

Synthesis and Characterization of Hybrid Mesoporous Materials Prepared with Triblock-Copolymer and Bridged Silsesquioxane

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Abstract In this study functionalized SBA-15 mesoporous silica materials have been synthesized through a simple co-condensation approach of bis-[3-(trimethoxysilyl)propyl] amine (BTPA) and tetraethyl orthosilicate (TEOS) using xylene like swelling agent, amphiphilic triblock-copolymer (PEO-PPO-PEO) Pluronic P123 as structural directing agent under acidic condition, and inorganic salt has been used to improve mesostructure ordering and tailor framework porosity. The influence of amount of BTPA on the structural properties of the resultant materials was investigated. The resultant materials have been characterized by powder X-ray diffraction, FT-IR, ²⁹Si MAS NMR, ¹³C CP MAS NMR, SEM and elemental analysis. In order to examine the potential of these materials as adsorbents for heavy metals Hg (II) adsorption experiments were also performed. The results from ²⁹Si MAS NMR and elemental analysis showed that with increasing the amount of BTPA in the synthesis mixture leads to increasing the incorporation of organic groups in the silica framework. Adsorption of Hg (II) ions from aqueous solutions showed high adsorption capacities suggested that these materials have good potential to be used as adsorbents for Hg (II) ions in acid solutions.

Keywords Silica-based Mesoporous Organic-Inorganic Hybrid Materials, Amine Functionalized Organosilicas, Surfactant Template Method

1. Introduction

In the last 20 years have been developed organic-inorganic hybrid silica-based porous materials, because of their fascinating properties including a regular mesostructure along 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 of functionalization[1-7].

Several researchers have reported various synthesis methodologies to prepare mesoporous oxide materials and proposed different mechanisms to explain the porous structures[8].

Various factors, such as starting materials (e.g., alkoxides, metal salts etc, surfactants as structure directing agent), reaction parameters (e.g. pH, temperature, solvent, co-solvent etc.) influence the formation of porous structures and dictate the pore size, its distribution and ordering[8, 9].

The possibility of introduction of organic groups with different nature and their homogeneous distribution during the synthesis is a very important advantage connected with the sol-gel synthesis.

The precursor BTPA (R'O)₃Si-R-Si(OR')₃ is capable of undergoing cross-linking reactions and concurrently carry the organic functionality R a priori on board, so leading to materials in which the density of the organic functional groups cannot be higher. These kinds of materials, where the functional group is bridged are called periodic mesoporous organosilicas (PMOs). The PMOs materials were firstly discovered 1999[10-12]. In some cases the 'dilution' of the reaction mixture with pure inorganic precursors (TMOS / TEOS) is helpful, although at the (disproportionate) cost of the density of organic groups. The fact that the organic groups are covalently bonded and embedded in these bis-silylated compounds leads to mesostructured hybrids in which the organic groups are an integral part of the pore walls, meaning that the framework itself is modified. These materials are called 'hybrids' since the inorganic and organic parts are completely homogeneously mixed at the molecular scale within the whole sample.[13] Integration of amine functional groups into the structure of mesoporous

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organic-inorganic silica hybrids is of big interest due to the versatile applications of the resultant materials provided by the chemistry of the amine functional group, which include base-catalysis[14] coupling and immobilization of functional molecules and biomolecules[15], drug delivery[16], adsorption and sequestration of heavy metal ions[17, 18], etc.

It has been suggested that preparing amine-functionalized materials with higher concentrations of functional groups will be important for enhancing their molecular accessibility in adsorbance and catalysis applications[19]

In this paper we report on synthesis of mesoporous amine functionalized organosilicas prepared via a sol-gel process by using a co-condensation of a basic amine-bridged polysilsesquioxane bis-[3-(trimethoxysilyl)propyl] amine (BTPA) and tetraethyl orthosilicate (TEOS) in the presence of nonionic surfactants. To estimate the influence of the amine-bridged polysilsesquioxane on materials structure we synthesized gels at different amounts BTPA. The samples were characterized by XRD, solid-state ^{29}Si MAS NMR, ^{13}C CP MAS NMR, FT-IR, SEM, elemental analysis. In order to examine the potential of these materials as adsorbents for heavy metals, Hg (II) adsorption experiments were also performed.

2. Experimental

2.1. Chemicals and Reagents

Materials were synthesized using triblock copolymer P123 $\text{PEO}_{20}\text{PPO}_{70}\text{PEO}_{20}$, (Sigma-Aldrich, Mn~5,800) as a structure directing agent. Tetraethyl orthosilicate (TEOS, MERCK) and bis[[3-(trimethoxysilyl)propyl]amine (BTPA, Aldrich) were used in order to synthesize the

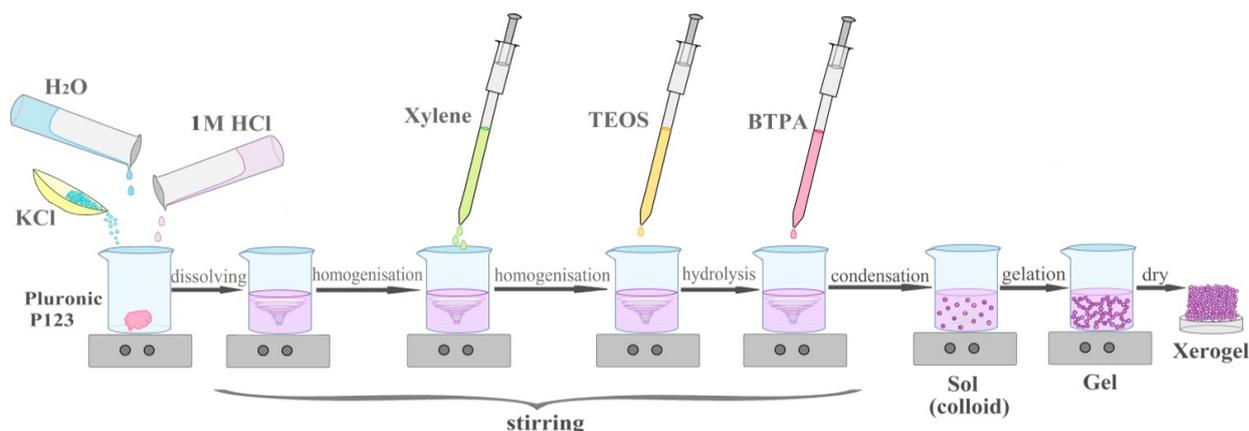
amine-functionalized mesoporous gels. Like swelling agent was used xylene (Aldrich). To improve mesostructure ordering and tailor framework porosity was used KCl (Aldrich). Ethanol (99.8%), distilled water and Fuming hydrochloric acid (HCl, 36%, Promark Chemicals) was used for removal of surfactant.

2.2. Synthesis of Mesoporous Silica

The gels were prepared through a one-step sol-gel process catalyzed by the $-\text{NH}-$ groups of BTPA. In a typical synthesis (Scheme 1) 1.2g of Pluronic P123 was dissolved in deionized water (10ml) and 52ml 1M HCl solution with stirring at 20°C. To this homogeneous solution xylene was added, after one hour stirring at the same temperature 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 (Scheme 1). The sample composition is presented in Table 1. The solid products were collected by filtration, washed thoroughly with water, and air dried at 60°C. This material is referred to as the as-synthesized material. The as-synthesized materials are designated a. ABMO 1, ABMO 2, ABMO 3 and ABMO 4.

2.3. Surfactant Extraction

The surfactant was removed by soaking. 1.0 g of as-synthesized sample was soaking in solution of 150 ml ethanol and 1.7ml 36% HCl at 60°C for 24 hours. The resulting solid was recovered by filtration, washed with ethanol, and dried in oven at 50°C for 24 hours. This material is referred to as the surfactant extracted material.



Scheme 1. Sol-gel/surfactant template synthesis of hybrid porous materials

Table 1. Composition of the samples

Sample	P123 [g]	KCl [g]	H ₂ O [ml]	1M HCl [ml]	Xylene [ml]	TEOS [ml]	BTPA [ml]
ABMO 1	1.2	3.5	10	52	2.64	2.64	1.16
ABMO 2	1.2	3.5	10	52	2.64	2.64	3.90
ABMO 3	1.2	3.5	10	52	2.64	2.64	5.85
ABMO 4	1.2	3.5	10	52	2.64	2.64	7.80

2.4. Characterization

The surface of the resultant materials were determined by scanning electron microscopy (SEM) images was recorded on a Hitachi S-4100 scanning electron microscope with an acceleration voltage of 15 kV. This technique was used to observe the external morphologies of the as synthesized and surfactant extracted materials. Fourier transform infrared (FT-IR) measurements were performed on a MATTSON 7000 Spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$ and 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) and ^{29}Si (79.49 MHz) MAS solid-state NMR experiments were recorded on a (9.4 T) Bruker Avance 400 spectrometer. The experimental parameters for ^{13}C CP MAS NMR experiments: 9 kHz spin rate, 5 s pulse delay, for ^{29}Si MAS NMR experiments: 5 kHz spin rate, 60s pulse delay. MAS NMR spectra were measured with $40\text{ }\mu\text{s}$ 1H 90° pulse, speed of rotation 50 kHz. ^{29}Si solid-state NMR spectra were recorded at 79.49 MHz on a (9.4 T) Bruker Avance 400 spectrometer. ^{29}Si magic angle spinning MAS NMR spectra were measured with $40\text{ }\mu\text{s}$ 1H 90° pulse, speed of rotation 50 kHz and a delay of 60 seconds. For X-ray phase analysis XRD (Rigaku/ New X-Ray Diffractometer System "Geigetflex" D/Max- C Series), working with $\text{Cu-K}\alpha$ radiation with a range of $0.4\text{--}5.0$ (2θ), and scanning speed 0.01° $2\theta/\text{min}$. Elemental analyses for C, N and H were performed with a Truspec 630-200-200 elemental analyzer at combustion furnace temperature 1075°C .

2.5. Metal Adsorption Studies

The adsorption properties of organic-inorganic hybrid materials towards Hg(II) ions were studied by means of the batch method. Experiments were carried out in acidic media (pH 2.5). Adsorption studies were performed using stoppered 50 ml Erlenmeyer flasks containing about 0.1 g sample and 10 ml of Hg(II) solution. For this study, aqueous solutions with concentrations from 600 mg/l to 2000 mg/l of Hg(II) ions were prepared. The mixtures were shaken at 25°C for 2 hours by an automatic shaker. On reaching equilibrium, the adsorbent was collected by filtration through a Millipore filter ($0.2\text{ }\mu\text{m}$). The initial and equilibrium concentrations of the Hg(II) ions were determined by flame atomic absorption spectrometry on a Pye Unicam SP 192 (UK). All adsorption experiments were replicated and the average results were used in data analyses. The results shows that with increasing of the initial concentration of Hg(II) ions in the solution, the adsorption on the investigated materials decrease which is connected with saturation of the active place of the adsorbent. At concentration to 900 mg/l the Hg(II) ions were retained practically fully on the investigated material. The adsorption capacities of ABMO 3 towards Hg(II) ions were determined at pH 2.5 using solutions with concentration of 900 mg/l

Hg(II).

3. Results and Discussions

3.1. Structural Properties

The XRD patterns of the synthesized and polymer extracted materials with different amount BTPA are shown in Figure 1. All samples shows a peak at about $2\theta = 1,16^\circ$, which shows characteristics of ordered two-dimensional materials (2D) hexagonal structure[20-22]. Such "single diffraction peaks" have also been used for the mesoporous materials by earlier authors[22]. Widening of the peak and the absence of others can be explained by the radial arrangement of mesoporous channels in microsize particles [23]. The absence of resolved higher-angle peaks indicates, however, that any structural order of the extracted hybrid materials does not extend over a long range, this could be to the faster gelation time of bis-[3-(triethoxysilyl) propyl] amine which provides inherently highly amorphous materials as well as the strong interface of amine groups on the co-assembly process caused by the electrostatic and hydrogen bond interactions between the amine groups and the block co-polymer and the silicate species[22]. Figure 1 show that the intensity of the peaks is the same for all samples, indicating that the rate of ordering of the resulting material is the same, i.e the amount of BTPA not affected.

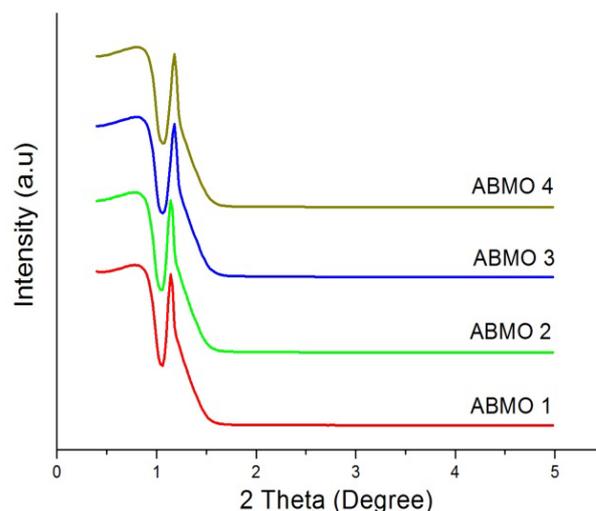


Figure 1. XRD patterns of the samples after polymer extraction

The morphology of the hybrid gels was studied with SEM analysis. Figure 2 show SEM micrographs of the studied hybrid gels. All samples have nanoporous structure typical for material obtained sol-gel route. The gels are characterized by a smooth surface with an amorphous structure composed of particles with a size around $0,2\text{ }\mu\text{m}$. Which formed aggregates with size about $1\text{--}2\text{ }\mu\text{m}$. The SEM images show that no significant differences in the morphology of the samples with increasing amount of BTPA.

In order to characterize the structure of the resulting

materials was carried infrared spectroscopy. Figure 3 are presented IR spectra of synthesized gels. All samples are characterized by typical band relating to Si-O bonds, at $440\text{-}460\text{ cm}^{-1}$ bending of O-Si-O bond[24, 25] at $760\text{-}790\text{ cm}^{-1}$ and $1000\text{-}1100$ is observed symmetric vibration band of Si-O-Si groups[26]. The appearance of the signal at $1415\text{-}1455\text{ cm}^{-1}$ is attributed to (Si-CH₂) and (N-CH₂) or (CCH₂) of the precursor (BTPA) and surfactant (P123), respectively[27]. The signals at $2800\text{-}2890\text{ cm}^{-1}$ and 1469 cm^{-1} detect the presence of CH links contained in the precursor (BTPA) and surfactant (P123), which would mean that the surfactant was not removed completely by soaking. The appearance of the band at $2977\text{-}2979\text{ cm}^{-1}$ is characteristic for stretching of methylene groups[-CH₂] building the BTPA molecules[28]. Another signal proving the inclusion of the bridging group in the structure of materials is the appearance of the signal at 1380 cm^{-1} related to the stretching vibration of n(CN) at C-N bonds[29], also the signal at 691 cm^{-1} typical of stretching of Si-CH₂[30, 31] and this one at 1375 cm^{-1} at which is observed stretching of CN bond[32]. The signals at 1640 cm^{-1} and 3450 cm^{-1} can be associated with the presence of NH groups[29,33] or stretching vibration of OH groups[25,34].

²⁹Si MAS NMR spectra of functionalized materials are presented on Figure 4. Clearly expressed six resonant peaks, three of which are at 110 ppm, 101 ppm and 92 ppm, respectively, as indicated Q⁴[Si(OSi)4], Q³[(OH)Si(OSi)₃] and Q²[(OH)₂Si(OSi)₂] and another three about 66 ppm, 57 ppm and 50 ppm are designated as T³[(SiO)₃SiC], T²[(SiO)₂(OH)SiC] and T¹[(SiO)(OH)₂SiC][35,36].

The appearance of the T^m peaks confirms that organic silane (BTPA) is included as part of the structure of the pore wall[37-39]. The ratio of the intensity of T^m and Qⁿ peaks (T^m / Qⁿ) increases with the increasing of the amount of BTPA, indicating that the bridging organic part in the pore walls increases with increasing the amount of BTPA[38, 39]. These ratios are 0.428, 0.544, 0.582 and 0.673 respectively for ABMO 1, ABMO 2, ABMO 3 and ABMO 4 which are in good agreement with the results from elemental analysis, who shows that with increasing the amount of BTPA the content of nitrogen increase (Table 2). In addition, the appearance of Q³, Q², T² and T¹ resonance peaks shows that the condensation between the both silicate precursors are not completed, this is confirmed by FT-IR spectra with appearance of signals around 920 cm^{-1} and about 940 cm^{-1} typical for vibration of Si-OH bond[31, 32, 40].

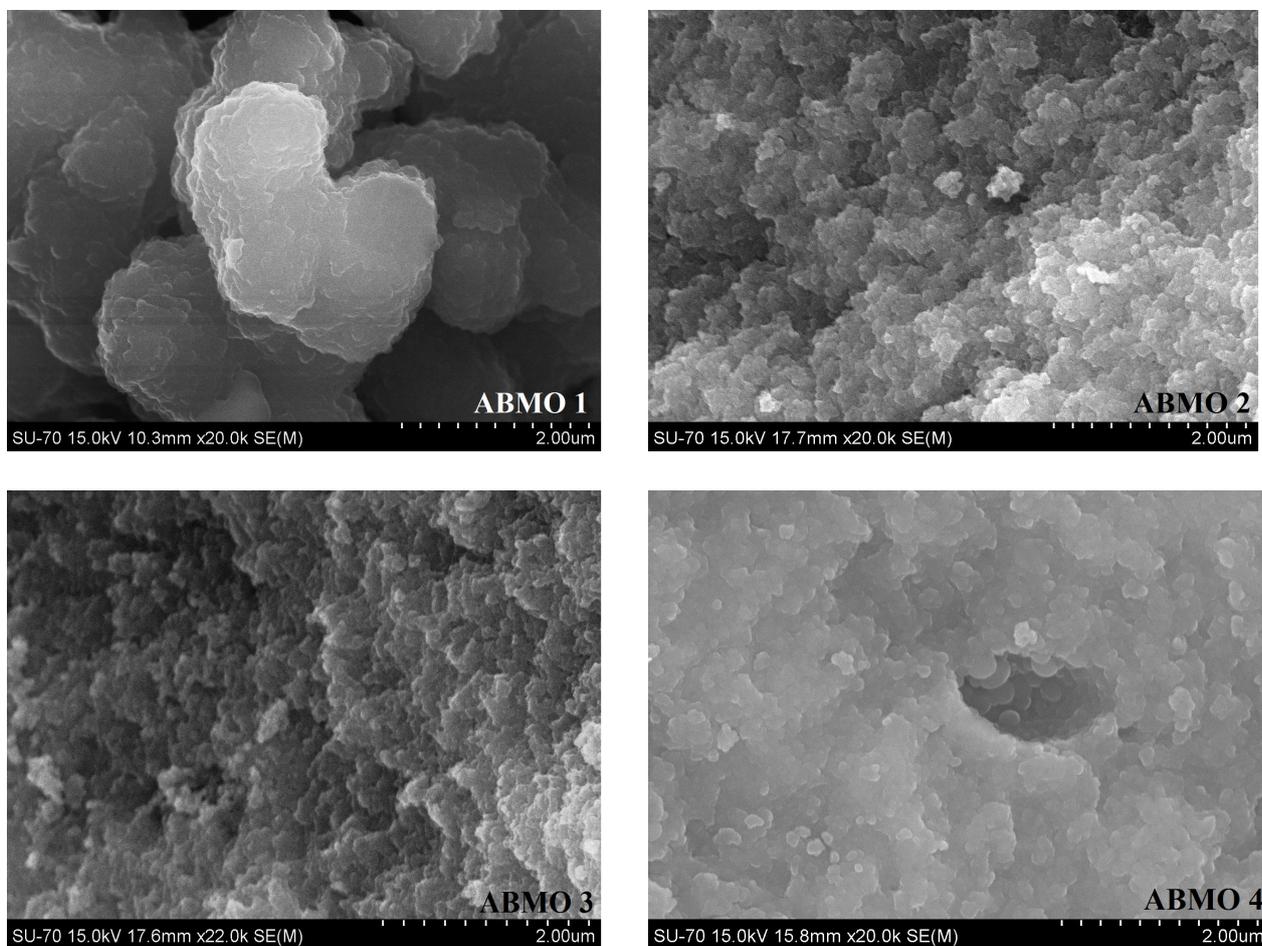


Figure 2. SEM images of the samples

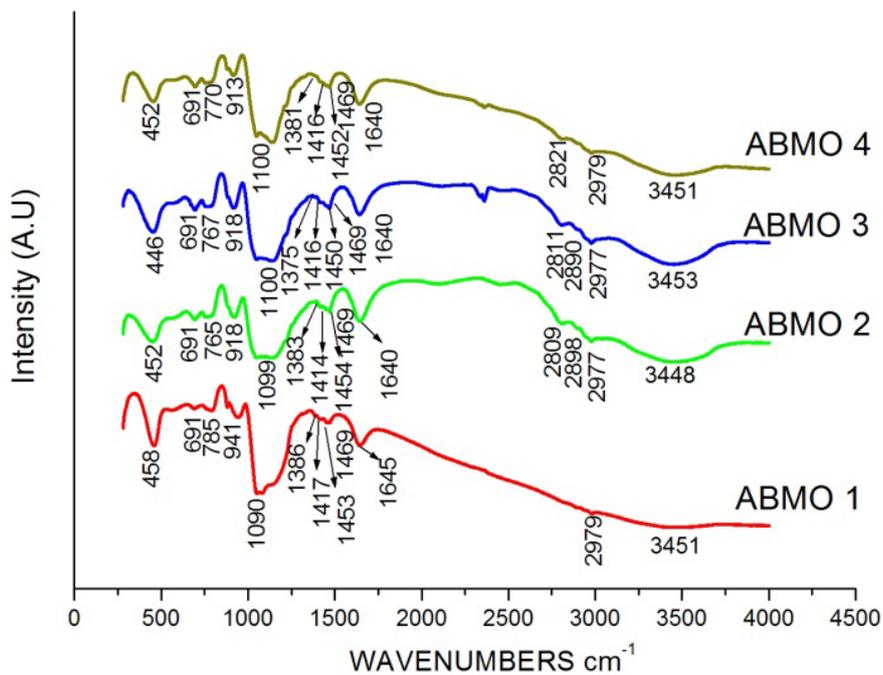


Figure 3. FT-IR spectra of the samples

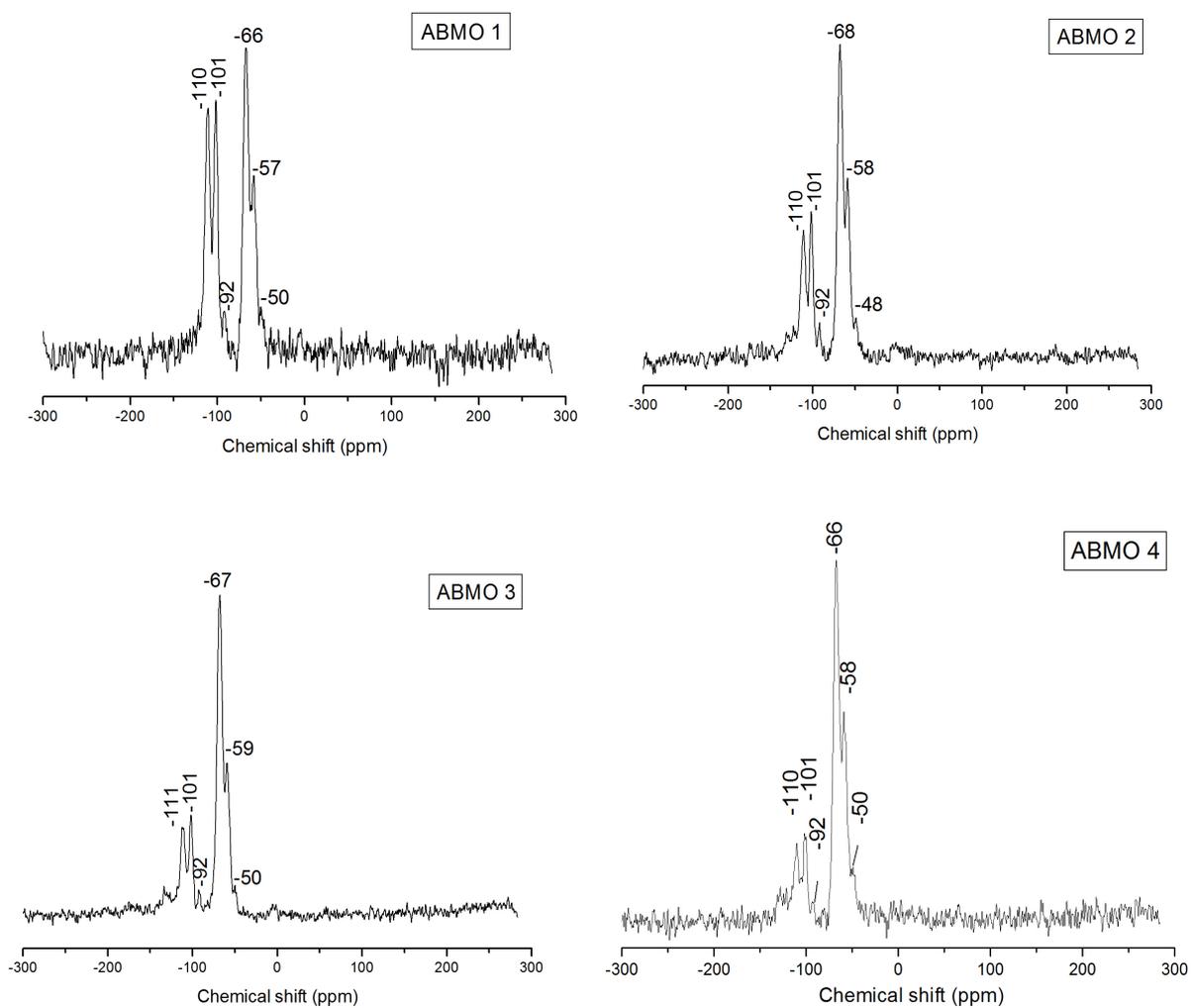
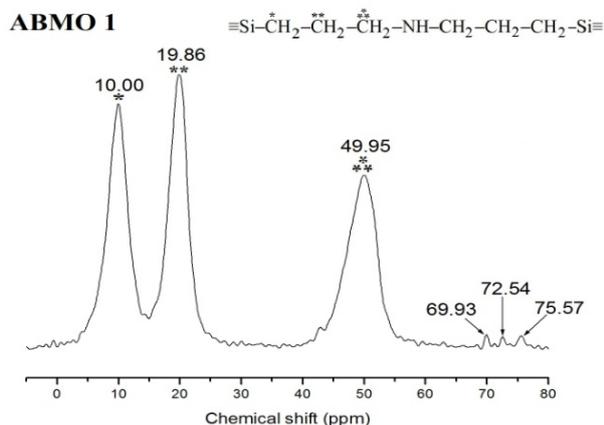


Figure 4. ^{29}Si MAS NMR spectra of the samples

Table 2. Results from elemental analysis

Sample	Mass[mg]	%C	%H	%N
ABMO 1	1.019	9.489	2.3104	1.8239
ABMO 2	1.204	18.481	4.9853	3.8301
ABMO 3	1.352	22.727	5.5204	4.2733
ABMO 4	1.087	22.767	5.3839	4.3004

The results from ^{13}C CP MAS NMR analysis of all samples shows resonans peaks from 10 to 50 ppm typical of sp^3 carbon atoms which characterize organic bridging group of BTPA[41-46]. 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 Figure 5[22, 47]. The appearance of peaks in the range from 70 to 75 ppm indicate the presence of surfactant P123 i.e. not completely extracted by soaking[22, 47-49], which is confirmed by FT-IR spectra in which the signal appears at about 2900 - 3000 cm^{-1} which are observed at stretching of CH bonds in CH_3 groups[50,51].

**Figure 5.** ^{13}C CP MAS NMR spectra of sample ABMO 1

3.4. Metal Adsorption Studies

The optimum time to establish adsorption equilibrium between investigated materials and Hg (II) ions of different concentrations was determined experimentally and was found to be within 20 minutes. The adsorption studies were performed taking into account these preliminary experiments. We investigated the influence of amount of BTPA over the adsorption. In Table 3 are presented the results from adsorption of Hg (II) ions from the solution with different concentration on the investigated materials.

Table 3. Influence of the BTPA amount on the materials adsorption

Adsorbent	Ion	C_0 [mg/ l]	Amount adsorbed matter[mg/g]
ABMO 1	Hg	2000	65.4
ABMO 2	Hg	2000	94.5
ABMO 3	Hg	2000	114.7
ABMO 4	Hg	2000	128.7

From these results we can conclude that the increasing of the amount of BTPA leads to increasing the adsorption

capacity of the materials i.e the increasing the amount of BTPA leads to increasing of active places, in this case the active places are -NH- groups from the bridged group from BTPA precursor, in the result of this the adsorption efficiency of the materials increase.

All materials are appropriate for Hg(II) removal form acidic aqueous solutions. The adsorption capacities were found to be 65.4 mg/g, 94.5 mg/g 114.7 mg/g and 128.7 mg/g for ABMO 1, ABMO 2, ABMO 3 and ABMO 4 respectively. The regeneration of the hybrid sorbents is from exceptionally importance. For the investigation of desorption of Hg (II) were used diluted mineral acids (0.1 M and 1 M HCl and 0.1 M, 1 M, 2 M HNO_3) and EDTA (0.01 M and 0.1 M). We suggested that the cations, released from the acids will change the adsorbed Hg(II) ions or they will obtain complex with EDTA. In Table 4 are presented the data for the adsorption (in %) for different desorption agents.

Table 4. Desorption of Hg(II) ions by hybrid material ABMO 3

Desorption agent	Time[hour]	ABMO 3
0.1 M HCl	3	1%
0.1 M HNO_3	3	100%
1 M HCl	3	6%
1 M HNO_3	3	100%
0.01 M EDTA	24	10%
0.1 M EDTA	24	100%

The obtained data shows that HCl is not appropriate for dsorption of Hg(II) ions, wile by using of 0.1M HNO_3 and EDTA were achieved 100% desorption. The last one can be used for effective regeneration of hybrid sorbents. On the base of the results, probably the adsorption of Hg (II) ions on the material ABMO 3 is mainly physical adsorption.

4. Conclusions

Amine functionalized mesoporous organosilica materials have been synthesized with direct co-condensation of tetraethylortosilicate (TEOS) and bis-[3-(triethoxyosilyl) propyl] amine (BTPA) under basic conditions catalyzed by the -NH- groups of BTPA. XRD results revealed that the materials have ordered structure but the absence of resolved higher angle picks indicates that the order does not extend over a long rage. FT-IR, elemental analysis and ^{29}Si MAS NMR data confirm that the materials are based on amine bridged polysiloxane and no degradation of the bridging groups occurs during the synthesis. FT-IR and ^{13}C CP MAS NMR analyses indicate that part of the surfactant P123 is not fully dissolved in the extraction step and is still present in the materials. Adsorption of Hg (II) ions from aqueous solutions shows high adsorption capacities suggesting that these materials have a potential to be used as adsorbents for Hg (II) ions in acidic solutions. On the base of the obtained results, probably the adsorption of Hg (II) ions on the material ABMO 3 is mainly physical adsorption. By 0.1M HNO_3 and EDTA were achieved 100% desorption of Hg(II) ions and regeneration of the hybrid material.

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