MODIFIED AND UNMODIFIED SILICA GEL USED FOR HEAVY METAL IONS REMOVAL FROM AQUEOUS SOLUTIONS

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ABSTRACT

Silica gel modified with 2–aminothiazole and pure silica gel are used as a sorbents for removal of Cu (II), Co (II), Ni (II), Cd (II), Pb (II) and Hg (II) ions from aqueous solutions. They are characterized with respect to their surface area, pore volumes, IR spectra, sulfur and nitrogen contents. It is found that their capacity depends on the medium pH. The modified sample has a greater sorption capacity than that of the other one in an acidic medium. In neutral and alkaline media both samples show identical sorption capacity. The highest sorption capacity is observed in regard to Hg (II) in modified silica gel presence, and which is why it can be successfully used for selective extraction of mercury ions from aqueous solutions.

Keywords: adsorption, silica gel, heavy metal removal, 2–aminothiazole.

INTRODUCTION

The availability of clean and uncontaminated water is an indispensable necessity for human life. Various technologies like mining, burning of fossil fuels and other anthropogenic activities have been found to be responsible for releasing Cu^{2+}, Pb^{2+}, and Cd^{2+} etc. ions into the environment at unprecedented levels. The high concentrations of some heavy metal ions in aqueous systems have necessitated the search for very efficient matrices for their removal. The silica gels have a wide application as inorganic supports [1-5]. They are characterized by a highly porous texture and therefore they can be utilized for synthesis of adsorbents with preset structural characteristics and various chemical surfaces. In addition, the structure of silica gel is corpuscular, i.e. it consists of interconnected particles forming a three-dimensional skeleton. The particle size affects the value of the specific surface area, while the compactness of binding influences the absorption volume of the pores. On the other hand, sulfur- and nitrogen-containing ligands are characterized by a high selectivity towards heavy metals [7, 8]. For this reason the modification of silica gel by S and N-containing organic substances is of great interest. Solid materials, such as silica, have been extensively used due to the presence of reactive hydroxyl groups on their surfaces. These groups enable the attachment of organic molecules containing Lewis bases, which can coordinate metal ions in a solution [9]. The correct choice of a desired functional group for immobilization on the silica surface can yield materials that are highly selective for a specific contaminant [10]. Recently, surface functionalization of ordered silica gel has attracted intensive interest in view of its use as a solid support, due to its large specific surface area and fast adsorption kinetics [11-14]. Several kinds of silica have been

functionalized with different ligands and to be used for mercury ions removal from water [7, 8]. The modifications of SBA-15 and MCM-41 with 2-mercapto thiazoline, 2-mercaptopyridine, or 2-mercaptobenzothiazol and MCM-48 with benzoyl thiourea have been recently reported [15-17]. Gu et al. [18] proposed the preparation of silica–polystyrene core–shell particles. In their work, silica particles were obtained through condensation and hydrolysis of tetraethyl orthosilicate in a water–ethanol–ammonia solution, and the silica particles were surface - modified with methacryloxypropyltrimethoxysilane acting as a coupling reagent. Yin et al. [19] reported the synthesis of novel composite adsorbent silica gel microspheres, encapsulated with 5-sulfosalicylic acid functionalized polystyrene (SG-PS-azo-SSA). The latter has a favorable effect and is used for the removal of Cu (II), Ag (I) and Au (III) metal ions. The purpose of the present paper is to synthesize silica gel modified with 2 -aminothiazole, containing sulfur and nitrogen as donor atoms, expecting selectivity toward heavy metals (Cu (II), Co (II), Ni (II), Cd (II), Pb(II) and Hg(II)) sorption. The properties examined will be compared to those of pure silica gel.

EXPERIMENTAL

Preparation of the sorbents

Modification of silica gel was achieved by tetraethyl orthosilicate (TEOS) hydrolyzed in advance at room temperature. Tetraethyl orthosilicate (10 ml) was hydrolyzed with distilled water at a TEOS: water ratio of 1:3. The hydrolysis proceeded at pH 3. An amount of 1.0005 g of 2 –aminothiazole ($C_3H_4N_2S$) was dissolved in 10 ml of dimethylformamide [DMFA – $(CH_3)_2NC(O)H$] and was added upon continuous stirring with a magnetic stirrer to the hydrolyzed TEOS. The stirring continued for 3 h at room temperature until complete homogenization of the solution was achieved. The solution thus obtained was dried for 24 h at 373 K. It was expected that the procedure described would provide the organic substance participation in the sorbent porous texture and globular skeleton formation. A powdery sample (S2A) was obtained, upon washing with distilled water and drying at 373 K. Pure silica gel (sample SG) was obtained by the classical sol gel method under identical conditions and initial component ratios [20].

Characterization of the sorbents

The amount of deposition of 2 -aminothiazole was determined by a thermal desorption method 0.5 g of the synthesized sorbent were heated in a furnace at 873 K for 1 h in air atmosphere. Then the sample was cooled down in air to room temperature. The amount of 2 -aminothiazole was calculated on the ground of the weight loss of the sample taking into account the weight change of the unmodified silica gel (blank sample). Elemental analysis was used to determine the sulfur and nitrogen content in the modified silica gel. Characterization of the surface and porous texture of the silica gel (SG) and the modified silica gel (S2A) was carried out by adsorption of nitrogen at the boiling temperature of liquid nitrogen (77K) using a conventional volumetric-measuring apparatus. The nitrogen adsorption isotherms were analyzed to evaluate the specific surface areas, A_{BET} (the BET equation was applied) and the total pore volume V_t, (the rule of Gurvich at a relative pressure of 0,95 was used). The average pore radius, R_p was evaluated as the ratio between the doubled V_t and A_{BET} parameters of the samples assuming a cylindrical pore model. The size distribution of the mesopores was estimated on the ground of the method of Pierce [15] using the adsorption branches of the isotherms. The IR spectra were taken on a KBr tablet using a Brucker IFS 25 Fourier transform interferometer (Germany) within the range of 400-4000 cm⁻¹.

Sorption studies

The stock standard solutions of 2 mg/L containing Cu (II), Co (II), Ni (II), Cd (II), Pb (II) and Hg (II) were prepared using Merck Titrisols. The Hg (II) solution, was of a concentration of 50 mg/L in accordance with the requirements of the atomic absorption analysis (AAA) device. The solutions, pH values varied in the range from 1 to 7 (pH-meter model pH 211, Hanna instruments, Germany) adjusted by adding dilute solutions of HNO_3 or NH_4OH. The sorbent was filtered away at the adsorption equilibrium while the filtrate was analysed by an AAA Pye Unicam SP 192 flame spectrometer (UK). To determine the sorption capacity, 20 mL of aqueous solution having 200 mg/L metal concentration were added to 0.2 g sorbent at optimum pH. After 24h the concentration of the investigated element was determined by flame atomic absorption analysis. The time dependence of the sorption percentage was followed in case of contact time of 15, 30, 60, 120, 180 min at pH 5.
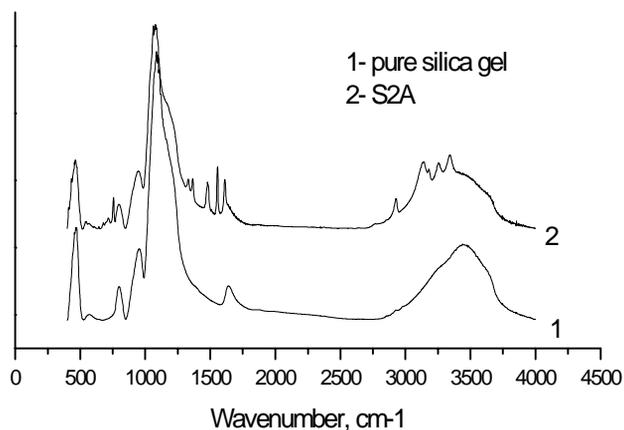
Fig. 1. IR spectra of the initial sample (SG) and modified sample (S2A).

Fig. 2. N_2 adsorption isotherms of the silica samples (SG and S2A).

RESULTS AND DISCUSSION

Characterization of the sorbents

Fig.1 shows the IR spectra of (SG) and (S2A). The specific bands of 2 -aminothiazole due to the presence of NH_2-group and C-N bonds are observed at about 1660 and 1500 cm $^{-1}$, respectively. This indicates their incorporation during the silica gel modification. The intensive band at 1050 cm^{-1} is due to the Si-O bond, while deformation of water is responsible for the band at 1630 cm^{-1}. The peaks at 3425 and 3600 cm^{-1} correspond to the stretching vibrations of the adsorbed water molecule.

Fig. 2 illustrates the nitrogen isotherms using the samples studied, while Table 1 presents the main textural parameters of the initial state of SG and S2A.
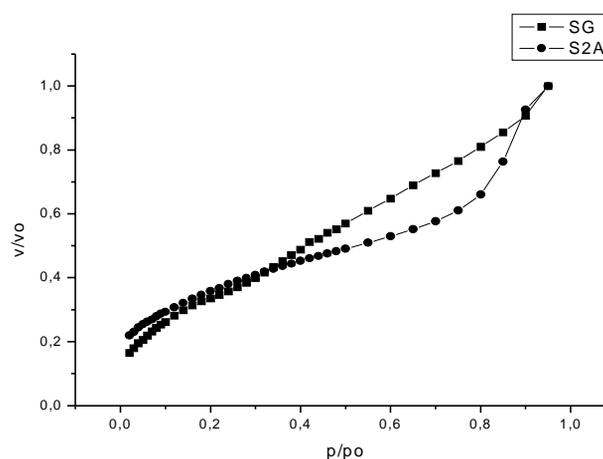
It is seen that the isotherms obtained using SG and S2A differ. This is an evidence of a change in the globular structure of S2A when compared to SG. This is most probably connected with the number of contacts [21] between the primary particles in S2A with varying R_P decrease (Table 1). Table 1 shows that 2- aminothiazole introduction to S2A leads to considerable decrease of A_{BET} value (21% for S2A) and the total pore volume when compared to the corresponding of SG.

The modification in the case of S2A (when compared to SG) results in decrease of R_P (again to an insignificant extent). This fact proves that the modifying agent in S2A case, included in the process of gel formation, is responsible in this effect .

The comparison of the pore size distribution curves plotted for SG and S2A (Fig. 3) shows the drastic change in

Table 1. Adsorption and texture parameters of the initial (SG) and of the modified samples (S2A).

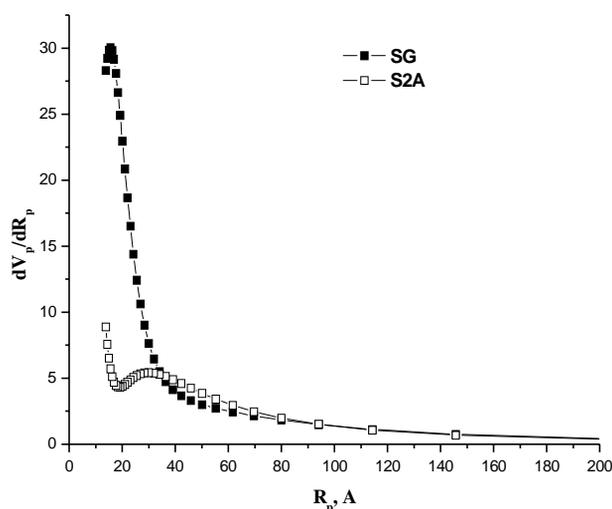| Parameters	SG	S2A
Specific surface area (A_{BET}), m^2/g	803	635
Total pore volume (V_t), cm^3/g	0,979	0,745
Average pore radius (R_p) Å	24,0	23,0
Nitrogen content, wt %	-	3,90
Sulfur content, wt %	-	4,40
Amount 2-aminothiazole mmol/g	-	1,38

Fig. 3. Mesopore size distribution curves for the initial and modified silica gel.

the porous texture of S2A in regard to that of the SG sample.

The pore size distribution goes from comparatively uniform (SG sample) to a wider-scope of distribution, including pores with quite different sizes. This shows that the addition of 2-aminothiazole results in the formation of globules of different size became of the increasing number of contacts of each single globule with its neighbours, the inter-globular growth and aggregation of the separate globules. Despite of the consid-

erable decrease in A_{BET} value (Table 1), the mesopores distribution type guarantees the sorbed ions access to the sorption sites on the sample contact surface.

Sorption properties

The changes in the adsorption capacity of the synthesized sorbents are studied as a function of the adsorption time. The kinetic curves of sorption of SG and S2A with respect to Hg(II) and Cu(II) ions are plotted in Fig. 4.

The sorption process on the two sorbents begins after 10 min. Complete sorption is observed within 60 min for both samples.

Fig. 5 shows the adsorbed amount percentage as a function of pH for Cu(II), Co(II), Ni(II), Cd(II), Pb(II) and Hg(II) ions.

It is seen that in the acidic pH region (1.5 – 4.0) the S2A sample is a better sorbent than SG the whole pH range investigated. The sorption of Hg (II) ions is the highest at S2A. Its highest values (99.0%) of this sorbent is attained in the neutral region. The same is valid for Pb (II) ions. In the acidic range the sorbed amount decreases in the line Hg(II)>Cu(II)>Co(II)>Cd(II)>Pb(II)>Ni(II) for the S2A. According to Pearson [22], in acid- base reactions the hard acids prefer to interact with the hard bases, while the soft acids - with the soft bases. Being soft bases, sulfur and nitrogen-containing sites should have a stronger
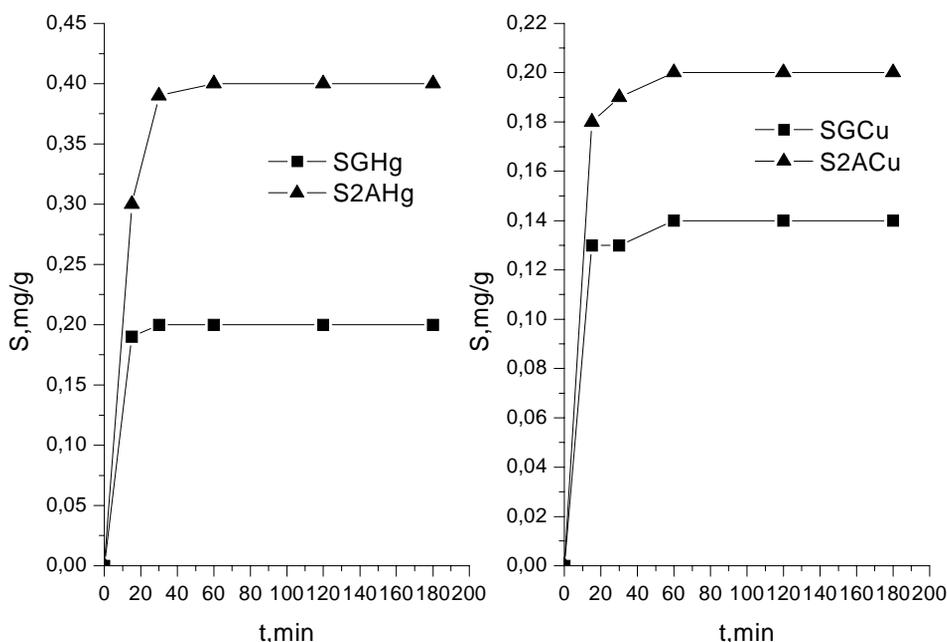

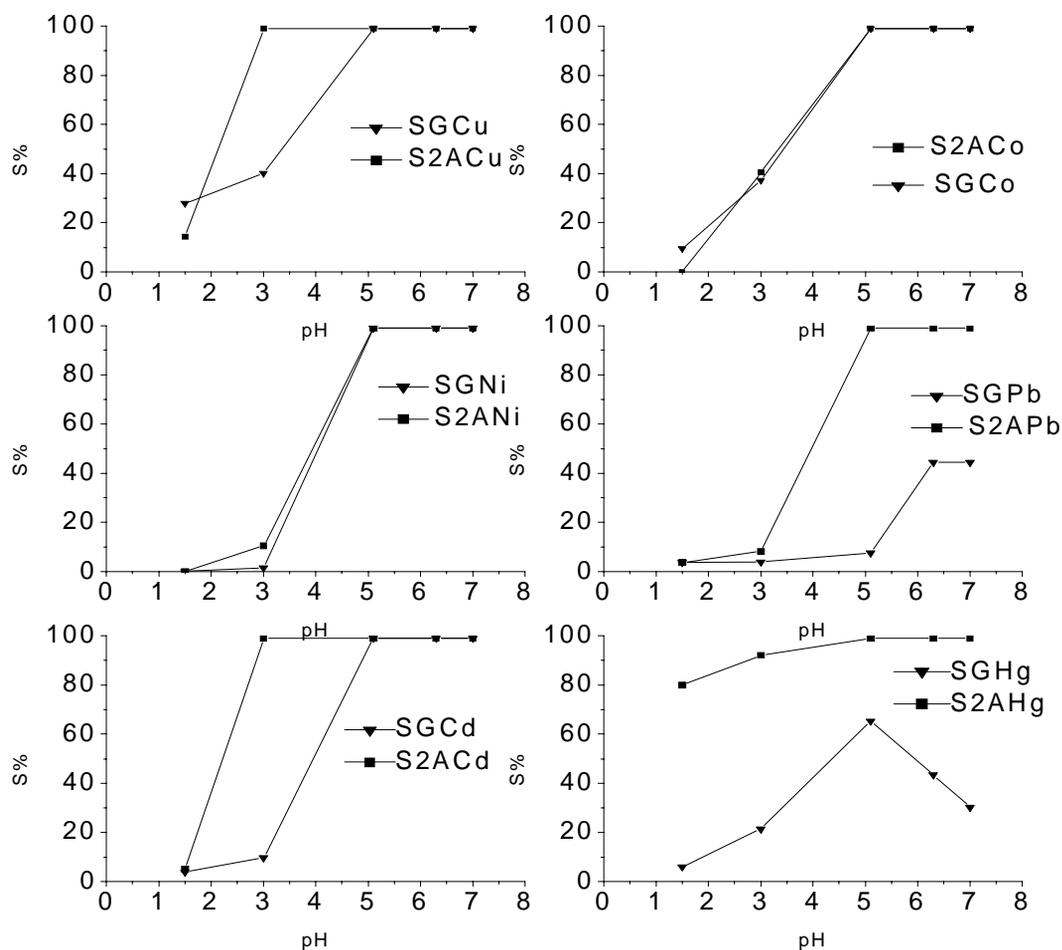Fig. 4. Kinetic curves of sorption of Cu (II) and Hg (II) on SG and S2A.

Fig. 5. pH - dependence of sorption (in %) of SG and S2A.

Table 2. Sorption capacity of silica gel (SG) and modified silica gel (S2A) (mg/g).

Capcity (mg/g) for	pH	Sorbents	
		SG	S2A
Cu(II)	5,0	0,07	5,53
Ni(II)	5,0	0,34	0,95
Co(II)	5,0	0,64	1,14
Cd(II)	5,0	1,13	1,20
Pb(II)	5,0	0,72	*
Hg(II)	5,0	2,67	8,43

* The sorption capacity of the synthesized sorbents has been studied at concentrations of the Pb(II) ions in the solution 200 mg L-1 and 400 mg L-1 and the sorption has been found to be completed. Higher concentrations of the Pb (II) ions have not been investigated.

affinity towards soft acids such as Hg (II) ions and a weaker affinity towards borderline acids like Cu(II) and Ni(II) ions. Probably S and N-containing sites are more accessible to sorption than are oxygen sites, which are probably protonized. In a neutral medium it is probable that all the active sites are taking part in the sorption process simultaneously, which explains the increase in sorption with pH. The static sorption capacity data are represented in Table 2.

The investigations indicate that S2A is characterized by a relatively higher sorption capacity than that of the SG. An exception in this respect is Cd (II) whose sorption capacity is slightly lower than that on unmodified silica gel. The highest sorption capacity is observed for Hg (II) ions in presence of SG, in view of which this sorbent can be used for selective extraction of mercury ions from aqueous solutions. The higher sorption capacity of S2A shows that all active sites (S, N and surface OH groups) participate in the sorption process, while on the SG sample the surface OH groups are the predominant active sites.

It is found out that S2A can be used for separating Hg (II) and Co (II) ions from the Ni (II), Pb (II), Cu (II) and Cd (II) ions an acidic medium.

CONCLUSIONS

The sorption of heavy metal ions on SG and S2A sorbents is studied. It is shown that of depends on the time and pH value. The percentage of metal ions removal reaches its maximum value at pH 5.0-7.0. The adsorbed amount of mercury ions is the highest in the whole investigated pH range in case of S2A. Its highest values (99.0 %) is attained in the neutral region. The same is also valid for Pb (II). It is found that in the acidic pH region (1.5 – 4.0) the S2A sample is better sorbent than SG. The investigations show as well that the modified silica gel is characterized by a relatively higher sorption capacity than that of the unmodified one. The highest sorption capacity is manifested with respect to Hg (II) ions in the presence of modified silica gel due to which this sorbent can be used for selective extraction of mercury ions from aqueous solutions.

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