



Fast, Efficient and Environmentally Friendly Extraction of Cu(II) and Zn(II) by Hybrid Silicas Impregnated with Acidic Organic Extractants

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ABSTRACT

The extraction of copper and zinc by mesostructured silicas impregnated with organic 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 performed in a sulfate medium. Various factors such as the pH of the aqueous phase, the chelators' concentration in the silica matrix, the extraction equilibrium time and the extraction capacity of the two cations on silica were studied. The cations were extracted at very acidic pH with very high extraction rates. The stripping of cations was achieved at pH's that were more acidic than those utilized for the extraction by maintaining the structure intact. Finally, their separation was successfully conducted in the cases of the three chelators.

KEY WORDS:

Solid-Liquid Extraction, Impregnated Mesostructured Silica, Cu(II)/Zn(II) Separation.

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)

1. INTRODUCTION

Several Industries such as mining, metallurgical and chemical factories massively contribute to the ongoing contamination of the environment. Furthermore, the mismanagement of sewage sludge contaminates soil with heavy metals such as cobalt, copper, zinc, lead, cadmium, and mercury. Naturally acidic rainwater can subsequently lixiviate these metals resulting in their disposal in the sea. Therefore, the necessity to remove these metals is two-fold:

1. To stop this source of pollution
2. To recover these precious metals in order to satisfy the global demand.

Consequently, the development of efficient and environmentally friendly systems for the extraction of metal cations, in synthetic solutions or industrial effluents, became a necessity. These performing systems are based on the synthesis of novel selective ligands on one hand, and on the other hand the elaboration of new porous organo-mineral hybrid materials, capable of trapping the metal cations. In this scope, one of the most used methods is the solid-liquid extraction, chosen in this work. Using this technique, various porous inorganic and organic (clays, zeolites, resins) solids have been widely used in the recovery of metal cations. However, the described extraction capacity in the literature is very limited [1-7]. In order to increase this latter, the materials used can be functionalized with organic extractants [1, 2, 8-14].

In this work, we have synthesized mesostructured silicas according to the protocol described by Firouzi *et al.* [15], and subsequently modified by Boos *et al.* [16]. These silicas were then calcined and impregnated with three acidic organic 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) [13]. The prepared silicas were used in the solid-liquid extraction of Cu (II) and Zn (II) in a sulfate medium. The various factors affecting the extraction were studied. The extraction equilibrium for the two cations was reached within 15 minutes, with very high extraction capacity and separations were carried out successfully.

2. EXPERIMENTAL

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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ respectively (analytical grade, Merck, Frankfurt, Germany) in deionized water and the correct concentrations were controlled by atomic absorption spectrometry ICP/AES (JY138 ultratrace, Horiba Jobin Yvon, UK). Standard solutions were prepared by acidic attack of copper and zinc chips (99.99%) purchased from Acros (Thermo Fisher Scientific, Geel, Belgium) using sulfuric acid (Merck, 95-97%). A solution of this latter as well as sodium sulfate and sodium hydroxide (analytical grade, Merck, Frankfurt, Germany) solutions were used to adjust the pH and the ionic strength of the different solutions.

The synthesis, impregnation and characterization of silicas used in this work were detailed in a previous work [13].

2.2 Metal extraction procedure

The extraction of the metal M(II) was carried out in polypropylene tubes thermoregulated at 25.0 ± 0.2 °C. In a typical experiment, 0.1 g of solid was mechanically stirred in 10 ml of aqueous phase for 1 h, a sufficient time to reach the equilibrium. Then, the two phases were separated with a high-speed centrifuge (10000 rpm for 10 min), the equilibrium pH of the liquid phase (pH_{eq}) was measured using a combined glass electrode connected to a Digilab 517 pH-meter (Crison, Barcelona, Spain) and the metal content in the aqueous phase was determined by ICP/AES (JY138 ultratrace, Horiba Jobin Yvon, UK). Aqueous solutions of the following composition were prepared: $[\text{H}^+, \text{Na}^+ \text{SO}_4^{2-}] = 0.33$ M, $[\text{M(II)}] = 100$ ppm ($\sim 1.6 \times 10^{-3}$ M for Cu(II) and $\sim 1.5 \times 10^{-3}$ M for Zn(II)), with different initial pH's (pH_i) between 1.0 and 5.8.

The extraction percentage %R of a metal M in a solid-liquid extraction, can be determined from its analytical concentrations in the aqueous phase before and after extraction (Eq. (1)):

$$R\% = \frac{[M^{m+}]_0 - [M^{m+}]_{\text{aq}}}{[M^{m+}]_0} * 100 \quad (1)$$

where R is the extraction percentage.

$[M^{m+}]_0$ is the initial concentration of the metal (mmol/l).

$[M^{m+}]_{\text{aq}}$ is the equilibrium concentration of the metal in the aqueous phase (mmol/l).

Another ratio can also be defined:

$$\frac{S}{M} = \frac{\text{Number of chelating sites in the solid}}{\text{Initial number of metal ions in solution}} \quad (2)$$

S = number of moles of HL_s in the impregnated solid.

Table 1 presents the concentrations of the ligands in mmol per 1 g of functionalized solid.

Table 1: Concentrations of ligands in mmol/g in the silica matrix.

Silica	Ligand	$[\text{HL}]_s$ (mmol/g)
MCM-CI	HPBI	0.55
	HPMSP	0.54
	DEHPA	0.57

The capacity of an extracting solid, expressed in m_{eq} / g , is defined by the maximum amount of metal ion that can be immobilized per unit of solid mass (solid). It depends essentially on the number of functional groups accessible on the surface of the material, on the specific surface area, and the dilution of the functional groups in the solid matrix and the stoichiometry of the complex between the metal and the ligand.

The Cu (II) capacity of impregnated silicas was determined in 0.33M sulfate medium by placing the same solid mass in contact with increasing amounts of metal ion, to allow the saturation of the solid. This was done by increasing the metal ion concentration in the solution without changing the volume ratio of the phases.

As for the stripping of metals and for each experimental point, an extraction of the metal was performed at a given equilibrium pH. The liquid and solid phases were then separated. During the extraction, we added to each solid phase a volume of nitric acid (in general HNO_3 , 1M) equal to the volume of the aqueous phase used. The pH of the nitric acid solution was less than that of the initial extraction pH determined in the previous study. The system was stirred for one hour. The stripped metal present in the aqueous phase by then was titrated.

The effect of the stripping on the silica structure was investigated through an analysis of the solids by X-ray diffraction XRD.

3. RESULTS

Our work revolves around the study of the extracting properties of silica supports impregnated by HPBI, HPMSP and / or DEHPA in order to confirm the importance of their use in the extraction of transition metals cations in sulfuric aqueous medium and their eventual separation. The preparation and characterization of the different silicas have been described in a previous work [10, 13].

We have investigated the kinetics and extraction capacity of the used supports towards the metal to be extracted. We also studied the pH of the aqueous medium and the concentration of ligands in the silica matrix as the main parameters influencing the outcome of the extraction.

We conducted Cu (II) and Zn (II) extraction tests on blanks (non-functionalized calcined silicas) [13], and no extraction was observed. This prompted us to incorporate chelating ligands in the silica for the cations extraction following their complexation within the silica matrix.

For each extraction system M^{2+} /(impregnated silica), we conducted a series of extractions for which the initial pH were the same. However, the contact time was ranging from 5 to 60 min. The initial pH and the pH at equilibrium are summarized in Table 2:

Table 2: Initial and equilibrium pH values for the kinetic study of the extraction.

System	pH _i	pH _{eq}
Cu-MCM-CI-HPBI	1.07	0.87 ± 0.02
Cu-MCM-CI-HPMSP	3.87	3.19 ± 0.01
Zn-MCM-CI-DEHPA	6.19	3.09 ± 0.03

Figure 1 represents the extraction percentage as a function of time. It is important to note that the equilibrium was reached in less than 15 min in all three cases.

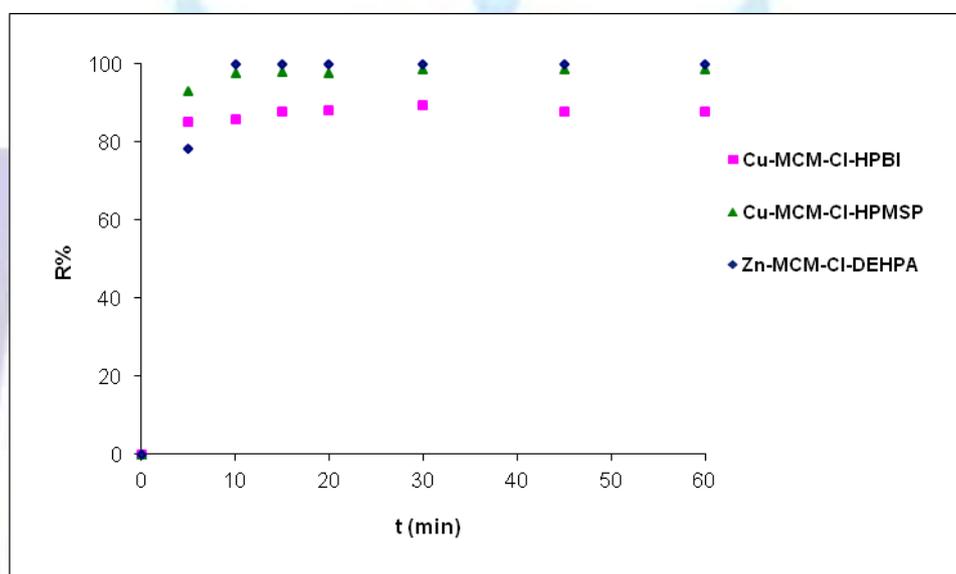


Figure 1: Time needed to reach equilibrium in the solid-liquid extraction of Cu(II) and Zn(II).

T = 25°C, medium [(Na,H)SO₄], ionic strength $\mu = 1$, [Cu]₀ = 1.57x10⁻³ M, [Zn]₀ = 1.53x10⁻³ M.

■ S/M=3.49 ▲ S/M=3.43 ◆ S/M=3.73

With the aim of determining the kinetic order of the extraction process, a pseudo-first order expressed in equations (3, 4) and a pseudo-second order expressed in equations (5, 6) were studied. For a pseudo-first order reaction, the rate law is expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Where

k_1 : the rate constant (min⁻¹),

q_e : quantity of the metal ion extracted at equilibrium (mmol/g),

q_t : quantity of the metal ion extracted at time t.

After equation 3 is integrated between 0 and t for the time and between 0 and q_t for the quantity of the metal ion extracted, we obtain:

$$\ln(q_e - q_t) = \ln q_e - k_1.t \quad (4)$$

For a pseudo-second order reaction, the rate law is expressed as:

$$\frac{dq_t}{dt} = k_2 \cdot (q_e - q_t)^2 \quad (5)$$

where k_2 is the rate constant ($\text{g} \cdot \text{mmol}^{-1} \cdot \text{min}^{-1}$)

After equation 5 is integrated, the following integrated law is obtained:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 \cdot t \quad (6)$$

Equation 6 can be rearranged as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad (7)$$

We determined the rate constants and correlation coefficients, by plotting $\ln(q_e - q_t)$ as a function of time t for pseudo-first order and t/q_t versus time for pseudo-second order. The results are summarized in Table 3 and are shown in Figures 2 and 3.

Table 3: Rate constants k of pseudo-first order and pseudo-second order reactions and correlation coefficients R of Cu(II) and Zn(II) extraction by the different silicas.

System	R_1^2	k_1	R_2^2	k_2
Cu-MCM-CI-HPBI	0.8917	0.09	0.9999	16.98
Cu-MCM-CI-HPMSP	0.7518	0.13	1	12.11
Zn-MCM-CI-DEHPA	0.9317	0.66	0.9904	2.28

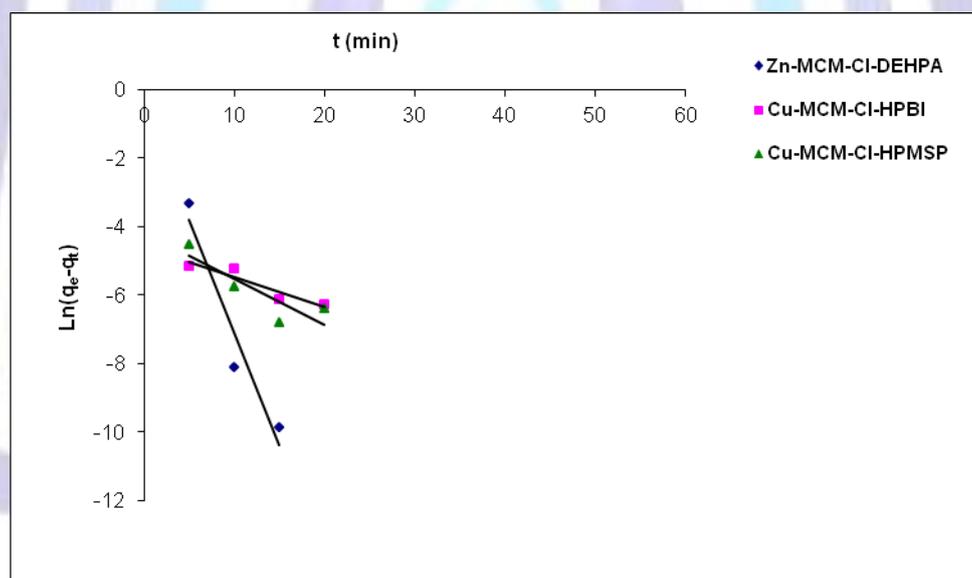


Figure 2: Representation of the kinetics of Cu(II) et de Zn(II) sorption by functionalized silicas as a pseudo-first order.

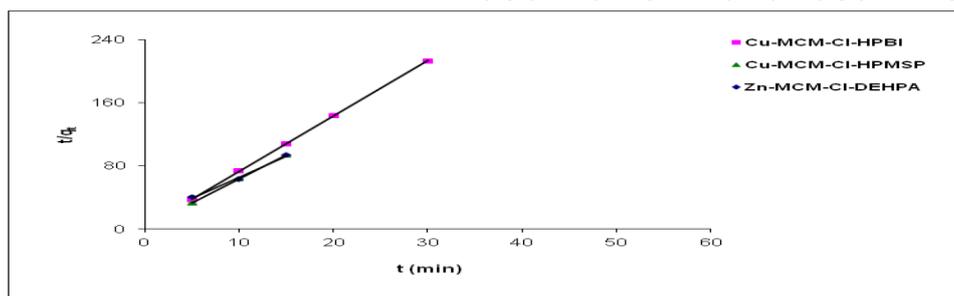


Figure 3: Representation of the kinetics of Cu(II) et de Zn(II) sorption by functionalized silicas as a pseudo-second order.

After comparing the correlation coefficients for the three different cases, we noted that the experimental points were consistent with the pseudo-second order model. Therefore, based on this model, we recalculated taking into account all the experimental points (Table 4).

Table 4: Kinetic parameters of the pseudo-second order Cu(II) and Zn(II) sorption by the different functionalized silicas.

Systèmes	C_0 (mol/l)	R_2^2	k_2	$q_{e,th}$ (mmol/g) ^a	$q_{e,exp}$ (mmol/g) ^b
Cu-MCM-CI-HPBI	1.57×10^{-3}	0.9999	174.15	0.139	0.139
Cu-MCM-CI-HPMSP	1.57×10^{-3}	1	24.50	0.162	0.160
Zn-MCM-CI-DEHPA	1.53×10^{-3}	0.9994	10.70	0.162	0.160

^a $q_{e,th}$: quantity of the metal ion extracted at equilibrium and determined by equation 7.

^b $q_{e,exp}$: quantity of the metal ion extracted at equilibrium and experimentally determined.

The correlation coefficients determined as well as the amounts of metal extracted at equilibrium were in good agreement with those determined experimentally.

Based on the theoretical study of Azizian [17, 18], the pseudo-second order model is best suited when the initial metal concentration is low. Indeed, in our case, we worked with a large excess of ligand ($S/M \geq 3.43$) and the kinetic order observed was certainly in agreement with the theory. However, it is to note that this result does not exclude in any case, second order possible chemisorption [19, 20] where the adsorption of metal cations taking place by complexation of this latter by ligands present in the solid phase.

In Table 5 we have summarized the data obtained by other research groups who worked with with the same ligands used in this study, on different functionalized solids. We also included the results of teams who used the liquid-liquid extraction technique [21, 26].

Table 5: Time needed to reach equilibrium in the liquid-liquid and solid-liquid extraction by different ligands of Cu(II) and Zn(II).

	Ligand	Cu (II)	Zn (II)
Liquid-Liquid Extraction	HPBI	15 min [21]	15 min [21]
	HPMSP	15 min [22]	15 min [23]
	DEHPA	60 min [24]	30 min [25]
Solid-Liquid Extraction <i>Impregnated silicas</i>	HPBI	15 min	*
	HPMSP	15 min	*
	DEHPA	*	15 min
Solid Liquid Extraction <i>Resins</i>	HPBI	*	*
	HPMSP	*	*
	DEHPA	120 min [26]	120 min [26]

It is of note that the equilibration time was reached more quickly in the case of the extraction of Zn (II) by DEHPA incorporated in the silica. The longest equilibration time corresponded to the extraction of zinc and copper by the resin impregnated by DEHPA. This was probably due to the textural properties of the two types of solids (Silica vs Resin). In general, for an extracting solid with a given chemical composition, the extraction kinetics of a metal ion depend on the solid's particle size and its average pore diameter. Decreasing the particles' size and increasing the average pore diameter help in achieving equilibrium more rapidly (Table 6) [27].

Table 6: Some textural properties of the MCM-C and the XAD-2 resin [27].

	Specific surface area (m ² /g)	Particles size	Average pore diameter (nm)
MCM-C	~ 1200	0.37 – 1.60 (μm)	~ 4
XAD-2	300	0.3 – 0.9 (mm)	9

Although the pore diameter of the resin is greater than twice that of silica, which promotes rapid kinetics, this is largely reduced by the other textural properties. The grain size of the mesostructured silicas is much smaller than that of the resin and their specific surface area is four times larger than that of the resin. This leads to a higher accessibility of the silica active sites to metal cations compared to the resin's.

In the remainder of the study, the contact time will be set to 60 minutes which will be sufficient to reach equilibrium.

3.1 Cu(II) extraction by silicas

3.1.1 Influence of the pH

The domain of extraction pH of Cu (II) by calcined impregnated silicas with different ligands was determined in a previous work [13]. The extraction was carried out at more acidic pH compared to those of the liquid-liquid extraction of copper with the same ligands [28] in the different cases, with an extracted amount of 0.16 mmol / g of impregnated silica.

3.1.2 Extraction capacity of MCM-CI towards Copper

The capacity was determined by measuring the amount of metal ion present in solution before (n_0) and after saturation (n):

$$C = \frac{(n_0 - n)}{m} \quad (8)$$

C: solid capacity (mmol / g)

m: mass of the solid before saturation (grams)

n_0 and n are expressed in mmol

In order to determine the Cu (II) extraction capacity of MCM-CI-HPBI and MCM-CI-HPMSP silicas, we have chosen initial pH's that were able to lead to maximum extraction. The initial pH's (pH_0) and equilibrium pH's are represented in Table 7.

Table 7: Initial equilibrium pH's of Cu (II) extraction by MCM-CI-HPBI et MCM-CI-HPMSP silicas.

	MCM-CI-HPBI	MCM-CI-HPMSP
pH₀	1.88 ± 0,05	3.48 ± 0.02
pH	1.81 ± 0,02	3.01 ± 0.02

Figure 4 shows the experimental results; In both cases, we observe two plateaus, the first one appears for Cu(II) initial concentrations of less than 600 ppm, and the second appears when the Cu(II) initial concentration is greater than 2000 ppm.

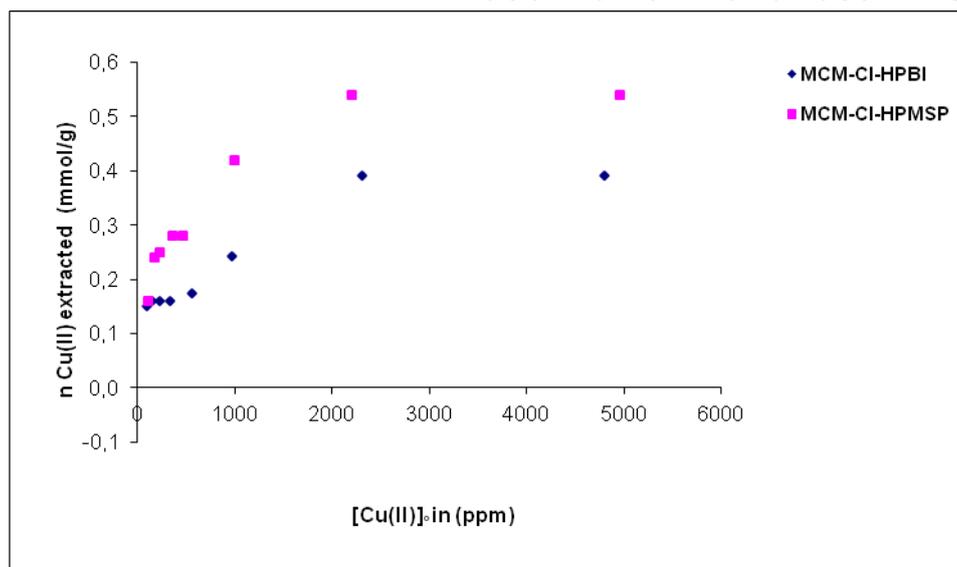


Figure 4: Cu (II) extraction capacity by MCM-CI-HPBI et MCM-CI-HPMSP silicas,

$T = 25^{\circ}\text{C}$, medium $[(\text{Na,H})\text{SO}_4]$, $t = 1 \text{ h}$, $[\text{HPBI}] = 0.55 \text{ mmol/g}$, $[\text{HPMSP}] = 0.54 \text{ mmol/g}$.

The amount of trapped ligand was practically the same in both silicas. Despite this, Cu (II) extraction capacity of the MCM-CI-HPMSP (0.54 mmol / g) was larger than that of the MCM-CI-HPBI (0.39 mmol / g).

The capacity value obtained in the case of MCM-CI-HPBI was in agreement with the values generally obtained by related materials [5]. However, those obtained by MCM-CI-HPMSP were substantially larger.

3.2 Zn(II) extraction by silicas

We have studied the extraction of zinc by non-functionalized silicas and silicas impregnated with different ligands.

3.2.1 Influence of the pH

The pH influence on Zn(II) extraction pH by the different impregnated silicas was studied in a previous work [13]. The best extraction was obtained with the silica impregnated by DEHPA. The extraction pH's were similar to those of the liquid-liquid extraction of Zn (II) by the same ligands [29].

3.2.2 Influence of ligand concentration

We have studied the effect of DEHPA concentration on the extraction of Zinc. The results are shown in Figure 5.

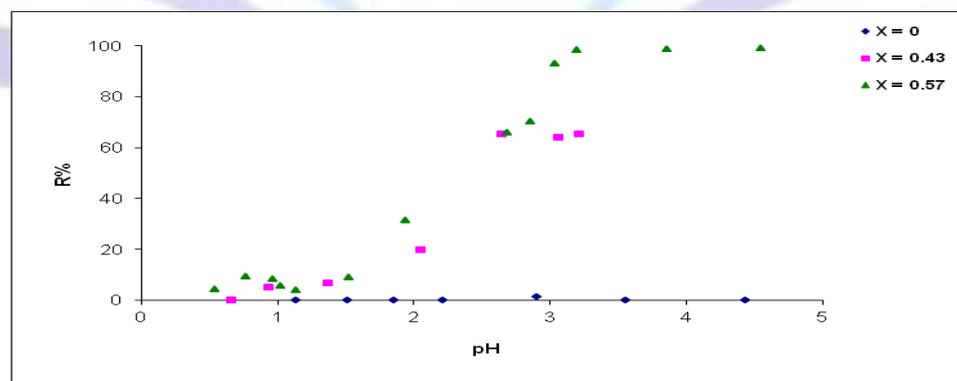


Figure 5: Effect of ligand concentration on Zn(II) extraction by

MCM-CI-DEHPA, $T = 25^{\circ}\text{C}$, medium $[(\text{Na,H})\text{SO}_4]$, ionic strength $\mu = 1$, $[\text{DEHPA}] = X$, $t = 1 \text{ h}$.

Two plateaus were obtained for the two different concentrations. The same phenomenon was obtained in one of our previous studies, in the research about the effect of the HPBI concentration on the extraction of copper by the MCM-CI-HPBI [10].

For 0.43 mmol/g of Zn(II), the MCM-CI-DEHPA was saturated with an extraction rate of approximately 66%. Whereas, for 0.42 mmol/g of Zn (II), the MCM-CI-HPBI was saturated with a 45% extraction rate. This difference may be due to the higher availability of DEHPA compared to HPBI.

3.2.3 Extraction capacity of MCM-CI-DEHPA towards zinc

We investigated the zinc extraction capacity of MCM-CI-DEHPA at $\text{pH}_0 = 6.20 \pm 0.08$ and $\text{pH}_{\text{eq}} = 3.14 \pm 0.05$. The results are presented in Figure 6.

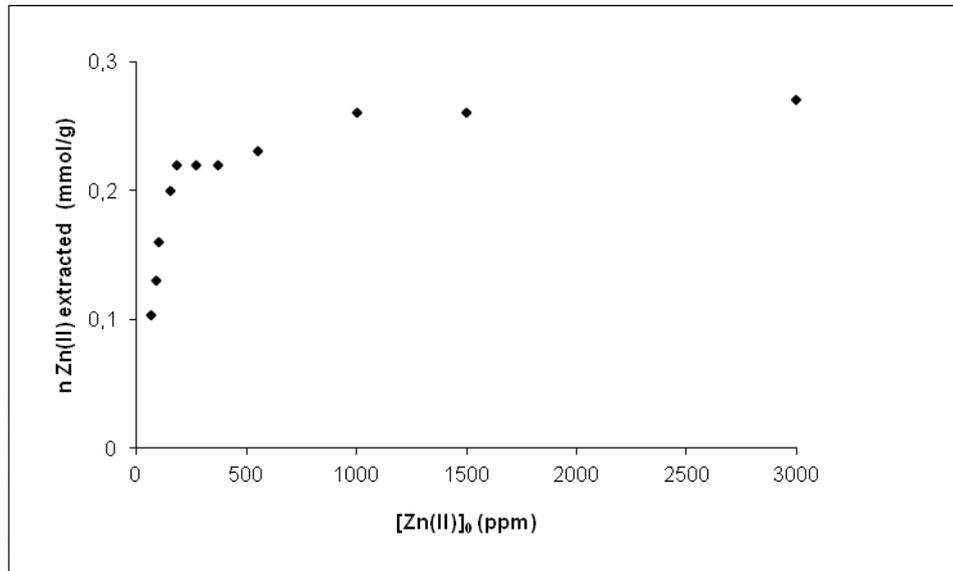


Figure 6: Zn(II) extraction capacity by MCM-CI-DEHPA, $T = 25^\circ\text{C}$, medium $[(\text{Na,H})\text{SO}_4]$, $t = 1$ h, $[\text{DEHPA}] = 0.57$ mmol/g.

As in the case of copper, the zinc extraction capacity of MCM-CI-DEHPA is represented by a curve having two plateaus: the first (0.22 mmol / g) was obtained at Zn(II) concentrations between 180 and 380 ppm and the second (0.27 mmol / g) at concentrations between 1000 and 3000 ppm.

3.3 Copper/zinc selectivity of the calcined impregnated silicas

For comparative reasons, we have presented on Figures 7, 8, and 9 the extraction curves of copper and Zinc previously obtained. The extracting solids were the calcined MCM's impregnated by HPBI, HPMSP and DEHPA, respectively.

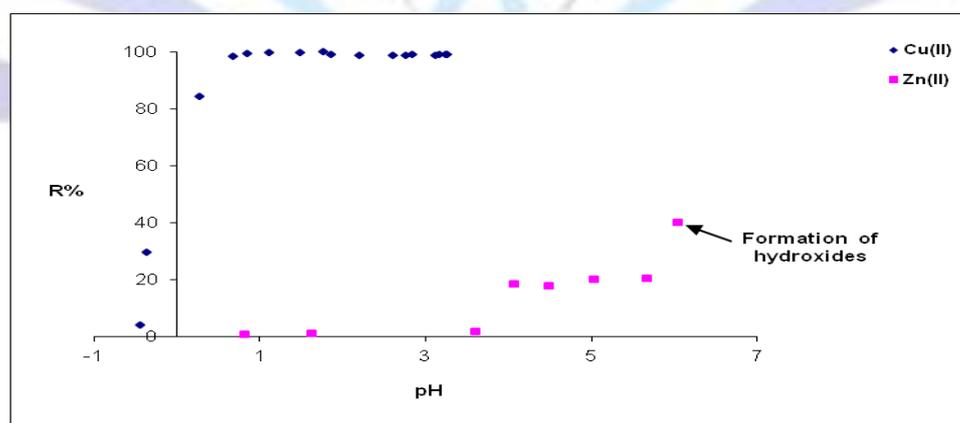


Figure 7: Cu(II) and Zn(II) extraction by MCM-CI-HPBI, $T = 25^\circ\text{C}$, medium $[(\text{Na,H})\text{SO}_4]$, ionic strength $\mu = 1$, $t = 1$ h, $[\text{HPBI}] = 0.55$ mmol/g.

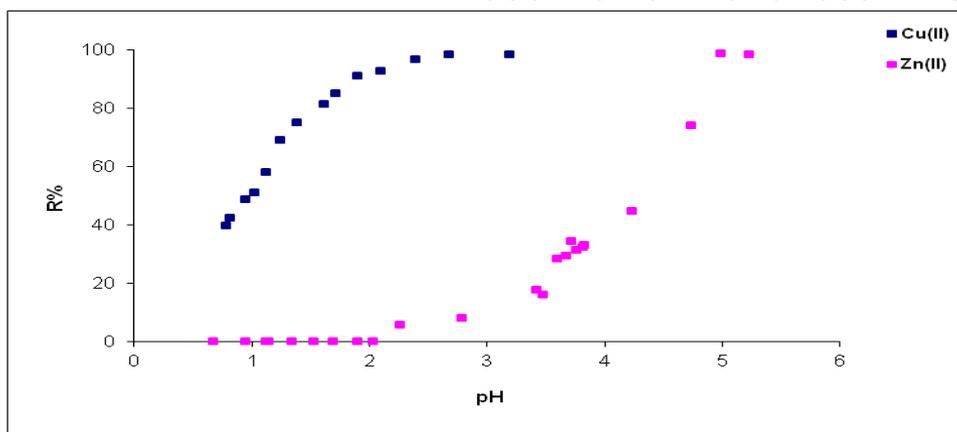


Figure 8: Cu(II) and Zn(II) extraction by MCM-CI-HPMSP,

$T = 25^{\circ}\text{C}$, medium $[(\text{Na,H})\text{SO}_4]$, ionic strength $\mu = 1$, $t = 1$ h, $[\text{HPMSP}] = 0.54$ mmol/g.

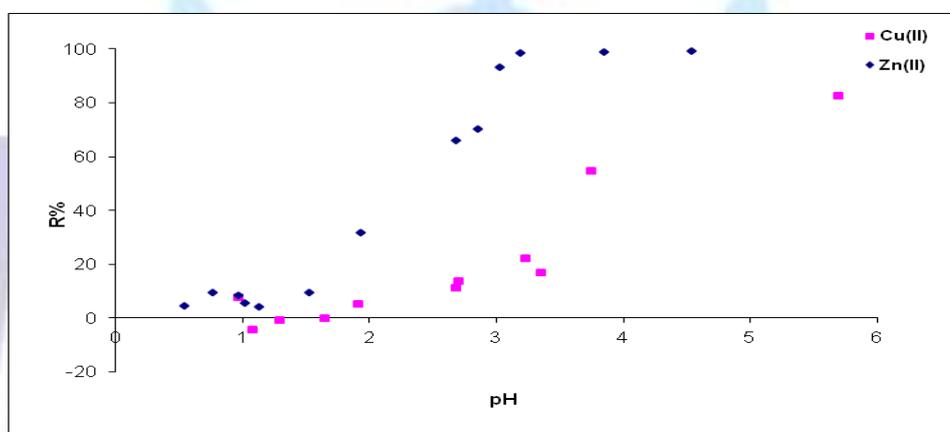


Figure 9: Cu(II) and Zn(II) extraction by MCM-CI-DEHPA,

$T = 25^{\circ}\text{C}$, medium $[(\text{Na,H})\text{SO}_4]$, ionic strength $\mu = 1$, $t = 1$ h, $[\text{DEHPA}] = 0.57$ mmol/g.

Figures 7, 8 and 9 show that it is possible to separate Cu and Zn in such systems. Thus, all copper should selectively be extracted at pH 2 by MCM-CI-HPBI and MCM-CI-HPMSP respectively. As for zinc, it should be extracted at pH 3 by the MCM-CI-DEHPA.

In order to test the above hypotheses, we performed the extraction of copper and zinc, from the same solution containing 100 ppm of each metal, by different systems, at two different pH's. The results are summarized in Table 8.

Table 8: Extraction percentages of copper and Zinc in the same solution, $T = 25^{\circ}\text{C}$;

$t = 1$ h; ionic strength $\mu = 1$ M, $[\text{Cu}] = [\text{Zn}] = 100$ ppm.

	S/M_t^c	pH	Cu(II) R%	Zn(II) R%
MCM-CI-HPBI	1.77	0.34	84.57	0
		2.70	98.03	0
MCM-CI-HPMSP	1.74	1.27	54.64	0
		2.67	97.63	0
MCM-CI-DEHPA	1.84	1.80	0	21.73
		3.12	0	91.22

^c S/M_t : Number of moles of HL / Total number of moles of metal (zinc + copper).

Based on Table 8, we can conclude that it is possible to selectively separate copper and zinc by using the systems we synthesized and elaborated. It should be noted that there was no further extraction of zinc by MCM-CI-HPBI nor by MCM-CI-HPMSP in the presence of copper. Furthermore, no extraction of copper by MCM-CI-DEHPA in the presence of zinc was observed.

The S/M_t ((Number of moles of HL / Total number of moles of metal (zinc + copper)) were 1.77; 1.74 and 1.84 respectively, under the conditions of these experiments. However, in the conditions of figures 7, 8 and 9, the S/Cu or S/Zn were practically doubled. It seems that the two metals compete for binding to the active sites, thereby disadvantaging the extraction of the less reactive (towards these sites) metal and even cancelling it.

3.4 Stripping of metallic cations

In order to recover the extracted metal cations and ensure the best performance of our functionalized silicas and their ability to be reused, we studied the stripping of copper and zinc by the silicas that have showed high extraction capacities towards these cations.

We presented the extraction-stripping by plotting the following experimental curves:

$$n(M_{ex}) = f(pH_{eq}) \text{ for extraction}$$

$$n(M_{str}) = f(pH_{eq}) \text{ for stripping}$$

pH_{eq} : extraction pH at equilibrium.

$n(M_{ex})$: number of moles of the extracted metal

$n(M_{str})$: number of moles of the stripped metal

A stripping percentage $R\%_{str}$ can be calculated as follows:

$$R\%_{str} = \frac{n(M_{str})}{n(M_{ex})} \times 100 \quad (9)$$

3.4.1 Cu(II) stripping from MCM-CI-HPMSP

Figure 10 shows the evolution of the number of moles of copper extracted by MCM-CI-HPMSP and stripped as a function of pH. The stripping was carried out using a solution of 1M solution of nitric acid.

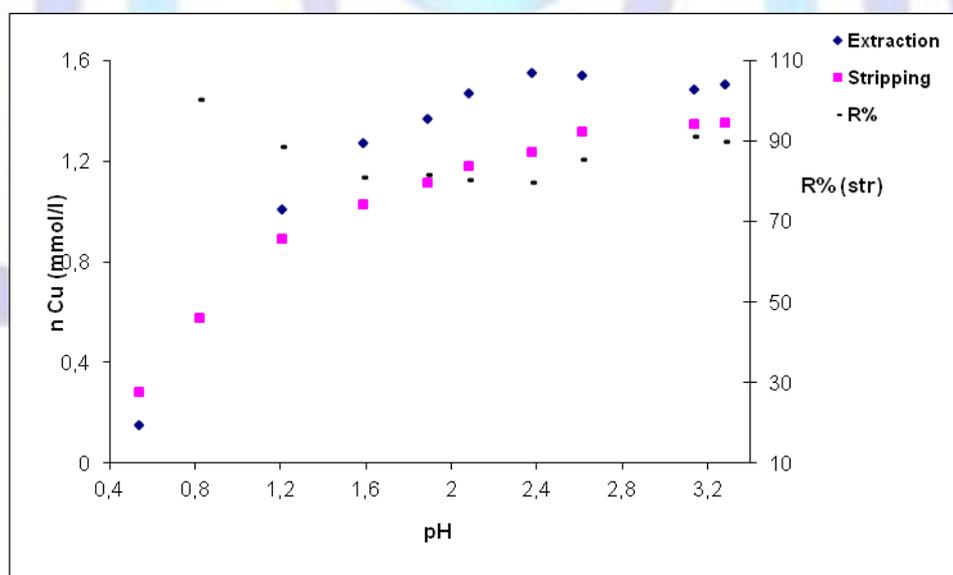


Figure 10: Extraction-stripping of Cu(II) by MCM-CI-HPMSP,

T = 25°C, t = 1 h, [HPMSP] = 0.54 mmol/g,

extraction solution: (Na,H)SO₄, ionic strength $\mu = 1$, stripping solution: 1M HNO₃.

Figure 10 shows that the copper recovery from the MCM-CI-HPMSP can be easily realized with more than 90% of the extracted copper being recovered. At low pH's, the stripping percentage $R\%_{str}$ can sometimes exceed 100%. In fact, the stripping was carried

out immediately after the phase separation following the extraction, by adding the acid solution to the silica still impregnated by the extraction. This was a source of error as the extraction is low at these pH's, the stripping percentage can surpass 100 %. However, this error becomes negligible for extractions with % R beyond 50%. Furthermore, XRD diffractograms showed that the structure was not affected by the stripping process.

3.4.2 Cu(II) stripping from MCM-CI-HPBI

Copper extraction by silicas impregnated with HPBI was high starting with pH= 0; therefore, the stripping must be carried out with very acidic solutions such as 6M HNO₃. We tried to recover the copper extracted by silicas impregnated with HPBI, playing on the stripping time. Experimental extraction-stripping curves are shown in Figure 11.

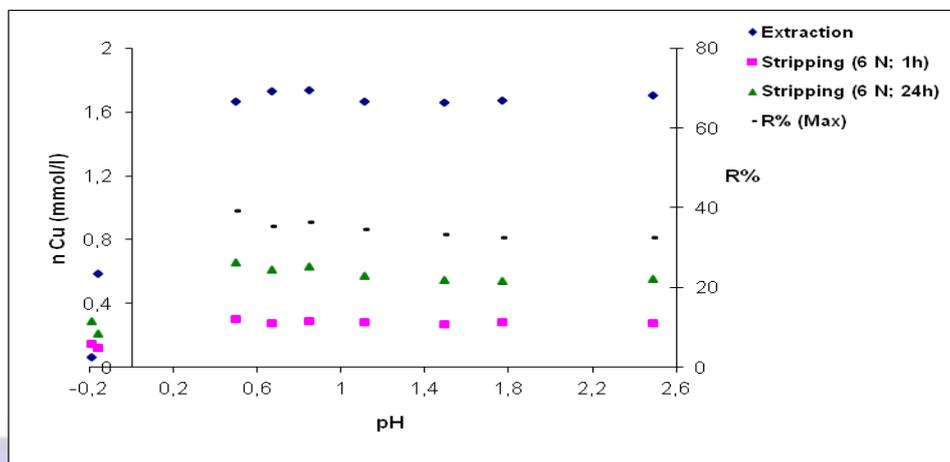


Figure 11: Extraction-stripping of Cu(II) by MCMCIHPBI,

**T = 25°C, medium [(Na,H)SO₄], ionic strength $\mu = 1$, t = 1 h, [HPBI] = 0.55 mmol/g,
 extraction solution: (Na,H)SO₄, $\mu = 1$, stripping solution: 6 M HNO₃.**

The maximum amount of recovered copper was approximately 35% after 24 hours. On the other hand, The XRD diffractograms, showed that the silica structure was completely destroyed by acid attack during the stripping; This may explain the low recovery of copper from the MCM-CI-HPBI.

3.4.3 Zn(II) stripping from MCM-CI-DEHPA

The extraction/stripping of zinc was realized with a 1M nitric acid solution. The results are presented in Figure 12.

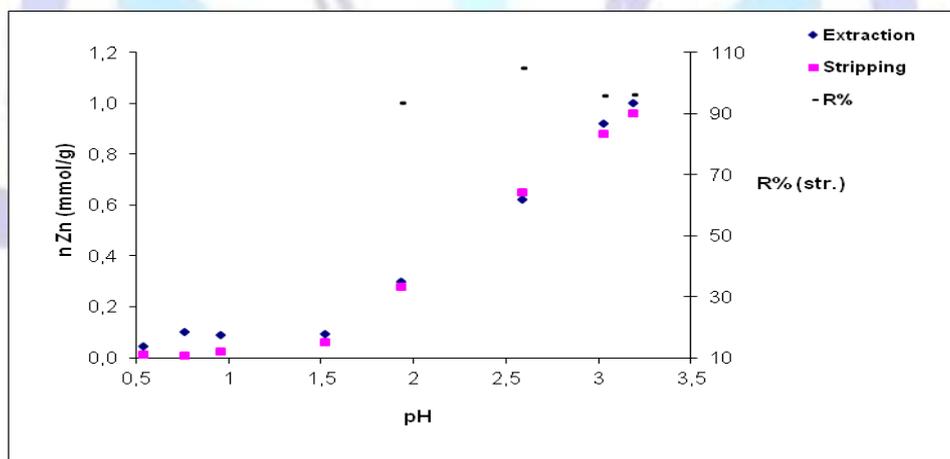


Figure 12: Extraction-stripping of Zn(II) by MCM-CI-DEHPA,

**T = 25°C, medium [(Na,H)SO₄], ionic strength $\mu = 1M$, t = 1 h, [DEHPA] = 0.57 mmol/g,
 extraction solution: (Na,H)SO₄, ionic strength $\mu = 1M$, stripping solution: 1 M HNO₃.**

Zinc can be recovered at more than 95% out of the quantity extracted by silica impregnated with DEHPA, without any change in the structure.

4. DISCUSSION



In the various cases of extraction capacity curves (Figures 4 and 6), we obtained the same shape presenting two plateaus. In Table 9, we have reported, for each system, the concentration of extracted metal at each plateau and the $R_{L/M}$ ratio which is defined as:

$$R_{L/M} = \text{amount of ligand (mmol/l)} / \text{Amount of extracted metal (mmol/g)}.$$

Table 9: $R_{L/M}$ Values at the two plateaus of capacity curves for all systems.

System	$R_{L/M}$	
	1 st Plateau	2 nd Plateau
Cu-MCM-CI-HPBI	3.4	1.4
Cu-MCM-CI-HPMSP	1.9	1
Zn-MCM-CI-DEHPA	2.6	2.1

Unlike liquid-liquid extraction, the amount of ligand in the solid-liquid extraction was limited and distributed over a large area. However, the formation of complexes ML^+X^- type, whose $R_{L/M}$ ratio was 1, could be favorable at high metal concentrations [5]. The charge of the complex would indeed be compensated by the anions of the aqueous phase (eg. HSO_4^-).

For Cu-MCM-CI-HPMSP systems, the $R_{L/M}$ ratio was 1 at the 2nd plateau, which corresponded to the formation of the complex CuL^+X^- . This ratio was 2 at the 1st plateau and corresponded to the formation of CuL_2 . This was in agreement with the liquid-liquid extraction by HPMSP where the concentration of the latter was largely in excess with regard to copper, which promoted the formation of CuL_2 . Thus, we could conclude that all HPMSP ligands were accessible, reactive and arranged to form a square planar complex with copper.

Concerning the Cu-MCM-CI-HPBI system, at high concentration of copper, a $R_{L/M}$ ratio of 1.4 (2nd plateau) was obtained. This corresponded to the formation of CuL^+X^- complex with the existence of some inaccessible sites (eg. crystallized HPBI). When the copper concentration was low, the ratio was 3.4 (1st plateau). This ratio corresponded to the formation of CuL_2 , with the presence of unreachable sites. Some of these sites are reactive, but could be hidden or poorly placed to coordinate a single copper, thus, we came to complex copper by these sites under CuL^+ form at high concentrations of copper. This was consistent with the plateau obtained at 0.42 mmol/g for copper extraction by MCM-CI-HPBI when the $R_{L/M} = 6$, which implies that some molecules were inaccessible to copper [10].

In the liquid-liquid extraction of Zn by DEHPA, different complex species could be formed such as for example ZnL_2 , $ZnL_2(HL)$, and $ZnL_2(HL)_2$. A high Zn/DEHPA ratio in organic phase promotes the formation of polymeric complexes of type $(ZnL_2)_n$ with: $2 \leq n \leq 3,5$ [25, 29]. In case DEHPA was immobilized on a mesostructured silica such as MCM-CI-DEHPA, it would be very difficult to accurately determine the stoichiometry of the complex formed during the extraction of zinc. The $R_{L/M}$ ratio was 2.1 at the 2nd plateau which may correspond to the formation of ZnL_2 complex. This ratio was 2.6 at the 1st plateau and could relate to the formation of $ZnL_2(HL)$ which was a very probable complex to form in the case of zinc [30]. The formation of ZnL^+X^- was unlikely to happen. These results were consistent with the plateau of the zinc extraction by the MCM-CI DEHPA with a rate of 66% of Zn, when the concentration of DEHPA was 0.43 mmol/g. The ratio obtained was 4.26 (Figure 5) most likely corresponding to the formation of $ZnL_2(HL)_2$.

The different silicas used in this work had almost the same ligand load and similar specific surface areas, despite this, the capacity to extract zinc was lower (0.27 mmol/g) than that for copper. This could be explained by the difference of stoichiometries of the formed complexes for copper and zinc.

5. CONCLUSION

In the first instance, we tested the extraction of Cu (II) and Zn (II) by the various impregnated silicas as a function of the pH of the aqueous phase. The different silicas extracted copper and / or zinc at very acidic pH's.

We then thoroughly studied the extraction process by investigating the extraction kinetics. The reactions were very fast for the different cases, and they were of pseudo-second order type. Extraction capacities were also considered. Up to 0.54 mmol/g and 0.27 mmol/g of Cu (II) and Zn (II) were respectively extracted by the impregnated silicas. We have highlighted the extraction of two complex types; ML^+ and ML_2 depending on the initial concentration and the nature of the ligand.

The stripping of Cu (II) and Zn (II) by the silicas impregnated with HPMSP and DEHPA, could easily be completed by a 1 M nitric acid solution without the structure of the silicas being damaged. In the case of the Cu (II) stripping by MCM-CI-HPBI, as extraction occurred starting at pH of -0.19, the process was only effective in more acidic media (6M HNO_3). Under these experimental conditions, the structure collapsed.

Further tests for the separation of Cu (II) and Zn (II) by the impregnated silica were conducted as a function of the pH. The silicas impregnated HPBI and HPMSP were selective for copper while those impregnated by DEHPA were selective for zinc.

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