Solid-Liquid Extraction of Co(II) by functionalized mesostructured Silica

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Abstract

The present work reports the synthesis of mesostructured silicas impregnated and/or doped by three different acidic chelators (HL), for the use in the extraction of Cobalt(II). The prepared solids were characterized by x-ray diffraction (XRD), the Fourier Transformed Infrared (FTIR) and N2-sorption at 77K. The quantity of the trapped ligand was determined by ultra violet visible spectroscopy (UV-Vis) and by calcination. The pH and the kinetics of Co(II) extraction were studied as well as the capacity of retention of the metallic cation in solids, while maintaining the ionic strength of the aqueous solution constant. The metallic cation was extracted at a very low pH and at a record time compared to any result previously reported in studies on silica supports.

Keywords

Extraction, functionalized Silica, Ligands, Co(II), Environment

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: the calcined silica (before the impregnation step)
MCM-CI-HL: the calcined and impregnated silica with HL (HPBI, HPMSP, or DEHPA)
MCM-NCI-HL: the non calcined and impregnated silica with HL (HPBI, HPMSP, or DEHPA)
MCM-D-HL: the doped silica with HL (HPBI, HPMSP, or DEHPA)

1. Introduction

The environmental protection and the fight against all types of pollution became major concerns and a big challenge for our modern societies. Indeed, the pollution is the result of the process of urbanization, the population boom and the development of the industrial, mining and agricultural activities. Therefore, international institutions and diverse associations, for the sake of the protection of the environment including flora and fauna, consolidate to monitor and enforce activities to either reduce or suppress any source of pollution. One of the most dangerous pollutions affecting the ecosystems being that causing the degradation of grounds and that is generated by industrial discharges containing micro-pollutants such as heavy metals [1]. Chemists, on their side, try to reduce the aforementioned problem, by the recovery of these metals through several methods like the chemical haste, the adsorption by adequate materials or by solvent extraction [2, 3]. Each of those techniques presents advantages and limits of application. By means of the scientific research, we were able to elaborate and use hybrid organo-mineral said materials; mesostructuredsilicas, in the treatment of the aqueous solutions and the extraction of heavy metals. Those silicas are beforehand functionalized by functional reactive groups, increasing by this fact their retention capacities for pollutants [4, 5]. The incorporation of the functional groups into the mesoporous silica can be achieved either by modification during the synthesis (doping or co-condensation) or by post-synthesis modification (grafting or impregnation) [6, 7].
The present work is the continuity of a research work of our team centered on heavy metals. Those metals are [4, 6, 8], well known for their beneficial roles for the biota at low concentrations, but also for their destructive impact on the environment, and thus fauna and flora. In fact, cobalt, as an example, takes part in the process of blood formation, stimulation of hemoglobin synthesis, metabolism of vitamins such as B12 and formation of enzymes, hormones and other vital compounds like DNA [9, 10]. However, when too much cobalt is assimilated into the body, it causes serious effects on the lungs (asthma, pneumonia and wheezing) and other severe hematological, cardiac, dermal and immunological effects [11, 12]. Exposure to cobalt can be by breathing air, touching materials, eating food and drinking water containing this element. The objective of our work is to eliminate or reduce Cobalt from nitrate medium by using solid phase extraction, as an alternative method which presents advantages compared to the solvent extraction. Among those advantages, we mention: sample to operate, rapid phase separation, absence of toxic organic solvent used and ability to combine it with different detection techniques [13]. The originality and the aim of our work is also a question of studying the extractive properties of functionalized silica by acid organic ligands such as β-dicetones (HPBI and HPMSP) and phosphoric acid (DEHPA) already used in solvent extraction, in order to compare the results obtained by the two methods. Furthermore, we intended to compare our results with the literature concerning the extraction of cobalt, by focalizing on parameters such as: pH’s effect, capacity of heavy metal retention and extraction kinetics. The functionalization of this silica was realized either during or after the synthesis by doping and impregnation, respectively. The various prepared silicas were characterized by various physico-chemical techniques of analysis.

2. Methodology
2.1. Synthesis
The method adopted in our work is the one proposed by Firouzi A. et al. [14] and by Boos A. et al. [15]. This method requires a source of silica, a structuring surfactant, water and methanol. All the syntheses were realized in a basic medium (NaOH 0.1M). The proportions are given in table 1.

Table 1: Molar composition of the reagents for MCM-41

<table>
<thead>
<tr>
<th>Reactant</th>
<th>TEOS</th>
<th>CTABr</th>
<th>H₂O (NaOH 0.1M)</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar composition</td>
<td>1</td>
<td>0.18</td>
<td>140</td>
<td>13</td>
</tr>
</tbody>
</table>

All reagents were used without any purification: TetraEthOxySilane TEOS (C₈H₂₀O₄Si, d=0.934, 98%) from Sigma-Aldrich, cetyltrimethylAmmonium Bromide CTABr (C₁₉H₄₂BrN, ≥ 96%) from Fluka Analytical, Sodium Hydroxide Laboratory Reagent (NaOH, ≥ 97%) from BiochemChemopharma and Methanol absolute Analytical Reagent (CH₄O, d = 0.791-0.793, ≥ 99.5%) from BiochemChemopharma.

In this work, we used calcined impregnated silica (MCM-CI) and non calcined impregnated silica (MCM-NCI). We also used silica doped by three ligands (HPBI, HPMSP and DEHPA), previously prepared and characterized by x-ray diffraction (XRD), the Fourier Transformed Infrared (FTIR) and N₂-sorption at 77 K [4]. In the table 2, we summarized the textural and structural data of the various silicas used in this study.

2.2. Extraction
2.2.1. Preparation of solutions
The solutions of extraction were prepared by dissolving the salt Co(NO₃)₂, xH₂O in water. The pH and ionic strength of the solutionswere adjusted by addition of HNO₃ or NaOH or by addition of NaNO₃ respectively. Solutions were analyzed before and after the extraction to determine the quantity of the metal extracted.

2.2.2. Extraction of Cobalt
0.1 g of functionalized silica were mixed with 10 ml of metallic solution in polypropylene tubes and put under magnetic stirring, until the transfer of the metal from the aqueous phase towards the solid phase was achieved. The various tubes were put in a thermoregulated cell at 25°C. The pH of the aqueous phase was measured
The aqueous phase was separated from the solid phase after the extraction by centrifugation, and then extraction supernatants were analyzed by UV-VISIBLE Spectroscopy.

**Table 2: Pores diameters and inter-reticular distances of silicas [6]**

<table>
<thead>
<tr>
<th>Silica</th>
<th>Structure</th>
<th>D_{BJH} (Å)</th>
<th>*d_{100} or **d_{002} (Å)</th>
<th>a_0 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-NC</td>
<td>H</td>
<td>---</td>
<td>38</td>
<td>43.9</td>
</tr>
<tr>
<td>MCM-C</td>
<td>H</td>
<td>25.8</td>
<td>34.2</td>
<td>39.5</td>
</tr>
<tr>
<td>MCM-CI-HPBI-0.55</td>
<td>H</td>
<td>21.8-26.0</td>
<td>35.9</td>
<td>41.5</td>
</tr>
<tr>
<td>MCM-D-HPBI-0.44</td>
<td>L</td>
<td>39</td>
<td>38.7</td>
<td>38.7</td>
</tr>
<tr>
<td>MCM-CI-HPMSP-0.54</td>
<td>H</td>
<td>21.2</td>
<td>34.2</td>
<td>39.5</td>
</tr>
<tr>
<td>MCM-D-HPMSP-0.53</td>
<td>L</td>
<td>38.9</td>
<td>31.1</td>
<td>31.1</td>
</tr>
<tr>
<td>MCM- CI-DEHPA-0.57</td>
<td>H</td>
<td>21.2-22.4</td>
<td>35.5</td>
<td>41.0</td>
</tr>
<tr>
<td>MCM-D-DEHPA-0.53</td>
<td>L</td>
<td>38.2</td>
<td>36.6</td>
<td>36.6</td>
</tr>
</tbody>
</table>

H: Hexagonal  
L: Lamellar  
*: Inter-reticular distance for impregnated silica  
**: Inter-reticular distance for doped silica

2.2.3. **Apparatus**

pH-meter, Jenway 3310, and UV-Visible spectrophotometer, Analytik Jena – Specrod ® 210 plus.

3. **Results and discussions**

3.1. **Evolution of pH for the aqueous phase**

During the extraction of cobalt by functionalized silicas, we noticed that the pH at equilibrium decreased after the extraction by the impregnated silicas, and increased after the extraction by the doped and/or non calcined impregnated silicas probably due to the surface quality of the materials and/or the presence of the cationic surfactant [16, 17].

3.2. **Effect of pH on the extraction of Co(II)**

In order to study the pH’s effect, we varied the initial pH of the aqueous phase without exceeding the pH corresponding to the formation of cobalt hydroxides (7.34 at the experimental conditions). The initial pH values were the same for the three studied systems: impregnated, doped and non impregnated silicas. All prepared solutions had an ionic strength of 0.1.

3.2.1. **Effect of pH on the extraction by calcined impregnated silicas**

The experimental curves of extraction are represented in figure 1. We noticed a pH at equilibrium lower than the initial pH.

![Figure 1: pH effect on the extraction of cobalt (II) by calcined impregnated silicas.](image)

The values of pH_{eq} were found to be between 1 and 4. In fact, the extraction of cobalt is preferentially made with the MCM-CI-HPMSP starting at a pH of 1.2. This extraction is inexisting with the MCM-CI-HPBI; whereas
with the MCM-CI-DEHPA the extraction is intermediate between both previous ones and it begins at pH 1.5 to reach its maximum at 2.8. This value is lower than the value obtained by Jafari et al. for the liquid-liquid extraction of cobalt by this same ligand (3.82) [18]. The absence of extraction by the MCM-CI-HPBI can be explained by the loss of HPBI in the aqueous phase in the form of PBI. This loss is due to the low value of the pKₐ of HPBI (~3.52); starting at pH 3.52, 50% of this ligand passes into the solution. The same result was previously observed for zinc by our team and by Torkestani et al. [6, 19].

3.2.2. Effect of pH on the extraction by doped silicas
Unlike the extractions by the calcined impregnated silicas, pH after extraction increased for the doped systems, and it varied from 1 to 8. We represented in figure 2 the extracted masses of cobalt versus the pH at equilibrium.

![Figure 2: pH effect on the extraction of cobalt (II) by doped silicas.](image)

Up to pH 6, the extracted quantities were practically insignificant for all used ligands. We noticed that at pH 6.8 the cobalt was significantly extracted by the MCM-D-HPMSP. Also, the pH of extraction by the doped silicas increased after extraction. This obstructed the study of the pH effect. At pH 7.7, the extracted quantity also increased, which was probably due to the cobalt hydroxides’ formation, beginning at pH 7.34. This result was not observed during the extraction of copper and zinc by this same silica [6].

The results obtained by the MCM-D-HPBI and MCM-D-DEHPA silicas could be explained by the inaccessibility of the ligand to the aqueous solution where the metallic cation resides; complexing sites would be probably trapped within the non calcined silica, phenomenon caused by the presence of the template which has a hydrophobic/hydrophilic behavior [20, 21] and a basic character, thus increasing the pH.

3.2.3. Effect of pH on the extraction by non calcined impregnated silicas
We tested the behavior towards the cobalt, of two non calcined silicas, one of which was impregnated by HPBI and the other one by HPMSP. The experimental results are presented in figure 3.

![Figure 3: pH effect on the extraction of cobalt (II) by non calcined impregnated silicas.](image)
The extraction of Co(II) by the MCM-NCI-HPBI was not significant, whereas the MCM-NCI-HPMSP presented a positive extraction between pH 6 and 7.2. Furthermore, we noticed that the MCM-NCI-HPBI had a similar behavior to the MCM-CI-HPBI and the MCM-D-HPBI, in terms of efficiency towards the cobalt. However, the MCM-NCI-HPMSP behaved rather like the MCM-D-HPMSP. We concluded that for these systems, ligands impregnated in silicas did not seem directly affected by the presence or absence of the surfactant in the same silica matrix.

3.2.4. Effect of pH on the functionalization mode of the same ligand

The functionalization type of the silicas plays an important role in the extraction of metals. Figure 4 presents the effect of this factor on the extraction of Co(II) extracted. In figure 4-A, the functionalization effect was not apparent, due to the release of HPBI in solution (50 % loss by pH 3.52), whereas in figures 4-B and 4-C, the effect was significant. Indeed, figure 4-B showed that Co(II) was extracted by MCM-CI-HPMSP at much lower values of pH than those obtained for MCM-NCI-HPMSP. Using MCM-D-HPMSP, the extraction was achieved at pH approximately 7.

3.3. Extraction capacity

The extraction capacity or the capacity of exchange of ions is defined by the number of active groups, or functional sites of the functionalized solid. This capacity is reached only when all these sites are saturated. In other words, it corresponds to the maximal quantity of metal, under all its forms, that can be adsorbed by unit mass of a solid. In this scope, we have studied the MCM-CI-HPMSP and the MCM-CI-DEHPA extracting...
capacity to determine the maximum cobalt load they can take. Figure 5 represents the Co(II) quantities that were extracted by the aforementioned silicas.

![Graph](image)

**Figure 4:** Effect of the silica functionalization mode on the extraction of cobalt.

**Figure 5:** Extraction capacity of cobalt by MCM-CI-HPMSP.

The capacities of Co(II) extraction by the MCM-CI-HPMSP and the MCM-CI-DEHPA were 0.32 and 0.67 mmol/g respectively. We also observed that the higher the concentration of cobalt was, the more elevated the extraction capacity. This was valid before the total saturation of the active sites of the extractant was reached. Also, the high cobalt extraction capacity achieved by the MCM-CI-DEHPA compared to the MCM-CI-HPMSP could be explained by the high number of active sites in the MCM-CI-DEHPA (0.57 mmol/g versus 0.54 mmol/g for the MCM-CI-HPMSP). It is important to note that both silicas were more performing than resins functionalized by Cyanex 272 [22], where the resins were nearly completely loaded (0.30 mmol/g) with 200 ppm cobalt solution at equilibrium.

3.4. Kinetics study

The rate of extraction of a metallic ion by silica supports plays a crucial role in the development of our method. The determination of the time of necessary contact to reach equilibrium is an essential parameter for the evaluation of the extraction efficiencies and capacities. For the extraction system Co^{2+} / MCM-CI-HPMSP, a series of extractions was realized with a stable initial pH and times of contact were varied from 5 to 120 min. The initial pH and the pH at equilibrium are presented in Table 3.

<table>
<thead>
<tr>
<th>System</th>
<th>pH (initial)</th>
<th>pH (equilibrium)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-MCM-CI-HPMSP</td>
<td>6.52</td>
<td>3.72</td>
</tr>
</tbody>
</table>

In figure 6, the Co(II) extracted quantity was plotted against the time of contact. We noticed that equilibrium was reached after 5 minutes. The fastest extraction reported until today being that conducted by J. Vaughan et al. [22] where the equilibrium was reached in 15 minutes.
In order to determine the order of Co(II) extraction reaction, we tried both pseudo-first order and pseudo-second order kinetic models (figure 7). In the table 4, we presented the correlation coefficients for the two models.

**Table 4: Correlation coefficients ($R^2$) of the Co (II) extraction by the MCM-CI-HPMSP for a pseudo-first order $R_1^2$ and a pseudo-second order $R_2^2$.**

<table>
<thead>
<tr>
<th>System</th>
<th>$R_1^2$</th>
<th>$R_2^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-MCM-CI-HPMSP</td>
<td>0.742</td>
<td>0.993</td>
</tr>
</tbody>
</table>

By comparing the coefficients of correlation, we noted that the experimental points were in agreement with a pseudo-second order. According to the theory of Azizian [23] and the results obtained by Bou-Maroun et al. [2], a pseudo-first order model applies better in case the initial concentration of the metal is high compared to the vacant complexation sites of the solid phase, whereas a pseudo-second order is better adapted when the initial metal ion concentration is low [24-27].

**Conclusion**

According to our presented practical results, the cobalt was preferentially extracted by the calcined impregnated systems, where the pH at equilibrium decreased with regard to the initial pH further to the ionic exchange between the Co$^{2+}$ ions in the liquid phase and the protons H$^+$ of the solid phase. On the other hand, the doped and non calcined impregnated systems presented no extracting capacities with a pH increasing after contact due to phenomena taking place during the acid-base equilibrium of the silica except for the MCM-NCI-HPMSP and the MCM-D-HPMSP. High quantities of extracted cobalt were obtained with HPMSP as a chelator, whereas intermediate or no extractions were observed for DEHPA or the HPBI respectively. This was due to the pK$_A$ values of these ligands affecting their ionization.

For their considerable practical importance, the extraction kinetics were studied for silicas that showed elevated extraction capacities towards cobalt. The time required to reach the equilibrium of extraction was 5 minutes (the best obtained by today for such silica systems). Moreover, the process of extraction was of pseudo-second order, compatible with a cation-ligand type of interaction: that is a chemical interaction and not only physical adsorption.
References


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