ORIGINAL ARTICLE

Preparation of silicas impregnated with HPBI, HPMSP and DEHPA and their application in the solid–liquid extraction of Cu(II) and Zn(II)

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Abstract The synthesis of mesostructured silicas impregnated with acidic chelators, an acylisoxazolone 3-phenyl-4-benzoyl-5-isoxazolone (HPBI), an acylpyrazolone 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP) and an organophosphoric acid di-(2-ethylhexyl)-phosphoric acid (DEHPA) was undertaken. The different solids were characterized by physico-chemical methods: XRD, FTIR, thermal analysis, TEM, and N2-sorption. The porous integrity of the silica was preserved after impregnation. The amount of ligand was evaluated by UV–Visible analysis of washings, weight loss after calcination and thermal analysis. More than 90% of the ligand used for the impregnation was trapped into the functionalized solids. These materials achieved encouraging...

Abbreviations: HL, one of the chelators HPBI, HPMSP, DEHPA; HPBI, 3-phenyl-4-benzoyl-5-isoxazolone; HPMSP, 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone; DEHPA, di-(2-ethylhexyl)-phosphoric acid; MCM-C, calcined silica (before the impregnation step); MCM-CI-HL, the calcined and impregnated silica with HL (HPBI, HPMSP, or DEHPA).

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1. Introduction

Waste water treatment is becoming more of a challenge for our modern civilization due to an ever increasing population and a corresponding consumer’s demand. Waste water contains all the products that we discard. The broad categories of the components of waste water are: biomass (Kaur et al., 2008) nutrients (Wong et al., 2003), salts (Bhattacharyya and Gupta, 2007), heavy metals (Kubilay et al., 2007), and pathogens (Pérez-Quintanilla et al., 2006). National governments and the European Union have introduced a wide range of legislative measures aiming to improve the quality of the environment. These legislative directives have particularly focused on ensuring that the discharge of contaminants has an extremely low residual concentration when deposited into an aquatic environment. The implementation of these directives has delivered significant ecological benefits, and the need for heavy metals to be removed from wastewater has become a priority.

Heavy metals are present in wastewaters from industrial applications, including mining, refining and production of textiles, paints and dyes. Among the several techniques available for heavy metal remediation, the most popular and cost efficient remains the method of adsorption. For example, activated carbon and a number of low-cost adsorbents such as rice husk, bagasse, used tea leaves (Kaur et al., 2008) and clays have been used for the removal of Cu(II) (Wong et al., 2003; Bhattacharyya and Gupta, 2007; Kubilay et al., 2007). Nevertheless, these materials present some problems such as low removal capacity, low selectivity, mechanical and thermal instability and long equilibration time.

More recently, the preparation of mesostructured silica-based adsorbents through a surfactant promoted alkoxylation autoassembly has generated considerable interest due to the unique large specific surface area and the regular pore structure of these silicas. The surface of these materials can be easily modified to give them interesting extractive properties, and in particular, it enhances their adsorption capacity and their selectivity for heavy metals. These structures can be functionalyzed with an organic functional group either by a post-synthesis surface modification or initially, through a one-pot sol–gel synthesis. For example, the removal efficiency of Cu$^{2+}$, Cd$^{2+}$, and Hg$^{2+}$ increased remarkably after mesoporous silicas such as SBA-15, MCM-41 and HMS have been coated by functional groups like –NH$_2$, –SH and –S–, respectively (Arakaki et al., 2006; Dubois et al., 2006; Pérez-Quintanilla et al., 2006, 2007; Walcarius and Delacôte, 2005; Wei et al., 2012; Wu et al., 2007; Zhang et al., 2007). MCM-41 silicas functionalized with mercaptopropyl groups by the co-condensation method were used to recover Ag$^+$, Cu$^{2+}$, Cr$^{3+}$, Hg$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$ (Liu et al., 1998; Wu et al., 2010). Bou Maroun et al. (2006) have shown that mesostructured silicas doped with mono- or bis-(acyl-hydroxy-pyrazole) are efficient in the extraction of highly diluted Eu$^{3+}$ and Cu$^{2+}$ due to the full accessibility of the ligand immobilized in the silica, to the metal ions. They have also demonstrated the dependence of the extraction on the pH, implying an extraction mechanism of the metal ions by exchange of the acylpyrazolone protons.

In an earlier work (Miloudi et al., 2007), we have shown that the Si-MCM-41 silica can be successfully impregnated by the organic cation exchanger HPBI (3-phenyl-4-benzoyl-5-isoxazolone). We have also proved that this support can act as a performing depolluting system for acid solutions contaminated by heavy metals. The present article completes this previous study. During this work, we have synthesized new mesostructured Si-MCM-41 supports impregnated by other proton exchangers such as HPMSP (1-phenyl-3-methyl-4-stearoyl-5-pyrazolone) and DEHPA (di-(2-ethylhexyl)-phosphoric acid). We have characterized the elaborated supports by physico-chemical methods and studied their application in the solid–liquid extraction of Cu$^{2+}$ and Zn$^{2+}$. Finally, we compared our results with liquid–liquid extraction data for which the ligands have been used as extractants.

2. Materials and methods

2.1. Chemicals and reagents

Deionized water obtained from a Milli-Q system (Millipore, Billerica, MA) was used for the preparation of all the solutions. Stock solutions of Cu(II) and Zn(II) (1 g/l) were prepared by dissolving CuSO$_4$.5H$_2$O and ZnSO$_4$.7H$_2$O respectively (analytical grade, Merck, Frankfurt, Germany) in deionized water and the correct concentrations were controlled by atomic absorption spectrometry. Standard solutions were prepared by acidic attack of copper chips (99.99%) purchased from Acros (Thermo Fisher Scientific, Geel, Belgium) using sulfuric acid (Merck, 95–97%). Nitric acid used in the washing of the impregnated silicas was purchased from Fluka (Sigma–Aldrich, St. Louis, MO, USA).

The different silicas were synthesized following the method proposed by Firoozi et al. (1995) and modified later by Boos et al. (2002), using cetyltrimethylammonium bromide (CTAB, 99%, Aldrich) as a surfactant and tetraethyl orthosilicate (TEOS, 98%, Aldrich, Sigma–Aldrich) as the silica source. The obtained solid was separated by filtration, dried at 333 K under atmospheric pressure for 24 h, then under vacuum for 24 h, and finally calcined at 773 K for 4 h under atmospheric pressure. The resulting solid was named MCM-C.

Di-(2-ethylhexyl)-phosphoric acid (DEHPA) was purchased from BDH (VWR International, England, UK). Its purity was determined by potentiometric titration in a 75% ethanol solution of the acid with 0.1 M aqueous NaOH using Gran method (Gran, 1950, 1952). The purity was found to be 98%.

1-Phenyl-3-methyl-4-stearoylpyrazol-5-ol (HPMSP) was synthesized according to the method detailed in reference (Lardon, 2006). Its purity was controlled by $^1$H-NMR and FTIR.

The preparation of 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) has been detailed in a previous paper (Messouadi et al., 1996). Its purity was verified by acid–base titration in extracted performances in removing copper with HPBI below pH 1 and in removing zinc with DEHPA below pH 3 in sulfate media.

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liquid biphasic system, TLC and $^1$H-NMR. Toluene (Alfa Aesar, MA, USA), acetone (Sigma–Aldrich) and chloroform (Riedel de Haën, Sigma–Aldrich) were used in the impregnation process.

2.2. Impregnation process

The impregnated materials ([MCM-CI-HL]) were prepared according to a dry impregnation method (Kabay et al., 2010 and references therein). The ligand HL (HPBI, HPMSP or DEHPA) was dissolved in toluene, acetone or chloroform, then the solution was put in contact with the calcined solid (MCM-C) in a ratio of 0.7 mmol for 1 g of solid, under magnetic stirring at room temperature and under atmospheric pressure until the total evaporation of the solvent. An additional material was prepared with an initial quantity of HPBI of 0.5 mmol/g. Finally, the obtained solid MCM-CI-HL was washed by HNO$_3$, 1 M, and dried under atmospheric pressure at 60°C for 24 h, then under vacuum at 60°C for 24 h.

The immobilized ligand can be regenerated by putting the functionalized solid in contact with an organic solvent such as chloroform, acetone or a heptane-ethanol mixture (1:1 by volume) for 1 h. Then, this step is repeated until the concentration of the ligand in the recuperated organic solvent becomes zero. The determination of the concentration of the ligand in the organic solvent is realized by UV spectrometry.

2.3. Instrumentation for solid characterization

$^1$H NMR (300 MHz) spectra were recorded with a Bruker Avance (Billericia, MA) spectrometer in the absence of an internal standard at 25°C. Samples were prepared in D$_2$O. FTIR spectra of ligands and solids were recorded with a Perkin Elmer FTIR spectrometer (Waltham, MA) (4000–400 cm$^{-1}$).

The amount of the ligand immobilized in/on the solid matrix was evaluated by three methods for the different solids.

a-. Analysis of the nitric acid aqueous solution used for the washing to evaluate the loss of ligand during this step: 10 ml of the washing solution was put in contact with an equal volume of chloroform, under vigorous agitation, in order to transfer HL in the organic phase. Afterward, the amount of HL in the organic solvent was determined by UV spectrometry at the maximum wavelength of each molecule, i.d. at 321, 270 and 244 nm for HPBI, HPMSP and DEHPA respectively.

b-. Calculation of the organic ligand: aliquots of dried samples were heated up to 500°C at 5°C/min and maintained at this temperature for 10 h. They were weighed before and after calcination, and the initial amount of HL was determined by difference.

c-. Thermal analysis (TGA, DTA): The degradation temperature of the ligand was determined from the DTA curve. Based on this temperature, we determined the initial ligand quantity from the TG plot.

Thermogravimetric analyses were performed in a SETARAM LABSYS instrument (SETARAM, Caluire, France), by heating the samples up to 700°C at a heating rate of 5°C min$^{-1}$ under air flow. The amounts of embedded ligand were determined by measuring ligand losses during washing by UV spectrometry using a HP 8453 UV spectrophotometer (Agilent, CA, USA), and also by measuring the mass losses during calcination. X-ray Diffraction (XRD) patterns were obtained using a D500 SIEMENS (Munich, Germany) diffractometer (Co K$_\alpha$, $\lambda = 1.78897$ Å X-ray source). All samples were scanned under the same conditions ($2\theta = 2$–10°). The surface area, pore size distribution and pore volume of the samples were determined according to BET and BJH methods from N$_2$-sorption isotherms using a SORPTOMATIC 1990 apparatus (Thermo Fisher Scientific). The different solids were examined by transmission electron microscopy TEM using a TOPCON 002B (FEI, OR, USA) apparatus operating at 200 kV with a resolution about 0.18 nm.

2.4. Metal extraction procedure

The extraction of the metal M(II) was carried out in polypropylene tubes thermostatted at 25.0 ± 0.2°C. In a typical experiment, 0.1 g of solid was mechanically shaken with 10 ml of aqueous phase for 1 h, a time sufficient to reach the equilibrium. Then, the two phases were separated with a high-speed centrifuge (10,000 rpm for 10 min), the equilibrium pH of the liquid phase (pH$_{eq}$) was measured using a glass electrode connected to a Digilab 517 pH-meter (Crisom, Barcelona, Spain) and the metal content in the aqueous phase was determined by ICP/AES (JY138 ultratracer, Horiba Jobin Yvon, UK). Aqueous solutions of the following composition were prepared: [H$^+$, Na$^+$] = 0.33 M, [M(II)] = 100 ppm ([H$_2$PO$_4$] = 0.33 M), [H$^+$] = 100 ppm (~1.6 × 10$^{-3}$ M for Cu(II) and ~1.5 × 10$^{-3}$ M for Zn(II)], with different initial pH’s (pH$_0$) between 1.0 and 5.8.

3. Results and discussion

3.1. Supports’ characterization by FTIR

The FTIR spectra of the three systems (HL, MCM-C and MCM-CI-HL) are shown in Figs. 1–3. In the different FTIR spectra, we observed the characteristic bands of the silicate network Si-O-Si: asymmetric stretching vibration at 1090 cm$^{-1}$, in-plane angle deformation at 790 cm$^{-1}$ and torsion at 470 cm$^{-1}$. We also observed the vibration band of Si-OH at about 960 cm$^{-1}$. Moreover, the band at 1637 cm$^{-1}$ corresponds to angular deformation vibrations of water absorbed in the silica pores.

The presence of the ligand in the silica matrix was proven by the appearance of new vibration bands in the corresponding impregnated silica spectra. Most bands were hidden by the silica vibration bands. In the case of HPBI, only the vibration band of C=O at 1691 cm$^{-1}$ appeared in the corresponding impregnated silica spectra displaced at about 1720 cm$^{-1}$ (Fig. 1). The stretching vibrations of P=O at 1230 cm$^{-1}$ and those of P–O–C at 1030 cm$^{-1}$ and 900 cm$^{-1}$ were hidden by the silica band in the case of DEHPA. The C=O band of the HPMSP was also hidden by the silica band. However, the presence of DEHPA and HPMSP in the corresponding impregnated silicas was proven by the appearance of stretching vibration bands of aliphatic C-H of the alkyl chain at 2960 and 2860 cm$^{-1}$ in the case of DEHPA and at 2920 and 2860 cm$^{-1}$ in the case of HPMSP (Figs. 2 and 3).
3.2. Ligand loading

The results of the different determinations of the amount of the ligand immobilized in/on the solid are reported in Table 1. We noticed that all the ligands were well immobilized in the silicas. However, we have observed a difference between the amounts of DEHPA obtained by the two methods: UV spectroscopy and thermal analysis. This difference is due to the
formation of a phosphate compound during the decomposition of DEHPA which was not eliminated during calcination. Therefore, the weight loss data were not taken into account. Notwithstanding, it is noticeable that a very high percentage of every impregnated ligand has been immobilized in the silicas.

3.3. Supports’ characterization by powder diffraction (XRD)

X-ray Diffraction (XRD) patterns of mesoporous Si-MCM-41 (calcined) and mesoporous silica impregnated with organic extractants are depicted in Figs. 4 and 5. The patterns clearly show the characteristic low-angle peaks of mesoporous materials. The pattern of the calcined silica (Miloudi et al. 2007) is similar to that generally obtained for the mesostructured materials (Huo et al., 1994; Oumi et al., 2002; Pauly et al., 2002) with a well ordered structure. The peaks are indexed as a hexagonal structure with corresponding (100), (110), and (200) reflections.

As proved by the presence of the (100) reflection, the porous structural integrities were preserved after the organic extractant impregnation step, regardless the nature of the extractant. However, the intensity of (100) reflection was lower for the impregnated silica than for MCM-C, perhaps due to the dilution of the ordered material by the organic ligand, leading to a decrease of the silica amount (85% for HPBI, 82% for DEHPA and 76% for HPMSP). In addition, (110) and (200) reflection peaks essentially merged into one broad peak, which indicates a partial loss of long-range crystallographic order due to impregnation. The physico-chemical parameters of all the samples are presented in Table 2.

Table 2 Textural parameters of MCM-CI-HL.

<table>
<thead>
<tr>
<th>Solid</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_t$ (cm$^3$/g)</th>
<th>$D_p$ (Å)</th>
<th>$d_{100}$ (Å)</th>
<th>% HL (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-C</td>
<td>1100</td>
<td>0.90</td>
<td>26</td>
<td>34.2</td>
<td>0</td>
</tr>
<tr>
<td>MCM-CI-HPBI-0.42</td>
<td>1020</td>
<td>0.88</td>
<td>26</td>
<td>34.2</td>
<td>11</td>
</tr>
<tr>
<td>MCM-CI-HPBI-0.55</td>
<td>870</td>
<td>0.62</td>
<td>&lt;20 and 28.9</td>
<td>35.9</td>
<td>15</td>
</tr>
<tr>
<td>MCM-CI-HPMSP-0.54</td>
<td>860</td>
<td>0.57</td>
<td>21</td>
<td>34.2</td>
<td>24</td>
</tr>
<tr>
<td>MCM-CI-DEHPA-0.57</td>
<td>880</td>
<td>0.59</td>
<td>&lt;20 and 22.4</td>
<td>35.5</td>
<td>18</td>
</tr>
</tbody>
</table>

$V_t$: total pore volume at $P/P_0 = 0.95$.

$D_p$ (BET): pore diameter calculated by BJH method.
was also studied. The three diffractograms were similar for all the solvents used in the impregnation. Therefore, the nature of the solvent used has no effect on the structural properties of the mesoporous silica materials.

The impregnated silicas were calcined before analysis by nitrogen adsorption at 77 K (see below). In order to show if this second calcination affects the porosity organization, we realized an XRD analysis of some samples that were later used for nitrogen adsorption measurements (Fig. 6). The diffractograms show that the porosity was preserved; however a slight decrease of the order and a shift of the $d_{100}$ peak toward higher diffraction angles corresponding to a lower $d_{100}$ distance (from 35.9 to 33.6 Å) were observed.

### 3.4. Characterization of the supports by nitrogen adsorption at 77 K

The different mesoporous silicas were characterized by nitrogen adsorption at 77 K before and after impregnation. Prior to the analysis, the supports were calcined at 500 °C for 10 h in order to remove both the surfactant and the ligand. The calculated textural parameters of all the samples are presented in Table 2.

The nitrogen adsorption–desorption isotherm of the calcined silica (Fig. 7) is a type IV isotherm of the IUPAC classification, featuring a narrow step due to capillary condensation of N$_2$ within the primary mesopores (Gregg, 1982). The obtained specific area was 1100 m$^2$/g, a characteristic of mesostructured silica materials. In our earlier work (Miloudi et al. 2007), we have shown that the textural properties of the silica impregnated by HPBI are not affected by low ligand loading, (type IV isotherms). On the other hand, as shown in Fig. 7, when the ligand concentration increased, N$_2$-adsorption isotherm changed from the type IV to the type I + IV, characteristic of super-microporous solids (Bastardo-Gonzalez et al., 2002; Casagrande et al., 2004) with a pore diameter about 20 Å. This variation occurred for all the ligands tested in the present work. A decrease in the pore diameter and the specific...
surface area was observed for high ligand concentrations (Table 2). This can be understood if we assume that the ligand–silica interaction as revealed by IR spectroscopy (shift of the C=O band at 1691 cm⁻¹ visible for HPBI) could move the silanols closer to each other, which would facilitate siloxane bridge formations by condensation under calcination.

The absence of the hysteresis loop indicates a pore-size uniformity and shows that there was no pore blockage during desorption (Casagrande et al., 2004; Guo et al., 2005).

In order to point out the effect of the impregnation solvent on the structural properties of silica, we have impregnated the calcined silica by using three different organic solvents: toluene, chloroform and acetone. The results showed that the solvent nature does not affect the textural parameters of the impregnated materials, as already observed with XRD.

BJH pore size distribution analysis has shown that calcined silica is narrow and centered around 26 Å (Miloudi et al., 2007). In our study, this distribution was observed for a low content of HPBI. However, when increasing the ligand content, the pore distribution of the different silicas impregnated with organic extractants was wider and lower in such a way that the center of the distribution could not be calculated by

Figure 9  Transmission electron micrographs (TEM) for: (a) MCM-C, (b) MCM-CI-HPBI-O.55, (c) MCM-CI-HPMSP-0.54, (d) MCM-CI-DEHPA-0.57.
the BJH method (Fig. 8). On the other hand, the organization of the mesoporosity was preserved for all the silica samples as proved by XRD patterns and not by N₂ adsorption. This latter did not allow a correct measurement of pore size lower than 20 Å as should be the case with the impregnated samples.

3.5. Characterization of the supports by TEM

TEM images showed that MCM-C has highly ordered mesostructure with regular channels characteristic of the hexagonal structure of MCM-41. The same was observed for the impregnated silicas (Fig. 9a–d). For example, in Fig. 9d, we recorded a highly-ordered hexagonal structure of MCM-CI-DEHPA, which is characteristic of MCM-41 structure. We concluded that the silica impregnation by the different ligands did not alter the ordered structure of the calcined starting material. These results were consistent with those of X-ray powder diffraction.

3.6. Metal extraction

The extraction percentage % R of a metal M, can be determined from its analytical concentrations in the aqueous phase before and after extraction (respectively [M]aq,i and [M]aq,e) (Eq. (1)):

$$ R = 100 \times \frac{[M]_{aq,i} - [M]_{aq,e}}{[M]_{aq,i}} \quad (1) $$

In order to determine the domain of the extraction pH of Cu(II) and Zn(II) by the impregnated silica, we carried out extractions by varying the initial pH of the aqueous phase. We noticed that the initial pH decreased after the extraction. This was an indication that the extraction process was probable an ionic exchange between Cu²⁺ ions of the aqueous solution and the H⁺ protons of the ligands HL in the solid phase. The same phenomenon was observed before in the liquid–liquid extraction of the Cu(II) by HBPI (Arichi and Goetz-Grandmont, 2009 and references therein).

Fig. 10 represents the experimental extractions of copper (% R = f (pHₑq)). According to this figure, Cu(II) was extracted at 100% by the silica impregnated by HPBI and HPMSP. The pH domains were more acidic compared to those of the liquid–liquid extraction of the copper by the same ligands (e.g., Cu(II) is extracted at pH ~0.5 for (HPBI)) (Arichi and Goetz-Grandmont, 2009 and references therein), which is favorable for the cation extraction from lixiviation solutions.

Fig. 10 shows a weak extraction capacity for Cu(II) by the MCM-CI-DEHPA (% R = 20 to pHₑq = 3.4).

The equilibrium pH seemed to be the only factor responsible for the extraction low rate. Thereafter, we have increased the equilibrium pH by adding NaOH, without reaching pH 5.5 at which starts the formation of the hydroxide Cu(OH)₂. The extraction rate reached 54.5% (pHₑq ≈ 3.75). Based on these results, we concluded that the Cu(II) extraction by MCM-CI DEHPA is total until the pH of the formation of Cu(OH)₂ is reached.

We also studied the zinc extraction by non functionalized silicas and by calcined silicas impregnated by different ligands, by varying the initial pH without reaching the pH of the formation of Zn(OH)₂.

No extraction was observed by the non functionalized silicas both calcined and not calcined.

Fig. 11 represents the extraction of zinc by the calcined and impregnated silicas.

We observed that the best extraction was obtained by the DEHPA impregnated silica: zinc was extracted at pH 1.5 and a yield of 100% was reached at pH 3 (pH½ = 2.35). This pH domain was the same as the one obtained by Kunzmann and Kolarik (1992) in the liquid–liquid extraction of Zn(II) by the same ligand, in a sulfate media. Indeed, this ligand presents a strong affinity toward Zn(II) (log $K_{ex}(ZnL_2)$ = 4.47 in the biphasic system: n-heptane-water (SO₄)²⁻) (Sastre and Mamoun, 1984); this affinity was maintained in the solid–liquid extraction.

Concerning the MCM-CI-HPMSP, the extraction was done at higher pHs (pH½ = 4.16), but it was complete at pH 4.7. In fact, the affinity of the zinc relatively to the 1-phenyl-3-methyl-4-octanoyl-pyrazol-5-one “HPMC₈” was weaker (log $K_{ex}(ZnL_2(\text{HL})_2)$ = -6.8) in the system (benzene-water) than the one of DEHPA (log $K_{ex}(ZnL_2(\text{HL}_2)_2)$ = 8.1) in the same biphasic system (benzene-water).

On the other hand, the zinc extraction by the MCM-CI HPBI did not exceed 20% (maximum yield reached at pH ~4). This phenomenon was most likely the result of the loss of HPBI in the aqueous phase at a higher pH, under an ionic form. Therefore, we tried to quantify the ligand in the

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**Figure 10** Cu(II) extraction by MCM-CI-HL (HL, HPBI, HPMSP, DEHPA), $T = 25$ °C, $\mu = 1$, medium [(Na,H)SO₄], $t = 1$ h.

**Figure 11** Zn(II) extraction by MCM-CI-HL, (HL, HPBI, HPMSP, DEHPA), $T = 25$ °C, medium [(Na,H)SO₄], $\mu = 1$, $t = 1$ h.
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extraction solutions, by UV–Visible spectroscopy. The results showed that 3% of HP MSP and DEHPA leached through the solution during the extraction of the metallic cation, until pH 6.5. However, 15% of HPBI went into the aqueous phase at pH 2.7% and 90% at pH 4.5 during extraction. This is due to the strong acidity of this ligand (pKa = 1.2) and explains the weak yield of the zinc(II) extraction by the MCM-CI-HPBI. The loss of HPBI in the aqueous phase was also observed in the biphasic system where more than 50% of HPBI went in the aqueous phase as PBI. The weak yield of the zinc(II) extraction by the MCM-CI-HPBI showed the stripping of the cations from the impregnated silica. We have shown that 3% of HPMSP and DEHPA leached through extraction solutions, by UV–Visible spectroscopy. The results are encouraging for the extraction of Cu(II) and Zn(II) in solid–liquid extraction. These results are indicative of the affinity of the ligands toward the aqueous media. The authors thank Dr. Z. Asfari for his help in the ligand synthesis and O. Tayeb and R. Hamacha for their help in the translation in English.

4. Conclusion

In this paper, we have demonstrated that the impregnation process is efficient in functionalizing MCM-41 silica without noticeable modifications of the porous structure. High contents of several ligands were achieved with amounts of ligand trapped exceeding 90% of the entire ligand we attempted to trap. The specific surface area of the silica decreased after impregnation, but it remained high and the inter-planar distance was preserved. The pore size was lowered but this should be the result of the second calcination step required for the nitrogen adsorption measurement. This observation was done for all the ligands at high concentrations.

On the other hand, this study has demonstrated the first potential environmental application of the mesostructured silicas impregnated with acidic chelating ligands. We have shown that the extraction of copper and zinc from sulfate media depends on the pH of the aqueous solution.

Copper was 100% extracted by MCM-CI-HPBI and MCM-CI-HP MSP at a very acidic pH range that was more acidic in the case of HPBI than HP MSP. MCM-CI-DEHPA extracted nearly 55% of Cu(II) at pH = 3.75. Zinc was almost 100% extracted by MCM-CI-DEHPA (pH 2–3) and by MCM-CI-HP MSP (pH 3–5). The ligands’ affinity toward the cations was maintained in solid–liquid extraction. These results are encouraging for the extraction of Cu(II) and Zn(II) in highly acidic leach solutions.

In a further paper, we will present the effect of the other parameters such as: ligand concentration, ionic strength of the aqueous solution. High contents of several ligands were achieved with amounts of ligand trapped exceeding 90% of the entire ligand we attempted to trap. The specific surface area of the silica decreased after impregnation, but it remained high and the inter-planar distance was preserved. The pore size was lowered but this should be the result of the second calcination step required for the nitrogen adsorption measurement. This observation was done for all the ligands at high concentrations.

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