

# Modified silica gel with 5-amino-1,3,4-thiadiazole-2-thiol for heavy metal ions removal

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**Abstract** A two sorbents was to synthesize for heavy metals removal: silica gel modified with 5-amino-1,3,4-thiadiazole-2-thiol (S5A) and pure silica gel. Modification of silica gel is achieved by tetraethyl orthosilicate (TEOS) preliminary hydrolyzed at room temperature. 5-Amino-1,3,4-thiadiazole-2-thiol is added, with continuous stirring with a magnetic stirrer, to the hydrolyzed TEOS. Pure silica gel (sample SG) is obtained by the classical sol–gel method using the same conditions and initial component ratios. The sorbents have been characterized as to their surface area, pore volumes, content of the functional groups, IR spectra, sulfur and nitrogen content. Their sorption properties to heavy (Cu(II), Co(II), Ni(II), Cd(II), Pb(II) and Hg(II) metals are investigated. The investigations indicate that modified silica gel is characterized by a relatively higher sorption capacity than is the unmodified one. The highest sorption capacity belongs to Hg(II) in presence of unmodified silica gel due to which this sorbent can be used for selective extraction of mercury ions from aqueous solutions.

**Keywords** Silica gel · 5-Amino-1,3,4-thiadiazole-2-thiol · Sorption · Heavy metals

## 1 Introduction

The toxic effect of heavy metals (Cd, Pb, Cu, Co, Ni, Hg etc.) has been known for a long time [1–3]. They may be present in water and food. For that reason, their

concentration in natural waters should be controlled with a view to their elimination. The most wide-spread and easiest method is adsorption applied to aqueous solutions using suitable sorbents [4, 5] that capture and immobilize harmful substances including heavy metals. In recent years there is a trend to use surface modified inorganic supports [6, 7]. In this way, new low-cost selective sorbents, which are effective catalysts and polymer fillers, have been obtained. Silica gels have a wide application as inorganic supports [1, 2, 8–10]. They are characterized by a porous texture and can, for that reason, be utilized for synthesis of adsorbents with preset structure characteristics and various chemical surfaces. In addition, the structure of silica gel is corpuscular, i.e., it is formed by particles connected with one another in a three-dimensional skeleton. The particle size affects the size of the specific surface area while the density 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 [6, 7, 11]. That is why the modification of silica gel by S and N-containing organic substances is very interesting. Silica gel modified with 5-formyl-3-arylazo-salicylic acid is used for extraction of Fe(II) [12]. Silica gel incorporating 3-amiopropyltriethoxysilane can be used for separating and concentrating Ag, Cd and Cl from sea water [13]. Gomes and co-authors [14] determined metal ions Cd(II), Co(II), Ni(II), Pb(II), Cu(II), Fe(III), Zn(II) in fuel ethanol by concentrating them with silica gel chemically modified with 5-amino-1,3,4-thiadiazole-2-thiol.

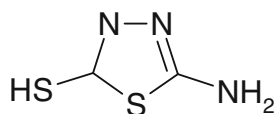
The purpose of the present paper was to synthesize silica gel modified with 5-amino-1,3,4-thiadiazole-2-thiol, containing sulfur and nitrogen as donor atoms and being selective to heavy metals (Cu(II), Co(II), Ni(II), Cu(II), Pb(II) and Hg(II)) and to compare its sorption properties with those of pure silica gel.

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## 2 Experimental

### 2.1 Preparation of the sorbents

Modification of silica gel is achieved by tetraethyl orthosilicate (TEOS) preliminary hydrolyzed at room temperature. TEOS (10 mL) is hydrolyzed with distilled water in a TEOS: water ratio of 1:3. Hydrolysis proceeds at pH 3: 5-amino-1,3,4 thiadiazole-2-thiol in an amount of 1.0 g is dissolved in 10 mL dimethylformamide (DMFA) and is added, with continuous stirring with a magnetic stirrer, to the hydrolyzed TEOS.



5-amino-1,3,4-thiadiazole-2-thiol

The stirring continues for 3 h at room temperature to the complete homogenization of the solution. The solution thus obtained is dried for 24 h at 373 K. In this way, the organic substance is expected to participate in the formation of the porous texture of the sorbent obtained, affecting at the same time the formation of the globular skeleton, i.e., the aggregation process. A powdery sample (S5A) is obtained, washed with distilled water and dried at 373 K. Pure silica gel (sample SG) is obtained by the classical sol gel method using the same conditions and initial component ratios [15].

### 2.2 Characterization of the sorbents

The amount of deposited 5-amino-1,3,4-thiadiazole-2-thiol was determined by a thermal desorption method as follows: 0.5 g of the synthesized sorbent were heated in a furnace at 873 K for 1 h under air atmosphere. Then the sample was cooled down to room temperature in air. The amount of 5-amino-1,3,4-thiadiazole-2-thiol was calculated from the weight loss of the sample, where the weight change of the unmodified silica gel (blank sample) was also taken into account. Elemental analysis was used to determine the percentage of sulfur and nitrogen in the modified silica gel. Characterization of the surface and porous texture of the silica gel (SG) and the modified silica gel (S5A) was carried out by low-temperature adsorption of nitrogen (77 K) using a conventional volumetric-measuring apparatus. The nitrogen adsorption isotherms were analysed to evaluate the following parameters. The specific surface areas ( $A_{\text{BET}}$ ) were determined on the basis of the BET equation, the total pore volume ( $V_t$ ) was estimated in accordance with the rule of Gurvich at a relative pressure 0.95. The average pore radius

( $R_p$ ) was evaluated as the ratio between the doubled  $V_t$  and  $A_{\text{BET}}$  parameters of the samples assuming a cylindrical pore model. The size distribution of the mesopores was estimated they bass on the method of Pierce [16] using the adsorption branches of the isotherms. The IR spectra were taken on a KBr tablet using a Bruker IFS 25 Fourier transform interferometer (Germany) in the range 400–4000  $\text{cm}^{-1}$ .

### 2.3 Sorption studies

The stock solutions of Cu(II), Co(II), Ni(II), Cd(II), Pb(II) and Hg(II) of a concentration of 2  $\text{mg L}^{-1}$  were prepared from Merck Titrisols (except for Hg(II)) where the concentration was 50  $\text{mg L}^{-1}$  since at lower values the device used for AAS would require preliminary concentration of the solution. The aqueous solutions containing the metals under consideration had different pH values varying between 1 and 7. The desired pH values (pH-meter model pH 211, Hanna instruments, Germany) were attained by adding diluted solutions of  $\text{HNO}_3$  and  $\text{NH}_4\text{OH}$ . After reaching adsorption equilibrium, the sorbent was filtered and the concentration in the filtrate of the element being investigated was determined by an AAS Pye Unicam SP 192 flame spectrometer (UK). Amounts of 20 mL of these solutions were added to 0.2 mg of the sorbent. After 24 h the concentration of the element under investigation was determined by flame atomic absorption spectrometry. To determine sorption capacity, 20 mL aqueous solution with a 200  $\text{mg L}^{-1}$  metal concentration were added to 0.2 mg sorbent at optimum pH. After 24 h the concentration of the element being investigated was determined by flame atomic absorption spectrometry. The dependence sorption percentage versus time was investigated for contact times of 15, 30, 60, 120, 180 min at pH 5.

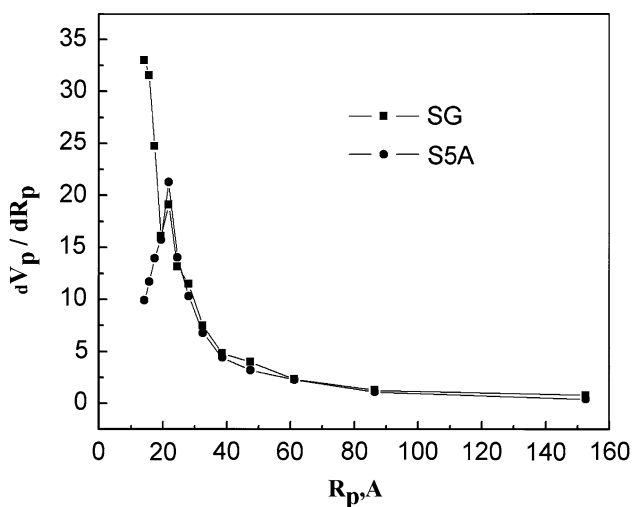
## 3 Results and discussion

### 3.1 Characterization of the sorbents

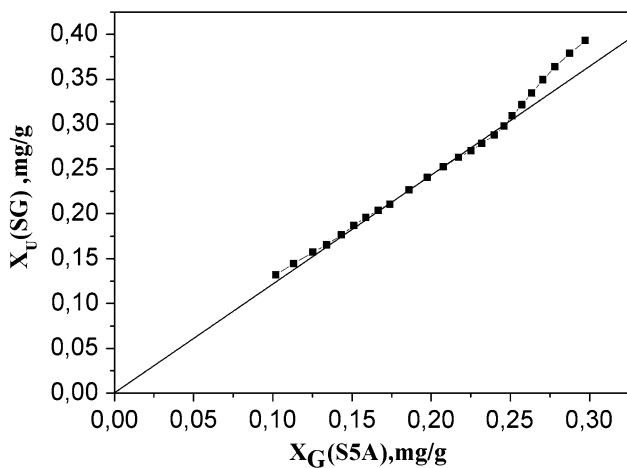
Table 1 shows some adsorption and texture parameters of the samples investigated. Figures 1 and 2 present their pore

**Table 1** Adsorption and texture parameters of the samples SG and S5A

Parameters	SG	S5A
Specific surface area ( $A_{\text{BET}}$ ), $\text{m}^2/\text{g}$	816	698
Total pore volume ( $V_t$ ), $\text{cm}^3/\text{g}$	1.01	0.81
Average pore radius ( $R_p$ ) $\text{\AA}$	24.8	23.1
Nitrogen content, wt%	–	5.4
Sulfur content, wt%	–	7.2
Amount 5-amino-1,3,4-thiadiazole-2-thiol, $\text{mmol/g}$	–	1.09

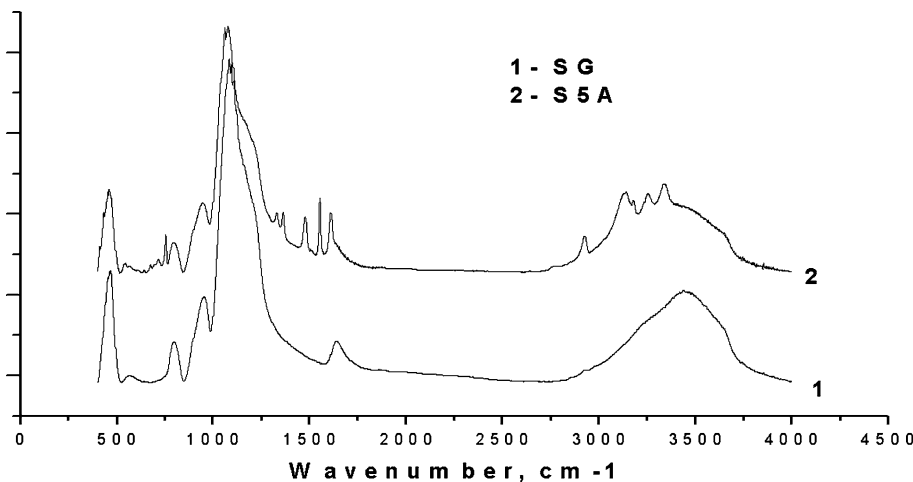


**Fig. 1** Mesopore size distribution curves for the silica gel SG and modified silica gel S5A



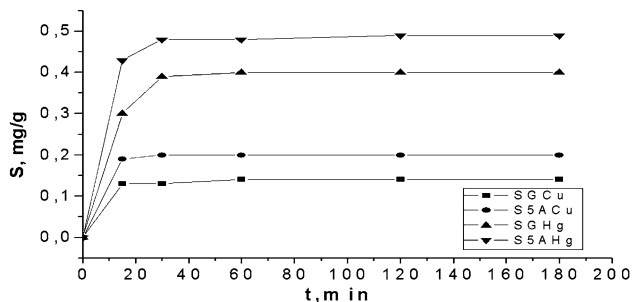
**Fig. 2** Comparison plots of nitrogen adsorbed ( $X_U$ ) on the SG with nitrogen adsorbed ( $X_G$ ) on S5A at the same relative pressure

**Fig. 3** IR spectra of SG and S5A



size distribution curves and the corresponding comparison curves [17, 18] plotted on the basis of the experimental adsorption isotherms. The comparison plots are a simple way of juxtaposing the shapes of the isotherms for a given solid with that of a reference sample. Analysis of the experimental results shows that sample SG is characterized by a suitable specific surface area and uniform fine-pore texture. Sample S5A, on its part, does not differ in porous structure type and pore size distribution from SG. The incorporation of 5-amino-1,3,4-thiadiazole-2-thiol into silica gel does not lead to a change in type of distribution and position of max  $R_p$  (20 Å). A certain, although negligible difference is observed in the  $R_p$  range of 25–60 Å of the pore size distribution curve, which indicates an effect of the organic substance on the aggregation of the particles forming the pores in this range. The latter is also confirmed by the disappearance of the shoulder at  $R_p$  27–35 Å in the S5A curve, which means blocking of the access to the adsorptive (nitrogen) molecules of S5A. This explains the specific surface area decrease (by 14% for a 1.09 mmol/g organic phase) with the S5A sample as compared to SG. Analysis of the  $n/C$  BET plots of Lecloux [19] shows that with SG there are a negligible amount of micropores ( $-0.003 \text{ cm}^3/\text{g}$ ) whereas with S5A they are altogether absent. Hence, the negligible amount of micropores with SG can be attributed to intraaggregate pores, which is confirmed by their disappearance with the S5A sample. Finally it may be noted that the incorporation of 5-amino-1,3,4-thiadiazole-2-thiol into the silicate matrix leads neither to a change in porous structure type and pore size distribution nor to an essential change in the BET specific surface area.

Figure 3 shows the IR spectra of silica gel (SG) and the synthesized sorbent (S5A). Both specific bands of 5-amino-1,3,4-thiadiazole-2-thiol due to the  $\text{NH}_3$  and C–N bonds are observed at about 1660 and 1500  $\text{cm}^{-1}$ , respectively.



**Fig. 4** Kinetic isotherms of sorption of SG and S5A for Cu(II) and Hg(II)

**Table 2** Sorption capacity of silica gel (SG) and modified silica gel (S5A) (mg/g)

Capacity (mg/g) for	pH	Sorbents	
		SG	S5A
Cu(II)	5.0	0.07	1.21
Ni(II)	5.0	0.34	0.76
Co(II)	5.0	0.64	0.67
Cd(II)	5.0	1.13	1.09
Pb(II)	5.0	0.72	1.54
Hg(II)	5.0	2.67	8.44

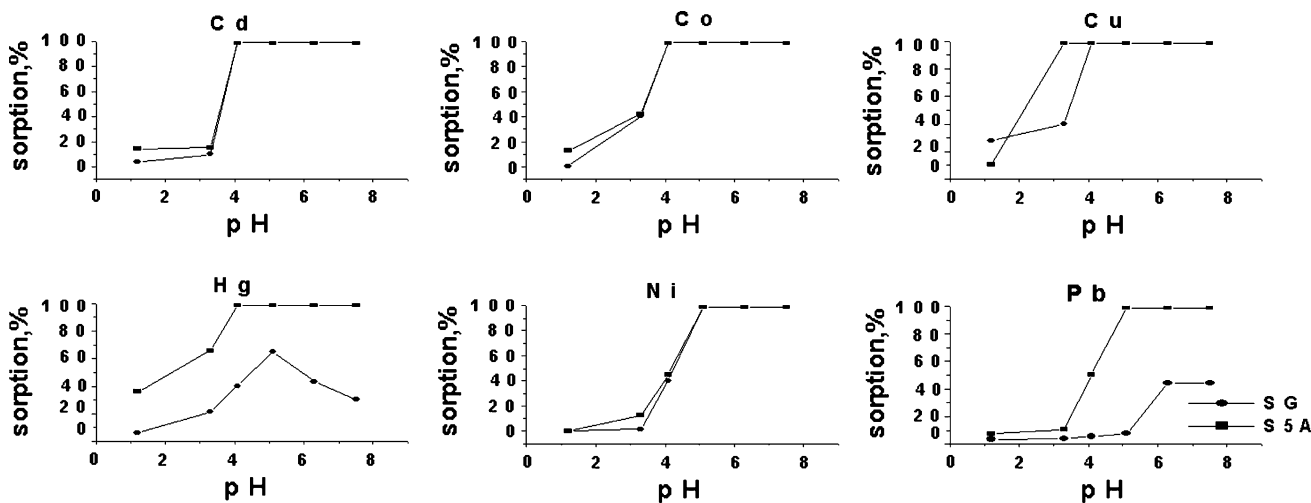
Their presence in the sorbent indicates their incorporation during the modification of silica gel. The intense band at  $1050\text{ cm}^{-1}$  is due to the Si–O bond while deformation water is responsible for the band at  $1630\text{ cm}^{-1}$ .

3.2 Sorption properties

The kinetic curves of sorption of SG and S5A for Hg(II) and Cu(II) ions are shown in Fig. 4. Sorption on the two sorbents begins after 15 min. Full sorption is observed in 30 min for both samples.

Figure 5 shows the sorption percentage as a function of pH for metal ions Cu(II), Co(II), Ni(II), Cd(II), Pb(II) and Hg(II). The sorption of the metal ions on sorbents SG and S5A is compared. It has been established that in the acid pH region (1.5–4.0) S5A adsorbs all metal ions better than SG. The mercury ions have the highest sorption values over the whole range investigated (pH 1.5–7) in the case of S5A. The sorption of Hg(II) attains its highest values (99.0%) in the neutral region. The same is also valid for Pb(II) in the whole range investigated (pH 1.5–7). In the acid range the percentage of sorption decreases in the sequence Hg(II), Cu(II), Co(II), Cd(II), Pb(II), Ni(II) for the modified

sorbent S5A. According to Pearson [20], in acid–base reactions hard acids prefer to interact with hard bases, and soft acids with soft bases. (Being soft bases, sulfur and nitrogen sites should have a stronger affinity to soft acids such as Hg(II) and a weaker affinity to borderline acids like Cu(II) and Ni(II)). Probably S and N sites are more accessible to sorption than are oxygen sites which are perhaps protonized. In a neutral medium maybe all active sites take part in sorption simultaneously, which explains the increase of sorption with pH. The static sorption capacity data are presented in Table 2. The investigations indicate that modified silica gel is characterized by a relatively higher sorption capacity than is the unmodified one. An exception is Cd(II) whose sorption capacity is a little lower than that of unmodified silica gel. The highest sorption capacity belongs to Hg(II) in presence of unmodified silica gel due to which this sorbent can be used for selective extraction of mercury ions from aqueous solutions. The higher sorption capacity of S5A shows that all active sites (S, N and surface OH groups) participate in the sorption process whereas on SG the surface OH groups are the predominating active sites.



**Fig. 5** Sorption (in %) of SG and S5A as dependent on pH

## 4 Conclusion

The sorption of the heavy metal ions on sorbents SG and S5A is compared. The sorption of the heavy metal ions depends on time and pH. The percentage of removal of the metals reaches its maximum value between pH 5.0–7.0. The mercury ions have the highest sorption values over the whole range investigated (pH 1.5–7) in the case of S5A. The sorption of Hg(II) attains its highest values (99.0%) in the neutral region. The same is also valid for Pb(II) in the whole range investigated (pH 1.5–7). It has been established that in the acid pH region (1.5–4.0) S5A adsorbs all metal ions better than SG. The investigations indicate that modified silica gel is characterized by a relatively higher sorption capacity than is the unmodified one. The highest sorption capacity belongs to Hg(II) in presence of unmodified silica gel due to which this sorbent can be used for selective extraction of mercury ions from aqueous solutions.

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