



kinetics is well described by a pseudo-second order model. The aerogels with intermediate and high contact angles show higher adsorption capacities, with favourable isotherms, for the phenolic compounds with higher hydrophobicity, which shows the important role of hydrophobic interactions in this process. The best results were obtained for the aerogel functionalized with  $\beta$ -cyclodextrin when adsorbing the 4-chlorophenol, proving the positive effect of the presence of the  $\beta$ -cyclodextrin hydrophobic cavity in the adsorption of this highly hydrophobic pollutant.

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## 1. Introduction

The presence of phenolic compounds in many industrial wastewaters, such as from petrochemical, pharmaceutical/cosmetics, polymers, paints/dyes, cork and textiles industries, among others, is of concern in terms of environmental/human health protection. Even in low concentrations, these compounds present high toxicity and low biodegradability and, as they also exhibit high volatility, they easily spread and migrate. More complex structures (higher degree of substitution in the aromatic ring) usually give rise to increased toxicity (e.g., alkylphenols, chlorophenols, bisphenol-A). The removal of phenolic compounds from wastewaters is also crucial to comply with the International Legislation, being their adsorption a conventional and effective route for industrial effluents, usually using activated carbon [1–3]. Adsorbents with high selectivity and adsorption capacity are needed, and the silica-based aerogels are promising materials and have attracted great interest for this purpose due to their extremely high porosity/surface area, chemical versatility and possibility of reutilization [4–7].

As the phenolic compounds have functional groups of hydrophobic and hydrophilic character, several types of interactions with the adsorbents are expected, namely hydrogen bonding, hydrophobic and electrostatic interactions, being these interactions also dependent on the pH of the solution, in particular the latter one [8–11]. Thus, an improved adsorption may be achieved by tailoring the aerogels surface chemistry. In addition, the aerogels characteristic extensive network of micro and mesopores [6] greatly favours the adsorption process.

The tailoring of the chemistry of silica-based aerogels may be performed by the co-precursor method [6,12], by co-condensation of silica precursors that give rise to inherently hydrophilic silicas, such as tetramethylorthosilicate (TMOS) and tetraethylorthosilicate (TEOS), with organosilanes that offer the possibility of compounding the silica network with hydrophobic groups. Examples of the later are alkyltrialkoxysilanes, such as methyltrimethoxysilane (MTMS), methyltriethoxysilane (MTES), vinyltriethoxysilane (VTES), and many others. Another possible method is the surface modification/derivatization of the gel [6,12], in which the silica native gel (hydrophilic) is obtained first and then kept in a bath containing a mixture of solvent and surface modifying agent/silylating agent (usually organosilanes) that will condensate in the gel surface. In this method, the mass transfer in the gel takes place by diffusion only. Therefore, large amounts of solvent and significant time are required to achieve solvent exchange and subsequent surface modification, respectively, being thus very costly.

Regarding to the adsorption of phenolic compounds on silica-based materials, including aerogels/xerogels, only a few studies were found in the literature. Wu et al. [9–11] compared the adsorption of organic dyes (alizarin and phenol red) on several xerogels, synthesized by the co-precursor approach combining TEOS with several triethoxysilanes and, also, with bis(trimethoxysilyl)hexane (BTMSH) and bis(trimethoxysilylpropyl)amine (BTMSPA). They concluded that the organic dyes adsorption in the xerogels is influenced by all types of interactions referred above, but the hydrophobic interactions are of major relevance. The adsorption

capacity of phenol red was the lowest among all the tested adsorbents (always below  $45 \text{ mg g}^{-1}$ ). You et al. [13] also tested a xerogel made from TEOS/BTMSH system, but for adsorption of bromophenol blue. The obtained adsorption capacity did not reach values above  $20 \text{ mg g}^{-1}$ . Haghbeen and Legge [14] studied the combination of TMOS and TEOS with propyltrimethoxysilane (PTMS) and methyltriethoxysilane (MTPS) to produce xerogel adsorbents for many types of phenolic compounds, but the adsorption capacities were not provided.

Concerning the surface derivatization method, An et al. have tested silica particles as adsorbents of phenol after performing the grafting of polyethyleneimine (PEI) [15,16] and polymethacrylic acid (PMAA) [8] onto the particles surface. They obtained a high adsorption capacity for phenol ( $160 \text{ mg g}^{-1}$  and  $163 \text{ mg g}^{-1}$  for PEI and PMAA, respectively) justified by the hydrogen bonding and electrostatic interactions. Faraji et al. [17,18] performed the modification of the surface of silica gel particles by compounding it with  $\beta$ -cyclodextrin, using the linking agent 3-glycidoxypropyltrimethoxysilane, and tested this adsorbent for phenol and many phenolic compounds with different types of functional substituent groups in the aromatic ring. Although it was referred that good adsorption performance was achieved, no numeric data was provided. Qin et al. [7] have modified the surface of a TEOS-derived xerogel with TMCS and got an adsorption capacity of  $142 \text{ mg g}^{-1}$  for phenol. Finally, Anbia and co-workers [19,20] had used mesoporous silica (MCM-41 and SBA-15) and made its surface derivatization with aminopropyltrimethoxysilane, in order to obtain better adsorption capacity for chlorophenols, bromophenols and iodophenols. They achieved very good adsorption performances and the best result was obtained for modified MCM-41, which showed an adsorption capacity of  $339 \text{ mg g}^{-1}$  for 2,4,6-trichlorophenol.

The literature results described above allow concluding that the hydrophobic/hydrophilic interactions between the silica-based adsorbent and the phenolic compounds are complex and very important to the adsorption capacity of the adsorbents. In an earlier work [4], we had tested MTMS-derived aerogels and xerogels, which were highly porous, flexible and hydrophobic [21–23], to the adsorption of the aromatic solvents benzene, toluene and phenol from water. The higher adsorption capacities were obtained for the aerogel in the cases of toluene ( $173 \text{ mg g}^{-1}$ ) and benzene ( $192 \text{ mg g}^{-1}$ ), which were remarkably high when compared to the available literature data. However, for phenol the adsorption performance was not the best. Thus, we have now focused on the chemical modification of the aerogels/xerogels obtained from MTMS, in order to improve their adsorption capacity towards phenolic compounds.

In this work, the co-precursor method is applied to obtain aerogels and xerogels of tailored hydrophobicity/hydrophilicity, by combining different proportions of MTMS and TMOS which contribute to have a balance of  $-\text{CH}_3$  and  $-\text{OH}$  in the final structure of the gel. In addition,  $\beta$ -cyclodextrin ( $\beta$ -CD) was added along with the precursors to one of the formulations in order to create a dispersion of this macromolecule in the gel matrix. It is recognized that the hydrophobic hole of  $\beta$ -CD can act as a cage for the aromatic ring of phenol. With these chemically tailored materials, the aim is to

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