Use of SiO$_2$ aerogel modified with mercapto functional groups for adsorption of Cu(II) and Hg(II) ions

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For adsorption of Cu(II) and Hg(II) ions a new adsorbent, SiO$_2$ aerogel modified with mercapto (-HS) functional groups was synthesized by standard sol-gel synthesis and then dried with supercritical drying using CO$_2$. This is very a porous high-tech material with very high specific surface area: therefore large quantities of ions in comparison to other used research materials can be adsorbed. The ability of modified silica aerogel with mercapto groups to remove Cu(II) and Hg(II) from aqueous solutions was assessed using batch adsorption technique under equilibrium conditions. The removal of heavy metal ions is dependent on the concentration, pH, contact time, adsorbent dose and temperature. Thus, optimal processing conditions for Cu(II) and Hg(II) ions adsorption on modified aerogel were firstly determined. The adsorbent exhibits very high adsorption potential for both heavy metal ions and more than a 99 % removal was achieved in the pH range from 4 to 6. Atomic adsorption spectrometer (AAS) and ion mass chromatography (ICP) were used for the determination of metal ions in aqueous solutions before and after adsorption.

INTRODUCTION

Some heavy metals can have toxic or harmful effects on many forms of life. The pollution of water resources with heavy metals is causing worldwide concern. Due to definitive regulations and precautions it becomes necessary to remove these heavy metals from wastewaters before releasing them into the environment. A number of materials have already been used to remove heavy metals from wastewater, such as agricultural and industrial solid wastes. The reason is in their proteins, carbohydrates and phenolic compounds, which have metal binding functional groups.

Conventional methods for the removal of heavy metals include precipitation, flocculation, ion exchange, reverse osmosis (1, 2), complexation/sequestration, electrochemical operation and biological treatment (3, 4). These methods become economically unviable for the removal of heavy metals at lower concentrations (5), when adsorptive treatment is more appropriate. A number of materials, especially naturally occurring lignocellulosic materials, have been used to remove heavy metals from wastewater (6-9). These materials were found to have good adsorption capacity due to substances inherently associated with cellulose such as lignin, tannin and pectin, which contain polyphenolic and aliphatic hydroxyl and carboxylic groups. The main disadvantages of these materials are their low resistance to abrasive forces in batch or column applications and leaching of some organics (water extractives) during adsorption (10).

For adsorption process adsorbents with high specific surface areas are needed. Pore size, pore distribution and surface area, as well as pore surface chemistry, are the most important factors

in the adsorption process (11, 12). Silica aerogels are extremely porous (up to 99 %) nanostructured materials with high specific surface areas (500–1000 m^2g^{-1}) and low density (as low as 5 kgm^{-3}) and they exhibit capacities which are comparable or even exceed that of commonly used adsorbents. One of the most important properties of silica aerogels is also the possibility to modify their surface chemical nature with the incorporation of organic functional groups.

SiO_2 aerogel modified with mercapto (-HS) functional groups was synthesized by standard sol-gel synthesis and then dried with supercritical drying using CO_2. It was found out that these modified aerogel is very efficient adsorbent of Cu(II) and Hg(II) ions from water. Cu(II) and Hg(II) ions are also very toxic metals (13-16) that have to be removed from wastewater.

The removal of heavy metal ions is dependent on the concentration, pH, contact time and adsorbent dose. Thus, optimal processing conditions for Cu(II) and Hg(II) ions adsorption on modified aerogel were firstly determined. At these conditions the adsorption isotherms were measured and results were fitted with Freundlich and Langmuir isotherm models.

MATERIALS AND METHODS

Materials

Chemicals used for preparation of modified silica aerogel by sol-gel synthesis were tetramethoxysilane (TMOS, 98 %- ABCR) and mercaptopropyltrimethoxysilane (MPTMS, 97 % - ABCR). Other chemicals included methanol (Merck, p.a.), 25 wt. % solution of NH_3 (TKI Hrastnik, p.a.) and distilled water.

The metal ion solutions were prepared by diluting 1g/L of stock solutions with distilled water. The pH adjustments were made with buffer solutions (sodium hydroxide/acetic acid, disodium dihydrogen phosphate/potassium dihydrogen phosphate) of appropriate pH (Merck).

Aerogel preparation

Silica gel doped with mercapto functional groups MPME was synthesised by mixing TMOS, MPTMS, methanol, water and ammonium hydroxide in molar ratio 0.67:0.33:15:4:0.075. The ratio MPTMS/TMOS was 0.5. The apparatus used for sol-gel synthesis is already presented in previous articles (17). Wet gel was aged in MeOH for five days. After that, wet gel was dried with supercritical CO_2 at 40 °C and 100 bars (18). For experiments of adsorption capacity measurements MPME aerogel was ground into powder with size less than 0.25 mm.

Aerogel characterisation

The physico-chemical characteristics of the MPME aerogel adsorbent were determined using standard procedures. The organic and inorganic bonds forming the aerogel structure were studied by Fourier transform infrared spectra (FTIR). From the Differential scanning calorimetry (DSC) and Thermal gravimetry (TG) measurements thermal stability of the aerogel was observed. The pore texture and BET surface area of aerogel adsorbent were determined by nitrogen physisorption.

Adsorption experiments

The adsorption of heavy metals on prepared functionalized silica aerogel MPME was studied by batch technique (19) at room temperature. These laboratory tests for measuring adsorption capacity are designed to be rapid screening methods for the determination of the performance of different adsorbents. Firstly, the effects of contact time and pH of the solution on the adsorption were studied. The results of these studies were used to obtain the optimum conditions for adsorption capacity measurements. Atomic adsorption spectrometer (AAS) and Ion coupled plasma (ICP) were used to analyze the concentration of heavy metals in water solutions.

The percent of adsorbate removal was calculated using Eq. (1)

$$E = (C_0 - C_e) \cdot 100 / C_0 \tag{1}$$

where E is metal ion removal in %, C_0 initial metal ion concentration of test solution and C_e final equilibrium concentration of test solution.

The correlation of equilibrium data by theoretical equations is essential to a practical design and operation of adsorption systems. Two isotherm equations have been tested in the present study, Freundlich and Langmuir.

The Freundlich equation predicts that the concentrations of metal ion on the adsorbent will increase as long as there is an increase in the metal ion concentration in liquid, as represented by Eq. (2)

$$\frac{x}{m} = K_F C_e^{1/n} \tag{2}$$

where x/m is the mass of adsorbate adsorbed per unit mass of adsorbent, K_F is Freundlich capacity factor, C_e is equilibrium concentration of adsorbate in solution after adsorption and $1/n$ represents Freundlich intensity parameter.

The Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness and that all sites are equal, resulting in equal energies and enthalpies of adsorption. The sorption data were analyzed according to the linear form of the Langmuir isotherm, as represented in Eq. (3)

$$\frac{m}{x} = \left(\frac{1}{ab}\right) \cdot \frac{1}{C_e} + \frac{1}{a} \tag{3}$$

where x/m is the mass of adsorbate adsorbed per unit mass of adsorbent, C_e is equilibrium concentration of adsorbate in solution after adsorption, a is a Langmuir constant which is a measure of adsorption capacity expressed in mg/g and b is also Langmuir constant which is a measure of energy of adsorption expressed in 1/mg.

The essential feature of the Langmuir isotherm can be expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter. R_L is calculated using the following Eq. (4).

$$R_L = 1/(1 + bC_0) \tag{4}$$

RESULTS

Aerogel characterisation

In Figure 1 the FTIR investigation of silica aerogel modified with mercapto functional groups MPME is shown. The peaks lower than 1100 cm^{-1} are due to asymmetric, symmetric and the bending modes of SiO_2, respectively. Peaks around 2900 cm^{-1} are related to S-H bonds and

that proofs a successful modification. Only a small peak at around 3500 cm^{-1} corresponds to O H bonding due to the presence of moisture.
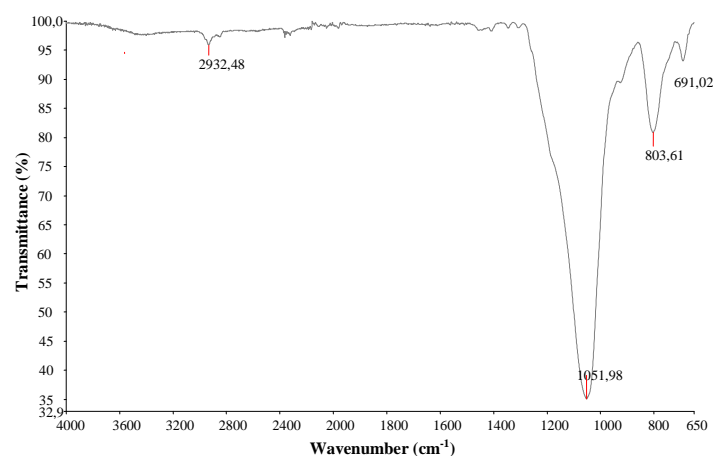

Figure 1: FTIR absorption spectra of aerogel sample MPME.

In Figure 2 DSC and TG curves for aerogel sample MPME are shown. It can be observed that there is a very little weight loss up to a temperature of 300 °C and a further increase of temperature causes weight loss along with exothermic peak corresponding to the oxidation of surface organic (-SH) groups.
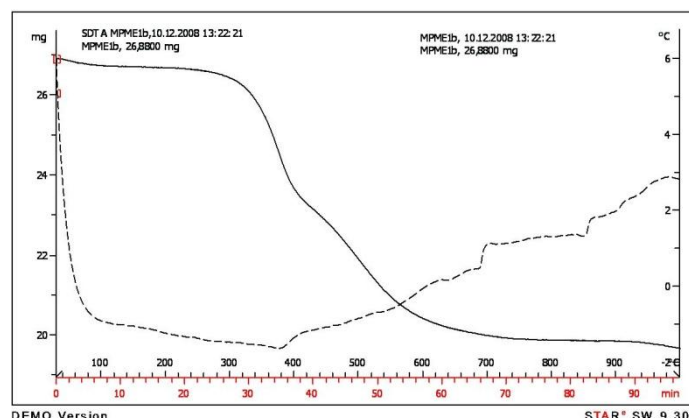

Figure 2: DSC-TG measurement of aerogel sample MPME.

Specific surface area, total pore volume and pore diameter were determined by nitrogen physisorption at -196 °C using a Micrometrics TriStar 3000 instrument. The BET surface area of MPME aerogel is 518 m^2/g, pore volume is 1.88 cm^3/g and average pore size is 14.5 nm. By adding co-precursor MPTMS, specific surface area, pore volume and average pore size decrease comparing to unmodified SiO$_2$ aerogel, because co-hydrolysis of MPTMS and TMOS proceeds one after another and thus results in different microstructures.

Removal of heavy metal ions from water solutions

From Figure 3 it can be seen, that the initial rate of adsorption was very fast. The removal of Hg(II) ions is almost 100 % after 15 minutes and for Cu(II) ions 77.7 %. The equilibrium was reached after 2 hours for Cu(II) ions and after 1 hour for Hg(II) ions. The reason for not

reaching the equilibrium time within a few minutes can be explained by the steric hindrance of the ligand within the matrix as compared to free ligands in solution.
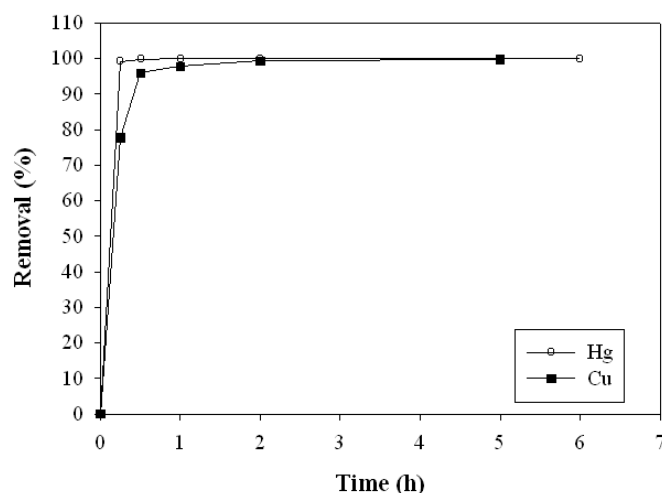

Figure 3: Effect of contact time on removal of heavy metals by aerogel MPME.

The results of pH effect on adsorption are presented in Figure 4. As it can been observed, the percentage adsorption generally increases with pH. These results are in agreement with the fact that metal ions are adsorbed by ion-exchange mechanism.
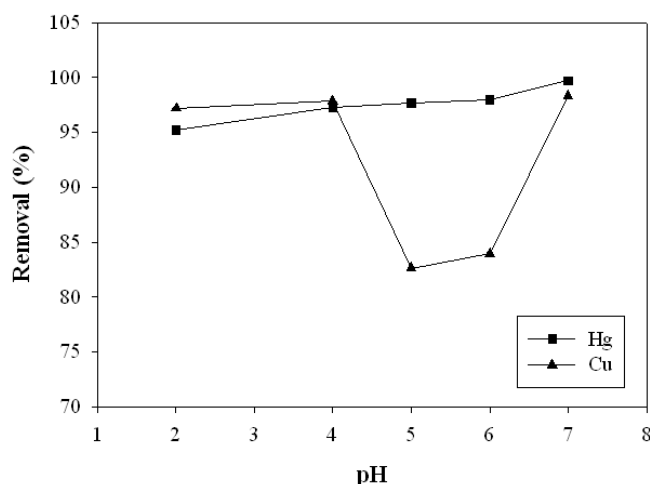

Figure 4: Effect of pH on removal of Cu(II) and Hg(II) ions by aerogel MPME.

When pH increases in the range of 2 to 6, metal is present predominantly as metal ions in the solution and also a concentration of H^+ ions will increase proportionally, which effects on competition between H^+ and M^+ ions for active adsorption sites on surface of aerogel. That consequently can influence on metal ions removal. The percent removal of Cu(II) ions decreases by increasing pH above 4. The reason may be also partial hydrolysis of M^+, resulting in the formation of MOH^+ and $M(OH)_2$. At pH between 6 and 7, percent removal increases again, because the formation of soluble hydroxyl complexes occurs. Higher adsorption of Hg(II) ions at higher pH values may imply that metal ions interact with adsorbent by chelating mechanism. As we want to adsorb metal ions on the adsorbent, the optimum pH is under pH 7 that is 4 in case of Cu(II) ions and 6 in case of Hg.

For determining the effect of adsorbent dose on adsorption and adsorption isotherms, the samples of aerogel and Cu(II) ions solution were prepared in range 0.2-5 mg/mL, with initial metal concentration 50 mg/L and pH 4. The results for percent removal of Cu(II) ions with regard to adsorbent dose are shown on Figure 5. They show the increase of percent removal with adsorbent dose and reaching 100 % removal at adsorbent dosage of ~2 mg/mL. In case of Hg(II) ions, aerogel dosages were between 0.05 and 1.25 mg/mL, initial metal concentration was also 50 mg/L and pH of the solution was 6. The results for percent removal of Hg(II) ions with regard to adsorbent dose are also shown on Figure 6. It can be seen that in case of Hg(II) ions, a 100 % removal is reached already with an adsorbent dosage of ~0.5 mg/mL. Obviously, percent removal of heavy metal ions increases with the increase in adsorbent dose due to a greater number of available exchangeable sites. Moreover, the larger the surface area, the greater availability of the exchangeable sites is.
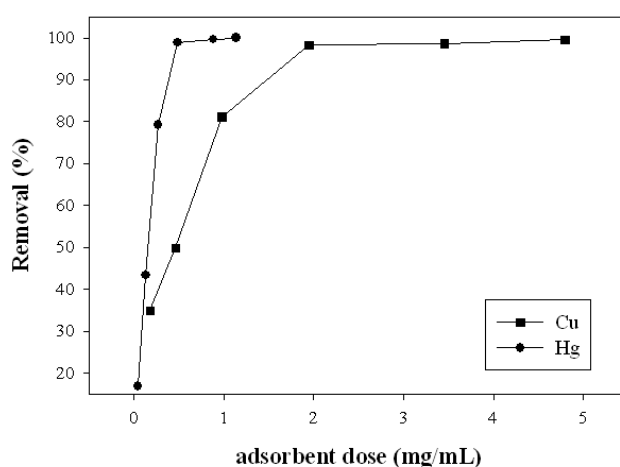

Figure 5: Effect of adsorbent MPME dose on removal of Cu(II) and Hg(II) ions.

Freundlich and Langmuir isotherm constants were determined from Freundlich and Langmuir isotherms in order to compare the obtained results with other adsorbents used for adsorption of heavy metal ions. The isotherms, presented on Figure 6 and 7, indicate that adsorption increases with an increase in equilibrium concentration of the adsorbate. The values of constants obtained from intercept and slope of the plots and values of R_L calculated according to Eq. 4 are given in Table 1. If the R_L values lie between 0 and 1, as in our case, then the adsorption process is favourable.
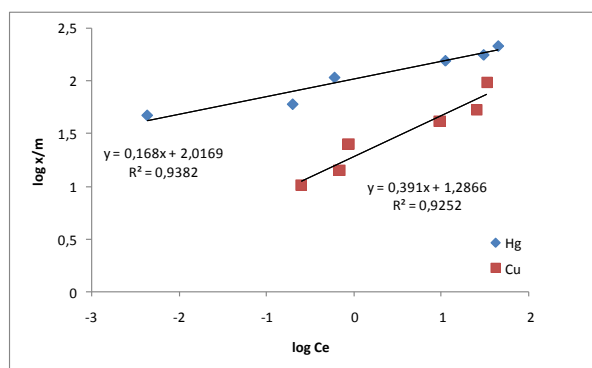

Figure 6: Freundlich isotherms for adsorption of Cu(II) and Hg(II) ions.
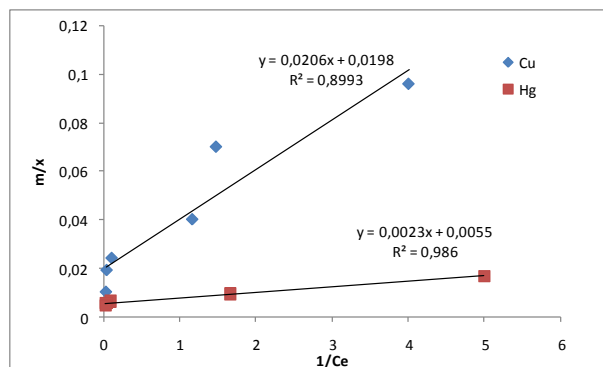
Figure 7: Langmuir isotherms for adsorption of Cu(II) and Hg(II) ions.

Table 1: Freundlich and Langmuir isotherm constants for adsorption of Cu(II) and Hg(II) ions on mercapto aerogel MPME.

Freundlich constants			
Metal ions	K_f (mg/g)(L/mg)$^{1/n}$	$1/n$	R^2
Cu	19.35	0.39	0.92
Hg	96.73	0.20	0.93
Langmuir constants			
Metal ions	a (mg/gm)	b (1/mg)	R^2	R_L
Cu	51.02	0.95	0.90	0.021
Hg	181.81	2.39	0.99	0.008

As it can been seen from the results, mercapto aerogel adsorb Hg ions in greater extent compared to Cu ions. But compared to other known adsorbents, modified silica aerogel with mercapto functional groups is a very efficient adsorbent of both Cu(II) and Hg(II) ions from water (10, 19-21).

On the basis of regression analysis of experimental data on the adsorptive behaviour of metal ions on modified SiO_2 aerogel with mercapto groups, it may be concluded that the adsorption behaviour of Cu(II) and Hg(II) ions on modified aerogel is in good agreement with both models, Freundlich and Langmuir.

CONCLUSION

The ability of modified SiO_2 aerogel with mercapto functional group (-HS) to remove Cu(II) and Hg(II) ions from water was investigated by batch technique. Modified SiO_2 aerogel was prepared by incorporation of co-precursor MPTMS in standard sol-gel synthesis and then dried by supercritical CO_2, by which excellent properties of aerogel were preserved. Optimal conditions for removal of Cu(II) and Hg(II) by this aerogel were determined. Cu(II) removal was the most efficient at pH 4 and Hg(II) removal was efficiently performed at the initial pH 6. The equilibrium time for both heavy metal ions was reached within 2 h. The equilibrium isotherm data were fitted well by Freundlich and Langmuir isotherm model as evidenced from the good agreement between the experimental and calculated values. The results of the present investigations illustrate that modified silica aerogel with mercapto functional groups could be used as an adsorbent for the effective removal of Cu(II) and Hg(II) ions from aqueous solutions.

REFERENCES

[1]   BINGAU, P., LONSDALE, H., PINHO, M., (Eds.), Synthetic Membranes: Science, Engineering and Application, NATO ASI Series, Series C: Mathematical and Physical Science, vol. 181, D. Ridelo Publishing Company, Dordrecht, 1986.

[2]   HARTIGER, L. Handbuch der Abwasser - und Recycling Technik Munchen, Carl Hanser Verlag, Wien, **1991**.

[3]   KIFFS, R.J., General inorganic effluents, in: Barnes D., Forster C.F., Hrudey S.E. (Eds.), Surveys in Industrial Wastewater Treatment - Manufacturing and Chemical Industries, vol. 3, Lonngman, New York, NY, 1987 (Chapter 1).

[4]   NAMASIVAYAM, C., RANGANATHAN, K., Environ. Technol., Vol. 16, **1995**, p. 851.

[5]   MEENA, A. K., MISHRA, G.K., RAI, P.K., RAJAGOPAL, C., NAGAR, P.N., J.Hazard. Mater. B, Vol. 122, **2005**, p.161.

[6]   BASSO, M.C., CERRELLA, E.G., CUKIERMAN, A.L., Ind. Eng. Chem. Res., Vol. 41, **2002**, p. 3580.

[7]   PARAB, H., JOSHI, S., SHENOY, N., VERMA, R., LALI, A., SUDERSANAN, M., Bioresour. Technol., Vol. 96, **2005**, p.1241–1248.

[8]   SAEED, A., IQBAL, M., WAHEED, M.W., J. Hazard. Mater. B1, Vol.17, **2005**, p. 65.

[9]   SCIBAN, M., KLASMJA, M., SKRBIC, B., J. Hazard. Mater. B1, Vol. 36, **2006**, p. 266.

[10] ANIRUDHAN, T.S., DIVYA, L., RAMACHANDRAN, M., J. Hazard. Mater., Vol. 157, **2008**, p. 620.

[11] YANG, R.T., Adsorbents: Fundamentals and Applications, Wiley-Interscience, **2003**.

[12] RUTHVEN, D.M., Principles of Adsorption and Adsorption Processes, Wiley-Interscience, **1984**.

[13] BANUM, S.J., Introduction to Organic and Biological Chemistry, third ed., Macmillan Publishing Co., New York, NY, **1982**, p. 541.

[14] SERPONE, N., BORGARELLO, E., PELIZZTI, E., Photoreduction and photodegradation of inorganic pollutants, in: Schiavello, M. (Ed.), Photocatalysis and Environment, Kluwer Academic, Dordrecht, **1988**, p.527.

[15] BERGLUND, F., BERTIN, M., Chemical Fallout, Thomas, Springfield, IL, **1969**.

[16] WHO Environmental Health Criteria 101, Methyl Mercury, Geneva, World Health Organization, **1990**, p.68.

[17] NOVAK, Z., KNEZ, Ž., J. Non-Cryst. Solids, Vol. 221, 1997, p. 163.

[18] METCALF & EDDY, Wastewater Engineering – Treatment and Reuse, fourth edition, **2003**.

[19] ANIRUDHAN, T.S., RADHAKRISHNAN, P.G., J. Chem. Thermodynamics, Vol. 40, **2008**, p. 702.

[20] HATAY, I., GUP, R., ERSÖZ, M., J. Hazard. Mater., Vol. 150, **2008**, p.546.

[21] YANG, H., XU, R., XUE, X., LI, F., LI, G., J. Hazard. Mater., Vol. 152, **2008**, p.690.