Contents lists available at SciVerse ScienceDirect

ELSEVIER





www.elsevier.com/locate/jcis

Application of hydrophobic silica based aerogels and xerogels for removal of toxic organic compounds from aqueous solutions

M.L.N. Perdigoto^a, R.C. Martins^a, N. Rocha^a, M.J. Quina^a, L. Gando-Ferreira^a, R. Patrício^b, L. Durães^{a,*}

^a CIEPQPF, Department of Chemical Engineering, Univ. Coimbra, Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal ^b AST – Active Space Technologies, Rua Coronel Júlio Veiga Simão, 3025-307 Coimbra, Portugal

ARTICLE INFO

Article history: Received 13 February 2012 Accepted 22 April 2012 Available online 4 May 2012

Keywords: Silica based aerogels/xerogels Hydrophobic adsorbents Toxic organic compounds Adsorption isotherms Adsorbent regeneration

ABSTRACT

This work is devoted to the application of hydrophobic silica based aerogels and xerogels for the removal of three toxic organic compounds from aqueous solutions. These materials were tested and characterized regarding their morphology, particle size distribution, surface area and porous structure. The equilibrium tests were carried out at different adsorbate concentrations and the experimental data were correlated by means of Langmuir and Freundlich isotherms. The equilibrium data were well described by Langmuir and Freundlich in most cases. The maximum adsorption capacity by Langmuir model was observed for the adsorption of benzene onto aerogel (192.31 mg/g), though the most promising results were obtained for toluene adsorption due to the greater adsorption energy involved. Comparing these results with other reported results, the hydrophobic silica based aerogels/xerogels were found to exhibit a remarkable performance for the removal of benzene and toluene. In addition, the regeneration of previously saturated aerogel/toluene was also investigated by using an ozonation process. The adsorption/regeneration tests with ozone oxidation showed that the aerogel might be regenerated, nevertheless the materials lost their hydrophobicity and thus different methods should be evaluated in forthcoming investigations.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

The increasing environmental concern on the deterioration of hydric resources is mainly due to the frequent pollutants discharge into the natural aquifers. In this sense, the governmental entities legislated based on a stringent control of the release of liquid effluents by manufacturing industries. On this matter, some organic compounds are significantly toxic and contribute to low biodegradability of industrial wastewaters. Sometimes the application of traditional cleaning methods, generally based on microorganisms, is not sufficiently efficient. Consequently, it is often necessary to apply pre-treatments that can remove some of those cumbersome substances [1,2].

The adsorption of organic compounds has become a relevant option for such pre-treatments, and the activated carbon adsorbent is commonly used for this purpose [3,4]. Currently, silica aerogels are the most studied group of aerogels and have been attracting great interest for wastewaters treatment [5]. In fact, silica-based aerogels have been studied in the adsorption of organic compounds [4,6–14]. Aerogels are the solids materials with the lowest

known density value, due to the existence of a unique nanostructured porous network [15–17]. These materials are composed essentially by micropores and mesopores that originate a large specific surface area, which favor the adsorption process. When used for wastewaters treatment, aerogels may exhibit good efficiency after several cycles of adsorption/desorption and higher adsorption capacities than the commonly used adsorbents [4].

The most relevant properties of silica aerogels are the high porosity (75–99.9%) resulting in a low density (3–500 kg/m³), high specific surface area (800–1000 m²/g) and pore size in the range of 1–100 nm [15]. The combination of its high porosity with the very small size of its pores leads to unique properties, such as low thermal conductivity (0.01-0.02 W/(m K)) and great accessibility to the internal surface through the porous network [12,15,17]. Moreover, one of the most interesting features of silica-based aerogels is the possibility to obtain different degrees of hydrophobicity by appropriately choosing the sol-gel precursors and controlling the chemical synthesis step [12]. Indeed, these unique properties make silica-based aerogels suitable for numerous applications. The low density and thermal conductivity values, make aerogels attractive for building insulation [18,19] and for spacecraft components; whereas their very high and controlled porous structure, make aerogels excellent candidates for catalysts, sensors and filters for gaseous pollutants. Other aerogel's applications include impact absorption, cosmic particles trap, dielectrics and spacers for vacuum electrodes [8].

^{*} Corresponding author. Fax: +351 239798703.

E-mail addresses: marisaperdigoto@eq.uc.pt (M.L.N. Perdigoto), martins@eq.uc.pt (R.C. Martins), nrocha@eq.uc.pt (N. Rocha), guida@eq.uc.pt (M.J. Quina), lferreira@eq.uc.pt (L. Gando-Ferreira), ricardo.patricio@activespacetech.com (R. Patrício), luisa@eq.uc.pt (L. Durães).

^{0021-9797/\$ -} see front matter @ 2012 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.jcis.2012.04.062

Additionally to aerogels, xerogel materials were also considered in this study. Xerogels are prepared using atmospheric pressure drying (APD), while aerogels are produced with supercritical fluids drying (SFD) [20,21]. During the drying of xerogels, the collapse of smaller pores may occur due to the higher capillary tension developed in the evaporation process. This phenomenon results in a contraction of the solid network, making it denser than that of aerogels. In supercritical fluids drying process the solvent is removed as a supercritical fluid, avoiding the formation of meniscus and decreasing the effect of surface tension, allowing the preservation of the porous network [5]. In some chemical systems the porosity of xerogels can reach values close to those of aerogels, in cases where the liquid inside the pores does not exhibit appreciable interaction with the solid structure of the material. This effect is seen when the synthesized gels, before undergo drying, have a highly hydrophobic solid network [22].

Previous research works have shown that hydrophilic aerogels have higher efficiency in removing soluble organic compounds from aqueous solutions, whereas the hydrophobic aerogels are more effective for the removal of water poorly soluble pollutants, including some important volatile organic compounds (VOCs) [6,9].

This work aims to determine the adsorption capacity of silica based aerogels and xerogels obtained by sol–gel technology using methyltrimethoxysilane (MTMS) precursor. With this precursor, the methyl groups linked to silicon are not hydrolyzed and remain in the gel structure, providing a higher hydrophobicity. Additionally, the presence of these groups in the network provides a higher porosity to the material, reducing the density and increasing the flexibility of the solid network, which is an advantageous feature to access new systems [16,20,22–25].

In this work, the removal process of the aromatic solvents benzene, toluene and phenol, when dissolved in water, was assessed. The obtained results are compared with several other studies on the adsorption of benzene [4,8,11,12] and toluene [4,6,8,11–13] with aerogels. In what concerns the phenol adsorption capacity of aerogels/xerogels, no reported data was found in the literature. Finally, one should note that industrially competitive adsorbents are required to be reusable. Thus, the feasibility of materials regeneration by oxidation with ozone and its effect on the adsorption efficiency was also evaluated.

2. Experimental

2.1. Materials

The adsorbent materials used in this work are aerogels and xerogels produced using methyltrimethoxysilane (MTMS) precursor, which were synthesized according to the methodology presented in a previous work [22]. Both aerogels and xerogels were obtained in the form of monoliths, then ground and passed through a 250 μ m sieve.

The three synthetic effluents tested in this work were prepared using reagent grade benzene, toluene and phenol. The used concentrations were selected to simulate real cases reported in the literature [26,27], and were 200 mg/L for benzene/toluene and 100 mg/L for phenol.

2.2. Adsorbents characterization

The characterization of aerogels/xerogels was carried out through different techniques. The microstructure of the material was observed and compared by scanning electron microscopy (SEM), with a *JMS-5310* microscope, from *JEOL*. For SEM analysis, the samples surface was previously coated with an Au film, using Physical Vapor Deposition during 20 s. The bulk density of the

aerogels/xerogels was determined by weight–volume measurements of monolithic pieces of material. The particles size distributions of the ground xerogels and aerogels were evaluated by laser diffraction spectroscopy (LDS), with a *Mastersizer 2000*, from *Malvern Instruments*. To perform this analysis, a small amount of aerogel/xerogel was mixed with water in a beaker using some dispersant drops. This diluted suspension was then analysed in the fluids module of the equipment. The surface area and the pore size distribution were determined by N₂ gas adsorption/desorption isotherms using an *ASAP 2000*, from *Micromeritics*. This technique considers the BET (Brunauer, Emmett and Teller) and BJH (Barrett, Joyner and Halenda) models, respectively, for the referred evaluations. The chemical structure of the materials after the cycles of adsorption/desorption was examined using FTIR spectroscopy by a *FT/IR-4200*, from *Jasco*.

2.3. Adsorption experiments

2.3.1. Determination of organic compounds concentration

The adsorption capacity of aerogels/xerogels was determined through several steps. In this work, a UV–Vis spectrophotometer *T60*, from *PG instruments*, was used to determine the concentration of the organic compounds. The concentrations of benzene, toluene and phenol used in the calibration curves were in the range of 0.002–0.2 g/L, which were analyzed at wavelengths of 254 nm, 261 nm and 272 nm, respectively.

2.3.2. Adsorption equilibrium and kinetics

Preliminary kinetic tests were carried out in order to determine the minimum contact time to establish equilibrium conditions between the adsorbents (aerogels/xerogels) and adsorbates (benzene, toluene and phenol). In these tests, an appropriate amount of adsorbent (0.05 g) and 50 mL of adsorbate solution with initial composition 0.2 g/L were poured into 60 mL glass bottles. These flasks were agitated at 16 rpm in a shaker (*Heidolph – REAX 20*) at room temperature, and samples for analysis were withdrawn after a certain contact time that varied between 1 and 120 min. For the three organic compounds, the preliminary tests showed that the adsorption equilibrium was reached within 60 min. Due to the moderate stirring speed used and because aerogels and xerogels were previously ground, further collapse of their structure was not noticeable to a significant extent.

Equilibrium adsorption curves were obtained by mixing 0.05 g of adsorbent with 50 mL of solution containing adsorbate in different initial concentrations varying between 0.002 and 0.2 g/L. These experiments were carried out under the same conditions as those used in the kinetic experiments (temperature and agitation) and in the optimum contact time -60 min.

2.3.3. Theoretical models

The adsorption isotherms describe how adsorbates interact with adsorbent materials and are fundamental to optimize the use of adsorbents. Thus, the correlation of equilibrium data using isotherm equations is important to the practical design and operation of adsorption systems. In the scope of this study, Langmuir and Freundlich equations were tested.

The Freundlich equation predicts that the concentration of adsorbate on the surface of the adsorbent will increase, while increasing the concentration of the adsorbate in the liquid solution, following a power law as represented by

$$q_e = K_f \times C_e^{1/n} \tag{1}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent, K_f is the Freundlich capacity factor, C_e is the equilibrium concentration of adsorbate in the solution after adsorption and 1/n

represents the Freundlich intensity parameter. The constants of the Freundlich isotherm were determined by linear regression, using the least squares method, applied to the experimental points and based on a logarithmic linearization.

The Langmuir adsorption isotherm assumes the formation of a monolayer of adsorbate on the surface of the adsorbent and that all sites are equivalent. This isotherm is expressed as:

$$q_e = \frac{ab \ C_e}{1 + b \ C_e} \tag{2}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration of adsorbate in solution, *a* represents the maximum adsorption capacity, and *b* is the Langmuir constant that is a measure of the energy of adsorption. As for the Freundlich model, the adsorption data were adjusted by linear regression, doing first the linearization of the Langmuir isotherm, which is represented in

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{C_e}{a} \tag{3}$$

The concentration of adsorbate retained in the adsorbent phase, q_e (mg/g), is calculated according to:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{4}$$

where C_0 and C_e are the initial and the equilibrium concentrations (mg/L), respectively, of adsorbate in solution, *m* is the mass (g) of the adsorbent and *V* (L) is the solution volume.

2.3.4. Regeneration of adsorbents

After the adsorption process, the surface of adsorbents was saturated with the adsorbate and the suspensions were filtrated to separate the adsorbent from the liquid solutions. In order to regenerate the adsorbent materials, the ozonation process was tested by filling a small column with the granular material and introducing in the bottom a stream of ozone of $\sim 54\,g/m_{air}^3,$ during 60 min [28,29]. The ozone stream was produced by a BMT 802N ozone generator and its concentration at the reactor inlet was monitored using a BMT 963 vent ozone gas analyzer. The ozone molecules react with the toluene rings of the adsorbates and break them into carboxylic acids of low molecular weight. But the ozone is not totally consumed, thus the experiment was carried out by installing a gas absorber column. A 10% (w/v) solution of potassium iodide was selected for breaking down the unreacted ozone molecules. This step was carried out to prevent environmental pollution and to garantee the safety in the laboratory [28].

3. Results and discussion

3.1. Adsorbents characterization

3.1.1. Morphology

As it can be seen in Fig. 1, both adsorbent materials consist of a network of interconnected structural units. Thus, when the monolith is grinded, the obtained particles of the adsorbent material are flakes but maintain the microstructure observed in the monoliths. Although the microstructure of both materials is very similar, it is verified that the aerogels have a slightly more porous structure than the xerogels. Thus, it is expected that the flakes of the xerogel have a more closed structure than those of aerogels.

3.1.2. Particles size distribution

The particles size distributions were obtained by LDS and the results are shown in Fig. 2. The average parameters of these distributions are presented in Table 1.



Fig. 1. SEM images of the (a) xerogel and (b) aerogel.



Fig. 2. Particle size distribution curves: (——) fractional and (——) cumulative undersize (<) for (a) xerogels and (b) aerogels.

For the aerogel (Fig. 2b), the fractional distribution curve is bimodal between 1 and 250 μ m: ~15 vol.% of the particles correspond to small particles in a range between 1 and 4 μ m, and the size of the other particles is in the range 8–250 μ m. In the particles size distribution of the xerogel (Fig. 2a), it is observed a narrower distribution curve. This curve is unimodal and asymmetric, with a small tail to the side of the fine particles. However, in accordance with the average parameters in Table 1, it appears that the average particle size (D_{mean}) and the median (D_{50}) of the both materials are very close.

Table 1

Average parameters and width of the particle size distribution for the xerogel and aerogel.

Adsorbent	$\text{Mode} \ (\mu m)$	D ₅₀ (µm)	$D_{\mathrm{mean}}\left(\mu\mathrm{m} ight)$	$D_{90}-D_{10}(\mu m)$
Xerogel	63.2	45.5 ± 0.2	52.3 ± 0.2	105.8 ± 0.5–8.9 ± 0.02
Aerogel	2.8; 100.2	41.7 ± 2.4	57.4 ± 2.9	136.1 ± 7.0–2.8 ± 0.05

Table 2	
Bulk density, specific surface ar	ea and pore size of xerogel and aerogel monoliths.

Adsorbent	Bulk density (kg m ⁻³)	BET surface area ^a $(m^2 g^{-1})$	BJH desorption pore size ^a (Å)
Xerogel	75.5 ± 4.8	426.5 ± 10.6	36
Aerogel	55.9 ± 8.6	512.4 ± 11.0	44

^a From Durães et al. [22].



Fig. 3. Pore size distribution obtained by nitrogen gas desorption for the grinded (_____) aerogels and (_____) xerogels.

3.1.3. Surface area and porosimetry

The obtained results of bulk density for the xerogel and aerogel are presented in Table 2. Concerning the BET surface area and BJH pore size, also presented in Table 2, we considered the results obtained in Durães et al. [22], since the used materials were synthesized with the same procedures and conditions and had similar bulk densities. The aerogel presented a porosity of about 96% and the xerogel of 93% [22]. Even though the aerogel and xerogel samples have close porosity values, for the adsorption process other structural properties are more relevant such as the surface area and the average pore size. The results presented in Table 2 show that the aerogel has a surface area and an average pore size that are 20% and 22% greater than those of xerogel, respectively. This increase is expected to lead to significant differences in their adsorption capacity.

In Fig. 3 are presented the pore size distribution curves for the ground xerogels and aerogels. It is observed that the aerogels had a larger amount of pores with diameters in the range 20-50 Å. Furthermore, it is also visible that the xerogel has a greater fraction of micropores (<20 Å).

The existence of more mesopores in the aerogel (20-100 Å) can be very important in the adsorption process, since this type of pores allows the formation of adsorption layers on the surface by capillary condensation phenomenon [30].

3.2. Adsorption/desorption experiments

3.2.1. Adsorption equilibrium

The description of adsorption equilibrium data with the Langmuir and Freundlich isotherms (Eqs. (1) and (2)) enabled to evaluate the adsorption capacity of the adsorbents aerogel and xerogel



Fig. 4. Experimental and calculated data for adsorption of (a) benzene, (b) toluene and (c) phenol into aerogel and xerogel.

for removing toxic organic compounds (benzene, toluene and phenol). Experimental and calculated results plotted as concentration of organic compound adsorbed into aerogel or xerogel, q_e , as function of its equilibrium concentration in solution, C_e , are depicted in Fig. 4a–c. On the basis of regression analysis of experimental data, it was possible to calculate the parameter values of the isotherms, as well as the correlation coefficients associated to each adsorbate/ adsorbent system (Table 3).

As shown in the adsorption curves represented in Fig. 4, the adsorbent material of type aerogel exhibits a better adsorption capacity than xerogel for all adsorbates. The main reason for its higher adsorption efficiency is the highly porous structure of the aerogel. Indeed, this material was synthesized under supercritical conditions, which allow pores to not collapse, contrarily to what occurs in the case of xerogels.

In addition, the interaction between the hydrophobic surface of the aerogel or xerogel and the adsorbate molecule is different for each organic compound. As shown in Fig. 4a and b, toluene is seemingly adsorbed to a greater extent than benzene. However, differences in the adsorption capacity for a given adsorbent/adsorbate can be more accurately described from the maximum adsorption capacity values and the energy involved in the adsorption process. These parameters were determined by the Langmuir

Table 3

Parameter	values of	Langmuir	and	Freundlich	isotherms
Falance	values of	Langinun	anu	rieununun	ISULIICI IIIS.

Adsorbate	Adsorbent	Langmuir			Freundlich		
		а	$b \times 10^2$	r^2	K _f	1/n	r^2
Toluene	А	173.47	2.50	0.954	8.44	0.63	0.964
	Х	102.42	5.84	0.980	19.91	0.33	0.981
Benzene	А	192.31	0.63	0.909	1.61	0.85	0.908
	Х	101.01	1.62	0.993	5.53	0.53	0.983
Phenol	А	21.06	0.64	0.958	0.00582	1.05	0.870
	Х	4.89	5.32	0.882	1.17	0.23	0.957

Units: a = mg/g; b = L/mg; $K_f = (mg/g)(L/mg)^{1/n}$; n, r = dimensionless.



Fig. 5. Comparison between experimental isotherms for benzene and literature data.

model and can be found in Table 3. Fig. 4c shows that phenol is adsorbed to a very lower extent by aerogel and xerogel than the other compounds. In fact, phenol is a hydrophilic solvent and, therefore, due to the super-hydrophobic nature of the adsorbent, there is a natural tendency for the solvent to be repelled by it. Moreover, phenol is able to form hydrogen bonds with water molecules establishing, this way, a strong interaction with the solvent which may unable its adsorption onto the solid material.

As previously mentioned, the parameters of the isotherms were obtained by fitting the Eqs. (1) and (2) to the experimental equilibrium data. The correlation coefficients shown in Table 3 indicate an adequate match of data with either Langmuir or Freundlich models in most of cases. The higher value for the maximum adsorption capacity by Langmuir model was observed for the case of adsorption of benzene onto aerogel (192.3 mg/g). Conversely, the most promising results were obtained for toluene adsorption since this involves greater adsorption energy. Both adsorbents exhibited the lowest adsorption capacities on phenol, i.e., 21.1 mg/g and 4.9 mg/g for aerogel and xerogel, respectively. In what concerns to the Freundlich model, the 1/n values ranging between zero and one indicate a favorable adsorption isotherm for all case studies.

The comparison of the results obtained in this work with those reported in the literature allows understanding the importance of the adsorbents under study. Several adsorption isotherms for benzene and toluene using adsorbent materials of the type aerogel and xerogel can be seen in Figs. 5 and 6.

The results in Fig. 5 clearly show that the materials used (aerogel-exp, xerogel-exp) exhibit better adsorption capacity than the MTMS-derived aerogels and TMES-derived aerogels reported in the literature for benzene adsorption [4]. Aerogels and xerogels synthesized in this work were obtained from methyltrimethoxysilane (MTMS), but their adsorption capacity differs greatly from that of aerogels synthesized by Štandeker et al. [4] with the same precursor. Thus, the discrepancies between the results obtained and those reported in the literature can be attributed to the preparation method which determined different pore structures of the synthesized materials. As aforementioned, the materials tested are



Fig. 6. Comparison between experimental isotherms for toluene and literature data.



Fig. 7. Adsorption capacity of aerogel for toluene after 4 adsorption/desorption cycles.

characterized by bimodal distribution of micropores and mesopores. The synergetic effect between the macroscopic morphology and intrinsic pore connections between mesopore channels and micropores contributes to achieving a large adsorption capacity [31]. In the case of aerogels tested in the work of Štandeker and co-workers, lower amounts of benzene adsorbed were found that could be attributable to their pore structures essentially based on micropores.

Regarding adsorption of toluene (Fig. 6), the results illustrate that the material with the highest adsorption capacity is the aerogel obtained from TFPTMOS/TMOS [6]. The greater adsorption capacity of TFPTMOS-based aerogels for toluene may be due to the greater polarity of the substituent group when compared to MTMS. The materials tested in this study showed better adsorption capacity than the other adsorbents until an equilibrium concentration of 125 mg/L, in case of the xerogel-exp, and approximately 160 mg/L, in case of aerogel-exp or aerogel-exp, the aerogels obtained with TMES/TMOS and MTMS by Standeker et al. [4]



Fig. 8. Infrared spectra of aerogel before and after 4 cycles of adsorption/desorption (v - stretching vibration; d - bending vibration; s - symmetric; as - asymmetric).

become those with greater adsorption effectiveness. The Nanogel, a commercial aerogel reported by Wang et al. [13], is the adsorbent that exhibits lower adsorption affinity for toluene. The inferior adsorption capacity of Nanogel may be attributed to the larger pore size (~200 Å) [32] when compared to the MTMS-based aerogels and xerogels prepared in this work and by Štandeker et al. [4], which have average pore sizes between 35 and 50 Å. An additional possible reason may be the different chemical nature of the substituent groups of these materials, but the information in the literature about the Nanogel chemical structure is very limited. Moreover, by observing the shape of all the adsorption curves in Fig. 6, it can be concluded that the TFPTMOS/TMOS-derived aerogel [6], as well as the aerogels/xerogels used experimentally in our study reveal favorable adsorption isotherms. The other adsorbents, in particular the MTMS-derived aerogels and TMES/TMOS-derived aerogels, obtained by Štandeker et al. [4], and the Nanogel [13] exhibit unfavorable adsorption isotherms. One should note that usually unfavorable isotherms are related to the heterogeneous surfaces of adsorbents, and this fact is directly associated to the synthesis and drying of these materials.

3.2.2. Regeneration of adsorbents

An adsorbent is industrially workable when it has a good adsorption capacity as well as a feasible regeneration. Based on the adsorption tests (Fig. 4), the system with best results was aero-gel/toluene, and thus this was the selected system to be subjected to cycles of adsorption/regeneration. These experiments were performed using the ozonation process, and the obtained results are shown in Fig. 7.

Ozone is an electrophilic resonance hybrid that tends to react with molecules of high electron density. Since the molecules of phenol, benzene and toluene have σ and π bonds with high electron density, ozone shall react effectively with the aromatic compounds, breaking them down into organic compounds such as carboxylic acids.

The obtained results suggest that, in the three initial cycles, the adsorption capacity remained nearly constant, being very close to the values that were presented previously, but at the fourth cycle the adsorption capacity has decreased significantly. One should note that, in opposition to what happened in the first three cycles, in the last cycle the aerogel was dispersed in the solution. Such behavior was not expected, since the initial material is highly hydrophobic. This evidence suggests that the aerogel may have lost part of its hydrophobicity on the regeneration process. A possible cause for this effect is the reaction of the ozone molecules with the functional methyl groups of the surface of the aerogel. Therefore, it can be concluded that the ozonation may have a limited application as a regenerating method for this type of material.

For a better insight on the effect of ozonolysis in the surface of the aerogel, FTIR analysis was undertaken to evaluate the differences in the chemical structure of aerogels after 4 cycles of adsorption/regeneration. The obtained spectra are presented in Fig. 8.

The FTIR spectra obtained for the original and the regenerated material reveals great similarity. Therefore, the chemical structure of materials remains largely intact after 4 cycles of adsorption/ desorption. The spectral peaks of these materials were assigned according to similar systems [2,22]. The observed vibrational bands confirm the existence of an inorganic network, predominantly based on Si-O-Si bonds (silica) with a methyl group per Si (hybrid materials) and -OH terminal groups. However, one difference can be found between both spectra, which is a small increase in the absorbance the -OH bonds, both bound with hydrogen bridges and unbound. The more significant presence of hydroxyl chemical functionality in the regenerated material can explain the improved dispersion of aerogels in aqueous solution in the last cycle. Further work needs to be carried out to evaluate the impact of the regeneration method type and conditions in the chemical structure of the aerogels.

4. Conclusions

In this work, aerogel and xerogel materials were synthesized using MTMS as chemical precursor to provide efficient adsorbents for toxic organic compounds of aqueous solutions.

It has been shown that the applied drying method to yield aerogels and xerogels leads to adsorbents with different microstructures. Aerogels are lighter, have greater specific surface area and have more mesopores than xerogels, whereas xerogels are richer in micropores. Such differences favor the adsorption of organic compounds at the surface of aerogels, leading to a greater adsorption capacity to benzene, toluene and phenol when compared to xerogels.

Both materials showed good adsorption capacity of hydrophobic compounds, whether they were polar or non-polar, respectively, toluene and benzene. For hydrophilic compounds, such as phenol, the adsorption capacity was found to be low. When compared to other reported data, the aerogels and xerogels that were prepared in this work have shown a significantly greater adsorption capacity for benzene. For toluene, in opposition to other aerogels, these adsorbents presented favorable isotherms, indicating that materials with more homogeneous surfaces could be obtained. The aerogels were shown to keep its adsorption capacity after three ozonolysis regeneration cycles. However, for longer regeneration cycles the chemical surface of the aerogels moves towards a more hydrophilic nature, leading to a poorer adsorption capacity.

References

- V.J. Inglezakis, S.G. Poulopoulos, Adsorption, Ion Exchange and Catalysis: Design of Operations and Environmental Applications, Elsevier Science, New York, 2006.
- [2] R. Al-Oweini, H. El-Rassy, Appl. Surf. Sci. 257 (2010) 276.
- [3] J.M. Dias, M.C. Alvim-Ferraz, M.F. Almeida, J. Rivera-Utrilla, M. Sanchez-Polo, J. Environ. Manage. 85 (2007) 833.
- [4] S. Štandeker, Z. Novak, Ž. Knez, J. Colloid Interface Sci. 310 (2007) 362.
- [5] Aerogels Handbook, first ed., Springer, New York, 2011.
- [6] L.W. Hrubesh, P.R. Coronado, J.H. Satcher Jr., J. Non-Cryst. Solids 285 (2001) 328.
- [7] S. Cui, X. Liu, Y. Liu, X. Shen, B. Lin, G. Han, Z. Wu, Sci. China Tech. Sci. 53 (2010) 2367.
- [8] J.L. Gurav, A.V. Rao, D.Y. Nadargi, H.-H. Park, J. Mater. Sci. 45 (2010) 503.
- [9] H. Liu, W. Sha, A.T. Cooper, M. Fan, Colloids Surf., A 347 (2009) 38.
- [10] J.A. Quevedo, G. Patel, R. Pfeffer, Ind. Eng. Chem. Res. 48 (2009) 191.
- [11] A.V. Rao, S.D. Bhagat, H. Hirashima, G.M. Pajonk, J. Colloid Interface Sci. 300 (2006) 279.
- [12] S. Štandeker, Z. Novak, Ž. Knez, J. Hazard. Mater. 165 (2009) 1114.
- [13] D. Wang, E. McLaughlin, R. Pfeffer, Y.S. Lin, Chem. Eng. J. 168 (2011) 1201.
- [14] D. Wang, T. Silbaugh, R. Pfeffer, Y.S. Lin, Powder Technol. 203 (2010) 298.

- [15] R.E. Kirk, D.F. Othmer, in: J.I. Kroschwitz, M. Hawe-Gant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, fourth ed., John Wiley & Sons, New York, 1998, p. 1.
- [16] A.V. Rao, N.D. Hegde, P.M. Shewale, Appl. Surf. Sci. 253 (2007) 4137.
- [17] S. Štandeker, A. Veronovski, Z. Novak, Ž. Knez, Desalination 269 (2011) 223.
- [18] K. Jensen, J. Schultz, F. Kristiansen, J. Non-Cryst. Solids 350 (2004) 351.
- [19] M. Schmidt, F. Schwertfeger, J. Non-Cryst. Solids 225 (1998) 364.
 [20] L. Durães, M. Ochoa, A. Portugal, N. Duarte, J.P. Dias, N. Rocha, J. Hernandez, Adv. Sci. Technol. 63 (2010) 41.
- [21] A. Soleimani-Dorcheh, M.H. Abbasi, J. Mater. Process. Technol. 199 (2008) 10.
 [22] L. Durães, M. Ochoa, N. Rocha, R. Patrício, N. Duarte, V. Redondo, A. Portugal, J.
- Nanosci. Nanotechnol. 12 (2012), http://dx.doi.org/10.1166/jnn.2012.4560. [23] A. Bhatnagar, M. Sillanpää, Chem. Eng. J. 157 (2010) 277.
- [24] D.Y. Nadargi, A.V. Rao, J. Alloys Compd. 467 (2009) 397.
- [25] A.V. Rao, N.D. Hegde, H. Hirashima, J. Colloid Interface Sci. 305 (2007) 124.
- [26] L. Cho, Environ. Eng. Res. 2 (1997) 201.
- [27] F. Su, C. Lu, S. Hu, Colloids Surf., A 353 (2010) 83.
- [28] M. Perdigoto, Treatment of Liquid Effluents Using Silica Based Aerogels, MSc Thesis in Chemical Engineering, University of Coimbra, Coimbra, 2011.
- [29] H. Valdés, M. Saánchez-Polo, J. Rivera-Utrilla, C.A. Zaror, Langmuir 18 (2002) 2111.
- [30] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, second ed., Academic Press, London, 1982.
- [31] K. Kosuge, S. Kubo, N. Kikukawa, M. Takemori, Langmuir 23 (2007) 3095.
- [32] H. Banda, in: Data Sheet Cabot Aerogel P100_200_300_400_4_2011_2:Layout 1, Cabot Corporation, 2011, p. 1. http://www.cabot-corp.com/Downloads/DL201005131356PM3125/> (16.04.12).