Adsorption of iron on crude olive stones

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ABSTRACT

The ability of crude olive stones, a residue of the olive-oil industry, for the adsorption of iron present in the industrial wastewaters was studied. Olive stones were used directly and characterized by mercuric porosimetry. The equilibrium adsorption capacity was higher when the particles size (from <1 to 4.8 mm) decreased. The percentage of iron adsorption increased from 30 to 70% when the initial concentration of biomass increased from 25 to 125 g dm^{-3}. The optimum concentration of olive stones was fixed at 37.5 g dm^{-3}. The adsorption of iron was determined as a function of their initial concentration and multiplayer formed at high iron concentration.

1. Introduction

Industrial wastewater is one of the major sources of aquatic pollution. Heavy metals stand out among the aquatic pollutants due to their persistence and toxicity. Aqueous industrial wastes from several activities, such as metal plating, mining, tanning, etc. cause contamination by heavy metals. Different methods of treating wastewater containing heavy metal ions have been developed over years which include coagulation, ion exchange, membrane separation, reverse osmosis, solvent extraction, chemical precipitation, electroflotation etc. (Namasivayam and Ranganathan, 1995). However, the above-mentioned methods are effective for treating high concentration of heavy metal ions. For low concentration of heavy metal ions (<100 mg dm^{-3}), adsorption is a much preferable technique and activated carbon has been widely applied for treating industrial wastewater. For the past few decades, attention has been devoted to develop adsorbents from agricultural by-products, also called biosorbents as alternative to activated carbon.

Hydrogen peroxide has been used to reduce BOD, COD, offensive odor and foaminess in domestic or industrial wastewater for many years. Hydrogen peroxide can be used as an autonomous treatment or as an improvement of existing physical or biologic treatment processes, according to the situation. Hydrogen peroxide can be used alone (Millero et al., 1989) or with a catalyst such as iron (Fe^{3+}) (Martinez Nieto et al., 2009).

The companies of olive-oil produce variable quantities of wastewaters, which require treatment for disposal or reuse. Today, regulations are becoming increasingly strict regarding the parameters measured in these effluents. In Spain, the resolution by the president of the Hydrographical Confederation of the Guadalquivir on water use 2006 set parameter limits as follows: pH 6.0–9.0, total suspended solid = 500 mg dm^{-3}; and maximum values for COD and BOD$_5^{20}$ were fixed at 1000 mg O$_2$ dm^{-3}. To solve this problem, Martinez Nieto et al. (2009) were proposed chemical oxidation based on the Fenton's process as a solution, to obtained irrigation water, to the above-mentioned effluents. This solution has made obtaining an irrigation water with some iron.

On the other hand, olives and olive-oil industry generate olive stones (OS) as by-product. In Spain, more than 370,000 tons of triturated olive stones are produced per year (Andalusian Energy Agency, 2008), most of which being destined for combustion and for production of active carbon (Rodriguez et al., 2008). Despite the environmental benefits of using this biomass as a fuel or a raw material for active carbon, some problems remain such as air pollution. Another economically and environmentally interesting alternative would be using it directly as an adsorbent for heavy metals. Following this line, different studies have show that olive stones could be used as biomass sources to eliminate pollutants such as phenols (Stasinakis et al., 2008), dyes (Akar et al., 2009), or heavy metals like Cd(II), Pb(II), Ni(II) (Gharaibeh et al., 1998; Pagnanelli et al., 2002; Blázquez et al., 2005; Fiol et al., 2006).

The purpose of the present study was to investigate the adsorption of iron(III) ions on olive stones. The experiments were done in a batch system and iron adsorption was investigated with respect to

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initial metal ion concentration, adsorbent dose and adsorbent size. The adsorption equilibrium was modelled by using the Langmuir isotherm model.

2. Materials and methods

2.1. Preparation of olive stones and iron solutions

Olive stones were a waste acquired from an extraction olive-oil plant, S.A.T. Olea Andaluza, located in Baeza in the province of Jaén (Spain). Olive stones were obtained from the separation from pulp (initial particle size <4.76 mm), were washed with water, and then boiled for two hours in order to remove the remaining organic matter which could interfere in the results. They were dried in a 333 ± 1 K oven, and then ground in the mill (IKA brand MF 10). The olive stones particles are separated into five fractions in a high vibration sieve ASTM brand CISA: 3–2, 2–1.4, 2–1, 1.4–1, and <1 mm.

The different iron solutions were prepared from a standard 30% (w/w) aqueous iron(III) chloride from QP Panreac. Metal iron concentrations range from 5 to 100 mg dm^{-3}.

2.2. Iron adsorption experiments

For the study of the iron adsorption in the olive stones biomass, after the characterization of several fraction with different particle size olive stones samples, the biomass of olive stones was introduced in iron solution with concentrations higher than those usually registered in the real wastewater condition (to detect the exact amount of iron adsorption).

Iron adsorption was carried out by mixing the iron solutions (5–100 mg dm^{-3}) with olive stones as adsorbent in 200 mL Erlenmeyer flask (final concentration 37.5 g dm^{-3}) with stirring (117 rpm) at 298 K. Samples were analyzed every 10 min during the first hour, and every 30 min during the remaining 2 h.

Moreover, Adsorption experiments with olive stones of different particle size (iron concentration solution 20 mg dm^{-3}) were studied. For that purpose, the particle size from <1 to 4.76 mm it have been varied. Also, experiments with different olive stones concentrations have been studied (25–125 g dm^{-3}) maintaining the same concentration in iron solution (20 mg dm^{-3}).

The amount of iron adsorbed has been determined by spectrophotometry by difference in the contents of iron before and after the adsorption, and the concentration of iron after the adsorption has been determined in the supernatant obtained by centrifugation.

2.3. Analytical methods

Mercury porosimetry (Thermo Electron Corporation, Pascal 440 and 140 Series) was employed to characterize the porosity of olive stones by applying various levels of pressure to a sample (0.3 g approximately) immersed in mercury and at environmental temperature. The pressure required to intrude mercury into the pore sample is inversely proportional to the size of the pores. The analysis was carried out loading the sample into a penetrometer, which consists of a sample cup connected to a metal-clad, precision-bore, glass capillary stem. The penetrometer is sealed and placed in a low pressure port, where the sample is evacuated to remove air and moisture. The cup of penetrometer and capillary stem are then automatically backfilled with mercury. As the pressure on the filled penetrometer increases, mercury penetrates into the pores, beginning with those pores of largest diameter. The instrument automatically collects low pressure measurement over the range of pressures specified (300 kPa). Then, the penetrometer is moved to the high pressure chamber, where high pressure measurements are taken (400 MPa).

Table 1
Crude olive stones composition (% dry matter).

Cellulose	40.4
Hemicellulose	32.2
Lignin	27.2

The olive stones were characterized (Table 1) according to the parameters of lignin (TAPPI T222 os-74), neutral detergent fiber (NDF) and acid detergent fiber (ADF) (Van Soest and Wine, 1967). The percentages of hemicellulose and cellulose in the solid residue were calculated according to the expressions:

$$\%\text{Hemicellulose} = \%\text{NDF} - \%\text{ADF} \tag{1}$$

$$\%\text{Cellulose} = \%\text{ADF} - \%\text{lignin} \tag{2}$$

All iron ions were reduced to iron ions (II) and, with thioglycolate medium and a derivative of triazine, formed a reddish-purple complex that was determined photometrically at 565 nm (Standard German methods ISO 8466-1 and German DIN 38402 A51).

The adsorption experiments and analytical methods were made at least three times each. The calculation and statistical methods used were available in the OriginPro 7.5 program.

3. Results and discussion

3.1. Characterization of olive stones and iron adsorption

Characterization of a biosorbent is an important analysis for understanding the behaviour or the mechanism of iron removal on the surface of biosorbent. Pore sizes are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC), that is, micropores (diameter <2 nm), mesopores (2 nm < diameter < 50 nm), and macropores (diameter > 50 nm). In Table 2, it can be see that the porosity of support (olive stones) has been separated in two different ranges, pores with diameter between 3.8 and 50 nm (varied between 12 and 38% of total specific volume of pores), and pores with diameter more than 50 nm (varied between 66 and 88% of total specific volume pores), therefore OS can be categorized as macroporous biosorbent.

Adsorption of iron on olive stones depends on the structural and morphological features of the support. The olive stones is a material with mesopores (pore width ca. 2–50 nm) and macropores (pore width >50 nm) (Table 2). This structure may allow its use in iron adsorption. The pore and particle sizes could be important to control the adsorption process. Firstly, the influence of the particle size on the adsorption of iron on olive stones was studied. The total specific surface area as the total cumulative specific volume has not been changed and we may consider the average values of 23 m^2 g^{-1} (SD = 2.4) and 0.12 cm^3 g^{-1} (SD = 0.019), respectively. The low total cumulative volume indicates that the surface has a not porous structure, but the surface has roughness which mainly manifests as macropores when the porosity was determined. The average diameter of the pores in the original crude olive stones is equal to 13.8 nm, this value is shifted to lower values with the crushing and separation of different particle sizes. Similarly one can observe the same for the data obtained after adsorption. In short, no significant changes in the distribution of the pores were detected (Table 2).

Fig. 1 compares the adsorption curves of iron onto olive stones with different particles sizes (from <1 to 4.8 mm). It seems that the adsorption rate and the equilibrium adsorption capacity depend on the fractions size: when the diameter decreases, the adsorption is higher because of the wider exchange surface offered by the sorbent to the iron metal ions. At equilibrium, the adsorption capacity slightly increases from 0.23 to 0.35 mg g^{-1}, ranging from the biggest

Table 2
Characteristics of crude olive stones.

Particle size (mm)	Pore diameter (nm)	Total cumulative volume ($cm^3\,g^{-1}$)	Pore diameter ranges (nm)	Specific volume ($cm^3\,g^{-1}$)
<4.8[a]	13.8	0.17	3.8–50	0.02
			>50	0.15
2–3	8.8	0.14	3.8–50	0.03
			>50	0.11
2–1.4	8.8	0.09	3.8–50	0.03
			>50	0.06
1.4–1	8.8	0.13	3.8–50	0.03
			>50	0.10
<1	8.8	0.12	3.8–50	0.03
			>50	0.09
<4.8[b]	4.4	0.11	3.8–50	0.02
			>50	0.09

[a] Original crude olive stones before the adsorption.
[b] Original crude olive stone after the adsorption. Adsorption conditions: Fe(III): $20\,mg\,dm^{-3}$; olive stone: $37.5\,g\,dm^{-3}$; stirring rate: 117 rpm; pH 2.9; temperature: 293 K.

size to the smallest. Due to the fact that the olive stones, a natural lignocellulosic biomass, is not a microporous material (Table 2), all the interactions that may happen between biomass and metal ions remain limited to the external surface of the biomass. Most research conducted on heavy metal sorption indicated that other effects may arise from the some processes, such as the predominant presence of hydrated species of heavy metals, changes in surface charge and the precipitation of the appropriate salt (Blázquez et al., 2005; Sarin and Pant, 2006; Kumar and Bandyopadhyay, 2006). Ion exchange has been reported as the predominant mechanism involved in many biosorption processes by lignocellulosic wastes (Ngah and Hanafiah, 2008; Fiol et al., 2006; Šćiban et al., 2006; Villaescusa et al., 2004).

In all cases, equilibrium is reached within 15–20 min in agreement with previous works on olive stones in which short equilibrium times of about 2 h were obtained. Many authors (Martín Lara et al., 2009; Pagnanelli et al., 2003; Fiol et al., 2006) have shown that most metal is removed within the first 20 min.

Also, olive stones used in this study were analyzed by scanning electron microscopy in order to examine its morphology. The SEM image of OS before iron adsorption is shown in Fig. 2a. OS has irregular structure, which favours the biosorption of Fe(III) ions on different parts of biosorbent. This image confirms the previous results obtained by the analysis of the porosity of olive stones. In Fig. 2b it can be observed the zones of iron accumulation after adsorption. The reason is the sorption of Fe(III) ions in the cavities of the material.

3.2. Influence of olive stones concentration

To confirm the influence of the external surface area on sorption performance of olive stones, iron adsorption percentages and
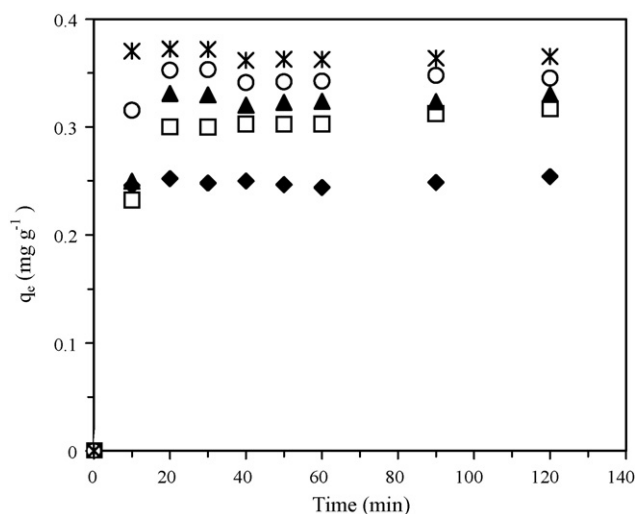

Fig. 1. Influence of the particle size of the crude olive stones on the Fe(III) adsorption. Supports: (◆) <4.8 mm, (□) 3–2 mm, (▲) 2–1.4 mm, (○) 1.4–1 mm and (✖) <1 mm. Adsorption conditions: Fe(III): $20\,mg\,cm^{-3}$; original crude olive stones: $37.5\,g\,dm^{-3}$; stirring rate: 117 rpm; pH 2.9 and temperature: 293 K.
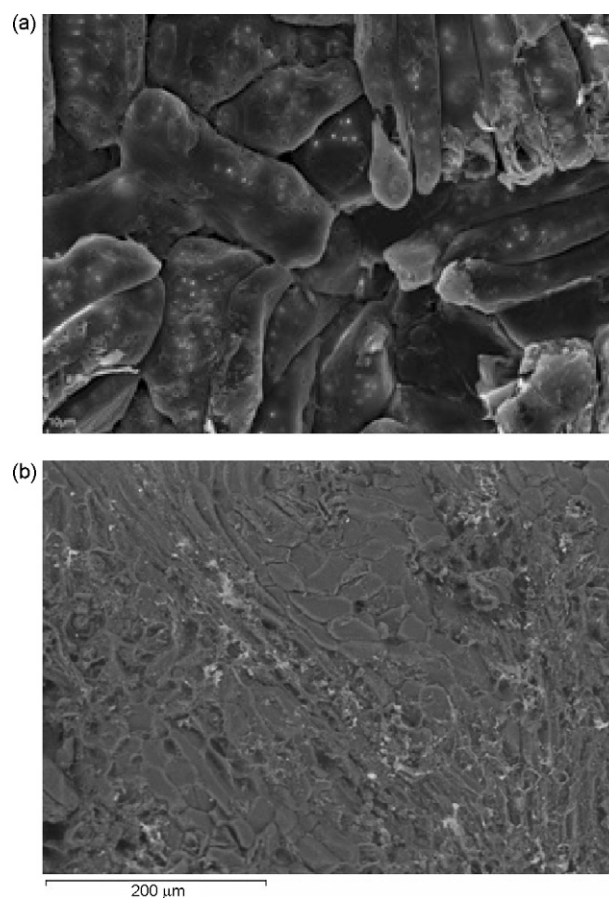

Fig. 2. SEM image of one particle of original crude olive stone. (a) Before iron adsorption and (b) after iron adsorption at different scale 10 and 200 μm, respectively. Adsorption conditions: Fe(III): $20\,mg\,dm^{-3}$; olive stone: $37.5\,g\,dm^{-3}$; stirring rate: 117 rpm; pH 2.9; and temperature: 293 K.
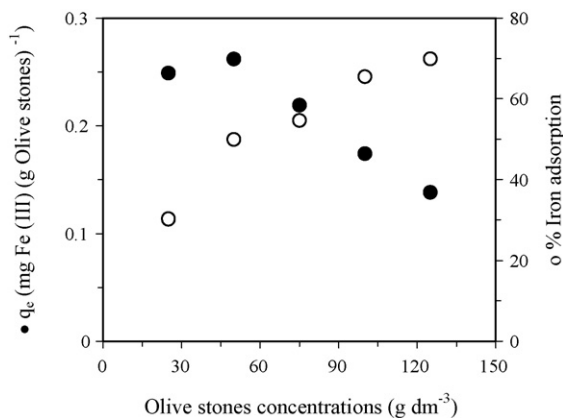
Fig. 3. Influence of initial olive stones concentrations on (●) equilibrium adsorption capacity (mg g^{-1}) and (○) iron adsorption percentage in the equilibrium. Adsorption conditions: Fe(III): 20 mg cm^{-3}; stirring rate: 117 rpm; pH 2.9; temperature: 293 K.

capacities were plotted against olive stones concentrations (Fig. 3). According to Fig. 3, the percentage of iron adsorption increased from 30 to 70% when the initial concentration of biomass increased from 25 to 125 g dm^{-3} because of a higher external surface area and thus availability of sorption sites, in agreement with the Langmuir hypothesis (Converti et al., 1992). Despite a higher removal, equilibrium adsorption capacity decreases for biomass concentrations ranging from 35 to 125 g dm^{-3}, a conclusion previously mentioned by other authors (Ozer et al., 1999). This result may have different explanations: (i) adsorption sites remain unsaturated during the adsorption reaction, (ii) the agglomeration of biomass particles at higher concentration reduces the available external surface area, (iii) at high biomass concentration, interaction of particles can cause desorption of sorbed metallic ions from the biomass surface area (Monahar et al., 2002). The optimum concentration of olive stones for an initial iron concentration of 20 mg dm^{-3} was thus fixed at 37.5 g dm^{-3} (Fig. 3).

3.3. Adsorption isotherm

In order to determine the adsorption isotherm the initial iron concentration was varied in the interval ranging from 5.0 to 100 mg iron dm^{-3}. Olive stones particle size <4.8 mm was selected as support to determinate the isotherm equilibrium. Firstly, equilibrium time for the adsorption was determinated. Fig. 4 shows the

Fig. 5. Influence of the initial iron concentrations on the equilibrium adsorption capacity. Adsorption conditions: original crude olive stones particles (<4.8 mm): 37.5 g dm^{-3}; stirring rate: 117 rpm; temperature: 293 K.

variation of iron adsorption over time for five experiments with different initial iron concentrations.

As presented in Fig. 5, the equilibrium adsorption capacity increases linearly from 0.06 to 0.7 mg g^{-1} when the initial Fe(III) concentrations varies from 5 to 50 mg dm^{-3}, as a result of the increase of the driving force (gradient of iron concentration). The same conclusion was obtained by Tiemann et al. (2000) and Ahluwalia and Goyal (2005) for the sorption of iron onto *Medicago Sativa* and *Tea leaves* biomass. Then, iron adsorption is possible even at low metal concentrations but it is favoured for high concentrations.

The adsorption proceeds at a high rate ($\approx$5 min) and the adsorption equilibrium is attained in 20 min (Fig. 4) being achieved in the first five minutes around 80% of the total adsorbed by the support. Fig. 6 shows the adsorption isotherms of iron on olive stones particles (<4.8 mm). The experimental data (Fig. 6) were adjusted to the Langmuir model Eq. (3),

$$q_e = \frac{K q_{max} C_{Fe}}{1 + K C_{Fe}} \qquad (3)$$

where q_e is the load of Fe (mg) adsorbed per gram of support on equilibrium and C_{Fe} is the iron concentration (mg dm^{-3}) on equilibrium. The maximum adsorption expressed in terms of iron
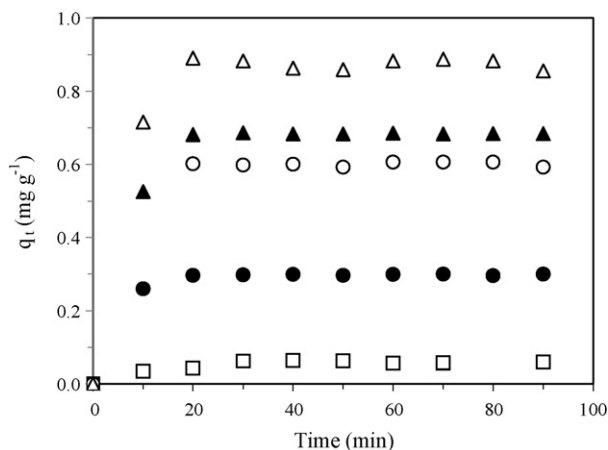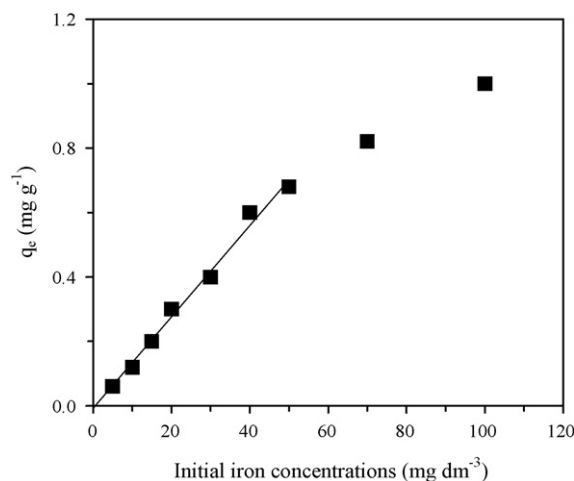

Fig. 4. Influence of the different initial iron concentrations on the olive-stones adsorption. Iron concentration: (□) 5, (●) 20, (○) 40, (▲) 50 and (△) 100 mg dm^{-3}. Adsorption conditions: original crude olive stones particles (<4.8 mm): 37.5 g dm^{-3}; stirring rate: 117 rpm; temperature: 293 K.
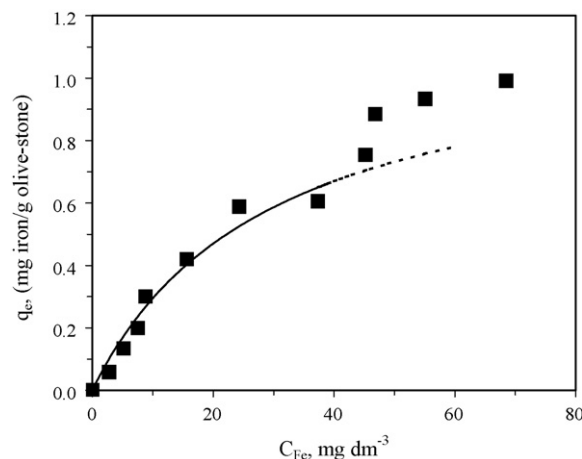

Fig. 6. Adsorption isotherm of iron to olive-stone. (■) Experimental data, (–) Langmuir model. Adsorption conditions: original crude olive-stones particles (<4.8 mm): 37.5 g dm^{-3}; stirring rate: 117 rpm; temperature: 293 K.

was q_{max} = 1.2 mg iron (g olive stones)$^{-1}$ and the model constant is K = 0.034 (mg dm^{-3})$^{-1}$ and R^2 = 0.963.

Fig. 6 shows the proper adjustment of Langmuir to the experimental data up to 37.3 mg dm^{-3} (0.65 mg/g olive stones). From this value the second layer adsorption appears. This second layer begins before reaching the maximum capacity of the model. The maximum adsorption expressed in terms of iron which determines the mathematical model (Eq. (1)) is an apparent value (dash line Fig. 6). Really, the second layer starts forming before it reaches the maximum adsorption corresponding to the first layer (Fig. 6). The real maximum value of iron adsorbed 0.65 mg/g on olive stones in the monolayer corresponds to the iron equilibrium concentration in the liquid phase C_{Fe} = 37.3 mg iron dm^{-3}. The adsorption of iron on olive stones occurs both in a monolayer (solid line in Fig. 6) and in a multilayer form.

The maximum real value of iron adsorbed on crude olive stones is similar or higher than other values registered for other metals such as Cd(II), Cr(III), Pb(II) in the same conditions (Blázquez et al., 2005; Calero et al., 2009). The importance of this adsorption process is determined by the fact that iron ions are present in some industrial treated or untreated wastewaters. Especially, in olive oil industry (Cañizares et al., 2006). Martinez Nieto et al. (2009) have demonstrated the effectiveness of the use of crude olive stones to eliminate residual iron ions from the wastewater of olive oil industry in real conditions.

4. Conclusions

Olive stones, agro-industrial abundant and cheap remainder from olive-oil industry, were demonstrated to become an alternative process for the detoxification of iron and good sorbent for these metal ions present in the wastewaters from the same industry. The sorption is affected by many factors: (1) The increase of the biomass and metal concentrations favours the adsorption. (2) The attractions between adsorbent–adsorbate only happen at the external surface of this non-porous biomass leading to a strong influence of the granular size. (3) The comparison between olive stones and other bio-adsorbent indicates the efficiency of its advantage as adsorbent. 4- The use of the olive stones without pretreatment on adsorption of the metals is possible. (5) The crude olive stones (without triturating) can be use as metallic cations adsorbent in industrial applications.

Acknowledgements

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