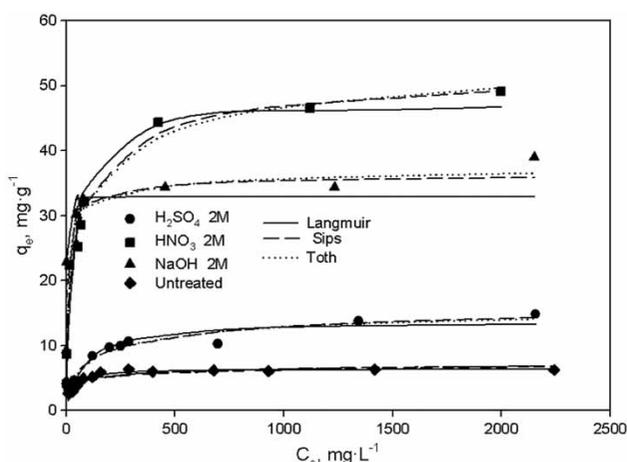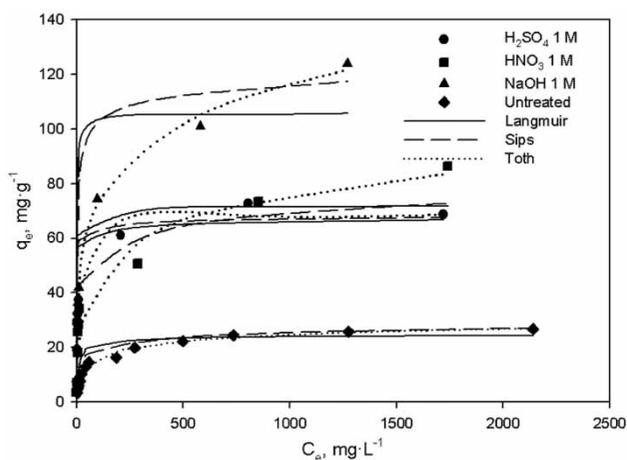
respectively. The maximum biosorption capacity of untreated OTP and chemically treated OTP with HNO_3, H_2SO_4, and NaOH was 26.7 mg g^{-1}, 86.4 mg g^{-1}, 72.78 mg g^{-1}, and 123.80 mg g^{-1}, respectively.

However, an important loss of mass is produced during treatment. Thus, for a more objective analysis, this is taken into account in the results of biosorption capacity. Table 1 shows the value of biosorption capacity of treated solid (q_e), a relative value of biosorption capacity which included the loss of mass and refers to 1 g of untreated biosorbent (q_{er}) and the relation between this value and the biosorption capacity of untreated biosorbent (q_{es}).

It is observed that the relation between relative biosorption capacity (q_{er}) and biosorption capacity of untreated biosorbent (q_{es}) was higher than 2 for all cases. The maximum value for each biosorbent was 6.62 for OS treated with 2 M HNO_3 and 2.47 for OTP treated with 1 M NaOH. Results show that all chemical treatments improve the biosorption capacity of untreated biosorbent, including the most unfavorable treatment, which duplicates this value. From the viewpoint of practical application it is interesting that this value is as high as possible.

Fitting data models

For a better understanding of the Pb(II) biosorption mechanism, data were fitted to several equilibrium isotherm models. In this work, a total of seven models were selected: four of two parameters (Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin) and three of three parameters (Redlich–Peterson, Sips, and Toth). Results are given in Tables 2 and 3 for OS and OTP, respectively.

Comparison between models

In general, models fitted better the OTP results than OS ones (higher values of R^2). Data were fitted by the Langmuir

Figure 1 │ Experimental biosorption isotherms for untreated and chemically treated OS and fitted isotherm by Langmuir, Sips, and Toth models.

Figure 2 │ Experimental biosorption isotherms for untreated and chemically treated OTP and fitted isotherm by Langmuir, Sips, and Toth models.

Table 1 │ Biosorption capacity of each chemically treated biosorbent, its relative value, and the relation between this value and the biosorption capacity of untreated biosorbent

Biosorbent		Loss of mass, %	q_e, mg g^{-1}	q_{er}, mg g^{-1}	q_{er}/q_{ers}
OS: q_{es} = 6.3 mg g^{-1}	HNO_3, 2 M	13.9	49.13	42.30	6.62
	H_2SO_4, 2 M	14.3	14.83	12.70	2.01
	NaOH, 2 M	36.8	38.93	24.60	4.00
OTP: q_{es} = 26.7 mg g^{-1}	HNO_3, 1 M	35.1	86.40	56.07	2.10
	H_2SO_4, 1 M	27.5	72.78	52.76	1.98
	NaOH, 1 M	46.7	123.80	65.98	2.47

Table 2 | Biosorption isotherm constants for lead ion onto untreated and chemically treated OS

Parameters	OS	HNO₃-OS	H₂SO₄-OS	NaOH-OS
Two-parameter models				
Langmuir model				
q_m, mg g^{-1}	6.412	47.467	13.769	32.934
b, L mg^{-1}	0.0390	0.0303	0.0126	1.9400
R^2	0.943	0.943	0.903	0.902
$\sum(q_{exp} - q_{cal})^2$	1.27	115.38	10.86	110.08
Freundlich model				
K_F, (mg g^{-1}) (L mg^{-1})$^{1/n}$	2.452	11.170	2.531	16.620
n	7.30	4.85	4.29	8.62
R^2	0.772	0.919	0.929	0.828
$\sum(q_{exp} - q_{cal})^2$	5.08	165.07	7.97	129.77
Dubinin–Radushkevich model				
q_m, mol g^{-1} (mg g^{-1})	4.51×10^{-5} (8.53)	3.41×10^{-5} (70.78)	1.04×10^{-4} (21.45)	2.16×10^{-4} (44.80)
B, mol kJ^{-2}	0.0017	0.0023	0.0029	0.0011
E, kJ mol^{-1}	17.24	14.61	13.04	21.22
R^2	0.839	0.965	0.951	0.885
$\sum(q_{exp} - q_{cal})^2$	8.35×10^{-11}	1.69×10^{-9}	1.27×10^{-10}	2.99×10^{-9}
Temkin model				
ΔQ, kJ mol^{-1}	20.76	19.29	17.13	22.84
K_0, L mg^{-1}	4.722	1.573	0.374	9.761
R^2	0.840	0.986	0.956	0.899
$\sum(q_{exp} - q_{cal})^2$	3.56	29.33	5.00	112.87
Three-parameter models				
Redlich–Peterson model				
A, L g^{-1}	2.110	4.970	0.525	90.200
B, (L mg^{-1})^g	0.784	0.256	0.112	3.650
g	0.88	0.87	0.84	0.95
R^2	0.816	0.984	0.959	0.949
$\sum(q_{exp} - q_{cal})^2$	4.10	33.44	4.63	57.38
Sips model				
q_m, mg g^{-1}	8.680	55.019	18.756	37.363
b, L mg^{-1}	0.231	0.104	0.063	0.799
n	2.78	1.73	1.95	2.25
R^2	0.863	0.985	0.955	0.913
$\sum(q_{exp} - q_{cal})^2$	3.04	30.33	5.09	97.72
Toth model				
q_m, mg g^{-1}	8.245	63.685	17.428	41.692
K_1, L mg^{-1}	1.091	0.400	0.032	2.219
n	2.93	2.81	1.95	2.00
R^2	0.891	0.988	0.955	0.953
$\sum(q_{exp} - q_{cal})^2$	2.42	24.63	5.04	52.45

Table 3 | Biosorption isotherm constants for lead ion onto untreated and chemically treated OTP

Parameters	OTP	HNO$_3$-OTP	H$_2$SO$_4$-OTP	NaOH-OTP
Two-parameter models				
Langmuir model				
q_m, mg g^{-1}	24.747	72.350	68.540	106.300
b, L mg^{-1}	0.0265	0.0699	0.1700	0.0779
R^2	0.952	0.908	0.960	0.926
$\sum(q_{exp} - q_{cal})^2$	38.38	600.34	211.04	1031.69
Freundlich model				
K_F, (mg g^{-1}) (L mg^{-1})$^{1/n}$	4.639	14.598	21.410	21.800
n	4.14	4.21	5.81	4.09
R^2	0.949	0.968	0.895	0.982
$\sum(q_{exp} - q_{cal})^2$	41.89	207.76	551.18	244.20
Dubinin–Radushkevich model				
q_m, mol g^{-1} (mg g^{-1})	1.96×10^{-4} (40.66)	5.63×10^{-4} (166.60)	4.67×10^{-4} (96.67)	8.59×10^{-4} (178.80)
B, mol kJ^{-2}	0.0028	0.0025	0.0018	0.0024
E, kJ mol^{-1}	13.34	14.16	16.77	14.33
R^2	0.979	0.966	0.926	0.994
$\sum(q_{exp} - q_{cal})^2$	3.95×10^{-10}	5.09×10^{-9}	9.09×10^{-9}	1.97×10^{-9}
Temkin model				
ΔQ, kJ mol^{-1}	17.31	21.09	22.20	24.26
K_0, L mg^{-1}	0.621	1.543	6.398	5.154
R^2	0.990	0.963	0.919	0.964
$\sum(q_{exp} - q_{cal})^2$	8.33	198.40	126.90	510.94
Three-parameter models				
Redlich–Peterson model				
A, L g^{-1}	1.34	18.57	13.22	44.75
B, (L mg^{-1})^g	0.138	0.932	0.238	1.487
g	0.86	0.81	0.97	0.80
R^2	0.990	0.975	0.962	0.998
$\sum(q_{exp} - q_{cal})^2$	7.96	162.86	196.74	30.82
Sips model				
q_m, mg g^{-1}	31.884	96.41	68.304	133.40
b, L mg^{-1}	0.074	0.128	0.161	0.143
n	1.780	2.130	0.956	1.950
R^2	0.988	0.953	0.960	0.986
$\sum(q_{exp} - q_{cal})^2$	9.48	304.69	210.57	191.83
Toth model				
q_m, mg g^{-1}	23.268	93.181	68.953	129.84
K_1, L mg^{-1}	0.147	0.252	0.185	0.210
n	2.67	2.39	1.09	2.03
R^2	0.990	0.950	0.963	0.995
$\sum(q_{exp} - q_{cal})^2$	8.05	194.93	196.38	76.05

isotherm with values of $R^2 > 0.90$ for all studied biosorbents. Values of maximum biosorption capacities (q_m) were similar to experimental results, confirming the validity of this model. Best results for q_m value were obtained for OS treated with 2 M HNO_3 and OTP treated with 1 M NaOH. This is in accordance with results obtained from characterization studies (Calero *et al.* 2013a; Martín-Lara *et al.* 2013), where it is shown that chemical treatments that more greatly improved the biosorption capacity of each biosorbent were the same. However, the operational parameter b, which relates the affinity of biosorbent to the sorbate, did not undergo important changes with chemical treatment, indicating that chemical treatment did not affect the affinity that biosorbent presents by the ion (according to the definition of parameter b). The Dubinin–Radushkevich isotherm provided high values of R^2. As well, values of mean free energy of biosorption (E) indicated that the mechanism of lead biosorption was mainly a chemical process, predominating the ionic interchange. These values were 17.24, 14.61, 13.04, and 21.22 kJ mol^{-1} for untreated OS, HNO_3-OS, H_2SO_4-OS, and NaOH-OS respectively, and 13.34, 14.16, 16.77, and 14.33 kJ mol^{-1} for untreated OTP, HNO_3-OTP, H_2SO_4-OTP, and NaOH-OTP, respectively. The Temkin model provided a good fit of results with values of energy change sorption (ΔQ) in the range between 17 and 24 kJ mol^{-1} for two biosorbents and the same magnitude order as that obtained by the Dubinin–Radushkevich model. Three-parameter models, in general, showed better values of R^2 (all higher than 0.90 except for untreated OS). Thus, for the Redlich–Peterson model, data were highly fitted by this isotherm with values of $R^2 > 0.95$ (except for untreated OS). Values of parameter g were close to 1 (higher than 0.80 for all studied biosorbents), indicating that the model had a trend to the Langmuir isotherm. The Sips model also represented adequately the experimental results, with obtained values of maximum biosorption

capacity very similar to experimental values and obtained by the Langmuir model. However, the parameter n was lower than 1. Finally, the obtained results by the Toth model were very similar to those obtained by Sips, both in values of biosorption capacity as well as in values of parameter n. For untreated and treated OS, in all cases the Langmuir model was the best to fit the data (highest values of R^2 and lowest values of $\sum(q_{exp} - q_{cal})^2$. However, for OTP, the Redlich–Peterson and Toth models were the best fitted for experimental results. Moreover, for OTP the difference between models was lower than for OS, giving all of them a good fit. This is also observed in Table 4, which shows experimental biosorption capacity and that obtained by better models. Figures 1 and 2 present the experimental results and fitted ones by the same models.

Comparison between biosorbents

Comparing values of biosorption capacity for each biosorbent (Tables 2 and 3), it is observed that values for treated OTP were higher than for treated OS. Moreover, comparing data obtained from the best models (Table 4), it is observed that results for OTP were better than for OS, with values of biosorption capacity around four times higher. Thus, the best results of q_m for OS and OTP were 49.13 mg g^{-1} and 123.80 mg g^{-1}, respectively, and they were obtained with HNO_3 treatment for OS and NaOH treatment for OTP.

However, taking into account values for untreated biosorbent (four times higher for OTP than for OS) and loss of mass (also higher for OTP during chemical treatment), it is concluded that chemical treatment for OS was more effective than for OTP, as values of q_{er}/q_{es} were higher for the first biosorbent. Regarding different chemical treatments for each biosorbent, it is determined that for OS the best results were obtained with treatment with 2 M HNO_3, giving a maximum value of biosorption capacity (49.13 mg g^{-1}) and a

Table 4 │ Experimental value of biosorption capacity and that obtained for models which reproduced better results

Biosorbent		Experimental	Langmuir	Sips	Toth
		q_m, mg g^{-1}			
OS	Untreated	6.33	6.41	8.68	8.26
	HNO_3	49.13	47.47	55.02	63.69
	H_2SO_4	14.83	13.77	18.76	17.43
	NaOH	38.93	32.93	37.36	41.69
OTP pruning	Untreated	26.72	24.75	31.68	36.27
	HNO_3	86.40	72.35	96.41	93.18
	H_2SO_4	72.78	68.54	68.30	68.95
	NaOH	123.80	106.30	133.40	129.84

minimum value of loss of mass (13.9%). For OTP the best result was obtained with treatment with 1 M NaOH, reaching a maximum value of biosorption capacity (123.80 mg g^{-1}); however the loss of mass was also high (46.7%). Maximum values of the relation (q_{er}/q_{es}) were 6.62 and 2.47 for HNO$_3$-OS and NaOH-OTP, respectively. It would be interesting to perform a more exhaustive economical analysis to determine from those values whether chemical treatment can be considered viable to use in real scale.

CONCLUSIONS

Two wastes of olive-oil production (OS and OTP) were chemically modified with three chemical solutions (HNO$_3$, H$_2$SO$_4$, and NaOH) and changes in physicochemical characteristics and biosorption properties were studied. Results showed that chemical treatments improved greatly the biosorption capacity of lead. Experimental isotherm tests were performed and the experimental maximum biosorption capacities obtained were 6.33, 49.13, 14.83, and 38.93 mg g^{-1} for untreated, HNO$_3$-OS, H$_2$SO$_4$-OS, and NaOH-OS, respectively, and 26.72, 86.40, 72.78, and 123.80 mg g^{-1} for untreated, HNO$_3$-OTP, H$_2$SO$_4$-OTP, and NaOH-OTP, respectively. Moreover, an effectiveness coefficient (q_{er}/q_{es}) was determined for each adsorbent material in order to take into consideration the loss of mass during chemical treatment. Results showed that the treatments that improved lead biosorption capacity more were treatments with HNO$_3$ for OS ($q_{er}/q_{es} = 6.62$) and with NaOH for OTP ($q_{er}/q_{es} = 2.47$). Data obtained were subject to equilibrium modeling using different isotherm models: Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Redlich–Peterson, Sips, and Toth. The better models were Langmuir, Toth, and Sips for OS, and Langmuir, Redlich–Peterson, and Toth for OTP.

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