

# Metal Ion Uptake from Aqueous Solution by Olive Stones: A Carbon-13 Solid-State Nuclear Magnetic Resonance and Potentiometric Study

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**ABSTRACT:** The use of biomasses that result from the agriculture and food industries in removing heavy metals from wastewaters is attracting increasing interest. We present a joined potentiometric and cross polarization magic angle spinning (CP-MAS) carbon-13 (<sup>13</sup>C) nuclear magnetic resonance (NMR) study on the interaction of olive stones with copper(II), nickel(II), and cadmium(II). The potentiometric measurements allow both to distinguish two kind of basic sites in the olive stones and to postulate the coordination models for the three studied metals. The NMR spectral analysis allows the attribution of the different signals to the components of the olive stone matrix. A comparison of CP-MAS <sup>13</sup>C NMR spectra of the samples after metal treatment suggests a specific complexation between metal ions and hydroxyl groups on guaiacyl and syringyl moieties. *Water Environ. Res.*, 79, 2363 (2007).

**KEYWORDS:** olive stones, solid-state cross polarization magic angle spinning carbon-13 nuclear magnetic resonance, heavy metals, cadmium, copper, nickel, potentiometric titration, metal uptake.

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## Introduction

In recent years, the use of biomasses from agriculture in removing heavy metals from aqueous solutions has attracted our interest (Villaescusa et al., 2000, 2002). The recovery and reuse of wastes as adsorbents, particularly in situations where reuse is envisaged within the same industry for water decontamination, may offer significant economic advantages over traditional water treatments (Al-Asheh and Duvnjak, 1998; Li and Yang, 1997; Sun and Shi, 1998). The reuse, in addition, contributes to an overall waste reduction strategy within the concerned industry.

Olive stones are obtained as a waste material from the olive oil industry. Considering that they are often simply burned, it would be advisable to find other uses for this type of waste. Several attempts to discover possible uses for olive stones have been made, including the following:

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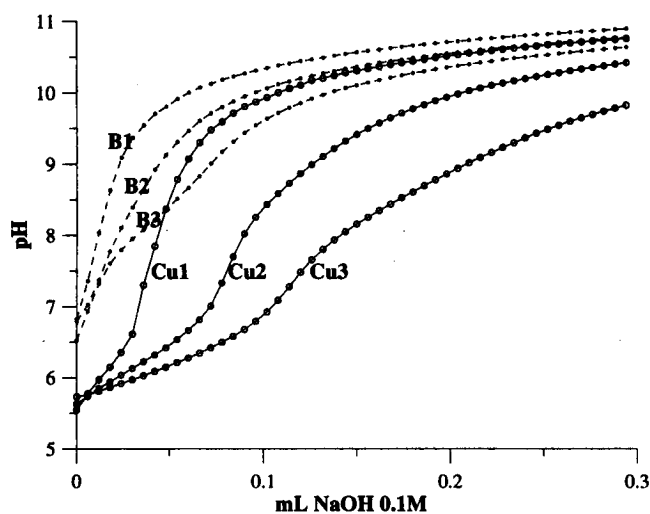
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- (1) Obtainment of cellulose and ethanol production from olive stones (Ballesteros et al., 2001; Fernandez-Bolanos et al., 1999);
- (2) Hemicellulose solubilization and enzymatic hydrolysis of cellulose by steam explosion of olive stones (Fernandez-Bolanos et al., 2001),
- (3) Conversion of olive stones to activated carbon for the removal of textile dyes and other organic molecules from aqueous solutions (Alaya et al., 2000; Pollard et al., 1992), and, recently,
- (4) Use of granulate olive stones as a possible substrate for hydroponics' cultures (Melgar et al., 2001).

While the use of olive mill solid residues (Gharaibeh et al., 1998; Pagnanelli et al., 2002) and olive pomace (Pagnanelli et al., 2003) for heavy metals removal has been reported, to our knowledge, no research has focused on the use of olive stones as an adsorbent of metal ions. We have recently reported the uptake of copper(II), cadmium(II), nickel(II), and chromium(VI) by crushed olive stone waste obtained after separation from olive cake, with both residues obtained after a second extraction of the residual olive oil contained in alperujo (Fiol et al., 2006). Alperujo is made up of a mixture of water (65% w/w), crushed olive stones (15% w/w), and olive pulp (20% w/w) (Montané et al., 2002). In this study, the influence of pH, sodium salts, and metal concentration on metal uptake was investigated. Maximum adsorption was found at approximately pH 5 to 7 for divalent metal ions and pH 3 for chromium(VI). High salt concentrations significantly reduced bivalent metal removal. The adsorption trend was described by noncompetitive Langmuir and Freundlich isotherms. Unfortunately, the mechanism of adsorption is still poorly understood. There is not yet complete knowledge of the chemical structure of olive stones or the fundamental mechanisms by which metal ions are bound to the olive stones. The identification of the binding sites and knowledge of the adsorption mechanism would be helpful for modeling and predicting the biomass yield in water purification systems. To this aim, we have investigated copper(II) and nickel(II) interactions with cork by potentiometric measurements and solid-state carbon-13 (<sup>13</sup>C) nuclear magnetic resonance (NMR) (Villaescusa et al., 2002); these same techniques are used in the present work to investigate metal ion interaction with the same olive stone waste used in our previous work (Fiol et al., 2006). The solid-state <sup>13</sup>C NMR analysis of spectral modifications induced in the olive stone matrix by metal binding, combined with the results of a potentiometric solution study, allow us to get some insight to the binding mechanisms. The



**Figure 1**—Titration curves with 0.1 M NaOH in 20 mL of water, in which 0.1, 0.2, and 0.3 g of untreated olive stones (B1, B2, and B3) and 0.1, 0.2, and 0.3 g of copper-treated olive stones (Cu1, Cu2, and Cu3) were suspended.

metal ions, copper(II), nickel(II), and cadmium(II) were selected for their highly hazardous potential in the environment and for their relatively different behavior in adsorption processes.

### Materials and Methods

**Reagents.** Crushed olive stones were supplied by an olive oil producer from Cordoba, Spain. Olive stones, washed three times with boiling water and three times with cold water, were allowed to dry at 110°C overnight. Once dried, they were ground and sifted at the desired particle size (<180 µm). Nickel(II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O) and cadmium chloride hydrate (CdCl<sub>2</sub>·H<sub>2</sub>O) were purchased from Carlo Erba Reagents SpA, Casella Postale 63, I-20090 Limite, Milan, Italy. Copper chloride and sodium hydroxide (NaOH) (97%) were Fluka Chemie GmbH (Buchs, Switzerland) products. Hydrochloric acid (HCl) volumetric standard solutions (0.1006 M) and inductively coupled plasma (ICP) standards for copper, nickel, and cadmium were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Metal ion solutions were prepared by dissolving the proper amounts of chlorides in HCl solutions (1 × 10<sup>-5</sup> M), to prevent metal hydrolysis.

**Metal Ion Uptake.** Olive stone samples were loaded with copper(II), nickel(II), and cadmium(II), by contact for 24 hours with solutions of different concentrations. We chose chloride salts because chloride can be considered the most common anion in natural and polluted waters. For potentiometric studies, the metal ion concentration ranged from 0.04 to 1.0 M, while, for NMR analysis, olive stones were loaded with saturated solutions (the low variations in NMR signals resulting from the presence of adsorbed metals led us to use saturated solutions to maximize the metal uptake). In both cases, the metal uptake procedure consisted in placing 2.0 g olive stones into 100 mL of metal ion solution under continuous agitation for 24 hours. Then, the samples were vacuum filtered through a Gooch crucible number 1 and abundantly rinsed with bi-distilled water to remove the nonbound metal ions. The samples prepared for NMR analysis were dried and kept in a desiccator until analysis.

**Potentiometric Titrations.** A set of experiments consisted of suspending different weights (0.1, 0.2, and 0.3 g) of untreated and

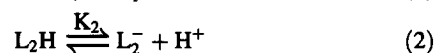
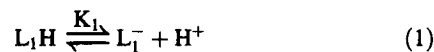
metal (1.0 M)-treated olive stone samples in 20 mL of bi-distilled water and titrating with either 0.1 M NaOH or 0.1 M HCl. Another series consisted of suspending 0.3 g of olive stones that had been in contact for 24 hours with metal ion solutions of different concentrations (0.04, 0.20, 1.00 M). All titrations were performed using an automatic titrator (model 702 SM Titrino, Metrohm AG, Herisau, Switzerland), in a glass cell maintained at 25°C, equipped with a magnetic stirring system, a Metrohm glass electrode for highly alkaline solutions, and a microburet delivery tube. The electrode was calibrated daily for hydrogen ion concentration by titrating standard HCl with carbonate-free 0.1 M NaOH; the resulting potentiometric data were analyzed with the Gran procedure (Gran, 1952) using our GRANPLOT program (Crisponi et al., 1993). The results of the potentiometric titrations were processed with the PSEQUAD program (Zekany et al., 1985) operating on the experimental data (titrant volume, log[H<sup>+</sup>]). These data were processed using the simplifying assumption that the measurements were performed in a homogeneous solution.

**Cross Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance Analysis.** The CP-MAS <sup>13</sup>C NMR spectra were recorded at room temperature (25°C) on a spectrometer Varian 400 Unity Inova (Varian Inc., Palo Alto, California) operating at 100.57 MHz, equipped with a 7-mm CP-MAS probe head. A matched Hartmann-Hann condition was established at the spin-lock field of 38 KHz. The rotor was spun at a rate of 4 KHz, and a contact time of 700 µs was applied to obtain polarization transfer. The 90-degree pulse was 6.6 µs, and a recycle delay of 5 seconds was used. Chemical shifts of CP-MAS spectra were obtained with respect to the methylene carbon resonance of solid adamantane, 38.3 ppm downfield from tetramethylsilane (Me<sub>4</sub>Si), determined before each measurement. Experiments were conducted on 65- to 80-mg samples of olive stones packed into a zirconium oxide (ZrO<sub>2</sub>) rotor.

### Results and Discussion

According to the procedure previously used in the work on metal adsorption using cork (Villaescusa et al., 2002), weighted amounts of untreated olive stones and metal-treated olive stones suspended in water were titrated with 0.1 M NaOH. Such titration data provide some insight to the acidic sites on olive stones and the properties of the binding sites. Titration data of untreated and copper-treated material are reported as an example in Figure 1.

In Figure 1, the titration curves of untreated (B1, B2, and B3) and copper-treated olive stones (Cu1, Cu2, and Cu3) refer to the titration of 0.1, 0.2, and 0.3 g of material, respectively. Concerning untreated olive stone titrations, despite some differences among repeated experiments, which can be ascribed to nonhomogeneous material and to a different contact between solution and solid suspended particles, these curves show characteristic trends, suggesting that two different kinds of basic sites occur on the olive stone matrix and can be fitted by a model that takes into account at least two different kinds of titrable protons on the olive stone matrix, characterized by the following ionization equilibria:



The concentrations of the L<sub>1</sub>H and L<sub>2</sub>H acidic groups were the same (i.e., 0.7 × 10<sup>-4</sup>, 1.4 × 10<sup>-4</sup>, and 2.1 × 10<sup>-4</sup> M) in the solutions in

**Table 1—Values of  $pK_1$ ,  $pK_2$ , and  $\log\beta$  calculated with the PSEQUAD program from the base titrations of untreated and metal treated olive stones.**

	$pK_1$ (mol L <sup>-1</sup> )	$pK_2$ (mol L <sup>-1</sup> )	Log $\beta$
Untreated olive stones	8.3	10.5	
Nickel-treated	6.9	8.7	
Cadmium-treated	6.9	10.4	
Copper-treated	8.1	9.7	-12.5

which 0.1, 0.2, and 0.3 g of untreated olive stones, respectively, were titrated in 20 mL of water. Optimized ionization constants ( $pK$ ) values are reported in Table 1. Titrations with acid of untreated samples provide evidence of basic groups on the olive stone matrix that bind protons with a  $pK$  6.8, according to the following equilibrium:



Titration curves of metal-treated olive stones are all lower than the corresponding untreated ones. The titrations of copper-treated olive stones can be accurately fitted by assuming the following two different processes:

- (1) Precipitation of adsorbed copper (the concentration of this ion was estimated as  $1.8 \times 10^{-4}$  M for the titration of 0.3 g of treated olive stones (compared with  $2.1 \times 10^{-4}$  of acidic sites) as hydroxide at pH 6.2 ( $\log\beta = -12.5$ ); and
- (2) Titration of two kinds of acidic groups, at the same concentration of untreated olive stones but with  $pK$  values slightly lower, as reported in Table 1.

The titration curves of cadmium- and nickel-treated olive stones do not present hydroxide precipitation and can be fitted assuming the titration of two kind of acidic groups, always at the same concentration of untreated olive stones, but with  $pK$  values significantly lower (see Table 1).

The above experimental observations can be explained by assuming that coordination of the metal ion took place in competition with protons for the same basic sites  $L_1$  and/or  $L_2$ , and the displaced protons were bound by the less basic site  $L_0$  with  $pK$  6.9.

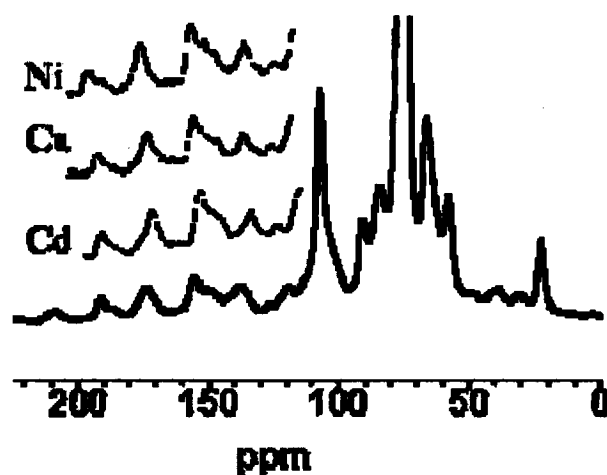
The different behavior for the three metal ions depends on different factors, such as the binding site involved in the coordination of the metal ion, strength of the binding, and pH of hydroxide precipitation. The following conclusions can be made:

(1) Nickel:

- The most involved site for nickel coordination is  $L_2$ ;
- Protons displaced from  $L_2$  are bound by the less basic site  $L_0$  and are titrated at  $pK$  6.9; and
- The protons of site  $L_1$  are titrated at  $pK$  8.7, slightly higher than in untreated olive stone ( $pK$  8.3), because the charge of the bound metal ion affects  $L_1$  proton acidity.

(2) Cadmium:

- The most implicated site for cadmium coordination is  $L_1$ ;
- Protons displaced from  $L_1$  are bound by  $L_0$  site and are titrated at  $pK$  6.9; and
- The protons of site  $L_2$  are titrated at  $pK$  10.4, approximately equal to untreated olive stone ( $pK$  10.5), and are not affected by the charge of the bound metal ion.



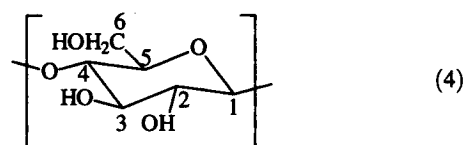
**Figure 2—CP-MAS <sup>13</sup>C NMR spectra of olive stones in the absence and presence of cadmium(II), copper(II), and nickel(II) (1 ppm = 1 mg/L).**

(3) Copper:

- The first observation during copper-treated olive stone titration is hydroxide formation at approximately pH 6.2;
- Copper concentration can be evaluated from the base used for its precipitation and comprises approximately 85% of the acidic site;
- Hydroxide formation liberates the copper coordination site ( $L_1$  or  $L_2$ ), on which protons transfer to  $L_0$ ; and
- Acidity of the  $L_1$  and  $L_2$  sites is slightly altered by copper hydroxide precipitation into cavities ( $pK$  8.1 to 8.3 and  $pK$  9.7 to 10.5, respectively).

A number of studies (Browning, 1975; Dudley et al., 1983; Garbow and Stark, 1990; Ha et al., 1997; Hatfield et al., 1987; Haw et al., 1984; Kolodziejewski et al., 1982; Pacchiano et al., 1993; Zlotnik- Mazori and Stark, 1988) have shown that CP-MAS <sup>13</sup>C NMR analysis enables elucidation of the major functional groups, cross-link sites, and polymeric domain structure of lignified plant materials, such as lignin; cell wall carbohydrates; and cuticular materials, such as cutin and suberin (Cordeiro et al., 1998; Lopes et al., 1998; Neto et al., 1995, 1996). In the present study, evidence is given on the principal chemical moieties that occur in olive stones by using the CP-MAS <sup>13</sup>C NMR technique. Figure 2 shows the CPMAS <sup>13</sup>C NMR spectra of an olive stone sample before and after treatment with metal ions. As shown, sets of resonances typical of cellulose, hemicellulose, and lignin polymeric components appear, and the assignments were made according to previous NMR investigations (Table 2).

The signals resulting from the cellulose are present in the spectral region from 105 to 50 mg/L (105 to 50 ppm), as follows:



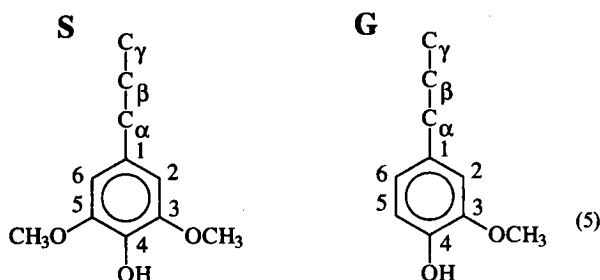
The C1 carbon atom of the glucose units resonates at 105 mg/L (105 ppm); the C4 carbon atom appears in the range 89 to 84 mg/L (89 to 84 ppm); the C2, C3, and C5 signals are from 80 to 70 mg/L (80 to

**Table 2—<sup>13</sup>C chemical shifts of olive stones.**

Carbon type	ppm	Carbon type	ppm
Polysaccharide residues		Phenylpropanoid residues	
C6	62	C1, C3, C4, C5	115 to 150
C2, C3, C5	72	COO	172
C4	83		
C1	101		

70 ppm); and the C6 carbon atom resonates at 66 ppm. Moreover, the signals at 22 and 174 ppm are respectively assigned to the methyl and carboxylic carbons of the acetate groups of hemicellulose, thus indicating the presence of a small amount of this polymeric component in the olive stones.

As far as the lignin component is concerned, it is well-known that this complex macromolecule mainly consists of phenylpropanoid residues, such as syringyl (S) and guaiacyl (G) units, whose ratio varies as a function of the plant species.



The signals of these aromatic carbon atoms are observed in the spectral region from 160 to 110 ppm; the peak at approximately 160 ppm is the result of oxygen-substituted aromatic ring carbons G3, S3, and S5; the resonance at approximately 148 ppm is attributed to carbons G4 and S4; the resonances in the range from approximately 80 to 65 ppm, partially overlapping with the signals of cellulose components, are assigned to the  $\alpha$ ,  $\beta$ , and  $\gamma$  carbon atoms; and the resonance resulting from the methoxy group of G and S units appears at 56 ppm.

A comparison between the CP-MAS <sup>13</sup>C NMR spectra of untreated and metal-treated olive stones shows that significant changes are induced by the presence of the metal ions, mainly in the signals at 150 to 140 ppm, while the signals at 110 to 50 ppm attributed to the glucose units remain substantially unchanged. These changes, which can be ascribed to the paramagnetic broadening of a part of these signals beyond detection, suggest that a specific coordination exists between the paramagnetic metal ions and hydroxyl groups of S and G aromatic rings.

Therefore, we must remark that two completely different techniques direct towards the same conclusions. Potentiometric results point out coordination by a basic site with pK of approximately 10, and this allows us to infer that a phenolic group is the most probable group implied in metal coordination. The NMR results give clear evidence that this presumable phenolic group is the located on syringyl and guaiacyl units.

## Credits

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