

## Assessment of metal adsorption onto an organo-functionalized silsesquioxane

Iago S. Reis<sup>a</sup>, Christiane Fernandes<sup>a</sup>, Eduardo S. Chaves<sup>a</sup>, Adolfo Horn Jr.<sup>a\*</sup>

<sup>a</sup> Department of Chemistry, Universidade Federal de Santa Catarina, Campus Trindade, Florianópolis, SC, 88040900, Brazil

### Abstract

Environmental pollution from metal ions has raised serious concerns due to their carcinogenic properties, indestructibility, and biological accumulation. Important sources of potentially toxic metal are mining stones and volcanic dust. In addition, humans also play a role in releasing potentially toxic metallic elements through activities such as dyeing, metal plating, and battery manufacturing. The removal of such toxic species from industrial effluents presents a significant environmental challenge and requires urgent attention. Therefore, this study aims to develop chemical systems capable of adsorbing toxic metal found in wastewater. To achieve this objective, a polyhedral oligomeric silsesquioxane (BMPA@POSS) functionalized with the ligand bis(pyridin-2-ylmethyl)amine (BMPA) was synthesized for metal adsorptions. The ligand was characterized by infrared (FTIR), <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopies. The BMPA@POSS was characterized by FTIR, solid-state <sup>13</sup>C and <sup>29</sup>Si NMR, elemental analysis of carbon, hydrogen, and nitrogen (CHN), and thermogravimetric analysis (TGA). The results showed that the compounds were successfully obtained. BMPA@POSS has a degree of functionalization of 1.50 mmol/g of material. The capacity for adsorption of cobalt, nickel, copper, zinc, lead, aluminum, manganese, vanadium, chromium, arsenic, beryllium, selenium, cadmium, barium, and uranium by BMPA@POSS was evaluated. A multi-element solution with a concentration of approximately 5 ppm of the mentioned metal ions was exposed to 10 mg of POSS in a batch for 24 h. BMPA@POSS showed higher adsorption capacity for V (97%), Cu (95%) and Pb (65%), while Co, Ni, Zn, Cd, and U were removed at 19-34%.

**Keywords:** organo-functionalized silica; metal adsorption; wastewater

### 1. Introduction

Contamination of water and air by potentially toxic metallic species is a topic of growing environmental concern, impacting millions of people worldwide. Exposure to heavy metals has increased due to the constant rise in anthropogenic activities, including mining, industrial growth, and the inadequate disposal of metallic materials harmful to human health. Food contamination with potentially toxic metals is also of high concern for human and animal health. This has led to increased monitoring of their concentrations in air, water resources, and food. [1,2,3].

Different strategies have been adopted to concentrate and, mainly, separate potentially toxic metallic ions in aqueous solution including ion exchange, electrodeposition, precipitation, membrane separation, and solvent extraction.

However, these approaches have drawbacks, such as high financial cost, complex execution, formation of toxic by-products, and/or incomplete recovery. Among the procedures implemented, adsorption stands out due to its adaptable operation, environmentally friendly working conditions, and recyclable adsorbents [4,5,6].

Therefore, it is relevant to develop new strategies and absorbent materials to reduce the presence of toxic metal ions in industrial effluents. One promising approach involves functionalizing silica-based materials with chelating groups. In addition to decontaminating the environment, capturing such elements allows for their isolation, concentration, and appropriate disposal or reintroduction into the production chain.

### 2. Material and methods

The syntheses of the ligand bis(pyridin-2-ylmethyl)amine (BMPA) and polyhedral oligomeric silsesquioxane (BMPA@POSS) were carried out as previously described [7,8].

The BMPA molecule was characterized using  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR). The spectra were obtained on a Varian-FT-NMR 400 MHz instrument. BMPA and BMPA@POSS were characterized by infrared (FTIR). The spectra were obtained on a Perkin Elmer FTIR-2000 spectrometer and the samples were measured in KBr pellets. The BMPA@POSS was characterized by solid-state  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy in Bruker Ascend equipment; the experiments were performed in cross-polarization mode;  $^{29}\text{Si}$  operating at 99 MHz and  $^{13}\text{C}$  operating at 125 MHz. Elemental analysis of carbon, hydrogen, and nitrogen (CHN) was performed in a PerkinElmer Model 2400 Series II, and thermogravimetric analysis (TGA) was conducted in a Shimadzu model TGA-50.

Inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer ELAN 6000) was employed to determine the metal concentration in solution. The analyses were carried out before,  $C_i$ , and after,  $C_f$ , contact with the adsorbent. The adsorption experiment was carried out in batch with the multi-element solution G17V SpecSol containing ions of Co, Ni, Cu, Zn, Pb, Al, Mn, V, Cr, As, Be, Se, Cd, Ba, and U. The initial concentration of the elements in the solution was  $5 \text{ mg L}^{-1}$  and adjusted to pH 3. 10 mg of adsorbent was used. The experiments were carried out in triplicates, under rotary agitation for 24 h.

### 3. Results and discussion

The chelating molecule bis(pyridin-2-ylmethyl)amine (BMPA) was synthesized according to the literature [8]. FTIR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR confirmed the structure and purity of the isolated compound. The obtention of the functionalized BMPA@POSS was carried out as described previously by us [7]. Its composition and possible structure were evaluated using different analyses. Figure 1 shows the FTIR spectra of the BMPA and BMPA@POSS molecules. Similar bands can be seen in the spectra of both molecules, confirming the presence of the ligand in the silica-based material. The main difference is the presence of an intense band between 1080 and

$800 \text{ cm}^{-1}$  in the BMPA@POSS, which characterizes the symmetric and asymmetric vibrations of Si-O-Si. The existence of this band and the absence of a band at  $3743 \text{ cm}^{-1}$  confirm that the methoxysilane groups of the silylating agent reagent were predominantly condensed into new siloxysilane bonds.

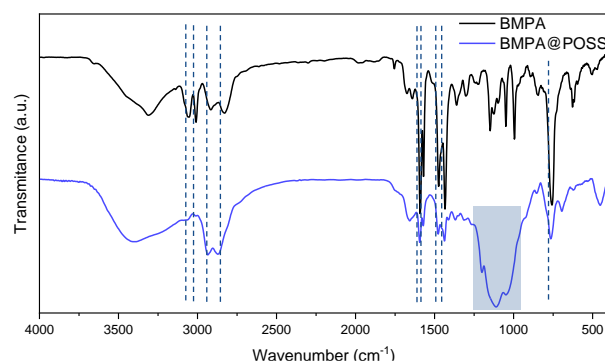


Fig. 1. FTIR spectra of BMPA and BMPA@POSS.

Figure 2 shows the solid-state  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR of the BMPA@POSS molecule. By analyzing the  $^{13}\text{C}$  spectra, the presence of the ligand in the respective silsesquioxane is confirmed, in agreement with the FTIR data. The  $^{29}\text{Si}$  NMR spectrum shows the presence of two silicon sites:  $T^2$  C-Si(OSi)<sub>2</sub>OH (-58.2 ppm) and  $T^3$  C-Si(OSi)<sub>3</sub> (-67.6 ppm), with a predominance of the last one.

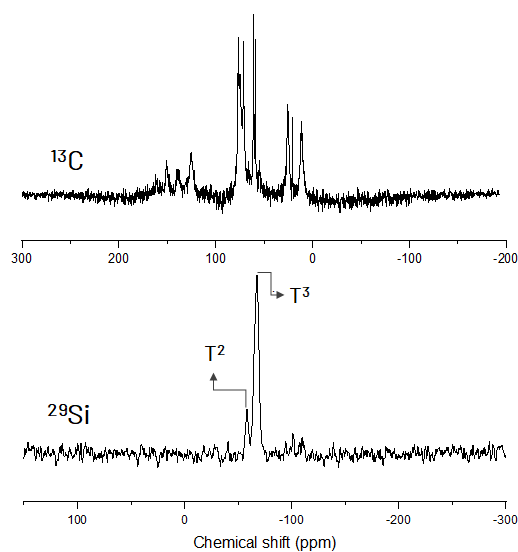


Fig. 2. Solid-state  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra for BMPA@POSS.

The organo-functionalization of the material, evidenced by NMR and FTIR analyses, was confirmed by CHN analysis (Table 1). It is consistent with open cage silsesquioxane containing T<sup>2</sup> sites and mostly T<sup>3</sup> sites, composed of four ligand molecules per unit, in addition to eight alkyl groups, one molecule of water and methanol. From this information, added to solid-state <sup>29</sup>Si NMR data, the structure for BMPA@POSS was proposed (see Figure 3), with a molecular weight of 2,642.93 g mol<sup>-1</sup>, and a functionalization degree of 1.5 mmol g<sup>-1</sup>.

Table 1. CHN elemental analysis for BMPA@POSS and the ligand load.

Data	C (%)	H (%)	N (%)	Load (mmol g <sup>-1</sup> )
Found	52.18	6.66	5.58	
Calculated	52.36	6.66	5.55	1.50

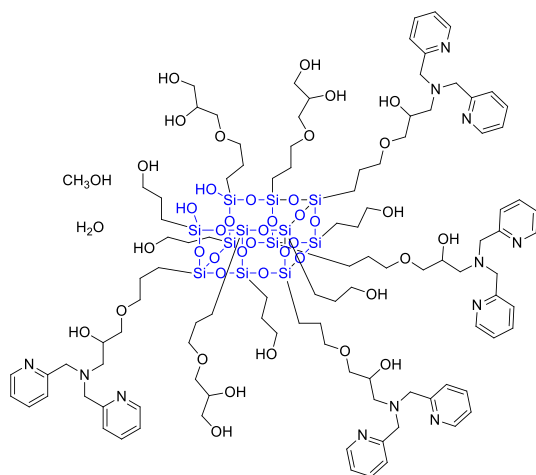


Fig. 3. BMPA@POSS structural proposal.

The TGA analysis indicated four significant mass losses, three of which are associated with the organic component of the material (Table 2). The first mass loss observed (up to 100 °C) agrees with the presence of solvents: one molecule of water and one of methanol (1.89%), as supported by the CHN data. The subsequent losses are attributed to organic backbone. The remained residue of the proposed compound is Si<sub>12</sub>O<sub>19</sub> (24.25%), in agreement with the proposed structure. The mass losses and the residue support the structure proposed by CHN and other previously discussed analyses.

Table 2. Weight loss (%) data obtained by TGA.

% Loss or residue (proposed)	% Loss or residue (founded)	ΔT (°C)	Loss or residue proposed
1.89	1.81	0-100	CH <sub>6</sub> O <sub>2</sub>
18.31	18.49	100-300	C <sub>28</sub> H <sub>32</sub> O <sub>2</sub>
38.87	38.25	300-510	C <sub>54</sub> H <sub>87</sub> N <sub>6</sub> O <sub>13</sub>
16.62	17.65	510-730	C <sub>23</sub> H <sub>51</sub> O <sub>7</sub>
24.25 (residue)	23.49 (residue)	>730	Si <sub>12</sub> O <sub>19</sub> (residue)

Equilibrium studies of metal ion adsorption by BMPA@POSS have been initiated. The material exhibited greater adsorption capacities for V (97%), Cu (95%) and Pb (68%). It also removed other metals, such as Co, Ni, Zn, Cd, and U, with percentages ranging from 19% to 34%. Beryllium was removed by 4%, while the remaining elements were not adsorbed.

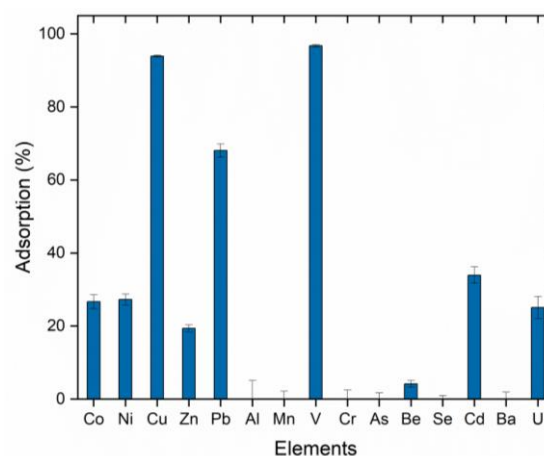


Fig. 4. Adsorption (%) in batch by BMPA@POSS.

#### 4. Conclusions

The synthetic route to obtain the ligand BMPA and BMPA@POSS proved to be adequate. The results obtained through FTIR, <sup>1</sup>H, <sup>13</sup>C NMR (ligand only), solid-state <sup>13</sup>C and <sup>29</sup>Si NMR, CHN, and TGA agree with the proposed structure. The adsorption of potentially toxic metal ions followed the order V~Cu>Pb>Cd>Co~Ni~U>Zn>Be. Showing that the material can remove toxic metal ions from the solution.

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