Silica Aerogels and Their Application for Different Adsorption Processes

Zoran Novak*, Željko Knez
University of Maribor, Faculty of Chemistry and Chemical Engineering,
Smetanova ul. 17, SI-2000 Maribor, Slovenia
E-mail: zoran.novak@uni-mb.si, Fax: +386 2 2527 774

Silica monolith aerogels with different degrees of hydrophobicity by incorporating methyltrimethoxysilane (MTMS) or trimethylethoxysilane (TMES) in standard sol-gel synthesis were prepared. Excellent properties of the aerogels, obtained with the sol-gel synthesis, were preserved with supercritical drying with CO_2. The degree of the hydrophobicity of the aerogels was tested by measuring the contact angle (θ) of a water droplet with the aerogel surface. The aerogels were also characterised by FTIR measurements. Adsorption capacity measurements show that silica aerogels are excellent adsorbents for different compounds dependent on its degree of hydrophobicity. Hydrophilic silica aerogels are shown to be better adsorbents of water moisture and vapours of volatile organic coumpunds from air than conventional adsorbents. On the other hand, for hydrophobic silica aerogels and mercapto (-HS) modified silica aerogels was proved that they are efficient adsorbents of organic and metal contaminants from water. Compared to the most used adsorbents - granulated active carbon (GAC) and silica gel, aerogels exhibit capacities which enormous exceed that of both mostly used adsorbents.

INTRODUCTION

Silica aerogels are nanostructured materials with open foam like structures having low density (as low as 5 kgm^{-3}), high surfaces area ($\approx$ 1000 m^2g^{-1}) and high porosity (> 95%). These features lead to unique properties, such as small index of refraction (1.01 to 1.1), low elastic modulus (<0.5 MPa), low thermal conductivity (0.01 $Wm^{-1}K^{-1}$) and to excellent accessibility of the inner surface through open porous network. One of the most important properties of silica aerogel is also the possibility to control its hydrophobicity.

Aerogels are synthesized by sol-gel process via hydrolysis of silicon alkoxides followed by condensation to yield polymeric network. A sol-gel is a porous network in a liquid, whose progressive densification leads to a biphasic medium. The process of gelation starts with aggregation of monomers into fractal clusters, which then interpenetrate to some extent and finally link together to form an infinite network. These wet gels are dried by the supercritical method. This technique attenuates the capillary forces and the structure of aerogels is under very little internal stresses that have minor effect on the gel properties.

Aerogels, based on tetramethoxysilane (TMOS) precursor, are hydrophilic and become wet with atmospheric moisture or water, but with appropriate chemical modification, the surface of the aerogel can be rendered hydrophobic so that the water molecules will be repelled [1]. The main reason for hydrophilicity of silica aerogels is the presence of Si-OH groups in aerogel structure as they promote the adsorption of water. By replacing Si-OH groups with hydrolytic stable Si-R groups (R = CH_3), the adsorption of water is hindered and thus

hydrophobic silica aerogels are obtained. The degree of the hydrophobicity of the aerogels was tested by measuring the contact angle (θ) of a water droplet with the aerogel surface.

Small pores, such as micropores and mesopores, result in large surface area responsible for adsorption. Pore size, pore distribution and surface area, as well as pore surface chemistry, are the major factors in the adsorption process. Silica aerogels meet these conditions because these materials have high specific surface areas, they are stable after several adsorption/desorption cycles with no loss of efficiency, they are easy recovered and they exhibit capacities which enormously exceed that of commonly used adsorbents such as granulated active carbon (GAC) and silica gel.

Due to above mentioned remarkable properties, aerogels could, besides other well-known applications [2], serve as good adsorbents for water and other organic vapours [3-4]. With change in hydrophobicity of aerogels they can be used also for removal of organic solvents from water. Aerogels, modified with mercapto (-HS) functional groups could be used for the removal of different heavy metals from water.

The aim of this work is to determine the feasibility of using hydrophilic and/or hydrophobic silica aerogels for cleaning certain organic and metal contaminants from wastewater and air and also for adsorption of water vapour, and to provide adsorption capacity data to compare with GAC and silica gel.

MATERIALS AND METHODS

Silica aerogels of different degree of hydrophobicity were prepared by sol-gel processing a tetramethoxysilane (TMOS - Aldrich, 98%) with methyl groups containing alkoxides methyltrimethoxysilane (MTMS - Aldrich, 98%) and trimethylethoxysilane (TMES – Fluka, 97%). For preparation of silica gels modified with mercapto functional groups mercaptopropyltrimethoxysilane (MPTMS, 97 % - ABCR) was used. Other chemicals include methanol (Merck, p.a.), 25 wt.% solution of NH_3 (TKI Hrastnik, p.a.) and distilled water.

Silica gels doped with methyl groups were synthesised by mixing TMOS, MTMS or TMES, methanol, water and ammonium hydroxide in different molar ratios. In order to prepare silica aerogels with different degrees of hydrophobicity, the molar ratios MTMS (or TMES):TMOS were varied as shown in Table 1.

Silica gel doped with mercapto (-HS) functional groups MPME was synthesised by adding coprecursor MPTMS, in standard sol gel procedure described above.

The apparatus used for sol-gel synthesis is already presented in previous articles [5]. Alcogels were aged in methanol for five days at room temperature. The second step in the production of aerogels was the drying of wet gels. In supercritical carbon dioxide drying, alcohol from the structure of the gel was replaced by carbon dioxide at 40 °C and 100 bars [5].

RESULTS

Characterisation of aerogels. For different adsorption processes silica aerogels with different degree of hydrophobicity were prepared by varying molar ratios MTMS/TMOS or TMES/TMOS. Hydrophobicity of aerogel adsorbents was tested and contact angles that were measured directly from the photograph image.

The results of the specific surface area, total pore volume and pore diameter measurements (Table 1) show that with the incorporation of MTMS or TMES the specific surfaces are lowered.

Table 1: Properties of different modified silica aerogels.

sample	mol. ratio MTMS /TMOS	contact angle [θ]	BET surface area [m^2/g][1]	pore volume [cm^3/g]	average pore size [nm]	C value
TMOS	0	/	812	3.67	18.1	90.0
MTMS1	2	133	719	2.28	12.7	47.6
MTMS2	5	144	560	1.26	9.0	99.4
MTMS3	10	157	112	0.13	5.8	5.9
MTMS4	∞	173	3.65[2]	0.005	4.8	-457
	mol. ratio TMES/TMOS					
TMES1	5	180	732	2.79	15.3	32.0
	mol. ratio MPTMSM/TMOS					
MPME1	0,5		518	1,88	14,5	44
MPME2	1		260	2,00	30,7	41
MPME3	2		79	0,44	22,2	44

[1] Determined using Braunauer-Emmett-Teller (BET) method using N$_2$ gas adsorption.
[2] Nitrogen sorption is not appropriate method, because of highly microporous material.

It can also be observed that with TMES modification compared to MTMS modification higher degree of hydrophobicity can be achieved at lower molar ratios and properties such as specific surface and pore volume are not significantly changed.

Adsorption of water vapour.
To compare adsorption capacities of water vapour from the air, hydrophilic TMOS based aerogel were used as well as two commercial adsorbents. From Figure 1a the affinity of different adsorbents for water vapour can be seen.
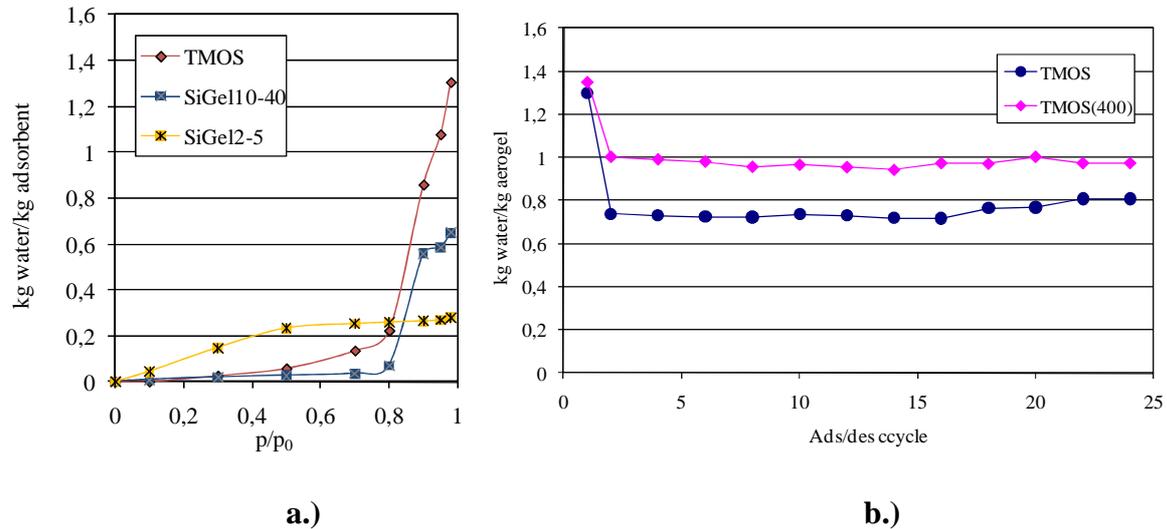

a.)   **b.)**

Figure 1. a.) water vapour adsorption on hydrophilic silica aerogel (TMOS) and two commercial silica gels and b.) adsorption capacities of TMOS aerogel during repeated adsorption/desorption cycles.

The saturated amount of water adsorbed on aerogels is the highest in the case of hydrophilic TMOS based silica aerogel (~1.35 kg/kg). The type of adsorption isotherm for commercial silica gel 10-40 is the same as that for silica aerogel (type V), but the saturated amount of water adsorbed is much lower and it is around 0.6 kg of water/kg of adsorbent.

Figure 1b shows results of repeated adsorption/desorption cycles of water vapour. The adsorptivity of silica aerogels decreased markedly after the first cycle, but after this drop, adsorptivity remained more or less stable in the next 25 cycles.

Adsorption of solvents from water.

Two silica aerogel samples with the highest degree of hydrophobicity, a sample prepared using pure MTMS (MTMS4) with contact angle of 173° and a sample prepared using TMES/TMOS = 5 (TMES1) with contact angle of ~180°, were used for the adsorption studies of various solvents from water.

Freundlich isotherms for different adsorbates adsorbed from water with hydrophobic silica aerogel MTMS4 are shown in Figure 2. The lines are a least-squares fits to the data and correlation coefficients are given. The Freundlich constants, K_f and $1/n$, are determined from the slope and intercept of this plots.

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

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 $1/n$ represent Freundlich intensity parameter
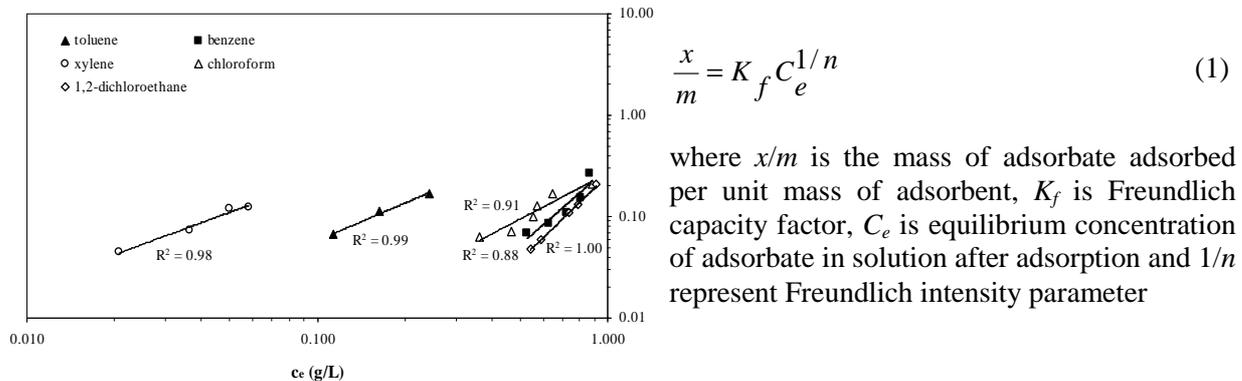
Figure 2: Freundlich isotherm plot for adsorption of different adsorbates from aqueous solutions by a superhydrophobic silica aerogel MTMS4. The lines are a least-squares fits to the data and correlation coefficients are given.

Table 2 Freundlich constants and adsorption capacities for two different superhydrophobic silica aerogels MTMS4 and TMES1 compared to GAC.

Adsorbate	MTMS4 aerogel		TMES1 aerogel		GAC[b]	
	K_f / adsorption capacity (mgg^{-1})[a]	$1/n$	K_f / adsorption capacity (mgg^{-1})[a]	$1/n$	K_f / adsorption capacity (mgg^{-1})[a]	$1/n$
toluene	1344	1.7	2704	1.7	26.1	0.44
benzene	300	2.5	311	2.9	1.0	1.6-2.9
ethylbenzene	4025	1.2	6215	1.3	53.0	0.79
chloroform	269	1.5	676	2.8	2.6	0.73
xylene	2514	1.0	3143	1.0	174.0-230.0	0.42-0.75
chlorobenzene	25194	2.9	37472	2.4	91.0	0.99
1,2-dichloroethan	256	2.8	219	5.8	3.6	0.83
trichloroethylene	1582	1.3	2002	1.6	28.0	0.62

[a] For adsorbate concentration of 1 g/L.
[b] Adapted from Dobbs and Cohen (1980) and LaGrega et al. (2001).

The capacities of superhydrophobic aerogel samples MTMS4 and TMES1 compared with GAC for the concentration of 1 gL^{-1} are shown in Table 2 for each of adsorbate tested.

The adsorption capacity of both superhydrophobic silica aerogels MTMS4 and TMES1 exceeds that for the GAC for all of the adsorbates tested. From the comparison between Freundlich constants for GAC and hydrophobic silica aerogels it can be concluded that aerogels are much better adsorbents. Adsorption capacity of aerogels is from 15 to 400 times higher.

Adsorption of BTEX vapours from air.
For the removal of different BTEX vapours from air various adsorbents were tested. The adsorption capacities of benzene vapours of all six aerogels and two commercial adsorbents (silica gel with mean particle sizes 100-200 µm and activated carbon – Bayer 01E 1179) tested are presented in Figure 3. The results show that the adsorbent with the highest adsorption capacity of benzene vapours from air is hydrophilic silica aerogel, and its adsorption capacity exceeds that of AC or SG significantly. With the increased degree of hydrophobicity, the performance of aerogels in sense of adsorption benzene vapours is lowered, probably due to the reduction of BET surface areas and micropore structure (see Table 1). Contrary to MTMS based aerogels, for TMES based silica aerogel which is also super hydrophobic, higher specific surface area is determined and consequently also higher adsorption capacity of benzene vapour. Because of its hydrophobicity it does not adsorb water vapour from waste gas streams, which is ubiquitous in indoor environments and in many types of industrial gas streams and could alter the adsorption capacity [6]. From this point of view, the hydrophobic aerogel (TMES1) is superior adsorbent of benzene or toluene vapours compared to other used adsorbents, especially to two commercial ones (SG and AC).
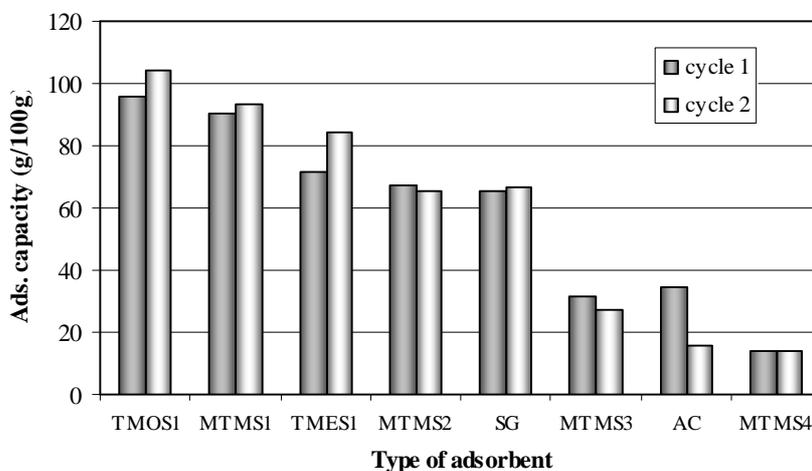

Figure 3: Comparison of adsorption capacities of different adsorbents used for the removal of benzene from air in two repeated adsorption/desorption cycles.

The comparison between two aerogel adsorbents (TMOS1 and TMES1) and two commercial adsorbents (SG and AC) used as adsorbents of diferent BTEX vapours is given in Table 3. The amounts adsorbed on adsorbents are almost the same irrespective of adsorbate (each of BTEX compound). The highest adsorption capacity has aerogel TMOS1 followed by aerogel TMES1, which adsorbs approximately 10-20 % less, but it is moisture resistant comparable to other adsorbents

Table 3: Comparison of adsorption capacities of four different adsorbents used for removal of BTEX vapours from air.

Adsorbent	Adsorption capacity [g/100g]*			
	Benzene	Toluene	Ethylbenzene	Xylene
TMOS1	95.91	91.14	93.98	102.54
TMES1	71.23	80.89	69.85	74.35
SG	65.39	64.64	64.85	64.12
AC	34.34	36.69	35.14	35.40

* STDEV ≤ 2.

The results in Figure 4 show that with the increased degree of hydrophobicity of the silica aerogels based on MTMS, the adsorption capacity decreases, which is probably due to the reduction of BET surface areas and micropore structure. The adsorption on micropores is limited by small micropore surface area available, although the location of adsorbate molecules occurs with stronger interaction due to hydrophobicity of the surface than in case of mesopores of hydrophilic silica aerogel with higher surface area. Contrary to MTMS based aerogels, for TMES based silica aerogel which is also superhydrophobic, higher specific surface area is determined and consequently also higher adsorption capacity of benzene vapour.
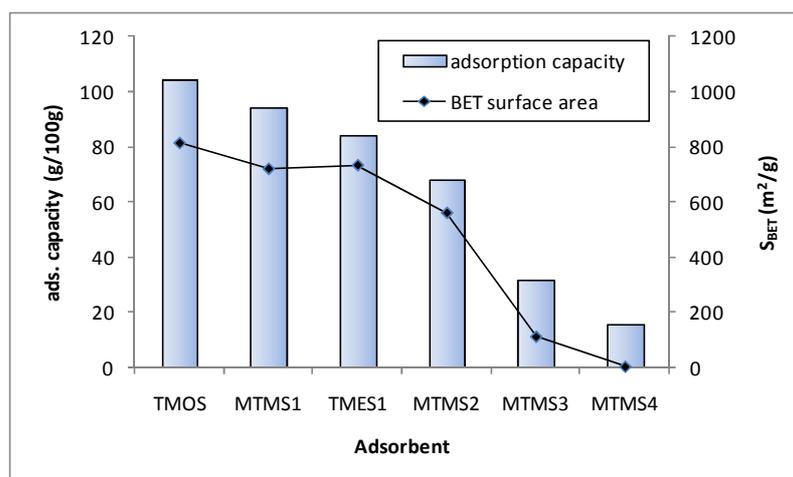

Figure 4. Dependence of adsorption capacity on BET surface area for the adsorption of benzene vapours on aerogel adsorbents with different hydrophobicity.

Adsorption of heavy metals from water.
The adsorption of heavy metals on prepared functionalized silica aerogel MPME was studied by batch technique [7] 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. At first it was determined for which heavy metal ions is the aerogel adsorbent selective and most effective. Mercapto modified aerogel was used as an adsorbent for the removal of seven different heavy metal ions.

From Figure 5 it can be seen that mercapto aerogel MPME1 is the best adsorbent for the removal of Cu and Hg ions. That is why only heavy metal ions of these two metals were used for further examination.
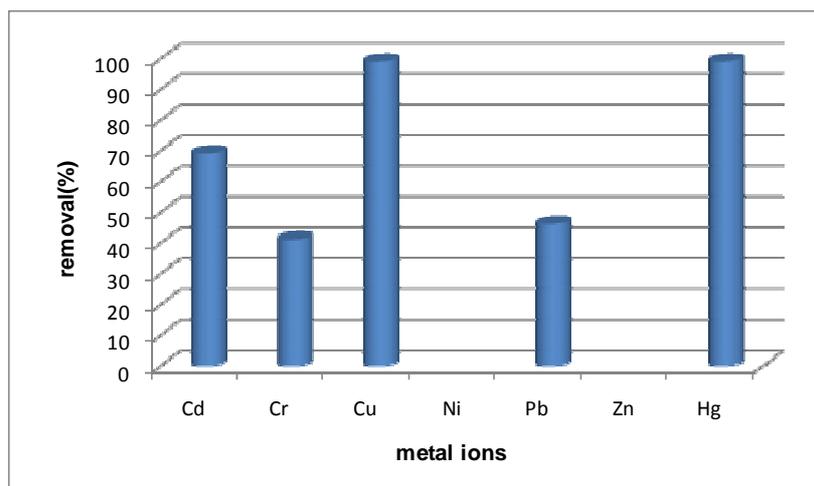
Figure 5. The effect of using different heavy metal ions on percent removal of heavy metals by mercapto aerogel.

To compare the obtained results with other adsorbents used for adsorption of heavy metal ions, Freundlich and Langmuir isotherm constants should be determined from Freundlich and Langmuir isotherms.
From the results it can be observed that mercapto aerogel adsorbs Hg ions in greater extent compared to Cu ions. But compared to other known adsorbents (listed in Table 4), modified silica aerogel with mercapto functional groups is a very efficient adsorbent of both Cu(II) and Hg(II) ions from water.

Table 4. Comparison of Langmuir constants q (i.e. adsorption capacity) for adsorption of Cu and Hg ions onto various types of waste biomass and synthesised materials reported in literature [8].

Adsorbent	q_0 (mg/g)
For Cu ions	
Rubber (*Hevea brasiliensis*) leaf powder	5.65
Tea waste	18
Litter of natural trembling poplar forest	29.76
Silica gel functionalized with 4-phenylacetophynone 4-aminobenzoylhydrazone	0.76
Hybrid surfactant-templated mesoporous silica	25.03
Activated carbon cloths	11.05
Polybenzoxazine aerogel	1.50
MPME aerogel (our research)	**51.02**
For Hg ions	
Biomatrix from rice husk	36.10
Guava (*Psidium guajava*) bark	3.36
Extracellular biopolymer poly(c-glutamic acid)	96.79
Poly(glycidylmethacrylate-methylmethacrylate), p(GMA-MMA-EGDMA) magnetic beads	148.60
MPME aerogel (our research)	**181.81**

CONCLUSION

With variation in molar ratios of precursors TMOS, MTMS and TMES monolith silica aerogels with different degrees of hydrophobicity were obtained. It was observed that molar ratios and the type of the precursor, water, solvent and catalyst affect hydrophobicity and structural properties of the aerogels significantly.

Hydrophilic silica aerogel that was used for water vapour adsorption exhibit adsorption capacity around 1.3 kg of water/kg of aerogel, which is markedly higher than that of any known adsorbent today. What is more, the adsorptivity of hydrophilic silica remains practically unchanged after 25 repeated ads/des cycles.

Superhydrophobic aerogels are shown to be very efficient adsorbents of volatile organic compounds (VOCs) from water. The adsorption capacity of both hydrophobic silica aerogels tested exceeds the capacity of comparable GAC for more than ~50 times. By complete regeneration with hot inert gas, silica aerogel adsorbents could be reused in many adsorption/desorption cycles without any significant loss of adsorptivity and BTEX vapours could be recovered as liquid.

The investigation has also shown that silica aerogel adsorbents are very efficient for the removal of toluene and benzene vapours from waste gas streams. The possibility to tailor hydrophobicity and consequently moisture resistance of silica aerogel adsorbents, their repeated use in many adsorption/desorption cycles make them superior to conventional adsorbents as silica gel and activated carbon.

The results of the investigation also 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] SCHWERTFEGER, F., EMMERLING, A., GROSS, J.,SCHUBERT, U., FRICKE, J. in: Y.A. Attia (Ed.), Sol-Gel Processing and Applications, Plenum Publishing Company, New York, **1994**, p.343.

[2] FRICKE, J. (Ed.), Aerogels, Proceedings of the 1st International Symposium on Aerogels, ISA1, Wűrzburg, 1985; Springer Proceedings in Physics, Springer-Verlag: Berlin, Vol. 6, **1986**

[3] ATTIA, Y.A., AHMED, M.S., ZHU, M., in: ATTIA, Y.A. (Ed.), Sol-Gel Processing and Applications, Plenum, New York, **1993**, p. 311.

[4] KNEZ, Ž., NOVAK, Z., J. Chem. Eng. Data, Vol 46, **2001**, p.858.

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

[6] SERRANO, D.P., CALLEJA, G., BOTAS, J.A., GUTIERREZ, F.J., Ind. Eng. Chem. Res. Vol.43, **2004**, p.7010

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

[8] ŠTANDEKER, S.,VERONOVSKI, A., NOVAK, Z., KNEZ, Ž., Desalination, Vol. 269, 2011, p.223