Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Synthesis and Characterization of Mesostructured Silica Doped with Acyl-Hydroxy-Pyrazole Derivatives. Sorption Tests of Cu(II) and Eu(III)

Elias Bou-Maroun[a]; Geneviève J. Goetz-Grandmont[a]; Anne Boos[a]
[a] Laboratoire de Chimie Analytique et Minérale de 1'E.C.P.M., I.P.H.C., Strasbourg Cedex 2, France

To cite this Article Bou-Maroun, Elias , Goetz-Grandmont, Geneviève J. and Boos, Anne(2006) 'Synthesis and Characterization of Mesostructured Silica Doped with Acyl-Hydroxy-Pyrazole Derivatives. Sorption Tests of Cu(II) and Eu(III)', Separation Science and Technology, 41: 13, 2933 — 2946
To link to this Article: DOI: 10.1080/01496390600786044
URL: http://dx.doi.org/10.1080/01496390600786044

Separation Science and Technology, 41: 2933–2946, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600786044

Synthesis and Characterization of Mesostructured Silica Doped with Acyl-Hydroxy-Pyrazole Derivatives. Sorption Tests of Cu(II) and Eu(III)

Elias Bou-Maroun, Geneviève J. Goetz-Grandmont, and Anne Boos
Laboratoire de Chimie Analytique et Minérale de 1'E.C.P.M., I.P.H.C., Strasbourg Cedex 2, France

Abstract: The synthesis and the characterization of mesostructured silica doped with acidic acyl-hydroxy-pyrazoles like extractants are described. The extractants have either a single chelating site, 1-phenyl-3-methyl-4-stearoyl-5-hydroxy-pyrazole (HPMSP), or two chelating sites, 1,12-bis(1′-phenyl-3′-methyl-5′-hydroxy-4′-pyrazolyl)-dodecane-1,12-dione (HL-10-LH). The so-called doped silicas were synthesized in basic medium according to a sol-gel process beginning with the solubilization of the extractant in a micellar phase followed by the precipitation of silica around micelles. The chemical composition of the synthesized materials, especially the ligand content, was determined. High quantities of ligand loadings (up to 0.69 mol/kg) are reached. The materials obtained were characterized by X-ray diffraction, laser granulometry, transmission and scanning electron microscopy and, after calcination, by nitrogen physisorption. Un-doped silica is mesostructured, lamellar, and has high pore diameter as well as high specific surfaces. Doping induces the disorganization of the lamellar structure, the increase of the pore diameter, and a slight decrease of the specific surface. The capacities of extraction of Cu(II) and Eu(III) by the doped materials and the corresponding extraction rate were measured: high values are reached.

Keywords: Mesostructured doped silica, acyl-hydroxy-pyrazole, solid-liquid extraction, preconcentration, europium, copper

Received 17 January 2006, Accepted 17 April 2006

Address correspondence to Elias Bou-Maroun, Laboratoire de Chimie Analytique et Minérale de 1'E.C.P.M., I.P.H.C., (UMR CNRS-ULP n° 7178), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France. Tel.: +33 3 90 24 27 29; Fax: +33 3 90 24 27 25; E-mail: boumaroune@ecpm.u-strasbg.fr or eliasbm@hotmail.com

INTRODUCTION

The concentration and the separation of trace metal ions, for an analysis purpose or for industrial waste processing, require the utilization and the application of some preconcentration techniques like solvent extraction or liquid-liquid extraction (1), solid-liquid extraction (2) and micellar extraction (3). These methods enable a selective extraction of the analyte from its initial matrix, often complex, and thus the elimination of major interferences.

Generally, the analytes of interest are concentrated in the extraction phase, which constitutes an essential step during the analysis of various metal species present in trace level, in order to exceed the detection limits (DL) of the principal analytical instruments, like Atomic Absorption Spectroscopy (AAS, DL = hundreds of $\mu g/L$) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, DL = tens of $\mu g/L$).

Among the techniques quoted above, the liquid-liquid extraction is the most studied and the most applied one both in hydrometallurgy and in chemical analysis. Its principal disadvantages are: frequent formation of additional phase, pollution of the aqueous phase by organic matter, and inadequacy for the concentration of trace amounts of ions in large sample volumes. The micellar extraction may be adapted for decontamination of aqueous effluents but in no case should it be considered as an alternative method to solvent extraction in the case of hydrometallurgical processes (3). The solid-liquid extraction may be a possible alternative technique especially as it implies fast, simple, and direct manipulation of the sample as well as saving of the solvent.

Functionalized mesoporous silica is a good candidate for its use as support. Silica supports have certain advantages compared to the polymeric resins. Silicas show a good mechanical resistance allowing them their use in columns (4). They are hydrophilic, which implies a good contact with the aqueous phase. They show a great resistance to acids, it may be an essential condition for the industrial waste processing that is frequently performed in acid medium. In addition mesostructured silicas have been chosen, as they are characterized by a great specific surface and a pore size in the nanometer range. This open-structure should allow a good access to every ligand immobilized in the structure and a fast extraction speed (5). In a previous paper (5) as well as in this work, we resorted to the immobilization of organic extractants by doping in order to increase the limited selectivity of the non-functionalized silica. Here, the term "doped silicas" means surfactant micelles solubilizing hydrophobic extractants immobilized in a mesostructured silica.

Surfactant-templated doped silicas were synthesized at low temperature (60°C) according to a sol-gel process, the extractants being solubilized in the mesostructured template, a micellar solution of cetyltrimethylammonium bromide CTAB. This method shows some advantages compared to other currently-used methods of ligand immobilization. A strong bonding between the porous material and the surfactant that solubilizes the extractant is obtained compared to the impregnation where the extractant is physically adsorbed on

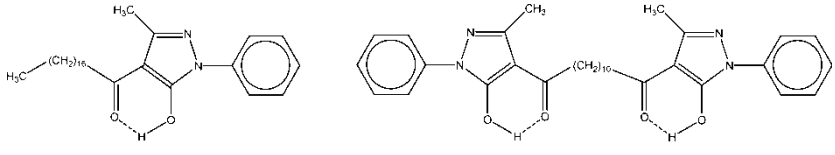
the support (6). No reagent derivatization is necessary compared to the grafting method. Moreover, in the latter case the limited mobility of the extractant entirely immobilized on the material may be a serious drawback when the formation of metal complexes requires the participation of several ligands.

In this study, the desired selectivity was brought by two acidic extractants derived from acyl-hydroxy-pyrazole. The first one 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone HPMSP, (ligand L, Fig. 1), already used in our team as a doping agent (5), is a well known ligand in liquid-liquid extraction of transition metals (7–9). The second one 1,12-bis(1′-phenyl-3′-methyl-5′-hydroxy-4′-pyrazolyl)-dodecane-1,12-dione HL-10-LH (ligand L_2, Fig. 1), is a better complexant than its parent compounds (acyl-hydroxy-pyrazoles) as it has been shown in liquid-liquid extraction of various metallic cations (10–15) and in micellar extraction (3). To characterize these new materials, the size and the shape of the particles, which constitute important parameters for their use as chromatographic support, were measured. Their specific surface, their pore volume and their pore distribution, physical factors that control the permeability to the aqueous phase, and their extractant loading were determined. Measurements of X-ray diffraction were made on various materials in order to determine their crystalline structure. A preliminary study of Cu(II) and Eu(III) sorption by these materials was made in order to test their usefulness in practice: the rate of metal sorption from dilute solutions and the capacity of sorbents in the presence of a large excess of metal ions were measured.

EXPERIMENTAL

Reagents

According to Jensen's synthesis of 4-acyl-5-hydroxy-pyrazoles (16), HPMSP and HL-10-LH were prepared from 1-phenyl-3-methyl-5-pyrazolone (Fluka, 98%) and stearoyl chloride and dodecane-dioyl dichloride (Merck, 98%) respectively. HPMSP was recrystallized from a toluene–ethanol (1/9) solution and controlled by ^{1}H NMR and IR spectroscopy. HL-10-LH was recrystallized from chloroform–ethanol (3/2) solution and its purity was established by titration with sodium hydroxide in the



HPMSP (L) HL-10-LH (L_2)

Figure 1. The extractants.

chloroform/(Na,H)ClO_4, 1 M two-phase system and by ^1H NMR (^1H NMR spectra available in Ref (17)).

Tetraethoxysilane (TEOS, 98%) was purchased from Aldrich, methanol (CH_3OH, 99.9%) was from Carlo Erba and cetyltrimethylammonium bromide (CTAB, 99%) was obtained from Acros. Europium solutions were prepared from europium oxide (Eu_2O_3, Prolabo, 99.9%) by dissolution with nitric acid ($\approx$1 M prepared from HNO_3, Prolabo, 68%) and dilution with deionized water (MilliQ RG, Millipore). Copper solutions were prepared from analytical grade nitrates. The pH of the aqueous solutions was adjusted with diluted HNO_3 or NaOH (Merck Titrisol) and their ionic strength was maintained at 0.1 M by addition of sodium nitrate (Prolabo, 99.5%).

Apparatus

UV-spectra were recorded on a HP 8453 UV-Visible spectrometer. The N_2 adsorption/desorption isotherms were obtained from a Sorptomatic 199 instrument. XRD experiments were performed with Siemens D5000 (copper anticathode, $\lambda_{K\alpha 1} = 1.5506$ Å) and Siemens D500 (cobalt anticathode, $\lambda_{K\alpha 1} = 1.7890$ Å) diffractometers. A JEOL JSM-6700F microscope was used for scanning electron microscope (SEM) studies. The transmission electron microscope (TEM) used was a TOPCON 002B working at 200 kV with a 0.18 nm resolution. The sample was first dispersed in alcohol and then deposited on a grid provided with a carbon membrane. The laser granulometer used was a MASTERSIZER 2000. It allows observation of a range of size from 0.02 to 2000 μm with an accuracy of 1% on the median diameter.

Copper ions in aqueous solutions were analyzed by Atomic Absorption Spectroscopy using a Perkin Elmer 2380 apparatus and europium ions were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry using a Jobin Yvon JY138 ultratrace apparatus.

Synthesis of Doped Mesoporous Silica

The molar ratio of the reagents in the mother liquor was fixed to: 1 TEOS: 140 H_2O: 13 CH_3OH: 0.18 CTAB: x extractant. The molar compositions of the templating phases and the corresponding terminology of the synthesized silicas are reported in Table 1. Si means silica, L refers to HPMSP, and L_2 to HL-10-LH and the number within the brackets indicates the number of chelating sites per gram of material determined after synthesis, see below (§ 3.1). The silicas Si@L(0.38) and Si@L_2(0.38) were prepared to have the same number of chelating sites in the target material.

The procedure adopted for all the synthesis is as follows: CTAB was dissolved in an aqueous solution of NaOH 0.1 M under agitation at 60°C.

Table 1. Composition of the initial templating phase and terminology of doped silicas for 0.18 mol of CTAB

Silica	Ligand/CTAB	Ligand (mol)	Chelating head (mol)
Blank	0	0	0
Si@L_2(0.38)	1/4.8	0.0375	0.075
Si@L(0.23)	1/6	0.03	0.03
Si@L_2(0.68)	1/3	0.06	0.12
Si@L(0.38)	1/3	0.06	0.06
Si@L(0.54)	1/2	0.09	0.09
Si@L(0.69)	1/1.26	0.143	0.143

This solution was mixed with methanol. The ligand was then added to the mixture. After dissolution, the TEOS was added and a precipitate appeared immediately. Agitation was maintained one hour at 60°C then 24 hours at room temperature. The product obtained was filtered at 0.45 μm, washed with water, dried for one hour at 60°C, and then one night under vacuum at 60°C. The more important the quantity of the encapsulated ligand, the yellower was the obtained solid, and the finer was the precipitate formed after aging, which led to a slow filtration.

Tests of Sorption of Cu(II) and Eu(III)

In order to determine the extraction capacity of a doped silica, 0.1 g aliquots were opposed to 10 mL of aqueous metallic solutions of increasing concentrations in a series of thermoregulated polypropylene tubes. The compositions of the aqueous phases were: $[(Na,H)NO_3] = 0.1$ M to ensure a constant ionic strength, initial pH ($pH_{initial}$) 2.10 ± 0.05, metal ion concentrations up to 1000 mg/L (i.e. up to 6.6×10^{-3} M of Eu or 15.7×10^{-3} M of Cu). The tubes were brought under magnetic stirring during 24 hours at 25°C. After separation of the phases by centrifugation at 12,000 rpm, the metal remaining in the aqueous phase was determined. Once the silica is saturated, its extraction capacity could be calculated as the difference between the initial and the remaining metal quantities.

The solid-liquid equilibration curves were carried out according to the following procedure: in a series of polypropylene centrifugation tubes, 0.1 g of doped silica was contacted with 10 ml of aqueous europium(III) solution under magnetic stirring during a given time "t". The chosen europium concentration and the silica mass ensure an excess of ligand (up to 25 times greater chelating sites than metal ions). The ionic strength of the aqueous phase was maintained constant $[(Na,H)NO_3] = 0.1$ M and its pH was selected in order to ensure a maximum of extraction without exceeding the pH of precipitation

of the europium hydroxide. Then, the solid was separated from the aqueous solution by centrifugation for 3 min at 12,000 rpm. Next, 1 ml of the aqueous solution was withdrawn and diluted for analysis by ICP-AES. The quantity extracted in the solid phase was calculated by the difference from the initial one. The contact time "t" is taken as the time elapsed between silica set in contact with the solution and the beginning of centrifugation.

RESULTS AND DISCUSSION

Chemical Composition of the Materials

The compositions of the doped and un-doped materials were determined by analysis of the filtrates after synthesis and mass balance of some reactants, and by analysis of aliquots of the materials themselves. This methodology was described and validated previously (5).

In addition, bromide ions remaining in the filtrate after synthesis were determined volumetrically for all doped silicas and for the blank material. The total amount of these ions was found in solution indicating that the surfactant had been incorporated in the form of CTA^+ or CTAOH, hydroxide ions being brought by the basic medium.

The measures relating to the material composition are gathered in Table 2. We notice that HPMSP (L) is completely loaded whatever the initial quantity used: Si@L(0.23-0.38-0.54-0.69). It is not the case of HL-10-LH (L_2) where the loaded percentage is ca. 80%. The interaction of the polymethylene chain of HL-10-LH with the surfactant is undoubtedly less stronger than the one created with the alkyl chain of HPMSP, which induces a loss of a considerable quantity in the supernatant of the synthesis. On the other hand, we did not observe any leaching of the entrapped ligand during the washing step after synthesis, which means a strong immobilization of both L and L_2 in the silica. A high loading of ligand L, about 0.693 mol/kg, was obtained. The "loss of mass" (second column of Table 2) is measured after calcination of

Table 2. Materials composition in ligand

Silica	Loaded ligand (%)	Loss of mass (%)	Ligand content (mol/kg)
Blank	0	49	0
Si@L_2(0.38)	81	53	0.191
Si@L(0.23)	100	54	0.229
Si@L_2(0.68)	79	56	0.342
Si@L(0.38)	100	57	0.383
Si@L(0.54)	100	63	0.543
Si@L(0.69)	100	69	0.693

the silica at 500°C during one night; it corresponds to the mass of (CTA^+ + ligand + H_2O), the remainder being SiO_2. It is noticeable that SiO_2 constitutes the half of the undoped material, whereas the doped materials only contain 47 to 31% of silica. Moreover, an increase of the loss of mass with the number of mol of the loaded ligand is observed (Fig. 2). This means that the ligand is added to the micellar phase, and that only a quite moderate decrease of entrapped CTA^+ occurs in comparison with the un-doped material.

Characterization of the Porous Structure

All nitrogen adsorption/desorption isotherms were reported after calcination of the sample at 500°C during one night and out-gassing at 300°C under vacuum for 3 hours just before the measurements. The isotherm of the un-doped material (Fig. 3) is characteristic of lamellar mesostructured silica of type IV with a hysteresis loop of type H4 according to the IUPAC nomenclature. In the presence of the ligand, the relative pressure at which we observe the increasing step of the adsorbed volume at $P_s/P_0 = 0.3$ for un-doped silica increases (Fig. 3), which means that the pores are larger. This increase is observed on a broader range of relative pressures; therefore, the pore distribution is broader. Moreover, Si@L(0.38) silica shows isotherms with a H3 type hysteresis (Fig. 3) usually obtained with pores in the form of slits or layers and the increasing step in the adsorbed volume is observed up to $P_s/P_0 = 0.9$, most likely due to a porosity in the high mesoporous range.

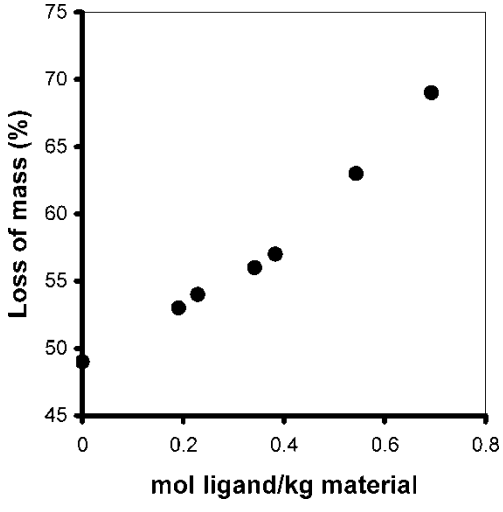


Figure 2. Loss of mass after calcination at 500°C for silicas of various loaded ligand content.

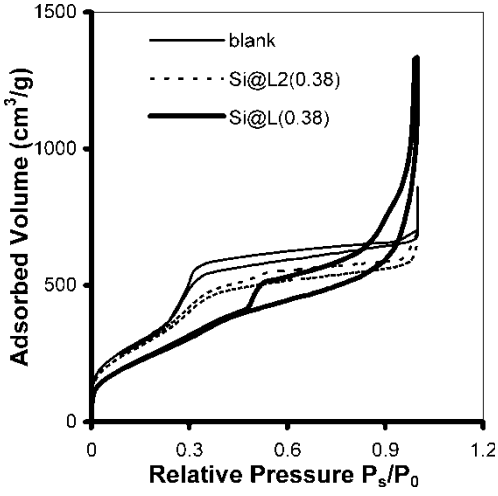


Figure 3. Nitrogen adsorption/desorption isotherms of the following silicas after calcination: un-doped, Si@L_2(0.38) and Si@L(0.38).

Specific surface areas (S_{BET}), pore volumes (V_p), and pore diameters (ϕ) of all the synthesized silicas were calculated from the nitrogen adsorption/desorption isotherm, using BET and BJH methods and they are reported in Table 3. The specific surface of the blank, 1290 m^2/g, is the usual value for mesoporous materials. It decreases as the material is loaded in the extracting molecule. Nevertheless, specific surfaces remain very high and thus are able to favor the exchanges with the liquid phase which is promising for the application in the removal of metals. Compared with the blank, the greater pore volume is likely due to a bigger pore size rather than due to the formation of more pores: in this case, we would have observed an increase in the specific surface. The pore distributions are in agreement with this assumption.

Table 3. Surface area, pore volume and pore diameter of the doped materials after calcination

Silica	S_{BET} (m^2/g)	Vp (cm^3/g)	ϕ (Å)
Blank	1290	1.01	25
Si@L_2(0.38)	1150	0.90	24
Si@L(0.23)	1110	0.91	26
Si@L_2(0.68)	1040	1.16	36
Si@L(0.38)	990	1.06	39
Si@L(0.54)	870	1.16	43
Si@L(0.69)	600	1.59	110–130[a]

[a]Wide distribution.

While un-doped silica has a pore diameter of 25 Å with a narrow pore distribution, the pore diameters of doped silicas increase with the quantity of loaded ligand. For example, by comparing Si@L_2(0.38) and Si@L_2(0.68), it is shown that the pore diameter increases from 24 to 36 Å when the quantity of HL-10-LH in silica increases from 0.38 to 0.68. A comparison between Si@L(0.38) and Si@L_2(0.38) shows that the introduction of one L_2 molecule seams to disturb the structure less than two molecules of L. It can be seen that for the same number of chelating heads, the introduction of L leads to a pore diameter of 39 Å instead of 24 Å.

The X-ray diffraction spectra of the un-doped silica (Fig. 4) shows a sharp peak corresponding to an interplanar distance equal to 31.3 Å. The presence of a second peak at d = 15.7 Å indicates a lamellar organization of this material which confirms the results given by the N_2 adsorption/desorption isotherm.

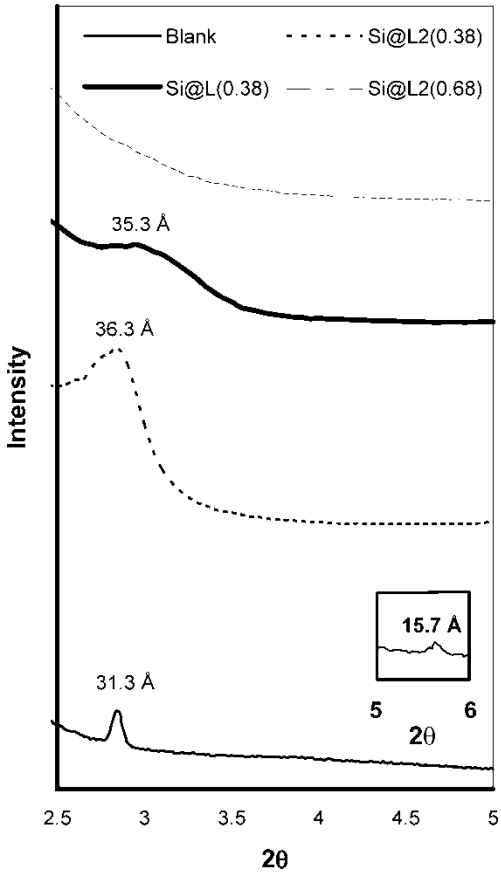


Figure 4. XRD spectra of un-doped silica, Si@L_2(0.38), Si@L(0.38) and Si@L_2(0.68). The insert figure shows the un-doped silica spectra for $5 < 2\theta < 6$.

The XRD diagrams of Si@L_2(0.38) and Si@L(0.38) are characteristic of poorly ordered mesostructured materials. The main diffraction peaks corresponding to an interplanar distances d = 36.3 and 35.3 Å respectively. When the number of ligands is reduced by half with a constant number of chelating sites, it seems that the bis(acyl-hydroxy-pyrazole) allows a better preservation of the organization at long distance of the material, even though the line of diffraction is broadened compared to the un-doped silica. The diffraction peak at d = 36.3 Å of Si@L_2(0.38) disappears for the most doped silica Si@L_2(0.68), which implies the destruction of the long distance order in the organization of the porosity.

The scanning electron microscopy (Photo 1) reveals that un-doped silica as well as the doped ones show an agglomerate of spherical grains. The order of magnitude of the grain size is about 0.1 to 0.5 μm. For laser granulometry, the use of a dispersing agent before the analysis induces a break of the agglomerates. Thus, the un-doped silica shows a narrow granulometric distribution centred on 0.1 μm while the grain size of doped silicas range between 0.1 and 0.2 μm. The ligand introduction causes a slight increase in granulometry but especially shows a widening of the distribution.

The observations carried out with the transmission electron microscope TEM on the un-doped silica as well as on the silica doped with HL-10-LH do not highlight any specific structure but confirm the spherical shape of these materials. The TEM observations of Si@L(0.23) (Photo 2) show spherical grains with a discoidal organization. Silicas strongly doped with HPMSP, Si@L(0.54,0.69) reveal the presence of zones organized in the

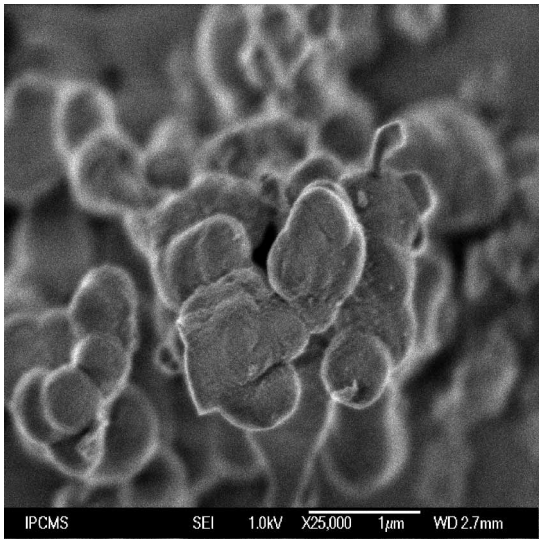


Photo 1. SEM photography of Si@L_2(0.38). Enlargement 25000×.

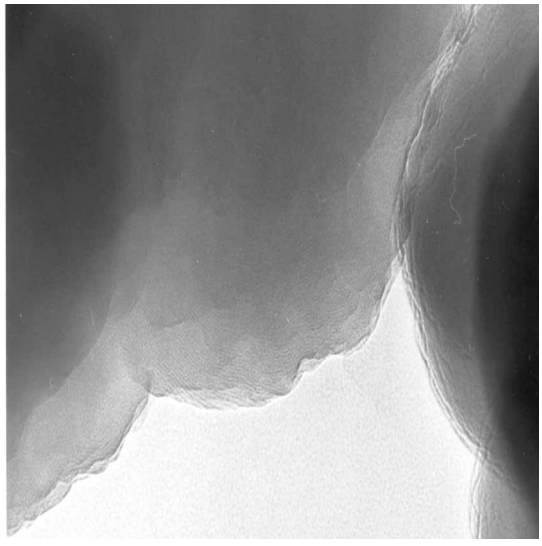


Photo 2. TEM photography of Si@L(0.23). Enlargement 78000×.

form of slides but they are rarer and smaller than those observed in slightly doped silicas. However, we have observed that some grains having a discoidal organization for Si@L(0.69).

Extraction Capacity and Equilibration Times

The extraction capacities, i.e. maximum loadings of metals, obtained for the different materials are gathered in Table 4. The equilibrium pH lay between 4 and 6. In this pH range, the sorption was maximum while no metal adsorption on the blank material was observed. When the number of chelating heads increases the complexation capacity increases. The ligand/Cu ratio is close to 2 for silica doped with HPMSP (L) and close to 1 for

Table 4. Extraction capacity of the doped materials

Silica	mol of ligand/kg	mol of chelating head/kg	mol Cu/kg	mol of ligand/mol of Cu	mol Eu/kg
Si@L_2(0.38)	0.191	0.382	0.20	0.96	0.11
Si@L_2(0.68)	0.342	0.684	0.33	1.04	0.18
Si@L(0.38)	0.383	0.383	0.21	1.82	0.13
Si@L(0.54)	0.543	0.543	0.28	1.94	ND[a]
Si@L(0.69)	0.693	0.693	0.34	2.04	ND[a]

[a]Not determined.

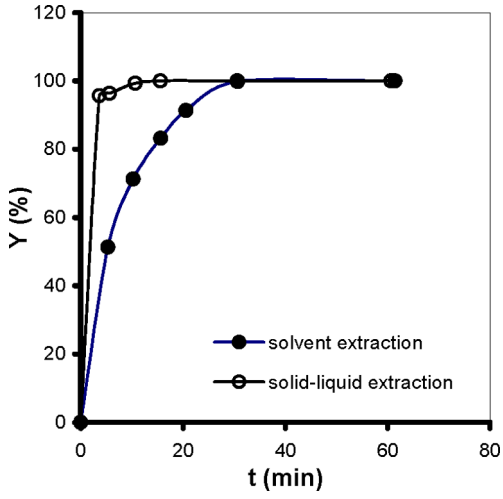


Figure 5. Equilibration curves of europium(III) extraction from 0.1 M nitrate medium at 25°C with 2.5×10^{-3} M of HL-10-LH initially solubilized in chloroform or with Si@L_2(0.38). $[Eu]_{i,aq} = 2 \times 10^{-4}$ M and 1.6×10^{-4} M respectively. Equilibrium pH = 4–5. The drawn lines are just a guide for the eyes.

silica doped with HL-10-LH (L_2). This means that the probable extracted complexes in the solid phase are Cu$(PMSP)_2$ and Cu(L-10-L). The latter complex implies a fold of the bis(acyl-hydroxypyrazole) ligand on the metallic center that was already observed in liquid-liquid extraction (17). More interesting, these results show that 90% to 100% of the trapped ligand is accessible to the metal, even with a porous structure filled with surfactants. This implies a great mobility of the ligand in the micelles filling the porosity. Thanks to that, the capacity values are high with all doped materials. Noticeably, they are higher than the capacity of silicas impregnated with HPMSP and containing the same amount of ligand (18).

Copper and europium extraction by Si@L_2(0.38) and Si@L(0.38) are very fast since the maximum capacity is reached within ten minutes. An example of europium extraction with time is shown in Fig. 5. This high exchange rate can be explained by the small size of the grains, the high specific surface as well as a great accessibility of the ligand to the aqueous solution. This fast reaction constitutes an advantage compared to the liquid-liquid extraction where the equilibrium is reached within 30 minutes (Fig. 5).

CONCLUSION

In order to remove copper and europium ions from aqueous solutions, silica based materials were functionalized with acyl-hydroxy-pyrazole ligands by a sol-gel method using a surfactant as a templating agent. Doping was

chosen as an immobilization method because it implies a one-step fast synthesis process simpler than grafting and impregnation. Doping is successful as 80 to 100% of the initial ligand quantity is entrapped. The synthesized silicas show high specific surfaces ($600-1300\ m^2/g$) after removal of the organic compounds filling the pores by calcination, they also show high quantities of ligand loadings (up to 0.69 mol/kg). The characterization studies of the porous structure show that the un-doped silica is mesostructured, has a lamellar structure, and a high pore diameter of 25 Å. Doping provokes the disorganization of the lamellar structure and the increase in the pore diameter.

The immobilized ligand offers high efficiency as it is readily accessible to the metal ions, which explains the high extraction capacities of these doped silicas in comparison with silica impregnated with the same ligand. Moreover, these extractions are very fast.

Finally, the use of these new supports in columns would have to be studied in order to check if their behavior with time enables them to compete with grafted silica. Moreover, since the above tests have shown that these materials could be quite efficient sorbents, thermodynamic studies of metal extraction processes are presently carried out in our laboratory, to better understand the sorption phenomena, particularly at weak or trace metal concentrations.

ACKNOWLEDGMENT

The authors acknowledge the scholarship for this work from the Lebanese National Council for Scientific Research (LNCSR).

REFERENCES

1. Takeishi, H., Kitatsuji, Y., Kimura, T., Meguro, Y., Yoshida, Z., and Kihara, S. (2001) Solvent extraction of uranium, neptunium, plutonium, americium, curium and californium ions by bis(1-phenyl-3-methyl-4-acylpyrazol-5-one) derivatives. *Anal. Chim. Acta.*, 431 (1): 69.
2. Jal, P.K., Patel, S., and Mishra, B.K. (2004) Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. *Talanta.*, 62 (5): 1005.
3. Hebrant, M., Provin, C., Brunette, J.P., and Tondre, C. (2001) Micellar extraction of europium(III) by a bolaform extractant and parent compounds derived from 5-pyrazolone. *Colloid. Surface. A.*, 181 (1–3): 225.
4. Deorkar, N.V. and Tavlarides, L.L. (1997) Zinc, cadmium, and lead separation from aqueous streams using solid-phase extractants. *Ind. Eng. Chem. Res.*, 36 (2): 399.
5. Boos, A., Intasiri, A., Brunette, J.P., and Leroy, M.J.F. (2002) Surfactant-templated silica doped with 1-phenyl-3-methyl-4-stearoylpyrazol-5-one (HPMSP) as a new extractant. *J. Mater. Chem.*, 12 (4): 886.

6. Dias Filho, N.L., Polito, W.L., and Gushikem, Y. (1995) Sorption and preconcentration of some heavy metals by 2-mercaptobenzothiazole-clay. *Talanta.*, 42 (8): 1031.
7. Akama, Y., Sato, K., Ukaji, M., Kawata, T., and Kajitani, M. (1985) Studies on extraction of copper(II) with 1-phenyl-3-methyl-4-acyl-5-pyrazolone. *Polyhedron*, 4 (1): 59.
8. Sigit; Goetz-Grandmont, G.J. and Brunette, J.P. (1992) Synergistic extraction of cadmium and cobalt with mixtures of 4-stearoyl-pyrazol-5-ol and tri-n-octylamine in toluene. *Monatsh. Chem.*, 123 (5): 373.
9. Umetani, S., Le, Q.T.H., and Matsui, M. (1997) Molecular design of highly selective ligands for group 13 metals. *Anal. Sci.*, 13 (4): 103.
10. Tayeb, A., Diantouba, B., Tsien, H.H., Goetz-Grandmont, G.J., Brunette, J.P., and Leroy, M.J.F. (Sept. 1986) *Proceedings of the International Solvent Extraction Conference ISEC'86*; München, II–481.
11. Tayeb, A., Goetz-Grandmont, G.J., Brunette, J.P., and Leroy, M.J.F. (1990) Analytical and spectroscopic study of zinc extraction with 1, 10-bis[1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl]-1, 10-decanedione and tri-n-octylphosphine oxide. *Solvent Extr. Ion Exch.*, 8 (1): 1.
12. Tayeb, A., Goetz-Grandmont, G.J., and Brunette, J.P. (1991) Analytical and spectroscopic study of indium extraction with 1, 10-bis(1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl)-1, 10-decanedione and its mixtures with tri-n-octylphosphine oxide. *Monatsh. Chem.*, 122 (6–7): 453.
13. Ensor, D.D., Glasgow, D.C., Smith, B.F., Jarvinen, G.D., and Jones, M.M. (1990) Distribution studies of actinides using a tetradentate extractant, 4,4′-nonanedioyl-bis(2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one). *Sep. Sci. Technol.*, 25 (13–15): 1629.
14. Miyazaki, S., Mukai, H., Umetani, S., Kihara, S., and Matsui, M. (1992) Steric effects of polymethylene chain length on the liquid-liquid extraction of beryllium(II), scandium(III), and yttrium(III) with bis(4-acylpyrazol-5-one) derivatives. *Anal. Chim. Acta.*, 259 (1): 25.
15. Uzoukwu, B.A., Gloe, K., and Duddeck, H. (1998) Kinetic studies of the solvent extraction of UO_2(II) and Hg(II) with 4-sebacoylbis(1-phenyl-3-methylpyrazolone-5) in chloroform. *Radiochim. Acta.*, 83 (2): 69.
16. Jensen, B.S. (1959) The synthesis of 1-phenyl-3-methyl-4-acyl-pyrazolone-5. *Acta Chem. Scand.*, 13 (8): 1668.
17. Miyazaki, S., Mukai, H., Umetani, S., Kihara, S., and Matsui, M. (1989) Steric effects of polymethylene chain length on the liquid-liquid extraction of copper(II) with bis(4-acylpyrazol-5-one) derivatives. *Inorg. Chem.*, 28 (15): 3014.
18. Tong, A., Akama, Y., and Tanaka, S. (1990) Preconcentration of copper, cobalt and nickel with 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone loaded on silica gel. *Analyst.*, 115 (7): 947.