Article

Production of Biosorbents from Waste Olive Cake and Its Adsorption Characteristics for Zn^{2+} Ion

Ana Fernando [1],*, Sofia Monteiro [1], Filomena Pinto [2] and Benilde Mendes [1]

[1] Grupo de Disciplinas de Ecologia da Hidrosfera/Unidade de Biotecnologia Ambiental, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Caparica, Portugal; E-Mail: pereira_sofia@sapo.pt (S.M.); bm@fct.unl.pt (B.M.)

[2] Departamento de Engenharia Energética e Controle Ambiental, INETI, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal; E-Mail: filomena.pinto@ineti.pt

* Author to whom correspondence should be addressed; E-mail: ala@fct.unl.pt

Abstract: In this study, waste olive cake (OC) was utilized as the raw material for the production of biosorbents by chemical treatment and its adsorption capacity for zinc ion was evaluated. Tests were conducted with the total biomass (T) and with the fraction > 2.00 mm (P), in order to determinate the influence of this fractionation step on subsequent treatments. Two chemical agents were used: sulfuric acid and sodium hydroxide. The parameters studied include physical and chemical properties of materials, contact time, pH, adsorbent dose and initial concentrations. The kinetic data were best fitted to the pseudo-second order model. Zinc binding is strongly pH dependent, with more zinc ions bound at a higher pH (5-7 in a range of 3-7). Both Langmuir and Freundlich models are well suited to fit the data on sorption of zinc by OC. Data on sorption of zinc by waste olive cake treated with sulfuric acid (OC-H) was better described by the Freundlich model. Zinc sorption by waste olive cake treated with sodium hydroxide (OC-OH) was better described by the Langmuir model. Results show OC-OH is a biosorbent with a superior adsorption capacity for zinc than OC-H. The maximum adsorption capacity obtained from the Langmuir isotherms increases in the order (mg/g): OC-HT (14), OCT (22) and OC-OHT (27). Results also indicate that the previous fractionation step doesn't produce a biosorbent with a superior adsorption capacity.

1. Introduction

The removal of Zn(II) from effluents is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods. The presence of zinc in wastewater is toxic to aquatic flora and fauna, even in relatively low concentrations. An excess of zinc in the human body can cause depression, lethargy, neurologic signs such as seizures and ataxia, and increased thirst [1]. The main sources of zinc in wastewater are discharged waste streams from metals, chemicals, pulp and paper manufacturing processes, steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, viscose rayon yarn and fiber production, etc [2,3].

Various treatment technologies have been developed for the decontamination of water and wastewater contaminated with heavy metals. The most commonly used methods for the removal of metal ions from industrial effluents include: chemical precipitation, solvent extraction, oxidation, reduction, dialysis/electro dialysis, electrolytic extraction, reverse osmosis, ion-exchange, evaporation, cementation, dilution, adsorption, filtration, flotation, air stripping, stem stripping, flocculation, sedimentation, soil flushing/washing chelation, etc [2,4]. Most of these methods suffer from drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries. For low concentrations of metal ions in wastewater, the adsorption process is recommended for their removal [5]. Activated carbon is one of the most widely employed adsorbent. It is mainly composed of carbonaceous material that has highly developed porosity, internal surface area and relatively high mechanical strength, making it suitable for the removal of heavy metals from wastewaters [1,4,6,7]. As a result, the demand for activated carbon is increasing, although remaining an expensive material.

Presently, low cost forest and agricultural wastes without or with little processing are considered promising adsorbents for heavy metals due to their high surface areas, microporous characters and surface chemical natures [8]. Besides, they are cheaper and readily available materials. Coconut shell, nutshells, oil palm waste, pine needles, sawdust, waste straw, rice husk, peanut hulls, hazelnut shells, almond shells, peach stones, tea dust leaves, apple wastes, sugarcane bagasse, coffee grounds, banana and orange peels, sugar beet pulp and different other materials were used and investigated [1,2,4-10].

Waste olive cake is the solid residue obtained from pressing the olives and is one of the most abundant agro-industrial wastes in the Mediterranean Region constituting a source of environmental problems caused by its accumulation and disposal [11,12]. The waste olive cake is currently used as fertilizer, natural or transformed into a more stabilized amendment [13-15], as an additive to animal food [16,17] and as a source of heat energy [12,18-25].

Recently some of these olive oil wastes (*in natura* or processed) have been tested as biosorbents for heavy metals [8,11,26-34]. Conversion of this waste to a useful adsorbent contributes not only for the treatment of heavy metals contaminated environment but also to minimizing the solid wastes. These research activities indicated promising results but further efforts are still required in order to maximize metal removal efficiency and minimize preparation costs.

In this work, waste olive cake, a major surplus waste produced in Portugal, was utilized as the raw material for the production of biosorbents by chemical treatent and its adsorption capacity for zinc ion was evaluated. The influence of several operating parameters, such as, particle size, different chemical treatment, contact time, pH, initial concentration and adsorbent dose was studied.

2. Results and Discussion

2.1. Characterization

The properties of the materials used in the adsorption tests, are given in Tables 1 and 2.

Table 1. Physical-chemical characterization of the materials derived from olive cake.

	Non activated (OC)		Activated with H_2SO_4 (OC-H)		Activated with NaOH (OC-OH)	
	Total (T)	>2mm (P)	Total (T)	>2mm (P)	Total (T)	>2mm (P)
Ash content (% dm)	21 ±2	14 ±1	23 ±3	18 ±4	22 ±1	15 ±3
pH	6.5 ±0.1	7.1 ±0.3	2.4 ±0.1	2.3 ±0.0	8.0 ±0.1	8.1 ±0.1
Iodine Number (mg/g)	135 ±10	64 ±5	329 ±13	247 ±5	217 ±39	64 ±5
C (% dm)	43 ±2	41 ±1	40 ±2	48 ±2	37 ±2	34 ±2
H (% dm)	5.9 ±0.8	6.4 ±0.2	3.3 ±0.6	2.9 ±0.2	6.3 ±0.3	6.6 ±0.3
N (% dm)	1.10 ±0.03	0.49 ±0.08	0.90 ±0.06	0.44 ±0.06	0.98 ±0.08	0.50 ±0.09

dm – dry matter

Table 2. Metals content of the materials derived from olive cake.

	Non activated (OC)		Activated with H_2SO_4 (OC-H)		Activated with NaOH (OC-OH)	
	Total (T)	>2mm (P)	Total (T)	>2mm (P)	Total (T)	>2mm (P)
Ca (% am)	1.8 ±0.2	1.3 ±0.2	0.37 ±0.09	0.25 ±0.09	< 0.0003	< 0.0003
Mg (% am)	0.52 ±0.01	0.51 ±0.04	0.09 ±0.01	0.03 ±0.02	< 0.00006	< 0.00006
K (% am)	2.8 ±0.4	1.2 ±0.1	1.4 ±0.1	0.6 ±0.1	0.5 ±0.1	0.12 ±0.03
Na (% am)	1.1 ±0.1	0.65 ±0.08	3.3 ±0.1	4.0 ±0.9	0.9 ±0.5	1.2 ±0.3
Fe (% am)	2.8 ±0.3	3.2 ±0.2	< 0.0012	< 0.0012	< 0.0012	< 0.0012
Mn (mg/kg am)	79 ±3	96 ±7	< 5.8	< 5.8	< 5.8	< 5.8
Zn (mg/kg am)	214 ±45	153 ±7	19 ±2	101 ±4	< 2.6	< 2.6
Cu (mg/kg am)	53 ±3	88 ±17	< 8.2	< 8.2	< 8.2	< 8.2

am – ash material

Results presented in Table 1 indicate that the fractions > 2 mm, chemically or non-chemically treated, presented lower iodine numbers than materials without fractionation. The iodine number is a relative indicator of porosity in a carbonaceous material and may be used as an approximation of surface area for some types of carbons [35]. Correlation between the BET surface area and the iodine number is established and well documented [4,26,34]. However, it must be realized that any relationship between surface area and iodine number cannot be generalized. It varies with changes in carbon raw material, processing conditions, and pore volume distribution [35]. As iodine number gives an indication on

microporosity (pores less than 1 nm in diameter), higher iodine numbers reflect better development of the microporous structure and higher adsorption abilities for low-molar-mass solutes [26,27]. Results of the iodine numbers for the fraction > 2 mm shows that those fractions have lower surface area for adsorption than materials that were not submitted to fractionation, resulting in materials with poorer characteristics for adsorption of low-molar-mass solutes. In fact, materials that were not fractionated are a mixture of particles with different size including smaller particle sizes, which have a greater rate of adsorption [6]. According to results presented in Table 1, chemically treated materials presented higher iodine numbers than non-chemically treated materials. So, though olive cake can be used as adsorbent without further treatment, chemical activation enhances its adsorption capacity. Comparing the different chemical activation, results show that material treated with sulfuric acid presented higher iodine numbers than material treated with sodium hydroxide, thus resulting in a material with better characteristics for adsorption. This is in agreement with the literature that reports that chemical activation using sulfuric acid at moderate temperatures produces a high surface area and high degree of microporosity [4]. Nevertheless, the iodine number of the materials in this study are lower than the iodine number obtained in the characterization of activated carbons from olive-waste cakes and from olive stones (waste olive cake activated with H_3PO_4 + pyrolysis: 583 mg/g [27]; olive stones activated with steam and N_2 gas mixture: 550 mg/g; solvent extracted olive pulp activated with steam and N_2 gas mixture: 478 mg/g [34]).

Results presented in Table 1 show that non-fractionated material have higher nitrogen content than fractionated material (> 2 mm fractions), but no significant differences are observed between fractionated and non-fractionated materials regarding the C and the H contents. Chemically treated materials showed a nitrogen content similar to the waste olive cake *in natura*. Treatment with sodium hydroxide produced a material with less carbon than the waste olive cake *in natura* and treatment with sulfuric acid produced a material with less hydrogen than the waste olive cake *in natura*. These materials presented lower carbon and hydrogen content, but higher nitrogen content than results for the waste olive cake reported in [30]. Results presented in Tables 1-2 also show that fractions > 2 mm have lower mineral content than materials without fractionation. Chemically treated materials also presented lower mineral content, namely calcium, magnesium, potassium, iron, manganese, zinc and copper contents, than materials *in natura*. So, as expected, the chemical treatments removed the inorganic matter. But, this removal mainly influences the larger pores [34].

Material pH may influence the removal efficiency. Material *in natura* presented a neutral pH, but treatment with sulfuric acid resulted in a carbonaceous material (OC-H) with an acid pH and treatment with sodium hydroxide resulted in a carbonaceous material (OC-OH) with an alkaline pH (Table 1). The very low pH value of OC-H is an indication of the presence of strong acid functional groups on the OC-H surface and this may hamper the surface properties of the materials to remove the zinc ions from the solution [6].
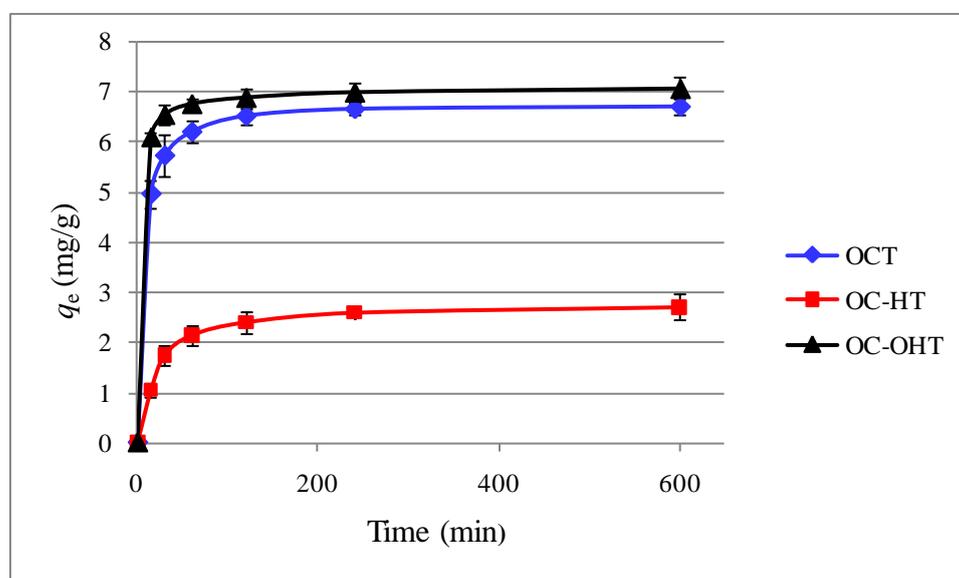
2.2. Zinc Adsorption

2.2.1. Contact time

The effect of contact time on zinc removal for the three different materials (OCT, OC-HT and OC-OHT) at natural pH of solution (6-7) is shown in Figure 1. In these experiments, only the non-fractionated materials were used, at a dose of 1g/L. The concentration of Zn(II) used in those experiments was 10 mg/L and the room temperature was 25 °C. The metal concentration retained in the adsorbent phase (q_e, mg/g) was calculated by using the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_o and C_e are the initial and final concentrations of metal ion in solution (mg/L), V is the volume of solution (l) and W is the mass of the adsorbent (g).

Figure 1. Effect of contact time on zinc removal (pH = 6-7; [Zn(II)] = 10 mg/L; biosorbent dose = 1g/L).

The zinc adsorption increased with time until equilibrium is attained between the amounts of zinc adsorbed on the biosorbents and the zinc remaining in solution. The figure shows that the adsorption of zinc increased with time from 0 to 120 min and then becomes almost constant up the end of the study. The rate of zinc binding with the biosorbents is higher in the initial stage and gradually decreases, becoming almost constant after 120 min. The rate behavior of the three different materials is similar, but it has been found that under identical conditions the material treated with sodium hydroxide (OC-OHT) and the waste olive cake *in natura* (OCT) presented higher removal efficiency for zinc than the material treated with sulfuric acid (OC-HT). The very low pH value of OC-HT (2.4, Table 1) is an indication of the presence of acid functional groups on the OC-HT surface. The smaller adsorption values observed with the acid material (OC-HT) can be attributed to the competition between the high concentrations of H^+ to be released by the biosorbent surface and the zinc ions in solution. Also the positively charged

surface can result in a repulsion of the adsorbing metal ion. Material treated with sodium hydroxide showed a higher removal efficiency for zinc than waste olive cake *in natura*, but these differences were not statistically significant (*P-value* = 0.58, t-Test).

2.2.2. Kinetic modelling

The sorption kinetics is an important aspect in the control of pollutants removal process, once it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions [36]. The Lagergren's first-order kinetic model and the Ho's pseudo-second-order model are the most frequently used in the literature to predict the mechanism involved in the sorption process [36]. The Lagergren's first order model is expressed by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

where q_t and q_e (mg/g) are respectively the amounts of sorbed metal at time t and at equilibrium and k_1 (min^{-1}) is the first order rate constant. The more recent pseudo-second-order model has been extensively used by several researchers in the same field [26]. This model is expressed by the following equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). The integration of equations 2 and 3 and its linearization allows the calculation of the rate constants and the equilibrium removal capacity q_e. Our results did not fit the Lagergren's first-order kinetic model but good correlation was obtained with the Ho's pseudo-second-order model (Figure 2).

Figure 2. Pseudo-second-order plot for zinc removal from aqueous solution (pH = 6-7; [Zn(II)] = 10 mg/L; biosorbent dose = 1g/L).
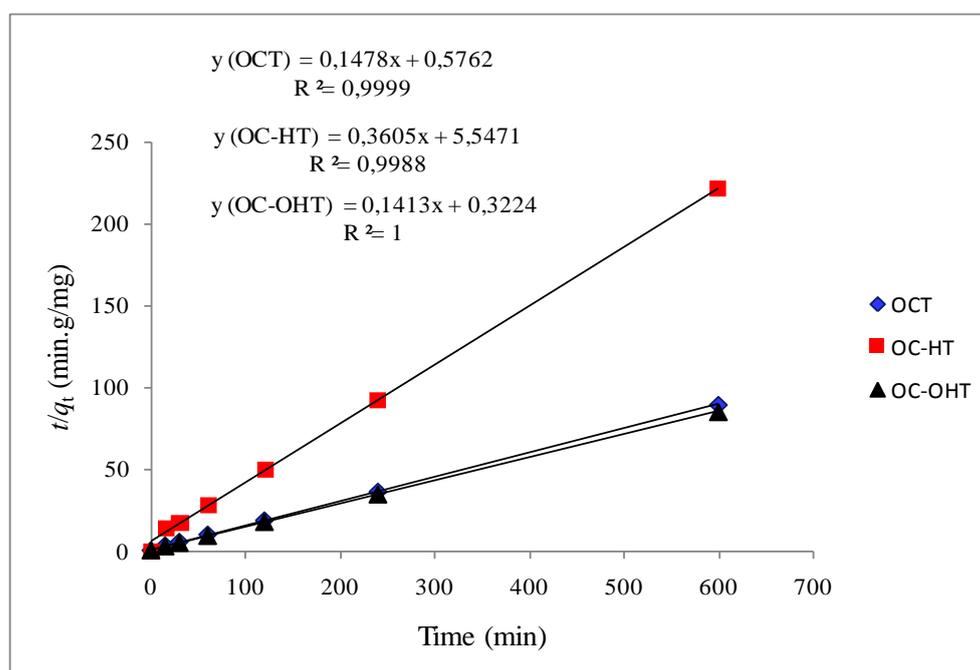
The calculated rate constants and q_e values and the corresponding linear regression determination coefficient R^2 values for both models are presented in Table 3. According to the results reported in Table 3, the first-order kinetic model did not fit well the experimental data. The experimental and the calculated values of the equilibrium removal capacity were significantly different. On the opposite, good correlation is observed between experimental data and the pseudo-second-order kinetic model with R^2 values higher than 0.99. For the three materials, the differences between the experimental and the calculated values of the equilibrium removal capacity were not significant. This suggests that the rate-limiting step in these biosorption systems may be chemical sorption or chemisorptions involving valence forces through sharing or exchange of electrons between sorbent and metal [36].

Table 3. Experimental and calculated values for the first-order kinetic model and for the pseudo-second-order model.

		First-order model			Pseudo-second-order model		
	q_e experimental (mg/g)	q_e calculated (mg/g)	k_1 (min^{-1})	R^2	q_e calculated (mg/g)	k_2 (g mg^{-1} min^{-1})	R^2
OCT	6.7 ±0.2	2.6	0.021	0.923	6.8	0.038	1.000
OC-HT	2.7 ±0.3	1.7	0.011	0.895	2.8	0.023	0.999
OC-OHT	7.1 ±0.3	1.6	0.019	0.812	7.1	0.062	1.000

The very fast sorption kinetics observed with the materials studied in this work represents an advantageous aspect when water treatment systems are designed, once these materials could be suitable for a continuous flow system. Values of the rate constants obtained in this study were compared with values reported in the literature for zinc ion adsorption onto agro based waste materials (Table 4).

**Table 4.** Comparison of rate constants for Zn(II) adsorption onto agro based waste materials.

Adsorbent	First-order model k_1 (min^{-1})	Pseudo-second-order model k_2 (g mg^{-1} min^{-1})	References
Activated carbon derived from bagasse	0.0079	-	[2]
Solvent extracted olive pulp activated with steam and N$_2$ gas mixture	0.0037-0.0090	-	[34]
Olive stones activated with steam and N$_2$ gas mixture	0.0035	-	[34]
Sugar beet pulp	-	0.102	[37]
Coffee husks	-	0.18-0.59	[38]
OCT	0.021	0.038	This study
OC-HT	0.011	0.023	This study
OC-OHT	0.019	0.062	This study

According to those results, the materials studied showed a better performance regarding the kinetics of the removal of Zn from the solution, compared to activated carbon derived from bagasse and compared to materials derived from waste olive cake and olive stones. But, compared to sugar beet pulp and to coffee husks, the materials studied presented lower kinetic constants. It should be noted also that variable kinetic constants are obtained due to different initial concentrations of metal, to different adsorbent dose and to different essay temperatures [2,6,8,31,36-38]. So, in this comparison (Table 4) results derived from different experimental conditions and this may be a source of variability that is not being considered.

2.2.3. Effect of solution pH

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process because the surface charge density of the adsorbent and the metallic species depend on the hydrogen ion concentration [8]. Thus the role of the pH was studied from solutions at different pH, covering a range of 3.0-7.0 for the three different materials (OCT, OC-HT and OC-OHT). In these experiments, only the non-fractionated materials were used, at a dose of 1g/L. The concentration of Zn(II) used in those experiments was 10 mg/L and the room temperature was 25 °C. The effect of solution pH on Zn(II) sorption is shown in Figure 3.

Figure 3. Effect of initial solution pH on zinc adsorption ([Zn(II)] = 10 mg/L; biosorbent dose = 1g/L).
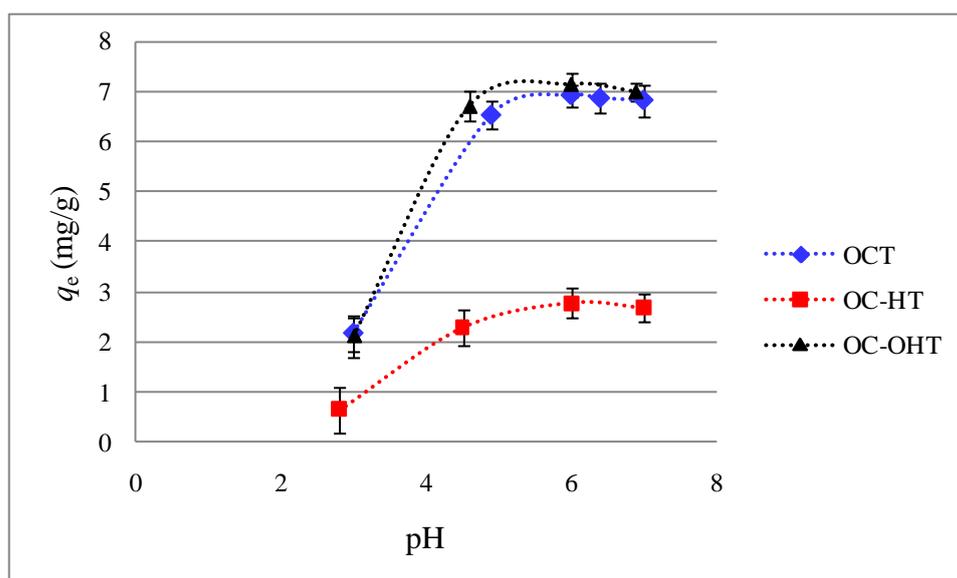

The amount of zinc ions sorbed by the materials increased sharply with the increase in pH from 3 to 4.5-5 and then increased more slowly with the increase in pH from 4.5-5.0 to 6.0. After pH 6.0 to 7.0 the amount of zinc adsorbed remained constant. Those results are in agreement with results reported in the literature which show that the pH range, where maximum adsorption occurs for zinc, lies within pH 5-7 [39]. From the speciation diagram for zinc [39], in this pH range (3-7) the metal will be mostly present in solution in its divalent ionic form, with smaller amounts in the form of $ZnOH^+$ at pH's > 6.0, making it favorable for biosorption in an increasingly negatively charged surface. At low pH values

there is a competition between H^+ and Zn^{2+} ion species for the sites of adsorption, due to the high H^+ concentration, while at higher pH this effect is diminished. According to these results, as the initial pH of sorption tests for the different biosorbents, were in the range 6.0-7.0 (OC: 6.5±0.1; OC-H: 6.0±0.1; OC-OH: 6.9±0.1), than maximum adsorption for the zinc ion was expected during the experiments. These results also show that no adjustment of the solution pH, for the sorption tests, is necessary in order to accomplish the maximum removal of zinc from the solution.

2.2.4. Effect of initial zinc concentration

The effect of initial zinc concentration on the adsorption is shown in Figure 4. Those sorption tests were conducted at 25 °C at natural pH of solution (6-7). Results presented are average results of the tests performed with different adsorbent doses (1, 2.5, 5, 7.5 and 10g/L). It can be seen from the figure that with increased Zn(II), the percentage removal of zinc decreased. As seen in Figure 4, while the initial Zn(II) concentration increased from 10 to 200 mg/L, the percent zinc removal by OCT, for example, decreased from 93 to 40% at equilibrium (average results of the tests performed with different adsorbent doses). But the amount of Zn(II) ions adsorbed per unit mass of adsorbent increased with the increase of the initial zinc concentrations. For example, for OCT, the adsorption capacity increased from 3.3 to 22 mg/g (average results of the tests performed with different adsorbent doses). This can be attributed to the effective pore diffusivity decrease with increasing initial metal concentration [31,40] and to a more efficient utilization of the sorptive capacities of the sorbent due to greater driving force (by a higher concentration gradient pressure) [41,42] .

Figure 4. Effect of initial concentration of zinc on the percentage removal of zinc (average results of the tests performed with different adsorbent doses; pH 6-7).
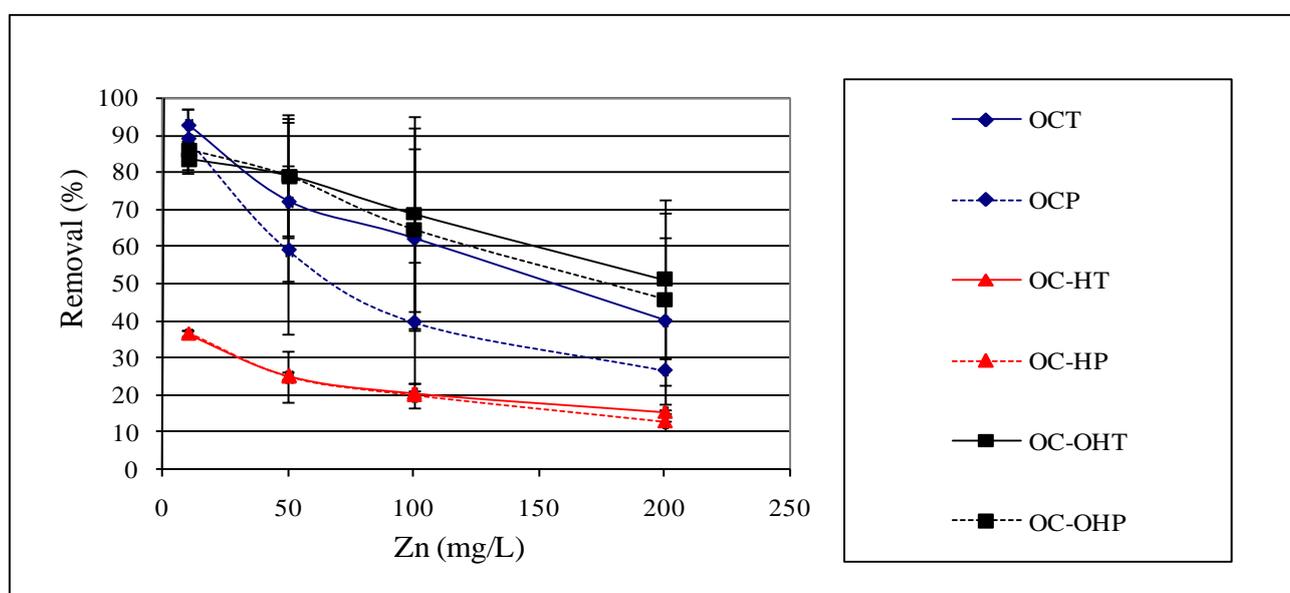
2.2.5. Effect of particle size

The effect of the previous fractionation step on the adsorption has been shown in Figure 4. It can be seen from the figure that the > 2.00 mm fraction removes lower zinc than the total biomass (treated

chemically or not treated), although these differences are not statistically significant (P-$value_{(OCT; OCP)}$ = 0.13; P-$value_{(OC-HT; OC-HP)}$ = 0.75; P-$value_{(OC-OHT; OC-OHP)}$ = 0.79; t-Test). Whole material is characterized by having not only particles with size > 2.00 mm (corresponding to 42 ± 3% w/w of the whole material) but also particles with smaller size (corresponding to 58 ± 3% w/w of the whole material). And those smaller particles present in the whole material led to an increase in metal adsorption. This is consistent with the literature once the smaller the particle sizes of the sorbents are, the greater the rate of diffusion and adsorption [6,11,43]. Intra-particle diffusion is reduced as the particle size reduces, because of the shorter mass transfer zone, causing a faster rate of adsorption [6]. Larger particles with spherical shapes, in general, present higher external mass transfer than smaller particles and adsorption from these particles is attributed to mass transport inside the sorbent particles [43]. When higher metal adsorption is verified on smaller particles, as observed with this study materials, the main process of metal adsorption onto solid adsorbents are those based on adsorption on the particle surface [43]. So, it is possible to conclude that the Zn(II) sorption on the materials tested in this study can be attributed to adsorption processes on the particle surface, mainly those related to ion exchange or surface complex formation [43]. According to the generic composition of the waste olive residues reported in the literature, smaller particles are especially characterised by cellulose, residual fats and polyphenolic substances, while particles with larger dimensions, by lignin and cellulose [44]. Thus, smaller particles are richer in active sites for adsorption not only due to the larger specific active surface but also to its specific composition, namely the acidic sites, such as carboxylic and phenolic groups present in the fat and polyphenolic compounds [11].

According to these results and to the results obtained in the characterization of the materials (*2.1*), this previous step shouldn't be considered in a commercial project, if the intention is to produce biosorbents from the > 2.00 mm fraction. Sorption tests should be done with the < 2.00 mm fraction in order to understand if it removes higher zinc than the whole material (with statistical significance). If so, fractionation could be considered in a commercial project. The < 2.00 mm fraction, canalized for the production of biosorbents and the > 2.00 mm fraction, as a source of heat energy.

2.2.6. Effect of chemical treatment

The effect of the chemical treatment on the adsorption has also been shown in Figure 4. It can be seen from the figure that treatment with sodium hydroxide resulted in a higher percentage removal of zinc. This may reflect not only the surface properties of the biosorbent, characterized by the high iodine number, but also the material pH, which was alkaline. Differences in the removal efficiency are not statistically significant to the untreated biomass (P-$value_{(OC-OH; OC)}$ = 0.095, t-Test) but they are statistically significant to the acid treated material (P-$value_{(OC-OH; OC-H)}$ = 1.9×10^{-16}, t-Test). Figure 4 also shows that though treatment with sodium hydroxide enhances the adsorption capacity to zinc of the olive cake (although without statistical significance), the treatment with sulfuric acid reduces significantly its adsorption capacity. The removal efficiency of the sulfuric acid treated material is statistically significantly lower than the removal efficiency obtained with the untreated biomass (P-$value_{(OC; OC-H)}$ = 4.5×10^{-10}, t-Test) and with the sodium hydroxide treated material (P-$value_{(OC-OH; OC-H)}$ = 1.9×10^{-16}, t-Test). In this case, the low pH of the acid biosorbent influenced negatively the removal efficiency although the sulfuric acid treatment produces a high surface area and a high degree of

microporosity (as already explained in *2.1* and in agreement with [4]). The very low pH value of OC-H (2.3-2.5, Table 1) is an indication of the presence of acid functional groups on the OC-H surface. The smaller adsorption values observed with the acid biosorbent can be attributed to the competition between the high concentrations of H^+ to be released by the biosorbent surface and the zinc ions in solution. Also the positively charged surface can result in a repulsion of the adsorbing metal ion. Partial degradation of the biomass matrix might also have occurred during the treatment with sulfuric acid, decreasing the active sites for adsorption and thus lowering the levels of adsorption of the acidic material.

In terms of cost-effectiveness of the process, since alkali treatment didn't augment the removal efficiency of zinc significantly face to untreated biomass, this treatment shouldn't be considered in a commercial process, for the removal of zinc ion from solutions. In fact, this treatment would only augment the consumption of chemicals and energy without a significant improvement of the biosorption process for zinc. Given that the sulfuric acid treatment produces a high surface area and a high degree of microporosity (*2.1*), it should be interesting to test the adsorption capacity of the acidic material to negatively charged ions, like chromate ion, dichromate ion or phosphates.

2.2.7. Adsorbent dose study

The effect of adsorbent dosage on the percentage removal of zinc is shown in Figure 5. Those sorption tests were conducted at 25 °C at natural pH of solution (6-7). Results presented are average results of the tests performed with different initial zinc concentrations (10, 50, 100 and 200 mg/L).

Figure 5. Effect of adsorbent dose on the percentage removal of zinc (average results of the tests performed with different initial zinc concentrations; pH 6-7).
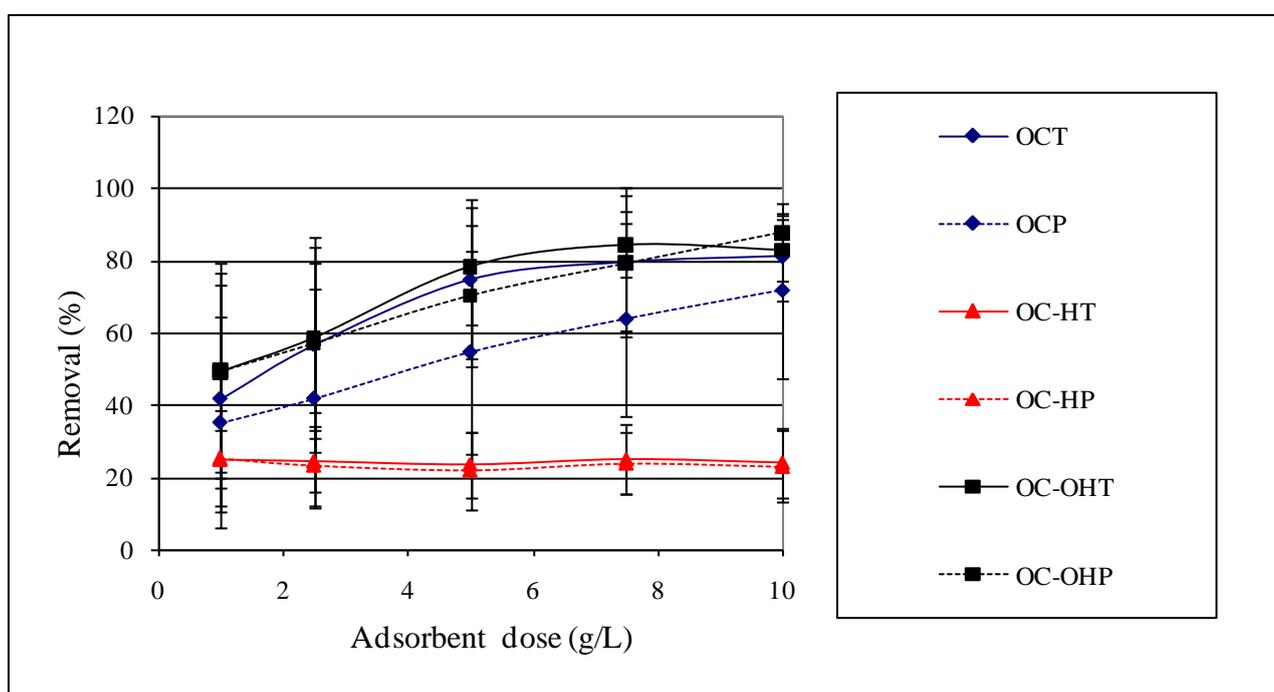
It can be seen from the figure that the percentage removal increases with the increase in adsorbent dosage (1 – 10 g/L), for the OC and OC-OH materials. As seen in Figure 5, while the adsorbent dose increased from 1 to 10 g/L, the percent zinc removal by OCT, for example, increased from 40 to 80% at equilibrium (average results of the tests performed with different initial zinc concentrations). This trend is expected because as the adsorbent dose increases the number of adsorbent particles increases and thus more Zn(II) is attached to their surfaces [6,31,38,45,46]. However, the unit adsorption capacity showed a reverse trend to the percent zinc adsorptions. By increasing the adsorbent dose from 1 to 10 g/L, the adsorption of Zn(II) ion per unit mass of OCT, for example, decreased from 26 to 6.9 mg/g. This may be due to overlapping and aggregation of adsorption sites when dose increased [31,46]. By increasing the adsorbent dose, the surface area for sorption is increased, although the initial zinc ion concentration is constant, thus decreasing the adsorption of Zn(II) ion per unit mass of adsorbent [41]. With OC and OC-OH materials, beyond 5 g/L, the percentage removal reaches almost a constant value. Therefore, the use of 5 g/L adsorbent dose is justified for economical purposes. As it can be observed in Figure 5, the effect of increasing OC-H concentration on the amount of zinc sorbed was not significant. As observed in Figure 4, Figure 5 shows that the > 2.00 mm fraction removes lower zinc than the total biomass, the treatment with sodium hydroxide enhances the adsorption capacity to zinc of the olive cake and the treatment with sulfuric acid reduces its adsorption capacity. Differences observed due to the particle size and to the chemical treatment were already discussed in 2.2.5 and 2.2.6.

2.2.8. Sorption isotherms

Both Langmuir and Freundlich models were tested for equilibrium description. Langmuir equation, based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface [31,38]. It does not take into consideration interactions between adsorbed molecules [38]. It can be represented by the equation:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4}$$

where q_e corresponds to the amount adsorbed per gram of adsorbent at equilibrium (mg/g), C_e is the solute concentration (mg/L) in the aqueous solution after equilibrium was reached, and q_{max} and K_L are constants related to the maximum adsorption capacity (mg/g) and the adsorption energy (l/mg), respectively. Freundlich's equation is an empirical model based on heterogeneous adsorption over independent sites [38] and is given by:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

where K_F is related to binding energy and adsorption capacity and n is related to the intensity of adsorption.

Figure 6. Sorption isotherms of zinc ions by the different biosorbents studied (biosorbent dose = 5g/L; pH 6-7). Solid lines correspond to Langmuir fits.
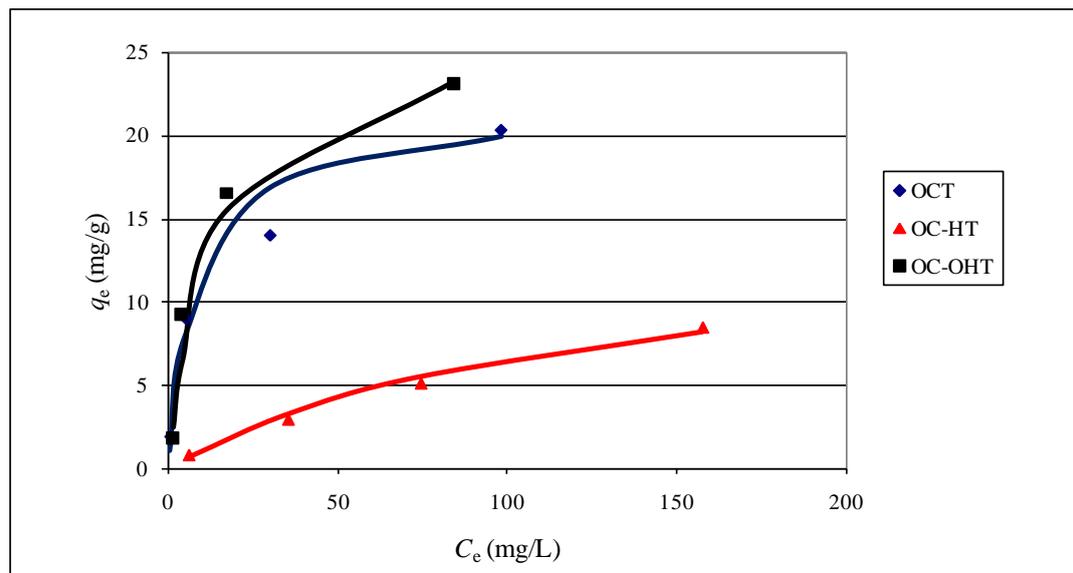
Sorption isotherms are presented in Figure 6. As can be seen, each compound adsorption data corresponds to convex upward curves, which are indicative of strong sorption [38,47]. Both Langmuir and Freundlich models were evaluated for description of metal sorption isotherms (Table 5). Results presented were obtained with the adsorbent dose of 5g/L (dose justified for economical purposes, 2.2.7).

Table 5. Lagmuir and Freundlich constants for sorption of zinc ions by the different biosorbents studied (biosorbent dose = 5g/L; pH 6-7).

	Langmuir			Freundlich		
	q_{max} (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
OCT	22	0.117	0.987	3.23	2.31	0.950
OCP	15	0.046	0.911	2.05	2.66	0.990
OC-HT	14	0.008	0.925	0.23	1.39	1.000
OC-HP	12	0.009	0.876	0.25	1.50	0.998
OC-OHT	27	0.081	0.987	2.45	1.74	0.830
OC-OHP	22	0.067	0.992	1.91	1.81	0.856

Both Langmuir and Freundlich models are well suited to fit the data on sorption of zinc by waste olive cake without any chemical treatment (OC). Data on sorption of zinc by waste olive cake treated with sulfuric acid (OC-H) represented acceptable fit to the Langmuir isotherms equation, though not as perfect as to the Freundlich isotherms equation. Zinc sorption from aqueous solutions by waste olive cake treated with sodium hydroxide (OC-OH) was better described by Langmuir model in comparison to Freundlich model. Zinc uptake capacity, represented by q_{max} in Langmuir equation, was higher for waste olive cake treated with sodium hydroxide (OC-OH) followed by non treated material (OC) and

was the lowest for waste olive cake treated with sulfuric acid (OC-H). A comparison of the zinc ions uptake capacities obtained in this study were compared with values reported in the literature for zinc ion adsorption onto agro based waste materials (Table 6).

Table 6. Langmuir based maximum adsorption capacity of several agro based waste materials for zinc adsorption.

Adsorbent	q_{max} (mg/g)	References
Activated carbon derived from bagasse	31	[2]
Waste olive cake extracted and roasted	5.4	[28]
Solvent extracted olive pulp activated with steam and N_2 gas mixture	31-33	[34]
Olive stones activated with steam and N_2 gas mixture	16	[34]
Peach stones activated with steam and N_2 gas mixture	6.4	[34]
Apricot stones activated with steam and N_2 gas mixture	13	[34]
Sugar beet pulp	18	[37]
Coffee husks	5.6	[38]
Coir	8.6	[48]
Papaya wood	14	[49]
Groundnut shells	7.6	[50]
Dye loaded groundnut shells	9.6	[50]
Teakwood Sawdust	11	[50]
Dye loaded teakwood sawdust	17	[50]
Rice husk alkali treated and autoclaved	8.1	[51]
Peanut hulls	9.0	[52]
Peanut hull pellets	10	[52]
Corncobs	2.0	[53]
Corncobs treated with citric acid	7.8-35	[53]
Corncobs treated with phosphoric acid	32-35	[53]
Cornstarch	6.9	[54]
Succinylated cornstarch	13	[54]
Oxidized cornstarch	37	[54]
OCT	22	This study
OCP	15	This study
OC-HT	14	This study
OC-HP	12	This study
OC-OHT	27	This study
OC-OHP	22	This study

However, qualitatively, it is evident that the zinc uptake capacity of the waste olive cake and derivates used in this study, in general, exceeds or is comparable to those for other sorbents presented in Table 6. These results reinforce the feasibility of employing waste olive cake and chemically modified olive cake as biosorbents for zinc ions removal from aqueous solutions, since they present good adsorption capacity in comparison to other low-cost sorbents. Aside from the zinc uptake capacity, the major advantage of waste olive cake as low-cost sorbents is that they are readily available in large quantities (in Portugal) and do not present an alternative profitable use. Also, after zinc sorption, the zinc-laden olive cake and chemically modified one can be used as a source of energy through combustion [12,18-25].

3. Experimental Section

3.1. Biosorbents Preparation and Characterization

The olive cake used for the experiments was obtained from "ProBeira", a producer of pitted table olives and also an olive oil factory, located in Envendos (Portugal). The waste, after an initial drying stage at ambient temperature, was roughly ground with a porcelain mortar and pestle. Part of the material was sieved in order to collect the fraction with > 2.00 mm, which corresponds mainly to the olive stones by-product, present in the olive cake. Both materials were then additionally dried in a vacuum oven at 60 ℃ for further 24 h. Tests were conducted with the total biomass and with the fraction > 2.00 mm, in order to determinate the influence that this fractionation has on subsequent treatments.

Two different activated agents were used: H_2SO_4 and NaOH. Activation with H_2SO_4 [4]: the materials were mixed in a 1:1 wt ratio with concentrated H_2SO_4, placed in an oven and heated to 200 ℃ for 24 h. After this, the samples were allowed to cool to room temperature, washed with distilled water and soaked in 1% $NaHCO_3$ solution to remove any remaining acid. The samples were then washed with distilled water until pH of the material reached 6, dried at 105 ℃ for 24 h and sieved to obtain the desired particle size (1.00-2.00 mm). Activation with NaOH [55]: the substrate (0.5 g) was added to 0.25 M NaOH solution and left for 1 h, after which the samples were neutralized with HCl. They were then washed thoroughly with distilled water, dried at 105 ℃ for 24 h and sieved to obtain the desired particle size (1.00-2.00 mm). Moisture content, ash content, elemental analysis and ash elemental analysis, pH and iodine number were determined in order to characterize the materials, before and after the chemical treatment processes.

The moisture content was determined after drying the biomaterials at 105 ± 2 ℃ to constant weight [56]. The ash content of all samples was obtained after burning a given amount of material in the presence of air at 550 ± 25 ℃ for 3 h and was calculated on a dry basis [56]. Elemental analysis was performed with a CHN 2000 elemental analyzer (Leco) [57]. Ash elemental analysis was determined after digestion of the ashes with HNO_3 [58]. The concentration of metals in the digested solution was measured by Atomic Absorption Spectrophotometry (Unicam Solaar 939). The pH of materials was measured after suspending 1 g of the material in 50 mL distilled water for 24 h [59]. The pH measurements were made using a micropH2001 meter (Crison). The iodine number is defined in terms of the milligrams of iodine adsorbed by 1 g of material when the iodine equilibrium concentration is 0.01

M [35]. This test method is based upon a three-point adsorption isotherm. A standard iodine solution (0.05M) is treated with three different weights of material under specified conditions. The carbon treated solutions are filtered to separate the carbon from the treated iodine solution (filtrate). Iodine remaining in the filtrate is measured by titration. The amount of iodine removed per gram of material is determined for each weighed sample and the resulting data used to plot a graph. The amount of iodine adsorbed (in milligrams) per gram of carbon at a residual iodine concentration of 0.01M is reported as the iodine number.

3.2. Adsorption Tests

To estimate the applicability of produced biomaterials as adsorbents for wastewater treatment, the adsorption tests were performed using zinc ion as the adsorbate. For the preparation of synthetic zinc wastewater, $ZnCl_2$ salt was used to make a 1,000 mg/L solution, which was diluted to 10, 50, 100 and 200 mg/L.

3.2.1. Effect of contact time

Batch experiments of biosorption were performed in a 250 mL conical flask. In all sets of experiments, 0.1 g of biomaterials was thoroughly mixed with 100 mL solution. In these experiments, only the non-fractionated materials were used. The concentration of Zn(II) used in those experiments was 10 mg/L. The mixture was agitated at a speed of 200 rpm in a thermostatic shaker bath at 25 ℃ for periods of time that ranged from 0.25 to 10 h. The initial solution pH of the mixtures ranged 6-7. All tests were carried out twice. After shaking, the material was separated from solution by filtration. The concentration of zinc ion remaining in solution was measured by Atomic Absorption Spectrophotometry (Unicam Solaar 939) after diluting the filtrate to an adequate concentration.

3.2.2. Effect of solution pH

The adsorption capacity of the materials at different pH was also studied. Batch experiments of biosorption were performed in a 250 mL conical flask. In all sets of experiments, 0.1 g of biomaterials was thoroughly mixed with 100 mL solution. In these experiments, only the non-fractionated materials were used. The concentration of Zn(II) used in those experiments was 10 mg/L. The initial pH of the solutions was adjusted to the required value, covering a range of 3.0-7.0, either by sulfuric acid and sodium hydroxide. The mixture was agitated at a speed of 200 rpm in a thermostatic shaker bath at 25 ℃ for 24 h and all tests were carried out twice. After shaking, the material was separated from solution by filtration. The concentration of zinc ion remaining in solution was measured by Atomic Absorption Spectrophotometry (Unicam Solaar 939) after diluting the filtrate to an adequate concentration.

3.2.3. Equilibrium isotherms

Known amounts of materials (0.1, 0.25, 0.5, 0.75 and 1.0 g) were placed in a 250 mL conical flask and 100 mL of zinc solution was added. Different initial zinc concentrations were tested in those experiments (10, 50, 100 and 200 mg/L). The mixture was agitated at a speed of 200 rpm in a

thermostatic shaker bath at 25 °C for 24 h. The initial solution pH of the mixtures ranged 6-7 and all tests were carried out twice. After shaking, the material was separated from solution by filtration. The concentration of zinc ion remaining in solution was measured by Atomic Absorption Spectrophotometry (Unicam Solaar 939) after diluting the filtrate to an adequate concentration.

4. Conclusions

The employment of the waste olive cake and chemically modified waste olive cake as biosorbents is a useful recycling process. Results showed that chemical treatment by sodium hydroxide produces a bio material with a superior adsorption capacity for zinc ion than treatment with sulfuric acid, although no significant differences were observed between the basic treated biomaterial and the untreated biomaterial. The maximum adsorption capacity obtained from the Langmuir isotherms increases in the order (mg/g): OC-HT (14), OCT (22) and OC-OHT (27). But, chemical treatment with sulfuric acid produces a biomaterial with better characteristics for adsorption than with sodium hydroxide. Furthermore, the superior adsorption capacity of the biosorbents studied, untreated or chemically treated with sodium hydroxide, for zinc ions, suggests that the process is potentially marketable. Results also indicate that the previous fractionation step, in order to obtain the > 2.00 mm fraction, doesn t produce an activated material with a superior adsorption capacity. So, this previous step shouldn't be considered in a commercial project.

Portugal is the 8th largest olive oil producer in the world and is characterized by a predominance of small to medium-sized olive oil industries. Most of those olive oil mills don't have a proper system to treat and dispose the waste olive cake. In order to minimize those problems related to the disposal of this residue, the development of economic technologies that can reuse these residues should be a priority. In this respect, this work tried to address this purpose, by chemically modifying the waste olive cake, with minimum processing, and trying to understand the behavior of these materials for the zinc ion removal of effluents (also a problem in Portugal).

Acknowledgements

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