

# Hydrophobic Silica Aerogels – Solvent Removal From Water

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Hydrophobic silica monolith aerogels were prepared by incorporating methyltrimethoxysilane (MTMS) in standard sol-gel synthesis following by drying of gels in supercritical CO<sub>2</sub> at 40°C. The hydrophobicity of the aerogels was tested by measuring the contact angle ( $\theta$ ). Adsorption capacity measurements show that hydrophobic silica aerogels are excellent adsorbents for different toxic organic compounds from water. In comparison to granulated active carbon (GAC) they exhibit capacities which are more than 70 times higher for all tested compounds.

## INTRODUCTION

Silica aerogels are nano-structured materials with open foam like structures having low density (as low as 5 kgm<sup>-3</sup>), high surface area ( $\approx 1000 \text{ m}^2\text{g}^{-1}$ ) and high porosity (> 95%). These features lead to unique properties and due to excellent accessibility of the inner surface through open porous network, the most important feature of silica aerogel is the possibility to control its hydrophobicity.

The main reason for hydrophilicity of silica aerogels is the presence of Si-OH groups in aerogel structure, because they promote the adsorption of water. By replacing Si-OH groups with hydrolytic stable Si-R groups (R = CH<sub>3</sub>), the adsorption of water is hindered and thus hydrophobic silica aerogels are obtained.

The hydrophobicity of the aerogels can be achieved by two methods: (i) surface chemical modification of the aerogels by gaseous reagents and (ii) surface modification of the colloidal particles by incorporating certain chemical additives in the alcisol itself [1-4]. Therefore, with appropriate surface chemical modification, the surface of the aerogel can be rendered hydrophobic so that the water molecules will be repelled [5].

Hydrophobic aerogels are shown to be efficient adsorbents of solvents from water [6]. A common approach to remove hazardous organic compounds from water is the filtration by using porous materials [7,8]. For this reason, and because it is relatively inexpensive product, granulated activated carbon (GAC) is usually selected as a filter medium and it is the standard for comparison. Sol-gel derived porous materials are being developed for special filtration applications because they have very high specific surface areas, and they can readily be made as membranes for filtration applications [6].

The aim of this work is to determine the feasibility of using hydrophobic silica aerogels for cleaning certain organic contaminants from wastewater, and to provide adsorption capacity data to compare with GAC. We have prepared silica aerogels of different degree of hydrophobicity with the contact angles between 0 and 173° by sol-gel route because it enabled a better control of hydrophobicity of the aerogel and was less expensive. Excellent properties of aerogels, obtained with the sol-gel synthesis, were preserved with supercritical drying with CO<sub>2</sub>. For the adsorption experiments of different organic toxic compounds from water, we used silica aerogels based on pure MTMS, which have the highest degree of hydrophobicity.

## I - MATERIALS AND METHODS

### Aerogel preparation

Silica aerogels of different degree of hydrophobicity were prepared by sol-gel processing a tetramethoxysilane (TMOS - Aldrich, 98%) with methyl groups containing alkoxide, methyltrimethoxysilane (MTMS - Aldrich, 98%). Other chemicals include methanol (Merck, p.a.), 25 wt.% solution of NH<sub>3</sub> (TKI Hrastnik, p.a.) and distilled water.

Silica gels doped with methyl groups were synthesized by mixing TMOS, MTMS, methanol, water and ammonium hydroxide in different molar ratios. In order to prepare silica aerogels with different hydrophobic properties, the molar ratio MTMS:TMOS:MeOH:H<sub>2</sub>O:NH<sub>4</sub>OH was varied systematically as shown in Table 1.

**Table 1:** Molar ratios for preparation of MTMS/TMOS based silica aerogels.

Serial number	MTMS/TMOS ( <i>M</i> )	Si	TMOS	MTMS	MeOH	H <sub>2</sub> O	NH <sub>4</sub> OH
1	0.15	1	0.870	0.130	5.674	3.869	0.027
2	0.35	1	0.741	0.259	5.352	3.741	0.048
3	0.5	1	0.667	0.333	5.167	3.667	0.06
4	1	1	0.5	0.5	4.75	3.5	0.088
5	1.5	1	0.4	0.6	4.5	3.4	0.104
6	2	1	0.333	0.667	4.333	3.333	0.115
7	5	1	0.167	0.833	3.917	3.167	0.143
8	10	1	0.091	0.909	3.727	3.091	0.155
9	∞	1	0	1	3.5	3	0.17

First a solution containing NH<sub>4</sub>OH and H<sub>2</sub>O was prepared. In a separate vessel, TMOS and MTMS were mixed and stirred at room temperature. To this solution MeOH was added. After homogenisation the NH<sub>4</sub>OH solution was added and the mixture was stirred for several minutes, and then poured into moulds where the gel was formed within 10 and 50 minutes. Wet gels were aged in MeOH for 5 days at room temperature. They were then dried supercritically in an autoclave at 40 °C and 100 bars [9].

The hydrophobicity of the aerogels was tested by measuring the contact angle ( $\theta$ ) of a sessile drop of water on the surface of a monolithic aerogel. For each measurement, a photograph of the droplet was taken and contact angle was measured directly from the photographic image.

The silica aerogel was ground into powder for experiments of adsorption capacity measurements.

### **Determining adsorption capacity**

Laboratory tests for measuring adsorption capacity are designed to be rapid screening methods for the determination of the performance of different adsorbents. A conventional batch equilibration procedure was used as isotherm testing. We have determined adsorption capacity of silica aerogel based on MTMS with the highest degree of hydrophobicity for different adsorbates: toluene, benzene, xylene, 1,2-dichloroethane and chloroform.

To achieve accurate results, the adsorption measurements had to be made under equilibrium conditions. Therefore, the first step was to determine the minimum contact time required to establish equilibrium conditions. To determine the optimum contact time, series of liquid samples, in our case prepared stock solutions, were exposed to the same adsorbent treatment dosage for different time periods using same test conditions (concentration, temperature, etc.). For different adsorbates the contact time was different and varied from half an hour to seven hours. Once the optimum contact time was determined, the next step was to measure the total adsorption capacity of adsorbent for different adsorbates. Different amounts of adsorbent were added in glass containers (between 0.005% and 2%). The prepared stock solution of adsorbate in water with initial concentration ( $C_0$ ) determined by GC/MS (concentration lower than solubility) was added to each container. These solutions were then thoroughly mixed by shaking capped containers under identical process conditions. After reaching equilibrium, a certain amount of solution was filtered and withdrawn for the analysis by GC/MS to determine the final concentration ( $C_e$ ).

For the purpose of comparing the adsorption capacity of hydrophobic silica aerogel based on MTMS with GAC, the Freundlich adsorption model is used because it takes into account the heterogeneity of real surfaces for adsorption [10]. The procedure is based on the determination of the amount of adsorbate removed by the powdered adsorbent, by measuring the concentration before and after exposure.

Derived empirically in 1912, the Freundlich isotherm is defined as follows:

$$\frac{x}{m} = K_f C_e^{1/n} \quad (1)$$

where  $x/m$  is 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. The constants in Freundlich isotherm can be determined by plotting  $\log(x/m)$  versus  $\log C_e$  from the best-fit straight line.

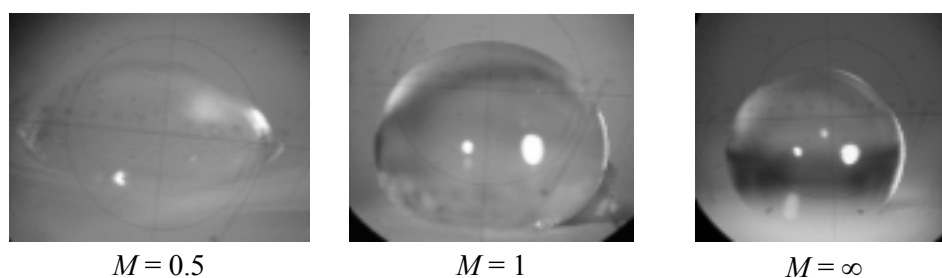
## II – RESULTS AND DISCUSSION

### Effect of MTMS/TMOS molar ratio on hydrophobicity

In order to obtain monolithic hydrophobic silica aerogels with different degree of hydrophobicity, the molar ratio MTMS/TMOS ( $M$ ) was varied from 0 to 10 and its effect on hydrophobicity was studied. Superhydrophobic silica aerogel was prepared using  $M = \infty$  (pure MTMS). For value of  $M = 0.15$ , it was impossible to obtain a contact angle as the water was immediately adsorbed by the aerogel, leaving a white mark where the water was adsorbed. It was found that  $\theta$  increased with the increased  $M$  values. Table 2 gives the results of  $\theta$  values measured directly from the photograph. Figure 1 demonstrates the contact angle for low ( $M = 0.5$ ), medium ( $M = 1$ ) and high ( $M = \infty$ )  $M$  values of the aerogels. From the figures it is obvious that the sphericity of the water droplet increased with the increased  $M$  values.

**Table 2:** Contact angle ( $\theta$ ) values of the hydrophobic silica aerogels prepared using different  $M$  values.

Serial number	MTMS/TMOS ( $M$ )	Contact angle ( $\theta$ )
1	0.15	0
2	0.35	42
3	0.5	55
4	1	96
5	1.5	110
6	2	133
7	5	144
8	10	157
9	$\infty$	173



**Figure 1:** Photographs showing a water droplet on the surface of silica aerogels prepared using different molar ratios of MTMS/TMOS.

### Adsorption capacity of superhydrophobic silica aerogel

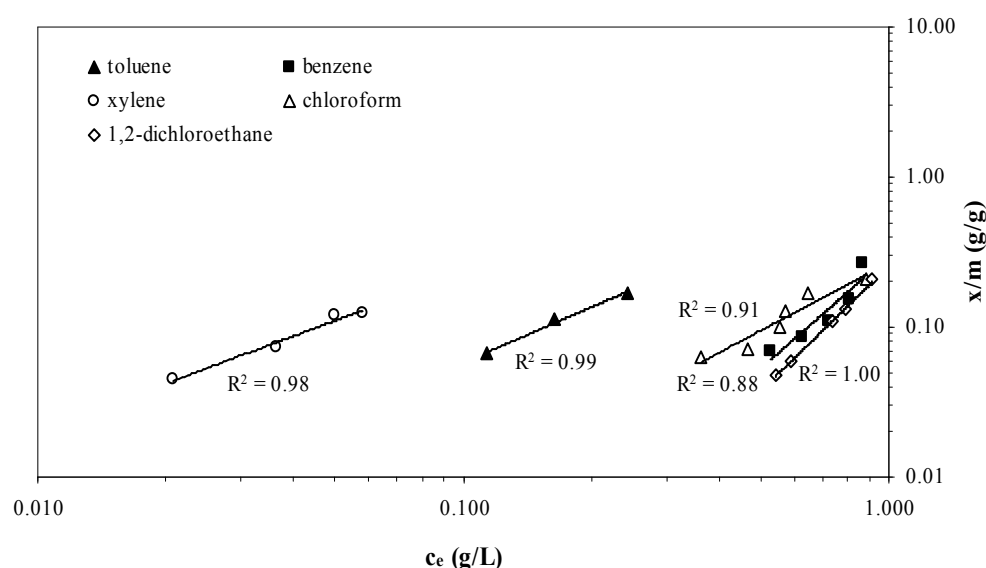
The highest degree of hydrophobicity was determined for the silica aerogel prepared using  $M = \infty$  (serial number 9) with contact angle of  $173^\circ$ . This silica aerogel doped with methyl groups was used for all of the adsorption studies.

First, we have determined optimum contact times for each organic compound (see Table 3) separately as it is written above. There is usually a sharp break in the curve at the optimum contact time.

**Table 3:** Optimum contact times determined for each adsorbate.

Adsorbate	toluene	benzene	xylene	1,2-dichloroethane	chloroform
Contact time (min)	30	60	420	120	180

Freundlich isotherms for different adsorbates adsorbed from water are shown in Figure 2.



**Figure 2:** Freundlich isotherm plot for adsorption of different adsorbates from aqueous solutions by a superhydrophobic silica aerogel. 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 plot. The capacities of aerogel compared with GAC for a concentration of 1 g/L, are shown in Table 4 for each of adsorbate tested.

**Table 4:** Comparison of Freundlich constants and adsorption capacities for hydrophobic silica aerogel and GAC.

Adsorbate	Aerogel (serial number 9)			GAC <sup>b</sup>		
	Freundlich constants		Adsorption capacity (mg/g) <sup>a</sup>	Freundlich constants		Adsorption capacity (mg/g) <sup>a</sup>
	$K_f$	$1/n$		$K_f$	$1/n$	
toluene	975	1.22	975	26.1	0.44	26.1
benzene	300	2.51	300	1.0	1.6-2.9	1.0
xylene	2541	1.05	2541	174-200	0.42-0.53	174-200
1,2-dichloroethane	256	2.77	256	3.6	0.83	3.6
chloroform	269	1.50	269	2.6	0.73	2.6

<sup>a</sup>For adsorbate concentration of 1 g/L.

<sup>b</sup>Adapted from Dobbs and Cohen (1980) and LaGrega et al. (2001).

The adsorption capacity of the hydrophobic aerogel tested exceeds that for the GAC for all of the adsorbates tested.

From the comparison between Freundlich constants for GAC and hydrophobic silica aerogel it can be concluded that aerogel is much better adsorbent. Adsorption capacity of aerogel is more than ~70 times higher.  $1/n$  constants for aerogel are in all cases higher than those for GAC.

## CONCLUSION

Hydrophobic aerogels are shown to be very efficient adsorbents of variety of volatile organic compounds (VOC) from water. The adsorption capacity of the hydrophobic silica aerogels exceeds the capacity of comparable GAC, on gram-per-gram basis, for all toxic organic compounds tested. The improved performance of adsorption capacity by the aerogel over GAC ranges from factors of ~70 times. These substantial improvement factors significantly offset the cost factors, which would otherwise favour the use of GAC for large-scale VOC trapping and solvent clean-up applications.

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