0273-2289/03/110/0137/$25.00

Olive Husk

An Alternative Sorbent for Removing Heavy Metals From Aqueous Streams

Angela Volpe,* Antonio Lopez, and Michele Pagano

Consiglio Nazionale delle Ricerche, Istituto di Ricerca sulle Acque, Via F. de Blasio, 5, 70123 Bari, Italy, E-mail: irsaav27@area.ba.cnr.it

Abstract

Sorption properties of olive husk were investigated under equilibrium (batch tests) and dynamic (column tests) conditions in order to assess the possibility of using such a waste material for removing heavy metals from aqueous streams. Husk samples were contacted, at 25°C, with aqueous solutions of nitric salts of Pb, Cd, Cu, and Zn. Sorption isotherms obtained from equilibrium data were fitted and interpreted by the Freundlich model. Metals-saturated husk samples resulting from column tests were air-dried and incinerated to simulate combustion in order to assess the fate of sorbed metals. The results demonstrated that, under both equilibrium and dynamic conditions, metal sorption capacity of the husk was in the sequence Pb>Cd>Cu>Zn. For all the metals, calculated Freundlich constants decreased by increasing initial metal concentration or decreasing solution pH. In dynamic tests, a significant reduction of sorption capacity was recorded (except for copper) when a metal was fed simultaneously to the others: Pb (77%); Cd (93%); Zn (68%). Combustion tests carried out on metals-saturated husk samples showed that the average losses of lead and cadmium, as volatile species, were always three to four times greater than the losses of copper and zinc, in both single-metal- and multimetal-saturated samples.

Index Entries: Heavy metals; sorption; olive husk; wastewater.

Introduction

Heavy metals contamination is an issue of great environmental concern because of the persistence of such pollutants in air, water, and soil and toxic effects to living systems through bioaccumulation *(1)*.

The main sources of heavy metals pollution are wastewaters from industrial activities such as mining; power production; electrodeposition;

*Author to whom all correspondence and reprint requests should be addressed.

tanning operations; and manufacturing of semiconductors, batteries, fertilizers, pigments, and paints *(2)*. Presently, the available technologies for removing metals from polluted wastewater are mostly based on precipitation, oxidation or reduction, sorption, ion exchange, and membrane filtration processes *(3)*. Among them, precipitation, although cheap, versatile, and simple, only permits the transfer of pollutants from a diluted phase (wastewater) to a concentrated phase (sludge), which, in turn, requires disposal. Furthermore, because precipitation does not allow trace metals removal, for some metals it is not possible to achieve the limits fixed by local regulations. Conversely, technologies based on ion exchange and membrane filtration not only reach very low residual concentrations of metals but also permit their quantitative recovery and recycle. Such technologies, as well as those based on oxidation/reduction processes, are complex and expensive. Regarding sorption technologies, their main drawback is the high cost of both sorbent materials (e.g., activated carbon) and their chemical or thermal regeneration *(4)*.

To reduce these costs, interest in alternative cheaper materials such as mineral oxides/hydroxides, zeolites, clays, and natural biosorbents (i.e., waste materials resulting from agricultural and industrial activities) is continuously growing *(5,6)*. In addition to their low cost, the main advantage of such materials is their "once-through" use, which avoids expensive regeneration.

As for natural biosorbents, those potentially effective for metals sorption can be substantially split into two categories: (1) living (microbial) biomass, for which metals retention is the result of the metabolic activity of microorganisms, which, in turn, is related to metal toxicity *(7)*; and (2) nonliving (vegetal) biomass, for which metals retention is owing to specific interactions with metal-selective functional groups (e.g., carboxyl, hydroxyl, sulfate, phosphate, amino, and amido) belonging to the chemical structure (e.g., polysaccharides, proteins, lipids) of these materials *(6)*.

So far, biosorbents already investigated to assess their sorption properties toward metals include algae *(8,9)*; fermentation products (bacteria, fungi, yeasts) *(10,11)*; chitin and chitosan *(5)*; peat *(12,13)*; and lignocellulosic residues such as sawdust and tree bark, straw, coconut and peanut shells, sugarcane, and beet pulp *(14–31)*. Most of them have shown sorption properties comparable with those of synthetic and costly materials *(5)*, confirming them as promising alternatives from both technological and economic standpoints.

On the basis of these considerations, taking into account that in Italy about 500,000 t/yr of olive husk is produced as waste material by the olive oil industry and that combustion for energy production is the main use of this material, we conducted an investigation to characterize the sorption properties of olive husk toward selected heavy metals and to assess the fate of sorbed metals during the combustion of metals-saturated husks.

Materials and Methods

Chemicals

Analytical-grade chemicals (Baker Analyzed, Deventer, The Netherlands) were used throughout the experiments.

Husk Conditioning

Samples of husk resulting from olive oil extraction were provided by a factory located near Bari, a town in Southern Italy. Husk samples were used after washing them with demineralized water to elute readily leachable organic matter, grinding (≤1 mm), and drying (105°C).

Acid-Base Titration

Two identical batches were prepared, each made of 1.0 g of conditioned husk suspended in 500 mL of demineralized water previously purged with N_2 and containing 0.1 mol/L of $NaNO_3$ as background electrolyte. Two titrations were carried out, one for each batch, adding H_2SO_4 or NaOH, both 0.02 *M*, under an inert atmosphere (N_2) to avoid the influence of external CO_2. After each addition of titrant, enough contact time (10 min) was allowed to achieve equilibrium conditions (i.e. constant pH values). A blank titration was carried out under the same conditions but without the husk.

Batch Sorption Experiments

Known amounts of husk (0.05–5 g) were contacted with fixed volumes (50–500 mL) of Pb, Cd, Cu, and Zn nitrate solutions at three different initial concentrations (10, 20, and 40 mg/L) and two pH values (3.5 and 5.0) in polyethylene bottles. During the tests at pH 3.5, the pH was maintained constant by adding 0.1 *M* HNO_3. During the tests carried out at pH 5.0, no pH adjustments were necessary because this pH (±0.5) remained constant throughout the experiments. Solid-to-liquid ratios were fixed to allow measurable residual concentrations of metals in the liquid phase at equilibrium. Batches were equilibrated in an orbital shaker at 180 rpm and constant temperature (25°C) for 24 h. Preliminary kinetic tests had confirmed that equilibrium was achieved within such a time span. After equilibration and filtration through 0.45-μm cellulose acetate filters, residual metal concentrations in the liquid phase were measured by inductively coupled plasma emission spectroscopy (ICP-OES). Blank tests (metal solutions without husk) were carried out to demonstrate the absence of any metal sorption owing to polyethylene bottles or cellulose filters. Blank equilibration tests were also carried out to quantify the eventual release of metals from pure husk by suspending known amounts of it in demineralized water. Organic matter release from husk was quantified by total organic carbon (TOC) measurements on filtered samples by an automatic TOC analyzer.

Column Experiments

Conditioned dry husk (2.5 g) was hydrated overnight in demineralized water and transferred into a glass column (id = 5 mm; height = 100 mm), yielding a final bed volume of 6 mL. Column tests were carried out at pH 5.0 (±0.5), feeding (upflow) nitrate solutions (flow rate = 1 mL/min) containing either a single metal (20 mg/L) or all the selected metals together (20 mg/L each).

Incineration Tests

Metals-saturated husk samples from column tests were washed with 100 mL of distilled water and dried overnight at 105°C. Dry sample (0.3 g) was mineralized by microwave digestion in 10 mL of 65% (w/w) HNO_3, and the resulting solution was diluted to a volume of 25 mL. Metal concentrations in these solutions were measured and related to the metal concentrations in the husk solid samples (milligrams/gram).

Dried husk samples (0.5 g) were incinerated in porcelain capsules at 550°C, the residual ashes were dissolved in 10 mL of 65% (w/w) HNO_3, and the solutions obtained were diluted to a volume of 25 mL. Metal concentrations in these solutions were related to the residual metal content in the ashes (milligrams/gram).

Analytical Methods

Percentages of total moisture, nitrogen, phosphorus, and organic carbon of the tested olive husk were measured according to standard procedures *(32)*. Titrations were carried out by a Titrino 719S system coupled with a pH electrode combined with an Ag/AgCl reference electrode, both from Metrohm (Herisau, Switzerland). Metal concentrations were determined by an Optima 3000 ICP-OES system from Perkin-Elmer (Norwalk, CT). Microwave digestion of husk samples was carried out using an MDS 2100 system from CEM S.p.A. (Bergamo, Italy). Soluble organic carbon concentration was determined by a TOC Analyzer 5050 from Shimadzu (Japan).

Results and Discussion

Table 1 reports the measured contents of total moisture, nitrogen, phosphorus, and organic carbon of olive husk conditioned as described in Materials and Methods.

From comparison of titration data referring to the husk suspensions and blank, it is possible to calculate the equivalents (H^+ or OH^-) necessary for the quantitative conversion of the husks in acid (up to pH 2.2) or alkaline (up to pH 11.5) form, i.e., 0.49 meq of H^+/g and 1.63 meq of OH^-/g, respectively. Such a result quantitatively proves the acidic nature of the husks confirmed even by the initial pH value of its aqueous suspension (i.e., pH 5.2). The qualitative discrimination among the different functional groups of

Table 1
Main Constituents of Tested Husk

Moisture (at 105°C)	Total nitrogen (as N) (%)	Total phosphorus (as P_2O_5) (%)	TOC (%)
21.99	1.36	0.44	39.53

the husks responsible for protonation-deprotonation reactions is beyond the scope of this article. Nevertheless, as for similar biosorbents *(17)*, considering the predominant lignocellulosic structure of this material, it is assumed that such functional groups are essentially a mixture of carboxyl, hydroxyl, and phenolic moieties.

Sorption properties of the husks were investigated at two pH values (3.5 and 5.0), each representative of specific experimental conditions. In fact, pH 5.0 (±0.5) is that resulting when the husk is suspended in neutral water, whereas pH 3.5 (±0.5) is that typical of many industrial wastewaters contaminated by heavy metals.

The sorption isotherms obtained from batch experiments were fitted and interpreted according to the Freundlich model *(33)* expressed by the following equation:

$$X = K_F c^n \quad (1)$$

in which X is the amount of metal sorbed per unit mass of sorbent under equilibrium conditions, c is the metal concentration in liquid phase under equilibrium conditions, K_F is the Freundlich constant related to the sorption capacity of the sorbent toward the reference metal, and n is the dimensionless parameter related to the intensity of sorbent-sorbate interactions.

The Freundlich model is perhaps the most widely used nonlinear sorption equilibrium model for physicochemically nonhomogeneous sorbents. Although both its origins and applications are for the most part empirical, the model has been proven to be thermodynamically rigorous in many instances of sorption on heterogeneous surfaces *(34)*. Table 2 reports the values of the correlation coefficients (R^2) for the Freundlich equation as well as those of the Freundlich parameters (i.e., K_F and n) together with their coefficients of variation (CVs) as obtained from the mathematical best fit of experimental equilibrium data. Both R^2 and CV values prove, in all the cases, the reliability of the data in Table 2, which, whatever the metal, indicate that when the initial concentration is 10 mg/L, the resulting K_F values sharply increase from pH 3.5 to 5.0. This trend cannot be ascribed to a pH-dependent speciation of metal ions in solution. In fact, as proven by the results of thermodynamic calculations done by means of the computer code MINEQL+ *(35)* and graphically shown in Fig. 1, at both pHs all the metals should always occur as free ions. To explain this trend, then, it must be assumed that, under equilibrium conditions, metal ions in solution cannot be present only in a free form [Me^{2+}] but are probably complexed with

Table 2
Freundlich Parameters Resulting from Mathematical Fit of Equilibrium Data

Metal	c_0 (mg/L)	pH	K_F	CV (%)	n	CV (%)	R^2
Pb	10	3.5	1.78	2.8	0.30	4.7	0.9762
	10	5.0	9.64	3.9	0.41	6.5	0.9750
	20	5.0	7.19	5.7	0.48	4.8	0.9895
	40	5.0	5.36	6.4	0.42	4.6	0.9920
Cd	10	3.5	0.52	3.8	0.37	5.9	0.9512
	10	5.0	1.77	3.8	0.70	2.8	0.9940
	20	5.0	1.72	6.8	0.67	3.8	0.9857
	40	5.0	1.07	11.2	0.72	4.7	0.9785
Cu	10	3.5	0.30	3.9	0.68	2.8	0.9904
	10	5.0	0.56	13.6	1.54	4.4	0.9866
	20	5.0	0.35	25.5	1.20	8.7	0.9459
	40	5.0	0.27	15.5	1.32	5.2	0.9650
Zn	10	3.5	0.21	5.9	0.69	4.0	0.9814
	10	5.0	0.44	9.3	1.05	4.4	0.9856
	20	5.0	0.23	7.9	1.01	2.8	0.9940
	40	5.0	0.17	17.3	0.88	5.7	0.9748

some ligands (L) occurring in the system. During batch experiments, in fact, whatever the pH and the metal, about 17 mg/L of TOC was constantly leached from the husks. This organic material (L) might complex some of the metal ions, preventing their sorption onto the husks. In such an instance, then, as demonstrated in previous studies for similar biosorbents, the following reactions could take place *(36)*:

Me(II) mass balance: $[Me(II)] = [Me^{2+}] + [Me(II)\text{-}L]$ (2)

Husk surface (S) reactions: $\underline{S}\text{-}H + H^+ \Leftrightarrow \underline{S}\text{-}H_2^+$ (3)

$$\underline{S}\text{-}H \Leftrightarrow \underline{S}^- + H^+ \quad (4)$$

$$\underline{S}\text{-}H + Me^{2+} \Leftrightarrow \underline{S}\text{-}Me^+ + H^+ \quad (5)$$

Leached organic matter (L) reactions: $L\text{-}H + H^+ \Leftrightarrow L\text{-}H_2^+$ (6)

$$L\text{-}H \Leftrightarrow L^- + H^+ \quad (7)$$

$$L\text{-}H + Me^{2+} \Leftrightarrow L\text{-}Me^+ + H^+ \quad (8)$$

Of course, the extent of metal sorption on the husk will be the result of all these simultaneous equilibria. In fact, at each pH, depending on the actual value of the equilibrium constants of these reactions, metal complexation with leached organic matter could prevail on complexation with husk surface, or vice versa, determining the actual K_F values. On the basis of such considerations, the increase in K_F values with pH could be justified assuming that, at pH 3.5, reactions 3 and 6 prevail, limiting metal sorption,

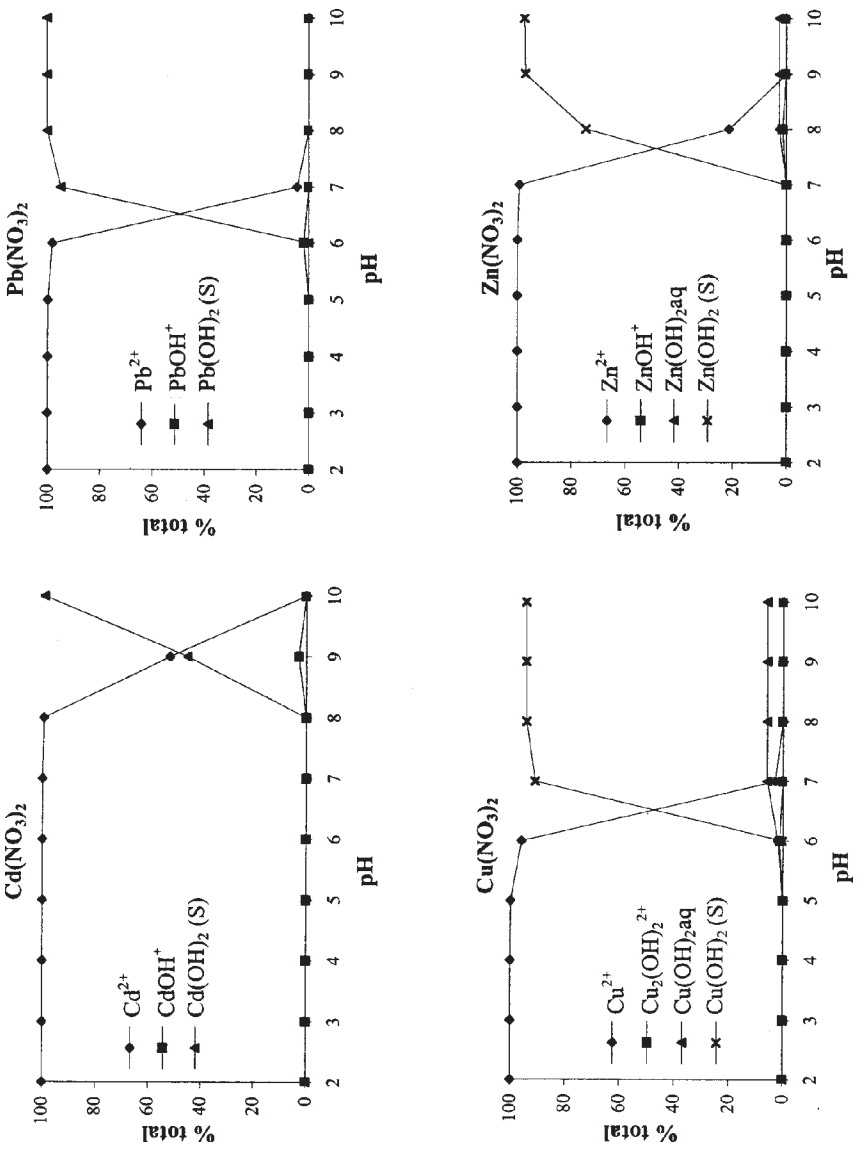

Fig. 1. Metal speciation as function of pH, calculated for 10 mg of (Me^{2+})/L solutions by means of computer code MINEQL+.

whereas, at pH 5.0, reactions 8 and 5 predominate, with the latter prevailing on the former. Such conclusions are also strengthened by the *n* values in Table 2. In fact, if one remembers that the value of the parameter *n* is related to the affinity of sorbate-sorbent interactions, the fact that, whatever the metal, the *n* value clearly increases from pH 3.5 to 5.0 strongly supports the conclusion that different reactions and/or mechanisms predominate at the two pHs.

In Table 2, by comparing the K_F values obtained for each metal at pH 5.0 at the three different initial concentrations (10, 20, and 40 mg/L), the effect of concentration on K_F value can be assessed. In fact, whatever the metal, a systematic decrease in K_F values is observed when initial metal concentration increases. Such a behavior can be ascribed to the electrical structure of the solid-liquid interface *(37)*. In fact, the surface electric potential associated with the surface charge of a solid is usually assumed to be responsible for the overall free energy of interaction, which, in turn, is related to the stability of the surface complexes of metal-functional groups. The overall binding energy for metal ions may be associated with the concerted action of a coulombic interaction (i.e., ion pair formation for maintenance of electroneutrality) accompanied by a Lewis acid-base interaction (i.e., covalent bonding) in which electron vacancies in the coordination sphere of metals are occupied by potentially ligand donor atoms of functional groups *(38)*. As observed in most ion-exchange controlled systems *(39)*, superimposition of additional covalent interactions to purely coulombic interactions, with the latter playing a major role, induces a sort of compression of the electric surface potential and, as a result, affinities toward metals are negatively influenced by increasing overall liquid-phase concentration and ionic strength. An analogous effect is supposed to be responsible for the reduced sorption (i.e., lower K_F values) recorded at higher concentrations in the investigated metal-husk system.

A comparison of the K_F values obtained for different metals can be done only at the same concentration, which, dealing with ions, cannot be expressed as milligrams/liter but as milliequivalents/liter. In Table 2, at pH 5.0, the different metals have the same normality (0.34 ± 0.04 meq/L) when their concentrations are, respectively, 40 mg/L for Pb, 20 mg/L for Cd, 10 mg/L for Cu, and 10 mg/L for Zn. The corresponding K_F values are 5.36 for Pb, 1.72 for Cd, 0.56 for Cu, and 0.44 for Zn, indicating for the husks the following sorption capacity trend: Pb > Cd > Cu > Zn. This result is quite consistent with the size of the hydrated ions of the considered metals *(40)*, which determines their sorption behavior. In fact, the lower the ionic radius, the higher the charge density and the extent of solvation, and the lower the extent of sorption *(41)*.

The data in Table 2 also demonstrate that pH influences *n* values much more than does the initial metal concentration. In fact, whatever the metal, *n* values sharply increase from pH 3.5 to 5.0, but they do not significantly change when initial metal concentration increases. This result confirms the previous conclusion that different sorption reactions and/or mechanisms

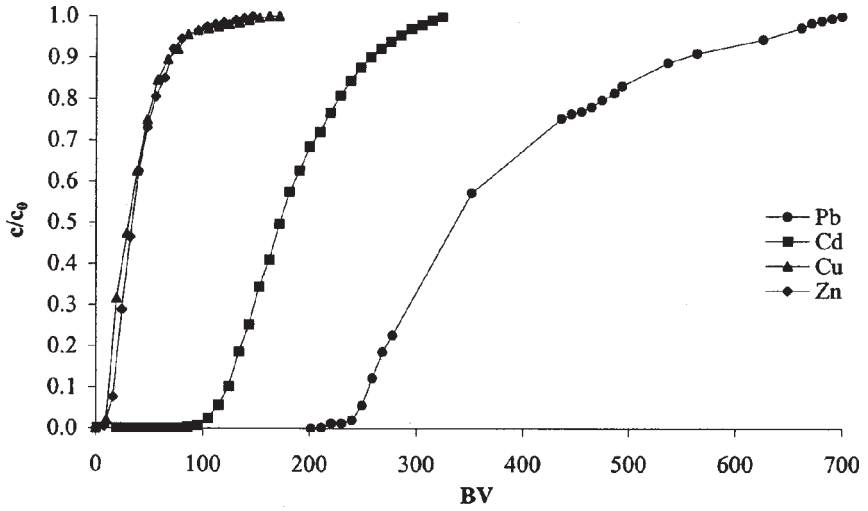

Fig. 2. Breakthrough curves obtained at pH 5.0 feeding solutions containing a single metal (c_0 = 20 mg/L).

prevail at the two investigated pHs and proves that metal concentration does not affect the intensity of metal-husk interactions.

According to this, comparing the average values of n (Table 2) obtained for each metal at pH 5.0, it is seen that the affinity of such interactions progressively decreases in the order Cu (n = 1.35) > Zn (n = 0.98) > Cd (n = 0.70) > Pb (n = 0.43).

Even though identification of the actual nature of such interactions was beyond the scope of the present work, considering the presence of carboxyl and hydroxyl functional groups on husk surfaces *(17)*, the greater stability of Zn and Cu carboxyl and hydroxyl complexes with respect to the corresponding Pb and Cd complexes *(42)* could justify the trend obtained for the parameter n.

Referring to the column tests, they were essentially aimed at studying the properties of husks under dynamic conditions. Batch or equilibrium tests, in fact, cannot provide scale-up data for flow columns used at real treatment plants. Therefore, the practical applicability of husks in large-scale column operations was evaluated by column tests as reported in Materials and Methods. The results of these tests are reported in Figs. 2 and 3, in which the breakthrough curves were obtained when the feed solutions contained a single metal or all the metals together, respectively. From these curves, and knowing the quantity of husks in the column (i.e., 2.5 g), it is possible to calculate the values of sorption capacities of the husks toward each metal under dynamic conditions. These values, reported in Table 3, indicate that, for a given metal, husk sorption capacity is much greater when the feed solution contained only a single metal. This result was expected because, in the case of solutions containing several metals, the total sorption capacity of the husk was saturated by all the metals simulta-

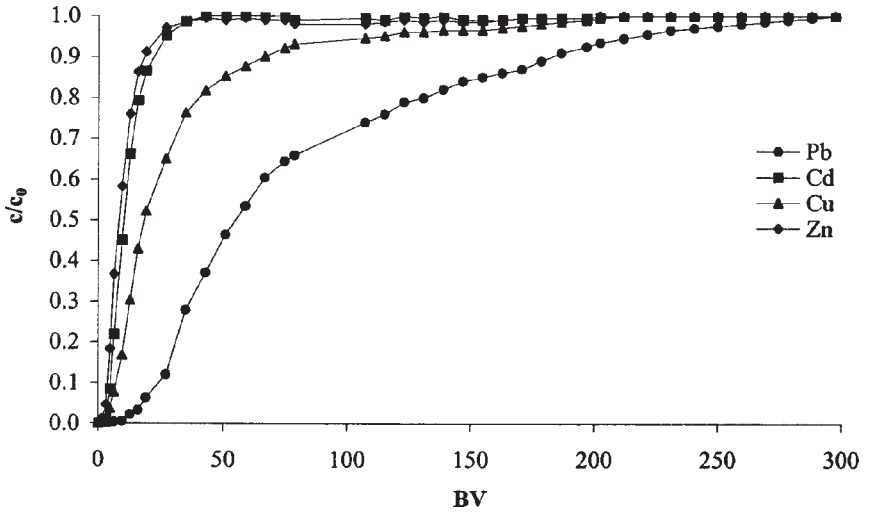

Fig. 3. Breakthrough curves obtained at pH 5.0 feeding a solution containing four metals together (c_0 = 20 mg/L each).

Table 3
Measured Sorption Capacities (meq/g) of Olive Husk[a]

Metal	A	B
Pb	0.160	0.036
Cd	0.152	0.010
Cu	0.054	0.046
Zn	0.050	0.016

[a]Dynamic tests were carried out by feeding solutions containing (A) a single metal (20 mg/L) and (B) four metals together (20 mg/L each).

neously fed. Such a trend was consistent except for copper, toward which the husk showed about the same value of sorption capacity under both conditions (i.e., single-metal or multimetals solutions). This latter result clearly indicates that the interactions between copper species and husk take place at surface sites specifically selective toward copper whose sorption capacity, in fact, remains basically the same in both cases.

The different behavior of copper can be justified by taking into account that the calculated affinity of its sorption interactions with husk (*n* value in Freundlich equation) was the highest among the investigated metals. In fact, considering the *n* values at pH 5.0 in Table 2, those referring to copper were only >1. Actually, then, the very strong affinity of the copper-husk interactions definitively prevails on the effect of the simultaneous presence of other metals on husk sorption capacity.

Table 4
Metal Recovered (%)
in Ash After Husk Incineration[a]

Metal	A	B
Pb	84.8	68.7
Cd	74.3	63.7
Cu	94.8	100
Zn	97.9	82.1

[a]Husk was saturated (A) with a single metal and (B) with four metals.

As reported in Materials and Methods, samples of metals-saturated husks resulting from column tests using both feeds (i.e., single-metal and multimetals feeds) were incinerated (simulating an eventual use of this material as combustible biomass) to assess the fate of sorbed metals that could be either recovered in the remaining solid ashes or disposed of with fly ashes. After analyzing metals in the remaining ash, and knowing the initial amount (milligrams/gram) of each metal in the saturated husks, we calculated the percentages of such an initial amount still present in solid ash recovered after incineration; the results are reported in Table 4. The deficient percentage with respect to the initial amount represents the fraction volatilized as fly ashes. From the data in Table 4, it is clear that lead and cadmium species, whenever in the feed, always resulted in more volatile losses than did copper and zinc ones. Finally, the higher volatility (i.e., lower metal recovery in remaining solid ashes) recorded for all the metals during the incineration of multimetals-saturated husk samples has to be ascribed to synergistic effects occurring among metal species in the course of the volatilization process *(43)*.

Conclusion

Our investigation aimed at assessing the possibility of using olive oil husks as an alternative sorbent for removing heavy metals from polluted wastewater obtained the following results.

1. The sorption capacity trend of the husks toward the different metals resulted in the sequence Pb > Cd > Cu > Zn, under both equilibrium and dynamic conditions.
2. Whatever the metal, the values of the Freundlich constant K_F sharply increased from pH 3.5 to 5.0.
3. Regardless of the metal, a regular decrease in the Freundlich constant K_F was recorded when the initial metal concentration in the liquid phase increased.
4. The affinities of metal-husk sorption interactions resulted in the sequence Cu > Zn > Cd > Pb.

5. As expected, under dynamic conditions, if sorption occurred from solutions containing several metals, the sorption capacity of the husks toward each metal resulted in lower values than those obtained from solutions containing a single metal; this was not true for copper, whose sorbed amount remained constant from single- or multiion solutions.
6. The incineration tests of metals-exhausted husk indicated the greater volatility of Pb and Cd over Zn and Cu species, for both single-metal- and multimetals-exhausted husk samples. In addition, in the latter case, for all the metals, volatility increased.

When heavy metals sorption capacity values of the tested husk are compared with those of conventional sorbents such as activated carbon, synthetic ion-exchange resins, and natural zeolites *(44,45)*, the outcomes are promising. In fact, just referring to lead, the sorption capacity measured for the husk (0.16 meq/g) is lower than the value for ion-exchange resins (2.5) and natural zeolites (1.8) but higher than the value for activated carbon (0.018).

In conclusion, although further studies are necessary, the results of our study appear encouraging, and the possibility of using a cheap natural biosorbent such as olive oil husk as a reliable alternative to currently marketed sorbents has been successfully assessed at least under the investigated conditions.

References

1. Chang, L. W., ed. (1996), *Toxicology of Metals*, CRC Press, Boca Raton, FL.
2. Edwards, J. D. (1995), *Industrial Wastewater Treatment—A Guidebook*, CRC Press, Boca Raton, FL.
3. Brooks, C. S. (1991), *Metal Recovery from Industrial Waste*, Lewis Publishers, Chelsea, MI.
4. Mc Kay, G., ed. (1996), *Use of Adsorbents for the Removal of Pollutants from Wastewater*, CRC Press, Boca Raton, FL.
5. Bailey, S. E., Olin, T. J., Bricka, R. M., and Adrian, D. D. (1999), *Water Res.* **33,** 2469–2479.
6. Drake, L. R. and Rayson, G. D. (1996), *Analyt. Chemistry* **68(1),** 22A–27A.
7. White, C., Wilkinson, S. C., and Gadd, G. M. (1995), *Intern. Biodeter. Biodegrad.* **35,** 17–40.
8. Volesky, B. (1990), *Biosorption of Heavy Metals*, CRC Press, Boca Raton, FL.
9. Yu, Q., Matheickal, J. T., Yin, P., and Kaewsarn P. (1999), *Water Res.* **33,** 1534–1537.
10. Kapoor, A. and Viraraghavan, T. (1998), *Water Res.* **32,** 1968–1977.
11. Chang, J. S., Huang, J. C., Chang, C. C., and Tarn, T. J. (1998), *Water Sci. Technol.* **38,** 171–178.
12. Crist, R. H., Martin, J. R., Chonko, J., and Crist, D. R. (1996), *Environ. Sci. Technol.* **30,** 2456–2461.
13. Ho, Y. S. and McKay, G. (1999), *Water Res.* **33,** 578–584.
14. Ajmal, M., Khan, A. H., Ahmad, S., and Ahmad A. (1998), *Water Res.* **32,** 3085–3091.
15. Bryant, P. S., Petersen, J. N., Lee, J. M., and Brouns, T. M. (1992), *Appl. Biochem. Biotechnol.* **34/35,** 777–788.
16. Alves, M. M., Beça, C. G. G., de Carvalho, R. G., Castanheira, J. M., Sol Pereira, M. C., and Vasconcelos, A. T. (1993), *Water Res.* **27,** 1333–1338.
17. Ravat, C., Dumonceau, J., and Monteil-Rivera, F. (2000), *Water Res.* **34,** 1327–1339.
18. Periasamy, K. and Namasivayam, C. (1995), *Waste Manage.* **15,** 63–68.

19. Filho, N. C., Winkler-Hechenleitner, A. A., and Gómez-Pineda, E. A. (1996), *Int. J. Polymeric Mater.* **34,** 211–218.
20. Özer, A., Tümen, F., and Bildik, M. (1997), *Environ. Technol.* **18,** 893–901.
21. Hawthorne Costa, E. T., Winkler-Hechenleitner, A. A., and Gómez-Pineda, E. A. (1995), *Separat. Sci. Technol.* **30,** 2593–2602.
22. Marañón, E. and Sastre, H. (1992), *Bioresour. Technol.* **40,** 73–76.
23. Baes, A. U., Umali, S. J. P., and Mercado, R. L. (1996), *Water Sci. Technol.* **34,** 193–200.
24. Tan, W. T., Ooi, S. T., and Lee, C. K. (1993), *Environ. Technol.* **14,** 277–282.
25. Orhan, Y. and Büyükgüngör, H. (1993), *Water Sci. Technol.* **28,** 247–255.
26. Munaf, E. and Zein, R. (1997), *Environ. Technol.* **18,** 359–362.
27. Verma, N. and Rehal, R. (1994), *Bioresour. Technol.* **49,** 277, 278.
28. Sharma, D. C. and Forster, C. F. (1994), *Bioresour. Technol.* **47,** 257–264.
29. Macchi, G., Marani, D., and Tiravanti, G. (1986), *Environ. Technol. Lett.* **7,** 431–444.
30. Tee, T. W. and Khan, A. R. M. (1988), *Environ. Technol. Lett.* **9,** 1223–1232.
31. Gharaibeh, S. H., Abu-El-Sha'r, W. Y., and Al-Kofahi, M. M. (1998), *Water Res.* **32,** 498–502.
32. American Society of Agronomy. (1996), in *Methods of Soil Analysis. Part 3: Chemical Methods.* Sparks, D. L., ed., Soil Science Society of America Inc., Madison, WI.
33. Weber, W. J. Jr., McGinley, P. M., and Katz, L. E. (1991), *Water Res.* **25,** 499–528.
34. Bolt, G. H. (1982), *Soil Chemistry—B: Physico-Chemical Models*, Elsevier, The Netherlands.
35. Schecher, W. D. and Mc Avoy, D. C. (1994), *MINEQL+: A Chemical Equilibrium Program for Personal Computers, Version 3.0*, Environmental Research Software, Hallowell, ME.
36. Lee, S. M. and Davis, A. P. (2001), *Water Res.* **35(2),** 534–540.
37. Stumm, W. (1992), *Chemistry of the Solid-Water Interface. Processes at the Mineral-Water and Particle-Water Interface in Natural Systems*, John Wiley & Sons, New York.
38. Zhao, D. and Sengupta, A. K. (1998), *Water Res.* **32,** 1613–1625.
39. Helfferich, F. (1962), *Ion Exchange*, McGraw Hill, New York.
40. Weast, R. C., ed. (1968), *Handbook of Chemistry and Physics*, 49th ed., Chemical Rubber Co., Cleveland, OH.
41. Habib, M. A. and Bockris, J. O'M. (1980), in *Comprehensive Treatise of Electrochemistry—1. The Double Layer*, Bockris, J. O'M., Conway B. E., and Yeager, E., eds., Plenum, New York.
42. Sillen, L. G. (1971), *Stability Constants of Metal-Ion Complexes*, Chemical Society, London.
43. Gerstle, R. W. and Albrinck D. N. (1982), *J. Air Pollu. Control Assoc.* **32(11),** 1119–1123.
44. Anderson, M. A. and Rubin, A. J. (1981), *Adsorption of Inorganics at Solid-Liquid Interfaces*, Ann Arbor Science Publishers, Ann Arbor, MI.
45. Blanchard, G., Maunaye, M., and Martin, G. (1984), *Water Res.* **18,** 1501–1507.