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Comparison of two models for the biosorption of Pb(II) using untreated and chemically treated olive stone: Experimental design methodology and adaptive neural fuzzy inference system (ANFIS)

A. Ronda*, M.A. Martín-Lara, A.I. Almendros, A. Pérez, G. Blázquez

Department of Chemical Engineering, University of Granada, Granada 18071, Spain

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ABSTRACT

The main objective of this work is to fit results from lead biosorption by untreated and chemically treated olive stone (OS) using two models: means of full factorial design methodology and fuzzy neural network. Concretely, OS was modified by three chemical agents: HNO_3, H_2SO_4 and NaOH, in order to improve its biosorption capacity. The examined operational variables were: concentration of chemical agent (0.1–2 M), pH (3–5) and initial lead concentration (50–250 mg/L), and the studied response was biosorption capacity (mg/g).

Results obtained from full factorial design methodology showed that all these factors considerably affected the studied response. Experimental results were fitted by a second-order equation showing the influence of each factor and their interactions. While the application of a fuzzy neural network model allowed to predict the results for the dependent variables as a function of the operating conditions used with errors less than 5% in all cases. Observed results were different when the biosorbent was treated with acid treatment or with basic one, although for all treatments the highest biosorption capacity was obtained with a concentration 2 M. Finally, models were compared and it is showed that ANFIS model predicted better experimental data with higher R^2 values.

1. Introduction

The pollution of environment with toxic heavy metals is spreading through the world along with industrial progress. Heavy metal ions can accumulate in the food chain, which posed a severe danger to human health [1]. The World Health Organization (WHO) recommends that the maximum acceptable concentration levels of lead in drinking water is 10 μg/L. Taking into consideration the necessity to reduce the emission of this metal to environment to diminish its negative impacts and its possible repercussion in the health of the population, it becomes necessary to look for feasible economic and environmental alternatives that allow keeping the levels of these polluting agents in the permissible range [2]. In this context, biosorption is an alternative to lead removal, because it has significant advantages in comparison with conventional methods, especially from economical and environmental viewpoints [3–6].

High number of agricultural waste materials have been utilized as adsorbents of heavy metals: tea and cactus leaves, almond shells, olive tree pruning waste, pine cone, black cumin, coconut shell, hyacinth roots, wastes of rice, *etc.* [7–10]. Agriculture waste materials contain proteins, polysaccharides and lignin, which containing multifunctional groups such as hydroxyl, carbonyl and carboxyl, play vital role for metal uptake purpose [10,11]. Moreover, chemical treatment of wastes determines an increase of active sites concentration and waste biosorbing capacity [12–20]. Rivera et al., in 1986 [21], were the first to use the chemically treated olive stone to obtain a activated carbons to remove lead from water. They crushed and sieved raw olive stones and then they treated them with 10% sulphuric acid. They obtained an increase in biosorption capacity. Recently, activated carbons have been considered unique adsorbents because of their extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity [22]. As current, nanotubes has been studied as biosorbent to heavy metals [23,24]. However, these materials are expensive and they have a complex preparation process. The use of chemically treated wastes has emerged as one of the most effective and most cheapest technologies for removing metals ions from wastewater. In this study the untreated and chemically treated olive stone are compared to remove Pb(II) ions.

* Corresponding author at: University of Granada, Department of Chemical Engineering, Avda. Fuentenueva s/N 18071 Granada, 18071 Granada, Spain. Tel.: +34958240445.

E-mail address: alirg@ugr.es (A. Ronda).

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Spain, Italy and Greece account for about 97% of Europe Union olive oil production, with Spain producing approximately 62% of this amount. Nowadays, the production of olive oil generates a high amount of olive stones. Taking into account that the olive cultivation is the fifth most cultivated product in Spain (the Spanish olive production in 2011 was nearly 7 million tons), high amount of olive stone as agroindustrial waste is produced in this country. Olive stone remains available as a waste product, for which no important industrial use has been developed, so it is normally incinerated or dumped without control. Although nowadays the olive stone is being used as fuel, a high amount of this waste remains without any application. Therefore the utilization, the study of other alternative uses, and the environmental concerns it presents are all extremely important [18].

The conventional studies during the development of a process involve variation of one factor at a time, keeping all other factors constant. In order to elucidate the influence of several operational variables jointly in a studied response, the experimental factorial design and statistical analysis by adaptive neural fuzzy inference system were used in this work. The factorial design [25] involves changing all variables from one experiment to the next. The design determines which factors have important effects on the response as well as how the effect of one factor varies with the level of the other factors [26]. The statistical analysis by adaptive neural fuzzy inference system (ANFIS) was originally developed by Jang [27] and it has been successfully used to simulate and control various processes [28,29].

The main objectives of the present study include the following:

- To study the effect of chemical treatment of olive stone to improve its biosorption capacity.
- To study all main individual and interaction effects on biosorption capacity of three operational parameters: concentration of chemical agent, pH and initial lead concentration.
- To model experimental data by two models: full factorial design to obtain a second-order regression equation and adaptive neural fuzzy inference system.
- To explain the biosorption capacity in two mathematical models.
- To compare both models by representing experimental and modeled data.

2. Materials and methods

2.1. Biomass

The olive stone (OS) is a waste produced in the olive oil extraction process. The OS used for this study was provided by an oil extraction plant located in Jaén (Spain). The stones were obtained from the separation process of the olive cake with an industrial pitting machine. The solid was milled with an analytical mill (IKA MF-10) and <1.000 mm fraction was chosen for the study. Finally, this fraction was treated with different chemical solutions to increase its biosorption capacity.

2.1.1. Modification by chemical treatment of the raw biomass

The chemical modification of OS was performed using three chemical solutions: nitric acid (HNO_3), sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH). The solutions for treatment were prepared at different concentrations (0.1 M, 1 M and 2 M) to analyze the effect of concentration of chemical agent on the biosorption capacity and lead removal percentage. One liter of these solutions and 10 g of biomass were mixed in a flask at constant temperature (50 °C). Biomass and chemical solution were kept in contact during 24 h. After, the biomass was repeatedly washed with distilled water until the pH of rising water remained constant. Finally, the chemically treated OS was dried in an oven at 40 °C during 24 h and after it was stored in a hermetic container for later use.

2.2. Preparation of lead solutions

A stock solution of 2000 mg/L Pb(II) was prepared by dissolving desired amount of $Pb(NO_3)_2$ in 500 mL of distilled water. Later, solutions of different concentrations were prepared by appropriate dilution of the above stock Pb(II) solution.

2.3. Characterization of untreated and chemically treated olive stone

Because the characterization of the waste is a very important aspect to analyze its behavior, a summary of obtained results in previous studies for untreated and chemically treated OS [18] is shown in Table 5.

2.4. Batch biosorption test

To compare two models, the biosorption capacity response was fitted for untreated and chemically treated OS. Thus, several biosorption experiments were performed in duplicate. They were conducted in a batch system and at constant temperature (25 °C). One gram of biomass and 100 mL of Pb(II) solution were mixed in a thermostatic flask. Experiments were carried out keeping the pH around 5 (pH was adjusted with 0.1 N HCl and 0.1 N NaOH solutions). After 120 min the final lead concentrations were measured using absorption spectrophotometer (PerkinElmer, model AAnalyst 200). The biosorption capacity at equilibrium q_e (mg/g) was calculated according to the following mass balance equation for the metal ion concentration:

$$q_e = \frac{(C_i - C_e) \cdot V}{m} \quad (1)$$

where C_i is the initial Pb(II) concentration (mg/L), C_e is the equilibrium Pb(II) concentration in solution (mg/L), V is the volume of the solution (L), and m is the mass of the biosorbent used (g).

2.5. Study of the operational factors

Parameters like pH, contact time, biosorbent dosage or temperature are very important in a biosorption process. However, these parameters have been studied before for untreated OS [17,26,30–32]. In this work the main goal is to study the effect to perform a chemical treatment on OS, therefore only parameters with highest influence in the treatment of biosorbents were studied in this work. Thus, the used chemical agent for the treatment, the concentration of the chemical solution for treatment and the pH were the studied factors. Other parameters were kept constant according to results of previous studies.

2.5.1. Effect of type of chemical treatment

First, the effect of type of chemical treatment of OS was studied. For this aspect it is important to know if the treatment improves the biosorption of lead process. Experiments with three agents were performed: two acid (HNO_3 and H_2SO_4) and one basic (NaOH) and the change of the biosorption capacity was studied. These experiments were carried out at followed conditions: treatment concentration = 1 M, pH 5, initial lead concentration =150 mg/L, biosorbent concentration = 10 g/L; contact time = 120 min; temperature = 25 °C and volume solution = 100 mL.

2.5.2. Analysis of three operational factors: chemical agent concentration, pH and initial lead concentration

After knowing that the treatment of OS improves the biosorption process of lead, the chemically treated OS were chosen to analyze the other operational factors. First, the influence of each factor onto biosorption capacity was analyzed. After, the effect of all factors together onto biosorption capacity was analyzed using two models.

Table 1
Values and levels of operating parameters.

Factors	Levels		
	−1	0	+1
A: Concentration of treatment solution (M)	0.1	1	2
B: pH	3	4	5
C: Initial concentration of lead (mg/L)	50	150	250

2.6. Modeling by full factorial design (FFD)

To develop a model for lead biosorption, factors previously analyzed were studied. Factorial designs allow the simultaneous study of the effects that several factors may have on the optimization of a particular process with less number of experiments [33,34]. It determines which factors have the important effects on the response as well as how the effect of one factor varies with the level of the other factors. The effects are the differential quantities expressing how a response changes as the levels of one or more factors are changed. Also, factorial designs allow measuring the interaction between each different group of factors.

The analysis of factors was performed for data obtained with chemically treated OS by HNO_3, H_2SO_4 and NaOH and the biosorption capacity of Pb(II) as response (Y). Studied factors were: chemical solution concentration for treatment (A), pH (B) and initial Pb(II) concentration (C) and the codified three levels: low (−1), intermediate (0) and high (+1). Then, 27 (3^3) measurements are required to perform a factorial design analysis. Table 1 shows values and levels of operating parameters. The factorial design analysis was performed for OS with three treatments and results were compared.

2.7. Statistical analysis by adaptive neural fuzzy inference system (ANFIS)

Fuzzy modeling, is a powerful tool for describing non-linear behavior in complex systems. Since the 1980s, the theory of fuzzy logic has been successfully used by a number of researchers to simulate and control fermentation and anaerobic digestion processes [35]. Neural networks, which were developed by analogy with the functioning of neurons in living beings [36], constitute one other powerful tool for modeling complex systems. The ANFIS paradigm is a multilayer feed-forward back-propagation network, which is an adaptive network functionally equivalent to a Sugeno fuzzy model. The adaptive network can tune the fuzzy system with a back propagation algorithm based on the collection of input–output data. This confers the fuzzy system the ability to learn [29]. The architecture and learning procedure for ANFIS are described in detail elsewhere [37]. Integrating fuzzy systems and neural networks combine advantages of two systems and provide an especially powerful modeling tool [29]. However, the main limitations of the ANFIS model can appear in area of studied range where experimental data are insufficient. For that, to obtain a good model it is necessary to use a significant number of data using different operational conditions (is to say, experimental data have to be representative of the whole range). On the other hand, the convergence of the ANFIS model solves the problem caused when the premise parameters are not fixed (which increases the search space and becomes the convergence of training slower). The ANFIS uses a learning algorithm, which decreases the search space and the algorithm converges faster. When experimental data are fitted using the ANFIS model, the convergence of solution can be forced to obtain a minimum error. However, though it may enhance performance it can cause a low stability of the response. To avoid this problem an error tolerance must be defined to obtain the model, instead to force the model to an error equal to zero [38]. In this case, the fixed error tolerance was 0.0001.

Table 2
Values and levels of operating parameters.

Fuzzy Rule	Constant	Levels		
		A	B	C
FR_1	c_1	Low	Low	Low
FR_2	c_2	Low	Low	Medium
FR_3	c_3	Low	Low	High
FR_4	c_4	Low	Medium	Low
FR_5	c_5	Low	Medium	Medium
FR_6	c_6	Low	Medium	High
FR_7	c_7	Low	High	Low
FR_8	c_8	Low	High	Medium
FR_9	c_9	Low	High	High
FR_{10}	c_{10}	Medium	Low	Low
FR_{11}	c_{11}	Medium	Low	Medium
FR_{12}	c_{12}	Medium	Low	High
FR_{13}	c_{13}	Medium	Medium	Low
FR_{14}	c_{14}	Medium	Medium	Medium
FR_{15}	c_{15}	Medium	Medium	High
FR_{16}	c_{16}	Medium	High	Low
FR_{17}	c_{17}	Medium	High	Medium
FR_{18}	c_{18}	Medium	High	High
FR_{19}	c_{19}	High	Low	Low
FR_{20}	c_{20}	High	Low	Medium
FR_{21}	c_{21}	High	Low	High
FR_{22}	c_{22}	High	Medium	Low
FR_{23}	c_{23}	High	Medium	Medium
FR_{24}	c_{24}	High	Medium	High
FR_{25}	c_{25}	High	High	Low
FR_{26}	c_{26}	High	High	Medium
FR_{27}	c_{27}	High	High	High

A: Concentration of treatment solution (M); B: pH; C: initial concentration of lead (mg/L).

Changes in biosorption capacity by untreated and chemically treated OS as a function of the operational variables of the biosorption process can be analyzed by model proposed by Jang et al. [39]:

$$y_e = \frac{\sum_{l=1}^{m} y^l \cdot \left[\prod_{i=1}^{n} \mu_{Fi}^l(x_i, \theta_i^l)\right]}{\sum_{l=1}^{m} \left[\prod_{i=1}^{n} \mu_{Fi}^l(x_i, \theta_i^l)\right]} \tag{2}$$

where y_e is the predicted response value, l is the number of level, m is the number of rules, n is the input operational variables, y^l is the defuzzifier and $\mu_{Fi}^l(x_i, \theta_i^l)$ is the members function. To simplify the expression, in this work, the expression $[\prod_{i=1}^{n} \mu_{Fi}^l(x_i, \theta_i^l)]$ is denoted by FR_l, due to it represents a fuzzy rule and it is expressed by the product of n functions. Thus, the expression (2) is replaced by:

$$y_e = \frac{\sum_{l=1}^{m} y^l \cdot FR_l}{\sum_{l=1}^{m} FR_l} \tag{3}$$

In this study, 3 operational variables and 3 levels per each variables have been analyzed. Thus, the Eq. (3) is rewritten as follows:

$$y_e = \frac{\sum_{l=1}^{27} c_l \cdot FR_l}{\sum_{l=1}^{27} FR_l} \tag{4}$$

where c_l is a single constant parameter per each variable and each level. Moreover, each FR_l is the combination of levels (low, medium and high) for each variable (chemical solution concentration for treatment (A), pH (B) and initial Pb(II) concentration (C)). Various methods are available to determine the fuzzy rule for the input data (linear, Gaussian, polynomial, logarithm, *etc.*) for independent variables. Each fuzzy rule determines the type of contribution of this variable in the final output.

Table 2 shows the combination of levels and variables, which give a rule (FR_l) and a constant (c_l).

To reproduce experimental values, Gaussian member functions has been used. A simpler member functions can be used (as a linear membership). However, a previous analysis showed that the minimum error of fitting was obtained with Gaussian functions. Therefore,

Table 3
Experimental results of biosorption test for chemically treated OS in each operational conditions.

Run	Operational conditions			Biosorption capacity (mg/g)		
	$C_{\text{Chemical solution}}$ (M)	pH	$C_{\text{initial Pb(II)}}$ (mg/L)	HNO_3-OS	H_2SO_4-OS	NaOH-OS
1	0.1	3	50	1.49	0.92	4.01
2	0.1	3	150	2.21	1.10	9.52
3	0.1	3	250	2.67	1.09	12.97
4	0.1	4	50	2.97	2.43	5.42
5	0.1	4	150	3.62	3.40	14.39
6	0.1	4	250	4.22	4.10	22.70
7	0.1	5	50	3.15	2.79	4.59
8	0.1	5	150	7.47	5.53	14.68
9	0.1	5	250	5.25	3.59	22.85
10	1	3	50	0.61	1.57	3.84
11	1	3	150	1.29	1.83	10.29
12	1	3	250	2.15	1.89	14.42
13	1	4	50	2.29	1.81	5.49
14	1	4	150	3.75	3.71	14.78
15	1	4	250	5.07	3.80	25.30
16	1	5	50	4.01	2.02	5.00
17	1	5	150	3.87	5.07	14.21
18	1	5	250	5.18	8.70	20.49
19	2	3	50	5.55	3.29	3.94
20	2	3	150	12.13	5.66	10.64
21	2	3	250	18.09	7.34	13.85
22	2	4	50	6.34	4.28	5.62
23	2	4	150	15.32	9.08	17.02
24	2	4	250	25.22	11.8	25.48
25	2	5	50	4.95	4.52	4.78
26	2	5	150	14.55	13.09	14.38
27	2	5	250	25.10	16.47	24.40

Table 4
Experimental data used to validate the proposed ANFIS model.

Run	Operational conditions			Biosorption capacity (mg/g)		
	$C_{\text{Chemical solution}}$ (M)	pH	$C_{\text{initial Pb(II)}}$ (mg/L)	HNO_3-OS	H_2SO_4-OS	NaOH-OS
1	0.5	3.5	100	3.32	2.25	8.95
2	0.5	4.5	200	7.73	5.01	19.46
3	1.5	3.5	200	14.47	7.68	19.01

they have been selected as they provided best results in the validating model. The mathematical expressions for the Gaussian member function and for each level are following:

$$\mu_{low} = exp\left(-0.5 \cdot \left(\frac{x - x_{low}}{L}\right)^2\right) \tag{5}$$

$$\mu_{medium} = exp\left(-0.5 \cdot \left(\frac{x - x_{medium}}{L}\right)^2\right) \tag{6}$$

$$\mu_{high} = exp\left(-0.5 \cdot \left(\frac{x - x_{high}}{L}\right)^2\right) \tag{7}$$

where x_{low}, x_{medium} and x_{high} are the values of each level (low, medium and high) for each variable and L is the width of Gaussian function distribution.

With all previous considerations, Eq. (4) can be expressed as:

$$y_e = \frac{c_1 \cdot FR_1 + c_2 \cdot FR_2 + c_3 \cdot FR_3 + \cdots + c_{25} \cdot FR_{25} + c_{26} \cdot FR_{26} + c_{27} \cdot FR_{27}}{FR_1 + FR_2 + FR_3 + \cdots + FR_{25} + FR_{26} + FR_{27}} \tag{8}$$

All parameters and constants in Eq. (8) were obtained using ANFIS Edit tool in the Matlab software. Finally the ANFIS model used were validated in three further different tests to experimental data used to training the model.

3. Results and discussions

3.1. Biosorption test

Table 3 shows all obtained results in biosorption test. All experiments were performed in duplicate and the average value was taken to study. These experimental data will be fitted according to full factorial design and statistical analysis by adaptive neural fuzzy inference system (ANFIS). Finally three further tests (listed in Table 4) were used to validate the obtained ANFIS model. Values were chosen in the middle of ranges for each operational variable with the objective to properly describe the whole range of data to study.

3.2. Study of the operational factors

3.2.1. Effect of type of chemical treatment

The OS was treated with three chemical treatments (HNO_3, H_2SO_4 and NaOH) to study the effect of chemical treatment in the biosorption capacity. Data obtained from treatment studies were compared with data obtained from untreated OS [40]. Results are shown in Fig. 1 where results obtained with untreated OS were also represented [40]. All treatments improve the biosorption capacity of OS. Improvements on lead biosorption obtained with treatments of OS with respect to untreated OS were 27.76, 29.66, 251.03% by HNO_3-OS, H_2SO_4-OS and NaOH-OS respectively. Although, all treatments improved results compared with untreated OS, the improvement with OS treated by HCl was very low, thus in this case the treatment is not viable. To following studies, this treatment was eliminated, and the effect of the

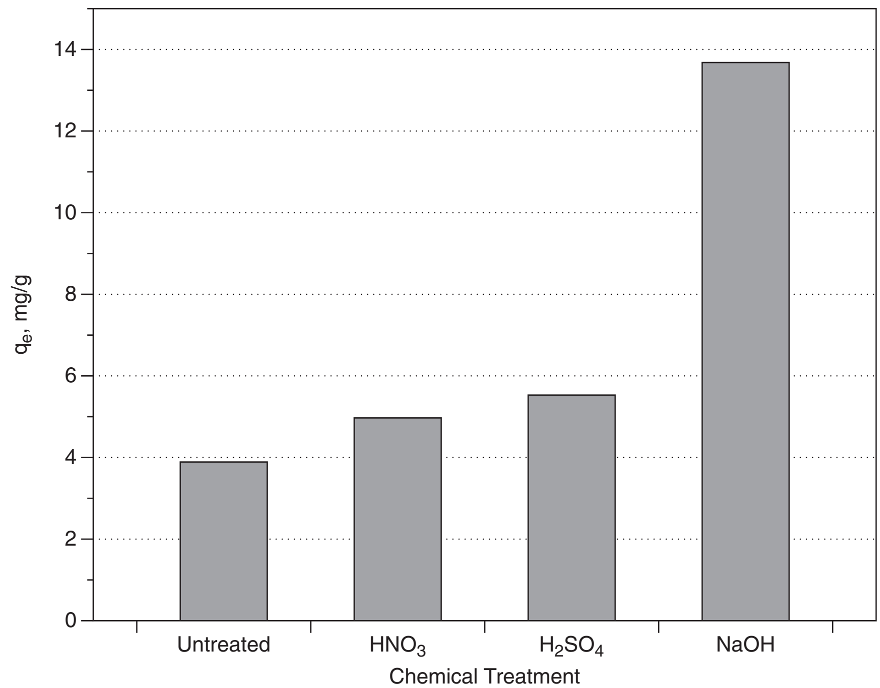

Fig. 1. Effect of type of chemical treatment in biosorption capacity of lead by untreated and treated OS (concentration of chemical agent = 1 M; pH 5; concentration initial of lead = 150 mg/L; concentration of biosorbent = 10 g/L).

other factors were studied only with OS chemically treated with the other agents.

Improvements observed when the biosorbent was treated with chemical agents were similar to results found by other authors: Shroff and Vaidya [14] obtained the best improvement of dead biomass of *Mucorhiemalis* with Na_2CO_3; Shroff and Vaidya [41] improved the biosorption capacity of dead biomass of *Rhizopus arrhizus* with nitric acid; Ofomaja and Naidoo [42] improved the biosorption capacity of pine cone with $Ca(OH)_2$, KOH and NaOH, obtaining the best results with NaOH treatment and Asgher and Bhatti [15] improved the biosorption capacity of *Citrus* waste biomass with acetic acid.

Most of them agree in that the chemical treatment of biomass changes the biosorption capacity of biosorbent, modifying the physicochemical characteristics of it. For this reason, the physicochemical characterization of biosorbent is vital to understanding the metal binding mechanism onto biomass.

Table 5 shows a summary of characterization of OS and the main changes produced with the three treatments. Although main changes were widely analyzed in a previous work [18], include: increasing of the specific area, the total pore volume and the number of binding sites, modification of chemical composition and decreasing of TOC content of the resulting solution after biosorption of lead, among others.

To analyze results, the loss of mass during treatments was taken into account (or yield of treatment), and it was observed that the nitric acid does soluble the lignin, increasing the concentration in weight of holocellulose. However, the opposite effect has the sulphuric acid, it does soluble much celluloses and therefore, the residual percentage of lignin increases. The treatment with sodium hydroxide behaves as a reactive which solubilize to lignin (according its traditional use), but it also attacks to holocellulose.

3.2.2. Study of the effects of factors

- Effect of solution pH

Experiments with OS treated with three chemical agents at concentration of treatment 1 M and at initial lead concentration of 150 mg/L were carried out at three different pH (3, 4 and 5), to study the effect of this factor onto biosorption capacity of olive stone by Pb(II). Results are shown in Fig. 2.

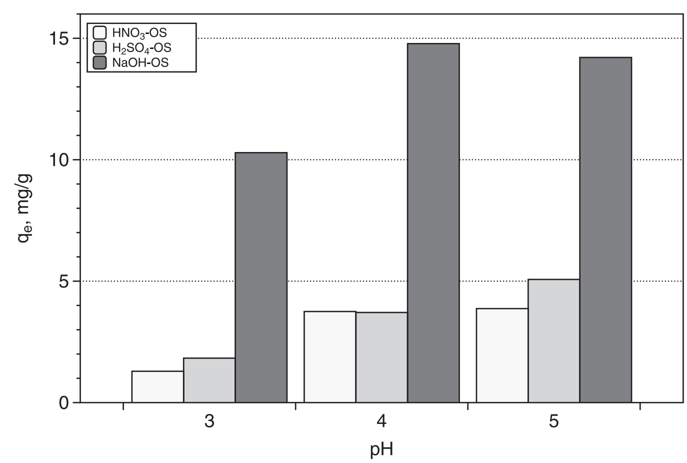

Fig. 2. Effect of pH in biosorption of lead onto biosorption capacity (Concentration of chemical agent = 1 M; concentration initial of lead = 150 mg/L; concentration of biosorbent = 10 g/L).

In Fig. 2 it is also observed that the general trend is biosorption capacity increases when the pH increases. The pH strongly affects biosorption capacity, being various reasons attributed to this relation. Thus, Congeevaram et al. [43] indicated that the pH of the solution had a significant effect on the heavy metal uptake since it controls the extent of surface protonation of the sorbent and the degree of ionization. But the pH value of a solution strongly influences not only the site dissociation of the biomass surface, but also the ionization and speciation of metals in aqueous solution. The diagram of lead species in solution (figure not shown) indicates that the lead precipitated as $Pb(OH)_2$ at pH higher than 5.5 being the process of retention really a combination of biosorption and microprecipitation. The diagram shows that when the pH is lower than 5.5 the main species in the solution is Pb(II). For this reason the study of pH was performed for pH lower than 5.5.

Table 5
Physico-chemical characteristics of biosorbents [18].

Treatment of OS		Untreated OS	HNO_3-OS	H_2SO_4-OS	NaOH-OS
Physical characterization					
BET surface area, m^2/g		0.1625	2.4468	0.5127	0.2543
Pore volume, cm^3/g		0.001840	0.003839	0.001880	0.000463
Pore diameter, Å		453.0230	62.7546	146.6377	72.7604
Particle size, mm		<1	<1	<1	<1
Composition of biosorbent					
Hot water soluble compound, %		12.16	20.45	9.22	19.59
E-B extractive compounds, %		0.76	0.84	0.60	4.98
Lignin, %		25.68	19.55	33.58	26.81
Holocellulose, %		54.70	61.88	56.36	60.82
Proximate analysis					
Moisture, %		5.43	–	–	–
Volatile material, %		74.66	79.00	83.95	78.68
Fixed carbon, %		19.54	20.96	16.03	17.80
Ash, %		0.37	0.04	0.02	3.52
Potentiometric titration					
Total titratable sites, mol/kg		0.0694	0.0767	0.1097	0.272
Acid titratable sites, mol/kg		0.0370	0.0662	0.0735	–
Basic titratable sites, mol/kg		0.0324	0.0105	0.0362	0.272
Point of zero charge (pH_{PZC})		5.17	2.97	2.95	6.77
Total carbon compounds					
TC, mg C/L		36.840	9.183	11.250	17.870
TOC, mg C/L		0.022	0.000	0.000	2.789
TIC, mg C/L		36.820	9.183	11.250	15.080
Loss of biomass					
Loss of biomass, %		–	13.9	14.3	36.8
FTIR analysis					
O–H	Wavenumber, cm^{-1}	3330.0	3331.9	3338.9	3336.8
	A, %	3.69	3.78	3.74	9.51
C–H	Wavenumber, cm^{-1}	2930.1	2898.6	2894.3	2915.5
	A, %	2.42	2.32	2.30	3.77
C=O	Wavenumber, cm^{-1}	1730.4	1737.1	1729.3	–
	A, %	3.13	1.87	2.02	–
C–O	Wavenumber, cm^{-1}	1233.0	1228.2	1227.2	1225.1
	A, %	6.02	4.27	4.70	6.58
C–O alcoholic	Wavenumber, cm^{-1}	1028.7	1027.5	1027.9	1028.5
	A, %	13.14	11.53	12.20	18.74

- Effect of initial lead concentration
  Three chemically treated OS at 1M were used as biosorbent to study the effect of initial lead concentration. Experiments at three concentrations (50, 150 and 250 mg/L) were performed and values of biosorption capacity were obtained. Results are shown in Fig. 3. Results show that in general, the biosorption capacity increases when the initial lead concentration increases. It is due to the driving force in biosorption capacity is the difference between initial and equilibrium concentrations. Thus, while this force increases, the response also increases. This force is higher when concentration of solution is further of equilibrium. It can be concluded that the biosorption capacity will increase with the initial lead concentration until it reaches the equilibrium concentration (it is obtained from the isotherm study).
- Effect of concentration of chemical agent
  The OS was treated at different concentrations of chemical agents (0.1, 1 and 2 M) to study the effect of solution concentration (Fig. 4).
  It is observed that the treatment with NaOH shows good results at all concentrations tested (biosorption capacity around 15 mg/g), nevertheless for acid treatment the behavior is different. The treatment at 1 M does not improve the biosortpion capacity with respect to treatment 0.1 M, even, it is worsen. However, the treatment at 2 M highly improve results, with improvements of 94.78 and 136.71% respect treatment 0.1 M for HNO_3-OS and H_2SO_4 respectively and respect. The chemical treatment changes physicochemical properties of the biosorbent, mainly changes in surface, functional groups and composition of materials. Thus, with the treatment 1 M, change this properties but not enough to obtain an improve. The acid treatment dissolve lignin compounds, but this loss is not compensated with increasing of surface area. There are changes in biosorbent, but the net balance between positive and negative effects is around 0, and for that there is no improvement in biosorption capacity. When the biosorbent is treated at 2 M, the net balance is positive (there are more beneficial than harmful changes) and the biosorption capacity increases highly.

4. Statistical analysis

4.1. Modeling by full factorial design (FFD)

Once studied all individual factors, two models were applied to study all factors together and to obtain a predicted equations to biosortpion capacity. Values of factors (treatment concentration, pH and initial lead concentration) with values of studied response (biosorption capacity) for each treated OS (HNO_3, H_2SO_4 and NaOH) are shown in Table 3.

From these experimental results, it is carried out the following analysis:

- Pareto plot
  The Pareto analysis indicates the extent of the influence of each variable on the response factor, and it is determined calculating

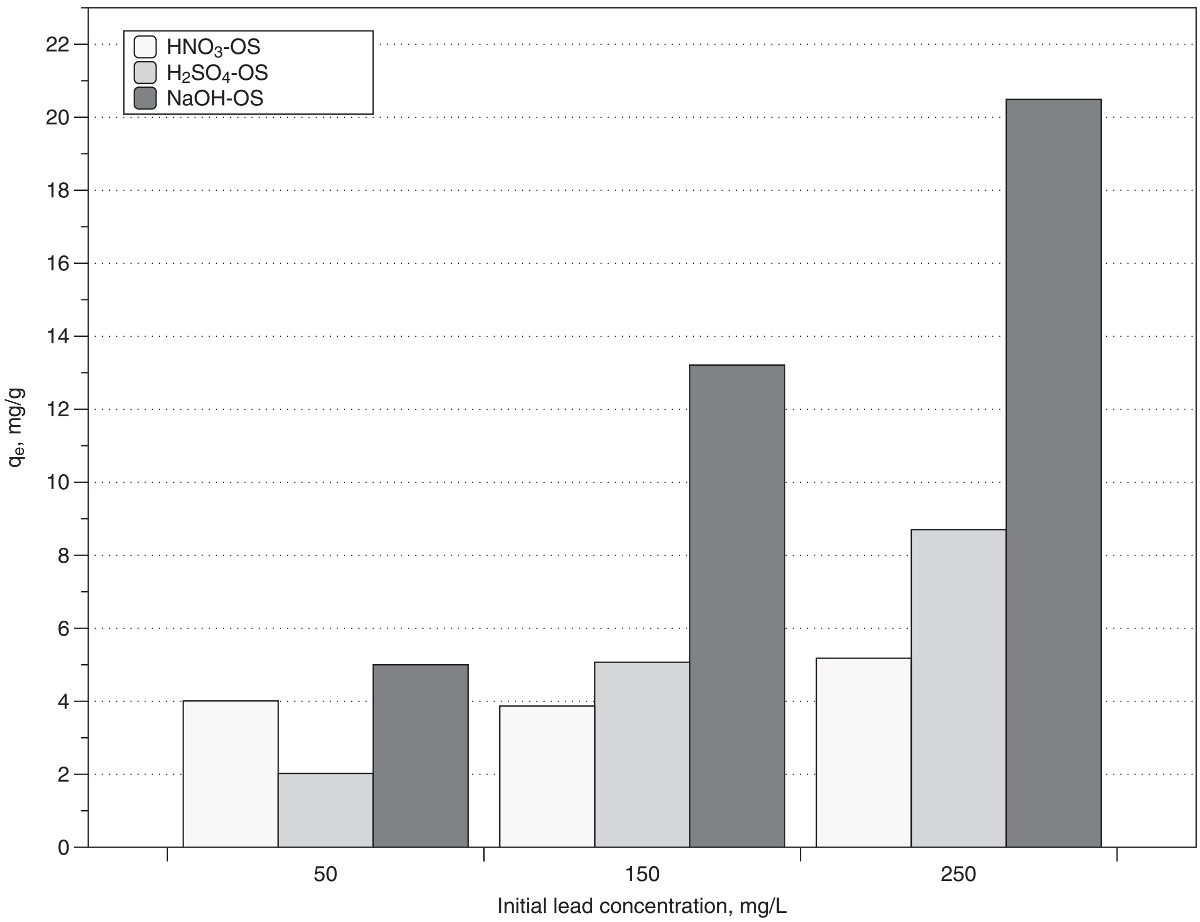

Fig. 3. Effect of initial lead concentration in biosorption of lead onto biosorption capacity (Concentration of chemical agent = 1 M; pH 5; concentration of biosorbent = 10 g/L).

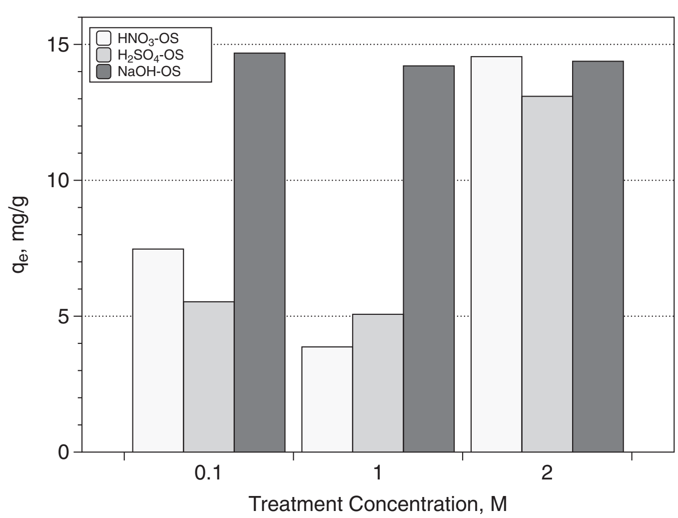

Fig. 4. Effect of chemical agent concentration in biosorption of lead onto biosorption capacity (pH 5; concentration initial of lead = 150 mg/L; concentration of biosorbent = 10 g/L).

the percentage effect of each term on the response [44]. Results obtained for biosorption capacity and for each chemically treated OS from Pareto analysis are shown in Fig. 5.

In Pareto plot, the vertical line indicates the minimum statistically-significant effect magnitude and the horizontal column lengths are proportional to the significance degree for each effect [45]. Negative factors indicate an unfavorable or antagonistic effect on the response, whereas positive factors indicate a favorable or synergistic effect on this [46]. Fig. 5 shows that for HNO_3-OS all the linear terms have a significant effect onto biosorption process. However, the quadratic terms have a different contribution, whereas the quadratic term of A has a high effect onto response, the other ones have a very low contribution, even below vertical line. Interactions between factors are introduced because in most cases the effect of each factor is affected by the effect of other factor. Several studies show that the interaction between two factors is highly significant onto response [1,47,48]. For example, the pH has influence on the biosorption process as it represents the pH of the solution (and therefore results of biosorption process are different according to pH) but, moreover, the effect of the other factors (as treatment solution or initial lead concentration) are also different according to pH of solution. Include the importance of the term A (both linear and quadratic), indicating the high effect of treatment concentration when OS is treated with HNO_3. Finally, note that the initial lead concentration (C) has a positive effect onto biosorption capacity as it was expected according to respective definition of equations. Similar effects are observed for H_2SO_4-OS: high importance of linear terms and the low effect of quadratic term of B. However, results for NaOH-OS are different. The most significant effect is the initial lead concentration, having a synergistic effect in case of linear one. Hence, for acid chemically treated OS the most significant effect is the treatment concentration, whereas for the basic one, the most significant is the initial lead concentration.

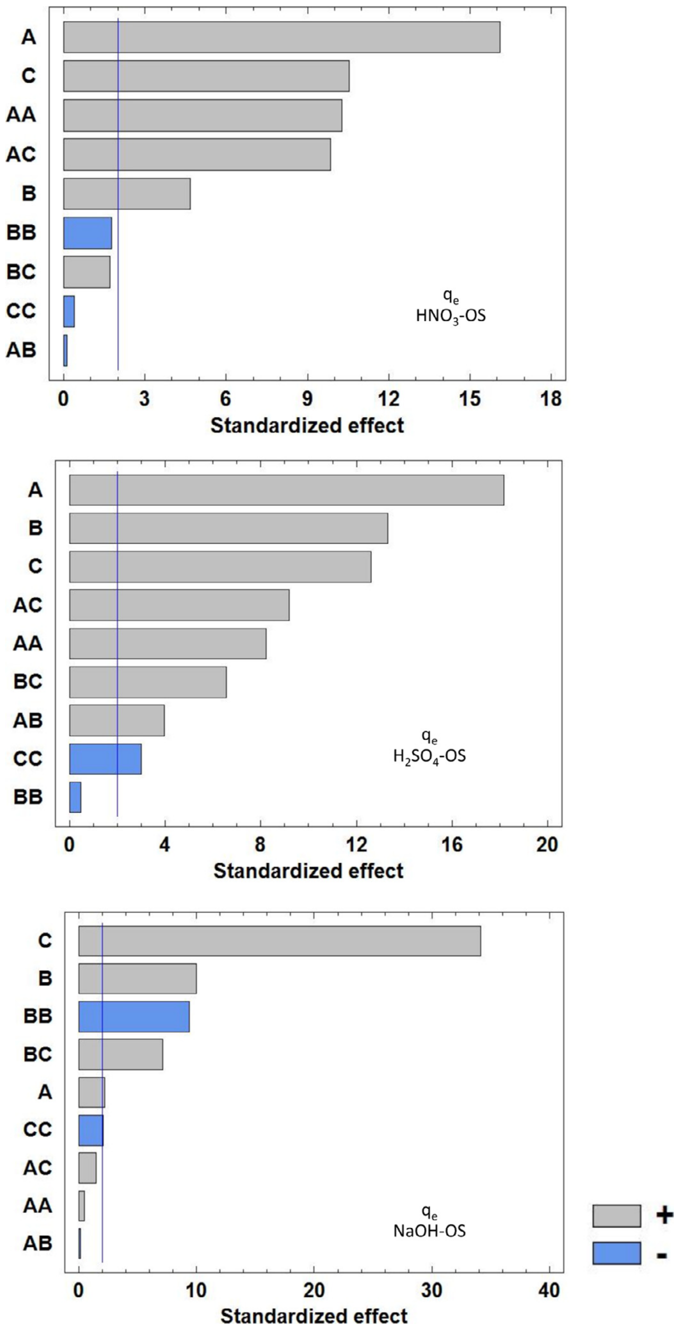

Fig. 5. Standardized Pareto plot of biosorption capacity for OS treated with HNO_3, H_2SO_4 and NaOH respectively.

- Regression analysis
  Data obtained were fitted to a second-order regression equation with the following form:

$$Y = a_0 + a_1 \cdot A + a_2 \cdot B + a_3 \cdot C + a_4 \cdot A^2 + a_5 \cdot A \cdot B + a_6 \cdot A \cdot C + a_7 \cdot B^2 + a_8 \cdot B \cdot C + a_9 \cdot C^2 \quad (9)$$

  where Y is the biosorption capacity, A, B and C are the studied factors, a_0 is the global mean and a_i are the regression coefficients. The fitted equation for each treated OS are obtained substituting the coefficients a_i in Eq. (9) by corresponding values from Table 6. Obtained values of standard deviation (Table 6) were higher 90 % in all studied cases. They indicated that the model provided a good fitting data and a high relation between observed and predicted values of biosorption capacity. Olmez [49] suggested that the correlation coefficient (R^2) should be at least 80% for a good fit of a model. Thus, obtained R^2 values showed that the regression models explained well the relation between factors and studied responses by corresponding second-order equations. On the other hand, values of R^2 indicate that the model with the best results are for OS treated with NaOH, as, it presents the highest value for R^2 to predict the biosorption capacity.

Table 6
Constants values for fitted model of two responses and for each treated-OS.

Constant	Fitted model of response		
	HNO_3-OS	H_2SO_4-OS	NaOH-OS
a_0	3.950	4.003	15.654
a_1	10.467	5.620	0.998
a_2	3.038	4.121	4.544
a_3	6.843	3.906	15.530
a_4	11.540	4.409	0.400
a_5	−0.112	1.499	−0.082
a_6	7.840	3.48	0.815
a_7	−1.987	−0.261	−7.393
a_8	− 1.360	2.482	3.987
a_9	−0.457	−1.614	−1.630
R^2	0.915	0.954	0.971

- ANOVA
  An analysis of variance was performed to study the significance of the model. Thus, an ANOVA was conducted to obtain the sum of squares (SS), degrees of freedom (Df), meansquares (MS), *F*-ratio (F-R), and *P*-values (P-V) by fitting the second-order polynomial equation from the experimental data. The results of the coefficients of the model and the analysis of variance (ANOVA) are shown in Table 7.
  It is observed from Table 7, coefficients for the main effects were highly significant for two acid treatment ($P = 0.000$), while for basic treatment, the effect A was not signifcant ($P > 0.034$). It is well known that larger the magnitude of the *F*-value and smaller the *P*-value, the more significant is the corresponding coefficient [50]. Therefore, it also implies that the variable with the largest effect was the treatment concentration for acid treatment. Moreover, all correlation coefficients (higher than 0.90) were very high showing good fitness of statistical model.

4.2. Adaptive neural fuzzy inference system (ANFIS)

Biosorption capacity of chemically treated OS was also predicted using several membership functions (linear, Gaussian, *etc.*) and the minimum error was obtained with Gaussian ones. Therefore, Gaussian membership functions were selected for the three operational variables (concentration of treatment solution, pH and initial lead concentration). Table 8 shows values of constant parameter per each variable and each level (c_l) for the fuzzy neural models used. Values of the width of Gaussian function distribution (L) for each variable and each level and values of each variable for each level (x_{low}, x_{medium} and x_{high}) is obtained function rules (FR_l). Predicted values for biosorption capacity are obtained using Eq. (8).

Table 9 shows obtained values for the width of Gaussian distribution (L) of each factor (concentration of treatment solution (A), pH (B) and initial lead concentration (C)) and each level (low, medium and high). According them, it is necessary to obtain the corresponding Gaussian functions for each level (Eq. (5)–(7)).

According the Eq. (8) and previous expressions and coefficients, the predicted biosorption capacity can be obtained. The values of the dependent variable estimated by the model is shown in Table 8. The estimates of the neural fuzzy models used departed little from their experimental counterparts (Table 3) and the average testing errors obtained by the model were: 4.1, 1.4 and 5.0 % for chemically treated OS with HNO_3, H_2SO_4 and NaOH respectively. Therefore, the

Table 7
Analysis of variance (ANOVA) for three chemically treated OS.

Factor	HNO_3-OS					H_2SO_4-OS					NaOH-OS				
	SS	Df	MS	F-R	P-V	SS	Df	MS	F-R	P-V	SS	Df	MS	F-R	P-V
A	985.96	1	985.96	259.61	0.000	284.3	1	284.3	329.3	0.000	9.0	1	9.0	4.8	0.034
B	83.1	1	83.1	21.9	0.000	152.9	1	152.9	177.1	0.000	185.9	1	185.9	99.8	0.000
C	421.5	1	421.5	111.0	0.000	137.3	1	137.3	159.1	0.000	2170.6	1	2170.6	1165.3	0.000
A^2	399.5	1	399.5	105.20	0.000	58.3	1	58.3	67.6	0.000	0.5	1	0.5	0.3	0.614
A · B	0.1	1	0.1	0.0	0.889	13.5	1	13.5	15.6	0.000	0.0	1	0.0	0.0	0.884
A · C	368.8	1	368.8	97.1	0.000	72.6	1	72.6	84.2	0.000	4.0	1	4.0	2.1	0.251
B^2	11.8	1	11.8	2.92	0.095	0.2	1	0.2	0.2	0.629	164.0	1	164.0	88.0	0.000
B · C	11.1	1	11.1	2.9	0.095	36.9	1	36.9	42.8	0.000	95.4	1	95.4	51.2	0.000
C^2	0.6	1	0.6	0.2	0.687	7.8	1	7.8	9.1	0.004	8.0	1	8.0	4.3	0.045
Total Error	163.3	43	3.8			37.1	43	0.9			80.1	43	1.9		
Total Error (corr.)	2445.8	53				800.9	53				2717.4	53			

Table 8
Constant parameter (c_l) obtained for chemically treated OS in each operational conditions.

Run	HNO_3-OS	H_2SO_4	NaOH-OS
1	0.0000	0.7429	2.517
2	0.7072	0.7358	5.082
3	1.003	0.785	3.573
4	2.925	2.205	4.852
5	3.6100	1.884	14.44
6	4.232	4.548	4.232
7	2.799	2.583	2.799
8	10.94	5.74	10.94
9	5.649	3.239	5.649
10	0.000	1.014	2.071
11	0.000	0.4111	5.30
12	0.000	0.00	3.957
13	1.646	0.7831	1.646
14	2.082	1.895	15.81
15	2.172	0.000	25.88
16	5.709	1.103	2.899
17	2.015	2.166	2.03
18	2.37	6.333	0.000
19	4.44	3.074	2.178
20	8.829	5.208	4.82
21	10.48	6.861	2.586
22	5.783	3.983	4.90
23	15.26	6.746	17.30
24	25.84	8.051	26.01
25	3.342	3.968	1.027
26	13.93	13.46	1.879
27	25.70	16.70	20.56

Table 9
Obtained values for the width of Gaussian distribution (L).

Factors	Levels		
	Low	Medium	High
A: Concentration of treatment solution	42.46	42.46	42.46
B: pH	0.3104	0.3146	0.7715
C: Initial concentration of lead	0.2967	0.2302	0.6358

mathematical model used provides accurate estimations of the experimental results. Moreover, the neural fuzzy modeling enables physical interpretation of constants (c_l), in as much as they represent the average value of the biosorption capacity under these conditions (defined by the specific neural fuzzy rule FR_l). For example, the predicted value obtained at a high treatment concentration, high pH and high initial lead concentration coincides with the parameter 27 of the equation (rule 27). This provides a substantial advantage over polynomial models.

In order to determine the values of the predicted biosorption capacity giving the optimum values of it, the response surfaces were plotted setting the value of one of the independent variables. The biosorption capacity was studied versus treatment concentration (A) and pH (B) for each levels of the initial lead concentration (C). The fixed variable in each representation of Fig. 6 was which had more influence on the process. Results are shown in Fig. 6.

The biosorption capacity is more markedly dependent on the initial lead concentration, as it is observed in the scale of obtained response (it is doubled for each level of the initial lead concentration). Besides, it is observed that the variation in the response is higher when the initial lead concentration increases. In this way, at an initial lead concentration of 50 mg/L, the ranges of biosorption capacity were between 0 and 6, 0 and 5 and 2.5 and 5.5 for chemically treated OS with HNO_3, H_2SO_4 and NaOH respectively. Contrary, at an initial lead concentration of 250 mg/L, these ranges were from 0 to 30, 0 to 16 and 10 to 25 for chemically treated OS with HNO_3, H_2SO_4 and NaOH respectively. Moreover, for the maximum value of C, there is a peak at high levels of both variables (A and B). This clearly indicates that the better conditions for the biosorption process is a pH nearly equal to 5 and a high concentration of treatment solution. This peak is not clear for NaOH-OS and it can be due to the charge of the biosorbent produces some precipitation of metal when the initial lead concentration is high. This allows to know the need to use pH controller during the process and to choose a lower value of pH when the initial lead concentration is high in order to avoid precipitation processes. Moreover, the same effect is observed in Section 3.2.2.

When the OS was treated with basic solution, it had a high biosorption capacity at all concentration tested, however, for acid treatment the behavior was different. The treatment at 1 M worsened the biosorption capacity with respect to the treatment at 0.1 M (it is observed a hole in response surfaces around the treatment concentration 1 M). However, values of biosorption capacities increased for a concentration 2 M, with a rising around this concentration. It can be due to that chemical treatment, as discussed above, changes physicochemical properties of biosorbent, mainly changes in surface, functional groups and composition of materials. Thus, with the treatment 1 M, change this properties but not enough to obtain an improvement. For example, the acid treatment dissolves lignin compounds, but this loss is not compensated with increase of surface area. There is a change in biosorbent, but the net balance between positive and negative effect is around 0, and for that there is not an improvement in biosorption capacity. When the biosorbent is treated at 2 M, this net balance is positive (there are more beneficial than harmful changes) and the biosorption capacity increases highly.

The trend of surface response is similar when OS was treated with acid solutions, however they were different for basic treatment. This shows a strong correlation between the biosorption capacity and the type of treatment (this confirms the importance of the characterization of biosorbent and the study of the changes produced during them). The better fitting by Gaussian functions indicate that the studied variables don't have a linear effect onto response, as they depend on all variables together, showing a Gaussian effect onto biosorption

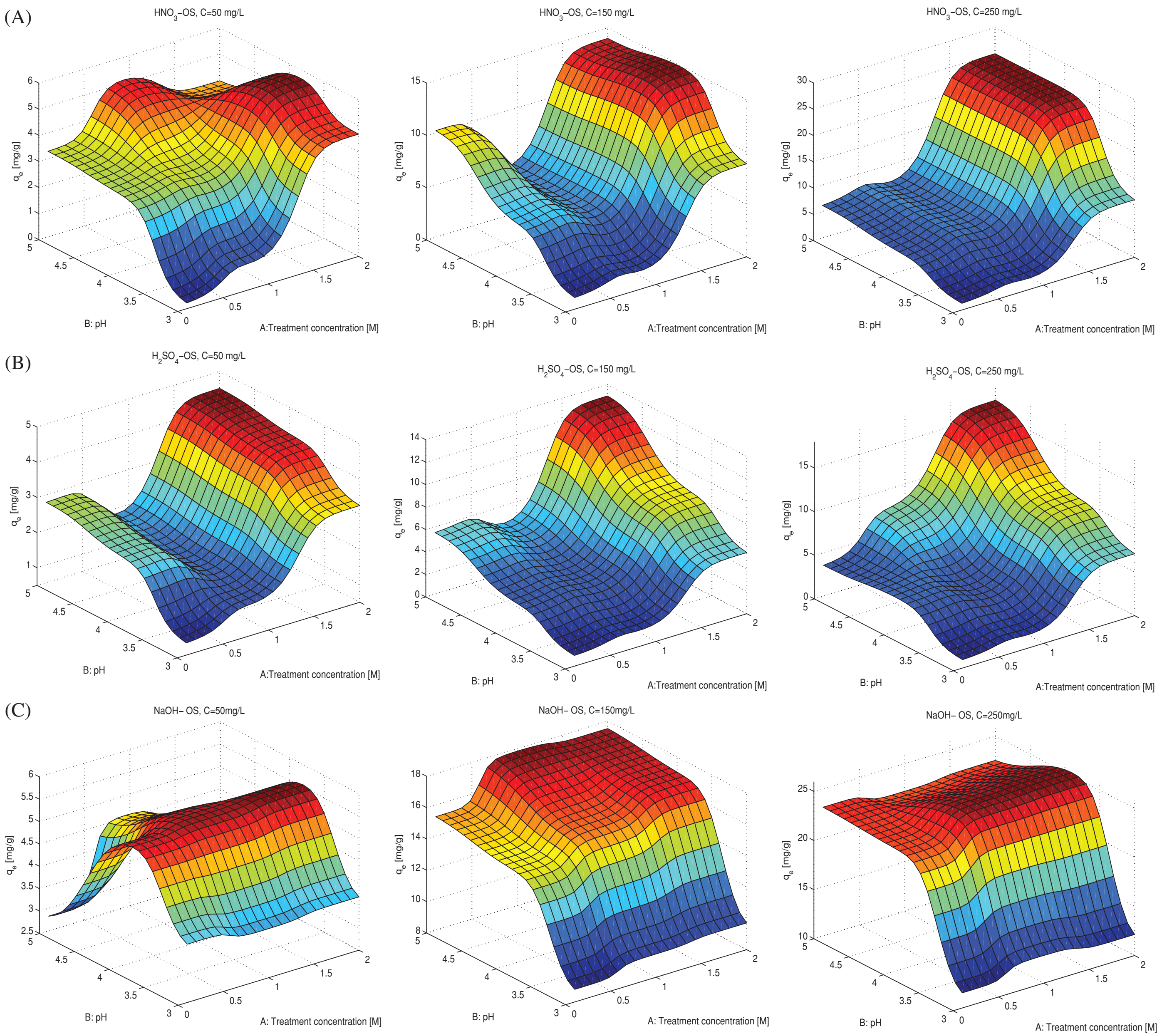

Fig. 6. Predicted biosorption capacity as a function of treatment concentration (A) and pH (B) for each levels of initial lead concentration (C) and for each chemically treated OS.

capacity. These Gaussian effects of process variables are very typical, which suggests the need to operate in the peak regions in order to maximize the lead removal.

4.3. Comparison between models

Comparing obtained values by both models with experimental values, in general, ANFIS model fits better results than FFD model (errors are smaller and value of R^2 are higher). Moreover, to analyze better the fitting results using both models, the predicted values (using both models) versus experimental values were represented (Fig. 7).

Moreover, the neural fuzzy modeling enables physical interpretation of constants (cl), in as much as they represent the average value of the biosorption capacity under these conditions (defined by the specific neural fuzzy rule FRl).

The fuzzy model best reproduces the experimental biosorption capacity values of Table 3 than the full factorial design model. It is observed that ANFIS model predicts better experimental results in studied range for three chemically treated OS. In all cases, value of R^2 is nearest to 1 when data are fitted by ANFIS model. However, both models have values of $R^2 > 0.91$.

5. Conclusions

Contamination by heavy metals are common in waste water worldwide. In this work, the use of biosorption by olive stone was studied to remove lead from aqueous solution. The olive stone underwent several chemical treatments to improve its biosorption capacity. Few studies have analyzed the relationship between chemical treatment of the biosorbent, characteristic changes of it and biosorption capacity values. In particular, the role played by chemical treatment together with other operational factors as treatment concentration, pH or initial lead concentration was analyzed by two mathematical models: full factorial design and adaptive neural fuzzy inference system. The biosorption capacity is marked by changes produced during chemical treatments and results were different according to acid or

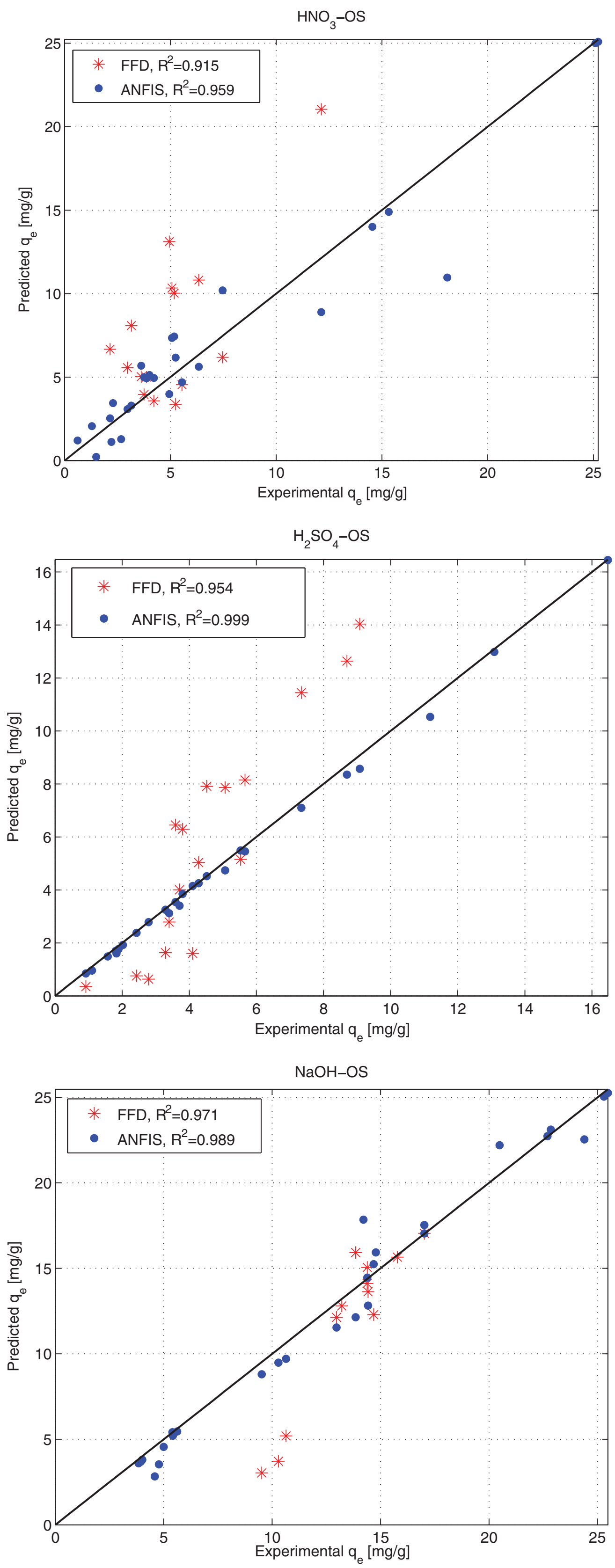

Fig. 7. Comparison between both used models: full factorial design (FFD) and adaptive neural fuzzy inference system (ANFIS) for chemically treated OS with HNO_3, H_2SO_4 and NaOH respectively.

basic treatment and concentration of the treatment. The following main conclusions were drawn:

1. Chemical treatments onto OS change its physicochemical properties (particularly, its surface, volume of porous, its main functional groups and its content in holocellulose and lignin).
2. Operational factors studied (chemical treatment, concentration of treatment solution, pH and initial lead solution) have a strong influence onto response.
3. Based on the R^2 values both models provided good fitting of data ($R^2 > 0.91$ in all cases) and both can be used to predict the biosorption capacity of OS.
4. The full factorial design provides poorer predictions of biosorption capacity results (lower values R^2).
5. Neural fuzzy models provide a physical interpretation of the constants c_l as they represent the average value of biosorption capacity under the conditions defined by the specific fuzzy rule.

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