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

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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.

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/m^3), high specific surface area (800–1000 m^2/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].

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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 μm 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 N_2 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 $1/n$