SILICA-BASED ORGANIC-INORGANIC HYBRID MATERIALS AS POTENTIAL ADSORBENTS FOR Hg(II) IONS

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ABSTRACT

In the present study four functionalized mesoporous silica materials denoted as BIS-1, BIS-2, BIS-3 and BIS-4 have been synthesized through a simple co-condensation of bis-[3-(trimethoxyosilyl)propyl] amine (BTPA) and tetraethyl orthosilicate (TEOS). The influence of the BTPA amount on the structural and adsorption properties of the resultant materials was investigated. The novel hybrid materials have been characterized by FT-IR, BET, \textsuperscript{13}C CP MAS NMR and elemental analysis.

The adsorption properties of mesoporous organic-inorganic materials containing amine functional groups, regarding Hg(II) ions were studied by the batch method. Experiments were carried out in acidic media. The material BIS-3 exhibits highest adsorption capacity for mercury ions. Kinetics of Hg (II) adsorption on BIS-3 was investigated. Equilibrium experimental data for BIS-3 were fitted to linear Langmuir and Freundlich models. All studied hybrid materials could be successfully used for effective removal of mercury ions from acidic aqueous solutions.

Keywords: silica-based mesoporous organic–inorganic hybrid materials; amine functionalized organosilicas; non-ionic surfactant; surfactant template method; mercury ion adsorption.

INTRODUCTION

Mercury is one of the extremely toxic metals and has drawn much attention due to its persistence, bioaccumulation, and non-biodegradability. Once admitted in the food chain, large accumulation of mercury compounds takes place in humans and animals [1]. The major sources of mercury pollution in the environment are industries like the production of chlor-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizers [2]. It is present in the environment from both natural sources and anthropogenic activities and the latter are believed to be responsible for the elevated mercury levels [3]. Much efforts have been expended on developing techniques for Hg(II) removal from wastewater, such as precipitation [4], ion exchange [5], membrane filtration [6] and adsorption [7]. Different materials as activated carbon [8 - 10], resins [11, 12], clays [13, 14], nitrogen-rich polymers [15 - 17] and silica [18, 19] have been studied for adsorption of Hg(II) ions. However, these materials have showed some disadvantages like low mechanical and thermal stability, weak chemical bonding strength, poor removal efficiency and high cost [20]. To overcome these drawbacks, hybrid organic–
inorganic silica gels, with high specific surface areas, thermal and mechanical stability, highly uniform pore distribution and tunable pore size, high adsorption capacity, as well as extraordinarily wide possibilities for functionalization [21 - 23] have been developed. Integration of amine functional groups into the structure of hybrids is of huge interest due to the versatile applications of the resultant materials, provided by the chemistry of the amine functional group. These include catalyses [24], chromatography [25], drug release [26], environmental control [27, 28], etc. In regard to the synthesis, different multi-amino-type groups have been introduced by using organoalkoxysilanes containing one, two and three amino groups [20].

The aim of the study was the synthesis and characterization of novel mesoporous amine functionalized organic-inorganic hybrid materials. In order to examine the potential of these materials as adsorbents for heavy metals, Hg (II) adsorption experiments were also performed.

EXPERIMENTAL

In the present study functionalized mesoporous silica materials have been synthesized through simple co-condensation of bis-[3-(trimethoxysilyl)propyl]amine (BTPA) and tetraethyl orthosilicate (TEOS) using xylene like a swelling agent. An amphiphilic triblock-copolymer poly (ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) ((PEO$_{20}$PPO$_{70}$PEO$_{20}$), commonly known by the trade name Pluronic P123), as a structural directing agent under acidic conditions, and an inorganic salt, has been used to improve the mesostructure ordering and tailor the framework porosity. The samples were characterized by nitrogen adsorption-desorption experiments, $^{13}$C CP MAS NMR, FT-IR and elemental analysis.

**Chemicals and reagents**

The materials were synthesized using the triblock copolymer P123 PEO$_{20}$PPO$_{70}$PEO$_{20}$ (Sigma-Aldrich, Mn~5,800) as a template. In order to synthesize the amine-functionalized mesoporous gels bis[3-trimethoxysilyl]propyl]amine (BTPA, Aldrich) and Tetraethyl orthosilicate (TEOS, MERCK) were used. Xylene (Aldrich) was used as swelling agent. To improve mesostructure ordering and tailor framework porosity KCl (Aldrich) was used. Ethanol (99.8 %), distilled water and hydrochloric acid (HCl, 36 %, Promark Chemicals) were used for surfactant removal.

**Synthesis of mesoporous silica**

The hybrid materials were prepared through a one-step sol-gel process, catalyzed by the –NH– groups of the amine functional precursor, BTPA. For the synthesis 1.2 g of Pluronic P123 was dissolved in 10 ml deionized water and 52 ml 1M HCl solution with stirring at room temperature. To this homogeneous solution xylene was added. After one hour stirring TEOS was added and then the mixture was stirred for 1 hour at the same temperature. After homogenization of this mixture BTPA was added (drop-by-drop) under continuous stirring. The chemical composition of the samples is presented in Table 1. The solid products were separated by filtration, washed thoroughly with water, and air dried at 60°C. The surfactant was removed by soaking. 1.0 g of the as-synthesized sample was soaked in a solution of 150 ml ethanol and 1.7 ml 36 % HCl at 60°C for 24 hours. The resulting solid was recovered trough filtration, washed with ethanol, and dried in an oven at 50°C for 24 hours. This material is referred to as the “surfactant extracted material”. The final materials are designated as BIS-1, BIS-2, BIS-3 and BIS-4.

**Characterization**

The specific surface area and the pore size distribution of the resultant materials were determined by nitrogen adsorption: nitrogen adsorption and desorption isotherms were measured at liquid nitrogen temperature using a Gemini 2370 instrument. The BET surface areas

<table>
<thead>
<tr>
<th>Sample</th>
<th>P123 [g]</th>
<th>KCl [g]</th>
<th>H$_2$O [ml]</th>
<th>1M HCl [ml]</th>
<th>Xylene [ml]</th>
<th>TEOS [ml]</th>
<th>BTPA [ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIS-1</td>
<td>1.2</td>
<td>3.5</td>
<td>10</td>
<td>52</td>
<td>2.64</td>
<td>2.64</td>
<td>1.20</td>
</tr>
<tr>
<td>BIS-2</td>
<td>1.2</td>
<td>3.5</td>
<td>10</td>
<td>52</td>
<td>2.64</td>
<td>2.64</td>
<td>3.90</td>
</tr>
<tr>
<td>BIS-3</td>
<td>1.2</td>
<td>3.5</td>
<td>10</td>
<td>52</td>
<td>2.64</td>
<td>2.64</td>
<td>5.90</td>
</tr>
<tr>
<td>BIS-4</td>
<td>1.2</td>
<td>3.5</td>
<td>10</td>
<td>52</td>
<td>2.64</td>
<td>2.64</td>
<td>7.80</td>
</tr>
</tbody>
</table>
were calculated from the adsorption data in the relative pressure range of 0.002–0.14. Pore size distributions were determined from the Barrett-Joyner-Halenda (BJH) desorption curve [29].

Fourier transform infrared (FT-IR) measurements were performed on a MATTSON 7000 Spectrometer in the range 4000–400 cm\(^{-1}\), with resolution 2 cm\(^{-1}\). The FT-IR spectra were recorded at room temperature using KBr pellets, 32 scans were signal averaged. FT-IR was used to confirm the removal of surfactants and the formation of organosilica materials. \(^{13}\)C (100.61MHz) cross-polarization magic angle spinning (CP MAS) spectra were recorded on a (9.4 T) Bruker Avance 400 spectrometer. The experimental parameters for the \(^{13}\)C CP MAS NMR experiments were: 9 kHz spin rate, 5 s pulse delay. NMR spectra were measured with 40 ms 1H 90° pulse, speed of rotation 50 kHz on a (9.4 T) Bruker Avance 400 spectrometer. Element analyses for C, N and H were performed with a Truspec 630-200-200 elemental analyzer at combustion furnace temperature, 1075°C.

**Adsorption studies**

The adsorption properties of silica-based hybrid materials towards Hg(II) ions were studied the batch method. Experiments were carried out in acidic media (pH 2.0). Adsorption studies were performed using stoppered 50 ml Erlenmeyer flasks containing about 0.2 g sample and 20 ml of Hg(II) solution. The mixture was shaken at 25°C for 24 hours with an automatic shaker. On reaching equilibrium, the adsorbent was removed by filtration through a Millipore filter (0.2 mm). The initial and equilibrium concentrations of the mercury ions were determined by flame AAS on a Pye Unicam SP 192 flame atomic absorption spectrometer (UK). The adsorption capacities of hybrid materials towards Hg(II) ions were determined at pH 2.0 using solution with concentration of 2000 mg l\(^{-1}\) Hg(II).

In order to optimize the contact time for the Hg(II) adsorption on the material BIS-3, kinetic experiment were carried out. The time intervals were from 5 min to 24 h. They were performed using solutions with initial mercury concentrations of 1800 mg l\(^{-1}\) (pH 2.0). The effect of initial Hg(II) concentration on the adsorption of BIS-3 was investigated using Hg(II) concentration in the range 500 - 2000 mg l\(^{-1}\) at pH 2.0.

Analytical grade reagents were used in all experiments. The working solutions containing different concentrations Hg (II) were prepared by stepwise dilution of the stock solution (Titrisol Merck, Germany). All adsorption experiments were replicated and the average results were used in data analyses.

**RESULTS AND DISCUSSION**

FTIR spectroscopy was carried for determination the structure of the resulting materials [30, 31]. The IR spectra of the synthesized gels are presented in Fig. 2. All samples show the typical band related to Si-O bonds, at 440 - 460 cm\(^{-1}\), bending of O-Si-O bond at 760 - 790 cm\(^{-1}\). At 1000-1100 a symmetric vibration band of Si-O-Si groups is observed. The signal at 1415 - 1455 cm\(^{-1}\) is attributed to (Si-CH\(_2\)) and (N-CH\(_2\)) or (CCH\(_2\)) of the

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BTPA (ml)</th>
<th>Nitrogen %</th>
<th>Adsorption capacity (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIS-1</td>
<td>1.16</td>
<td>1.82</td>
<td>65.4</td>
</tr>
<tr>
<td>BIS-2</td>
<td>3.90</td>
<td>3.83</td>
<td>94.5</td>
</tr>
<tr>
<td>BIS-3</td>
<td>5.85</td>
<td>4.27</td>
<td>178.6</td>
</tr>
<tr>
<td>BIS-4</td>
<td>7.80</td>
<td>4.30</td>
<td>171.7</td>
</tr>
</tbody>
</table>
amine functionalized precursor (BTPA) and surfactant (P123), respectively. The signals at 2800 - 2890 cm\(^{-1}\) and 1469 cm\(^{-1}\) identify the presence of CH links, contained in BTPA and P123. The band at 2977 - 2979 cm\(^{-1}\) is characteristic for stretching of the methylene groups [-CH\(_2\)] building the BTPA molecules. Another signal proving the inclusion of the bridging group in the structure of the materials is the appearance of the signal at 1380 cm\(^{-1}\), which is related to the stretching vibration of n(CN) at C-N bonds, the signal at 691 cm\(^{-1}\) typical of stretching of Si-CH\(_2\), and the one at 1375 cm\(^{-1}\), at which stretching of CN bond is observed. The signals at 1640 cm\(^{-1}\) and 3450 cm\(^{-1}\) can be associated with the presence of NH groups or stretching vibration of OH groups (Fig. 1).

The results from the \(^{13}\text{C}\) CP MAS NMR analysis of all samples show resonance peaks from 10 to 50 ppm, typical of sp\(^3\) carbon atoms which characterize the organic bridging group of BTPA [32]. The three most intense peaks at around 10, 20 and 50 ppm correspond to the carbon atoms of the bridging group in the direction from left to right, as presented in Fig. 2. The appearance of peaks in the range from 70 to 75 ppm indicates the presence of P123, this means that the surfactant extraction is not completed [33], which is confirmed also by the FT-IR spectra, through appearing of the signals at about 2900 - 3000 cm\(^{-1}\) which are typical for stretching of CH bonds in CH\(_3\) groups.

Fig. 2. \(^{13}\text{C}\) CP MAS NMR spectra of the BIS-2 sample.

Fig. 3. BET and pore size distribution of the synthesized hybrid materials.
The results of the elemental analysis show that with increasing of the BTPA amount, the nitrogen amount increases steadily, thus proving that saturation of the silicate network with amine groups is not reached (Table 3).

The porous structure of the samples was determined by N\textsubscript{2} adsorption-desorption measurements. According to IUPAC, the shape of an adsorption isotherm can be classified into one of six groups [34]. The type of the isotherms of all hybrid samples is IV. The gels are mesoporous according to the IUPAC classification (the average pore size is in the range between 2 - 50 nm). The adsorption/desorption curves of the hybrid materials in the present study show hysteresis loops that resemble the H2 type in the IUPAC classification [34] (Fig. 3). This type of hysteresis loop is characteristic of inkbottle-type pores and tubular – non-perfect cylindrical – pores with heterogeneous pore widths [35].

With increasing of the BTPA amount changes in the ratio silica /surfactant occur. This is connected with improving of texture parameters up to sample BIS-3, which exhibits the highest surface area, pore size and pore volume. For larger SiO\textsubscript{2}/P123 molar ratio (BIS-4) a slight decrease in the values of texture parameters is observed. This might be due to the fact that after the extraction process, part of the polymer rests still entrapped in the materials. The FT-IR and 	extsuperscript{13}C CP MAS NMR analyses confirm the presence of alkyl groups from the residual P123 amount after the extraction and prove this assumption.

**Adsorption studies**

The adsorption capacities of silica-based hybrid materials (BIS-1, BIS-2, BIS-3 and BIS-4) towards Hg(II) ions are presented in Table 2. These results are in good agreement with the results for the surface and texture parameters. The highest capacity was obtained for the material BIS-3, characterized by the highest surface area and pore volume (Table 4). Nevertheless, all hybrid materials effectively adsorb Hg(II) ions and could be used as adsorbents for their removal from aqueous solutions. Finally, we selected the material BIS-3 for more detailed studies of adsorption properties towards Hg(II) ions.

The effect of the agitation time on the Hg(II) adsorption on material BIS-3 is presented on Fig. 4. The degree of adsorption was found to increase with the increase in agitation time and reached a maximum value within 30 min.

An increase of adsorption with increasing of the initial Hg(II) concentration was observed also for BIS-3. The removal efficiency of mercury ions was 100 % for concentrations exceeding 900 mg l\textsuperscript{-1}.

The experimental adsorption isotherm on BIS-3 is presented on Fig. 5. The adsorption data were analyzed with the following linearized forms of Langmuir and Freundlich isotherms:

\[
\frac{C_e}{Q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \quad (1)
\]

\[
\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)
\]

**Table 3. Element analysis of the samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass [mg]</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIS-1</td>
<td>1.019</td>
<td>9.489</td>
<td>2.3104</td>
<td>1.8239</td>
</tr>
<tr>
<td>BIS-2</td>
<td>1.204</td>
<td>18.481</td>
<td>4.9853</td>
<td>3.8301</td>
</tr>
<tr>
<td>BIS-3</td>
<td>1.352</td>
<td>22.727</td>
<td>5.5204</td>
<td>4.2733</td>
</tr>
<tr>
<td>BIS-4</td>
<td>1.087</td>
<td>22.767</td>
<td>5.3839</td>
<td>4.3004</td>
</tr>
</tbody>
</table>

**Table 4. Texture parameters of the amine functionalized organosilica samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore volume [cm\textsuperscript{3}/g]</th>
<th>Surface area [m\textsuperscript{2}/g]</th>
<th>Pore size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIS-1</td>
<td>0.11</td>
<td>157</td>
<td>3.1</td>
</tr>
<tr>
<td>BIS-2</td>
<td>0.31</td>
<td>258</td>
<td>3.8</td>
</tr>
<tr>
<td>BIS-3</td>
<td>0.48</td>
<td>296</td>
<td>5.8</td>
</tr>
<tr>
<td>BIS-4</td>
<td>0.40</td>
<td>282</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Fig. 4. Effect of contact time on the adsorption of Hg(II) ions on BIS-3.
where \( C_e \) is equilibrium concentration of metal ions (mg l\(^{-1}\)); \( Q_e \) = amount of ions adsorbed (mg) per unit of mass of the adsorbent (g); \( Q_0 \) = adsorption capacity (mg g\(^{-1}\)); \( K_L \) = Langmuir constant; \( k_F \) = Freundlich constant; \( n \) = intensity of adsorption.

The values of the Langmuir and Freundlich parameters were obtained based on the linear correlation between the values of (1) \( (C_e / Q_e) \) and \( C_e \) and (2) \( \ln Q_e \) and \( \ln C_e \), respectively (Table 5).

The Langmuir model is based on the assumption that all adsorption sites are equally active, the surface is energetically homogeneous and a monolayer surface coverage is formed without any interaction between the adsorbed molecules. According to the correlation coefficient \( R^2 \) (0.9982) the fit to the Langmuir model is very good. The equilibrium adsorption capacity for the Hg(II) ions was 178.57 mg g\(^{-1}\) which is comparable with data reported in the literature [36, 37].

The Langmuir model parameter can be used to predict the affinity between adsorbate and adsorbent using the dimensionless separation factor, \( R_L \).

\[
R_L = \frac{1}{1 + K_L C_0} \tag{3}
\]

The \( R_L \) values for the BIS-3 material were found to vary: from 0.005 to 0.012.

All values of \( R_L \) were within the range from zero to one, which indicated that the adsorption process was occurring favourably on the material BIS-3 [38, 39].

The Freundlich model is valid for heterogeneous surfaces and predicts an increase in the concentration of the ionic species adsorbed on the surface of the solid, when the concentration of certain species in the liquid phase is increased. On the basis of the correlation coefficient \( R^2 \) (0.9232) calculated from the Freundlich plot, there is a good agreement between the Freundlich model and the experimental data but not as good as for the Langmuir model. In the present study the n-value is 1.718, which indicates favourable adsorption of Hg(II) onto BIS-3 [38,39].

It is important to assume that the mechanism of Hg(II) adsorption on the studied material cannot be attributed directly to the Langmuir or Freundlich models. From the data listed in Table 5 it may be concluded that the adsorption isotherm of mercury ions exhibit mainly Langmuir behaviour, which indicates, for the most part, a homogeneous surface binding and monolayer adsorption.

**CONCLUSIONS**

Novel mesoporous amine functionalized organic-inorganic hybrid materials were synthesized by co-condensation of tetraethylortosilacate (TEOS) and bis-[3-(triethoxysilyl)propyl] amine (BTPA). FT-IR, BET, \(^{13}\)C CP MAS NMR and element analysis were used for their characterization.

With increasing of the BTPA amount, changes in the ratio silica / surfactant occur. This is connected with improving of texture parameters up to sample BIS-3 which exhibits the highest surface area, pore size and pore volume. These results are the main reason for the highest adsorption capacity of the material BIS-3 for mercury ions. The best fit of the experimental isotherm data for BIS-3 was observed for the Langmuir model. Nevertheless, all synthesized hybrid materials exhibit high adsorption capacity for mercury ions and could be used as potential adsorbents for their removal from waste waters.
REFERENCES

22. Y. Wan, D. Zhao, On the controllable soft-templating