



Special Issue on Ciência e Tecnologia dos Materiais

Adsorption of phenol on silica aerogels using a stirred tank and a fixed bed column

Joana Marques^a, Telma Matias^a, Artur J. M. Valente^b, António Portugal^a, Margarida J. Quina^a,
Lícínia Gando-Ferreira^a, Luís Durães^{a,*}

^aCIEPQPF, Department of Chemical Engineering, University of Coimbra, Rua Silvio Lima, 3030-790 Coimbra, Portugal

^bCQC, Department of Chemistry, University of Coimbra, Rua Larga, 3004-535 Coimbra, Portugal

Abstract

The potential of a hydrophobic aerogel-like material for phenol adsorption from aqueous solutions was studied. Firstly, the effects of phenol concentration and adsorbent dosage on the adsorption equilibrium were investigated. The adsorption capacity of phenol at equilibrium increased with the increase of initial phenol concentration and decreased by increasing the adsorbent dosage. The optimum adsorbent dosage was 0.45g/45 mL, corresponding to a removal percentage of 54% and a liquid-solid ratio of 100. Langmuir and Freundlich isotherm models fitted fairly the experimental equilibrium data, but the Freundlich model was adopted as the more suitable for describing the studied system. Secondly, the performance of the adsorbent was investigated by using two different system layouts: perfectly stirred tank in batch conditions, and fixed bed column tested in continuous regime. Pseudo-first and pseudo-second-order kinetic models were fitted to have an assessment on the kinetic parameters and adsorption mechanism. Finally, feasibility of chemical regeneration of the adsorbent, using an acid solution, and its effect on the phenol adsorption capacity were also examined. The changes in the chemical structure of the adsorbent after 4 regeneration cycles were assessed by Fourier transform infrared spectroscopy (FTIR). High regeneration efficiency of the adsorbent was observed in all performed cycles.

© 2014 Portuguese Society of Materials (SPM). Published by Elsevier España, S.L. All rights reserved.

Keywords: Adsorption; phenol; silica-based aerogel; equilibrium isotherms; kinetic models; batch and continuous regimes.

1. Introduction

Phenol and its derivatives are organic compounds present in the effluents of many industries, such as pharmaceutical, petrochemical, cork and textiles [1]. The high toxicity, low biodegradability and high volatility (ease spreading) of these compounds may lead to serious effects in the water/air natural environments and human health [1]. Strategies for removal of phenolic compounds from wastewaters are welcome and will help to comply with current and future legislation. The adsorption technology, due to

its simplicity, has been widely used, mainly with activated carbon as adsorbent [2,3]. However, some issues have been identified, *e.g.* the low selectivity and regenerability of the adsorbent. Silica-based aerogels are promising materials in this context due to their extremely high porosity/surface area, chemical versatility and possibility of reuse [4-7]. In an earlier work [8], the potential of these materials for adsorption of phenol-derivative compounds was confirmed. In this work, a hydrophobic silica aerogel, based on mixing methyltrimethoxysilane (MTMS) and tetramethyl orthosilicate (TMOS) precursors, was studied for phenol adsorption from aqueous solutions by testing both batch and continuous systems. Chemical regeneration tests were also performed.

* Corresponding author.

E-mail address: luisa@eq.uc.pt (L. Durães).

2. Materials and methods

2.1. Materials

For the synthesis of the silica aerogel-like material, TMOS ($\geq 98\%$), MTMS ($\geq 98\%$) and NH_4OH (25% NH_3 in H_2O) were purchased from Sigma-Aldrich. Ethanol ($\geq 99.8\%$, EtOH) was obtained from Fisher. All reagents were used without further purification.

To prepare the synthetic effluent and elution solution, analytical grade phenol (99%) and HCl (37%) were obtained from Aldrich. All experiments used deionized water of high purity (from *Millipore* ultra-pure water system). Before the tests, the aerogel-like adsorbent was ground and passed through two sieves to retain the particle sizes in the range 74–250 μm .

2.2. Synthesis of the aerogel-like material

The preparation of the silica-based adsorbent followed the procedure described in an earlier work [8]. Briefly, MTMS e TMOS precursors were diluted in an EtOH/ H_2O mixture and an alkaline solution of NH_4OH (1M) was added, under stirring. The resultant sol was transferred to test tubes and aged during five days at 27°C. The molar ratio of MTMS:TMOS was 0.8:0.2. The gels were dried by ambient pressure drying (APD), evaporating the solvents in an oven [8].

2.3. Aerogel-like material characterization

FTIR spectroscopy was performed on a *Jasco FT/IR 4200* equipment. The spectra were obtained in the KBr mode, using KBr pellets composed by 80 mg of KBr and 0.2–0.3 mg of the sample, in a wave number range of 400–4000 cm^{-1} and resolution of 4 cm^{-1} .

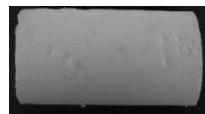
Contact angle measurements were performed with water droplets in a *Dataphysics model OCA 20* apparatus to assess the hydrophobicity of the aerogel. Helium pycnometry (*Micromeritics, Accupyc 1330*) was applied to measure the skeletal density of the silica-based material. The bulk density was obtained by the measurement of mass and volume of regular pieces of aerogel. By combining the skeletal and bulk densities it was possible to evaluate the porosity.

The specific surface area and average pore size were obtained by nitrogen gas adsorption, with BET theory and NLDFT method, respectively, using *Autosorb iQ-MP* equipment, from *Quatachrome Instruments*. Previous degasification of the samples was performed in a vacuum oven at 50°C, during 3 days, and also in the equipment.

The properties and aspect of the adsorbent are shown in Table 1.

Table 1. Properties and aspect of the adsorbent.

Bulk density (kg m^{-3})	154 ± 14
Contact Angle (°)	148 ± 3
BET surface area ($\text{m}^2 \text{g}^{-1}$)	569 ± 1
Porosity (%)	86.7
Average pore size (nm)	1.4



2.4. Adsorption equilibrium and kinetic tests

The phenol concentration was determined by measuring UV absorbance at 270 nm wavelength using a UV-Vis spectrophotometer (*PG Instruments – Model T70*). Quartz glass cells (Hellma) of 10 mm path length were used.

2.4.1. Phenol adsorption equilibrium

Equilibrium isotherm of phenol on the aerogel was determined through batch experiments. Initial concentrations of phenol varied in the range 50–500 mg L^{-1} . A mass of 0.09 g of adsorbent was added into glass bottles (50 mL) containing 45 mL of each solution. These flasks were rotated at 16 rpm in a shaker (*Heidolph – REAX 20*) at room temperature (RT), and supernatant aliquots were collected after 24 h of contact time and filtered through a 0.45 μm filter before analysis.

In order to investigate the effect of liquid-solid ratio on the adsorption process, several adsorbent dosages were tested (0.09–0.9 g/45mL) with an initial phenol concentration of 100 mg L^{-1} . These experiments were carried out under the same conditions as described above. All tests were performed in two replicates. The adsorption performance of the silica aerogel towards phenol was evaluated by equations (1,2).

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e (mg L^{-1}) are the concentrations of phenol initially and at equilibrium, respectively, $V(\text{L})$ is the volume of the solution, $m(\text{g})$ is the mass of adsorbent, and q_e (mg g^{-1}) is the phenol uptake, expressed as phenol removal per unit mass of aerogel. In this work, the Langmuir and Freundlich isotherm models were used to describe the relationship between the adsorption capacity and the corresponding equilibrium concentration in the solution [8].

2.4.2. Performance of the adsorbent in a perfectly stirred tank

The performance of the adsorbent was evaluated by a perfectly stirred tank (11 cm of diameter and 12 cm of height), tested in batch conditions. This tank has a set of four parallelepiped baskets, where the adsorbent is placed, coupled to a rotational stirrer (*CAT - Model R50D*). For kinetic tests, 10 g of adsorbent and 1 L of phenol solution with initial concentration of 100 mg L⁻¹ were poured into the tank under 150 rpm of stirring rate at RT. Samples for analysis were collected after contact times between 5 and 180 min. The phenol uptake on aerogel during time was modeled by the pseudo-first-order and pseudo-second-order kinetic models, using the methodology described in a previous work [8].

2.4.3. Performance of the adsorbent in a fixed bed column

A continuous flow adsorption experiment was conducted at RT in a fixed bed column (10 mm diameter; 100 mm height). 1.6 g of adsorbent was placed into the column and was compressed so as to decrease the interparticle voids. The phenol solution (50 mg L⁻¹) was fed to the column by a peristaltic pump (*GILSON Minipuls 3*) with a flow rate of 2 mL min⁻¹. Samples were collected at the column outlet at different time intervals, during 3 h, and the phenol concentration was determined in order to obtain the breakthrough curve.

2.5. Regeneration tests

Industrially competitive adsorbents are required to be reusable. Thus, the feasibility of regeneration of the aerogel was also evaluated, using an acid solution and its effect on the phenol adsorption uptake. Elution experiments were performed using a 0.1 M hydrochloric acid solution as eluting agent. Phenol adsorption-desorption experiment was repeated four times by using the same adsorbent. The procedures of phenol adsorption were carried out under the same conditions as those used in section 2.4.3.

3. Results and discussion

3.1. Equilibrium adsorption of phenol into the aerogel

The adsorption equilibrium data of aerogel for phenol are shown in Fig. 1. From the termination coefficient analysis, it can be seen that Langmuir ($R^2=0.961$) and

Freundlich ($R^2=0.966$) equations have similar values, although slightly higher for the later one. The Freundlich model was adopted for further comparisons in this work, as it has been successfully applied to describe the removal of organic contaminants from aqueous solutions by adsorption on heterogeneous surfaces. The model parameters found are: $K_F = 3.39 \times 10^{-1}$ (mg g⁻¹(L mg⁻¹)^{1/n}); $1/n = 0.709$. The n value is higher than 1, which indicates that the adsorption of phenol on the aerogel is a favorable process, in the studied range of concentrations. The maximum percentage of phenol removed from the aqueous solution was 18.8% (with phenol initial concentration of 100 mg L⁻¹). These results suggest a limited affinity between phenol and the aerogel.

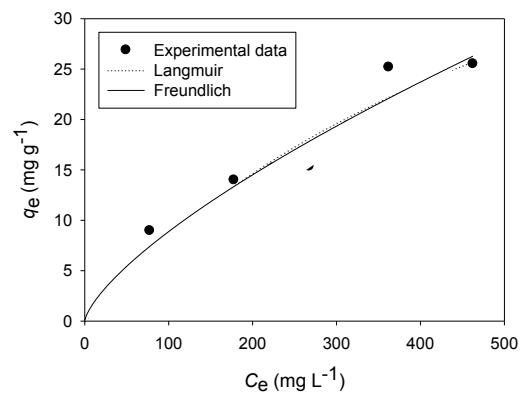


Fig. 1. Experimental and calculated equilibrium data for adsorption of phenol on the aerogel.

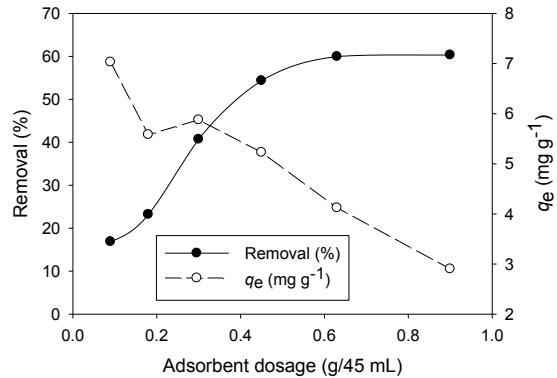


Fig. 2. Effect of adsorbent dosage on phenol removal and adsorbent capacity.

The effect of adsorbent dosage on the adsorption of phenol is presented in Fig. 2. This is an important parameter because it determines the capacity of adsorbent for a given phenol concentration as well as

the reaching of adsorbent-adsorbate equilibrium. The experimental data show that the percentage of removal of phenol increases by increasing the adsorbent dosage, while the adsorption capacity gradually decreases. This decrease observed in the adsorption capacity may be caused by sites that remain unsaturated during the adsorption process and/or due to partial agglomeration of the adsorbent [9]. The maximum adsorption capacity was found to be 7.0 mg g^{-1} at an adsorbent dosage of 0.09 g (liquid-solid ratio of 500). The increase in the percentage of removal is due to the availability of greater number of active sites of adsorbent. However, after a certain dosage, the increase of the percentage of removal is negligible, being the optimum amount $0.45\text{g}/45 \text{ mL}$, which corresponds to a phenol removal of 54% and a liquid-solid ratio of 100.

3.2. Kinetic adsorption in a batch stirred tank

The kinetics of phenol adsorption in a batch stirred tank was evaluated applying two different models. Fig. 3 shows experimental data and the best fitting corresponding to the pseudo-second-order model, with a termination coefficient of 0.99 and the following parameters: $k_2 = 0.0125 \text{ min g mg}^{-1}$; $q_e = 3.848 \text{ mg g}^{-1}$. The theoretical q_e value agrees well with the experimental one (3.448 mg g^{-1}), corresponding to a removal of phenol of 33.4%. Fig. 3 also shows that more than 2 h are required to achieve equilibrium. These results indicate that both physical and chemical adsorption may have a role in the observed behavior, or it is difficult to access the active sites of the adsorbent surface [8]. Furthermore, the low value of the adsorption capacity (less than a q_e of 5.9 mg g^{-1} estimated through the Freundlich model – see section 3.1) may be due to the fact that the adsorbent was not entirely confined into the baskets of the stirred tank.

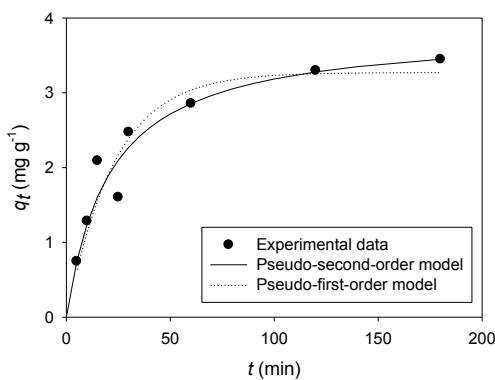


Fig. 3. Adsorption kinetic of phenol on aerogel in a stirred tank ($T = 20^\circ\text{C}$, $V = 1 \text{ L}$, $m = 10 \text{ g}$, $C_0 = 100 \text{ mg L}^{-1}$).

3.3. Kinetic adsorption in a fixed bed column (continuous)

The aerogel performance was also evaluated through the breakthrough curve of a continuous fixed bed column. The breakthrough curve obtained at 50 mg L^{-1} of feed phenol concentration is shown in Fig. 4 (corresponding to the cycle 1). In this system, the equilibrium adsorption capacity can be determined from Eq. (3).

$$q_e (\text{mg g}^{-1}) = \frac{m_{\text{adsorbed}}}{m_0} = \frac{Q \int_0^{t_F} (C_0 - C) dt}{m_0} \quad (3)$$

where m_{adsorbed} is the adsorbed mass in mg, m_0 is the initial mass of adsorbent, Q is the flow rate (L min^{-1}), C_0 and C are the inlet phenol concentration and the outlet phenol concentration (mg L^{-1}) at time t , respectively, and t_F is the time required for full bed exhaustion (min). Moreover, there are other important parameters to describe the behaviour of the system, namely the stoichiometric time (t_{ST}), estimated from Eq. (4), the break time (t_{bp}) and the exhaustion time (t_E), being the later given by the times at which the outlet phenol concentration corresponds to 1% and 95% of the inlet phenol concentration, respectively.

$$t_{\text{ST}} (\text{min}) = \int_0^{t_F} \left(1 - \frac{C}{C_0} \right) dt \quad (4)$$

From the breakthrough curve, the values of t_{bp} , t_{ST} and t_E were 91, 107 and 118 min, respectively. The equilibrium adsorption capacity of phenol in the fixed bed column system was 6.6 mg g^{-1} (cycle 1) which is slightly higher than a q_e of 5.4 mg g^{-1} estimated through the Freundlich model. The obtained results indicate that this system leads to a better performance of the aerogel when compared with the stirred tank system, since it enables a better contact between aerogel and phenol.

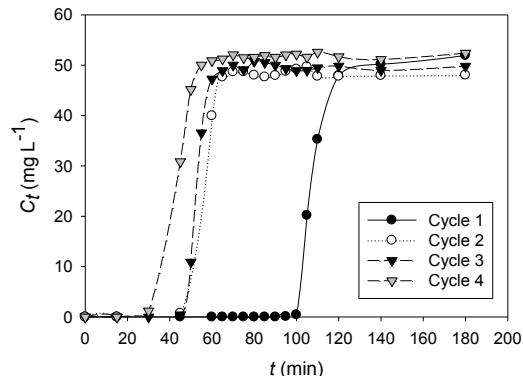


Fig. 4. Breakthrough curves of phenol on aerogel in a fixed bed column ($T = 20^\circ\text{C}$, $Q = 2 \text{ mL min}^{-1}$, $m = 1.6 \text{ g}$, $C_0 = 50 \text{ mg L}^{-1}$).

3.4. Chemical regeneration

The regeneration of the adsorbent is one of the most important factors, since it affects the overall cost of the adsorption process. In order to investigate the regeneration of the aerogel, the adsorption-desorption cycle was repeated 4 times by using the same material. Figs. 4 and 5 show the breakthrough and elution curves of phenol from aerogel, respectively, in a fixed bed column. The regeneration efficiency was calculated by the ratio between the adsorbed mass (see Eq. 3) and the desorbed mass, m_{desorbed} , obtained by Eq. (5). The regeneration efficiencies (%) are very high in all the performed cycles, as can be seen in Table 2. This result indicates that the hydrochloric acid used in the regeneration phase can break easily the bonds between phenol and aerogel.

$$m_{\text{desorbed}} = Q \int_0^{t_F} C dt \quad (5)$$

However, the adsorption capacity of phenol on the aerogel decreased from 6.6 (Cycle 1) to 3.4 mg g⁻¹ (Cycle 2). This reduction in the adsorption capacity may be due to the change in OH groups and a slight change in the CH₃ groups of the adsorbent, as was confirmed by FTIR spectra.

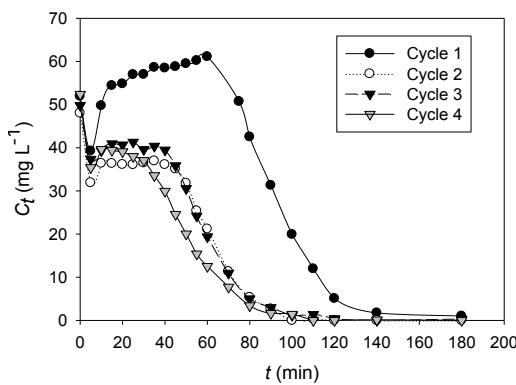


Fig. 5. Elution curves of phenol from aerogel in a fixed bed column.

Table 1. Parameters of the saturation and elution curves in the fixed bed column.

	Adsorption-desorption cycle			
	1	2	3	4
Adsorption capacity, q_e (mg g ⁻¹)	6.6	3.4	3.3	2.7
Break time, t_{bp} (min)	91	45	42	26
Exhaustion time, t_E (min)	118	65	61	57
Stoichiometric time, t_{ST} (min)	107	57	54	43
Regeneration efficiency (%)	99	84	93	95

4. Conclusions

The results of the equilibrium adsorption study showed that the adsorption capacity of phenol increased with the increase of initial phenol concentration and decreased with the increase of adsorbent dosage. Furthermore, the optimum adsorbent dosage was 0.45g/45 mL, corresponding to a phenol removal of 54% and a liquid-solid ratio of 100. The Freundlich isotherm model was recognized as the more suitable to fit the obtained equilibrium data. The Freundlich capacity factor (n) is higher than 1, indicating a favourable adsorption of phenol on the aerogel. The kinetic adsorption results indicate that the aerogel has a better adsorption performance in the fixed bed column system than in the stirred tank. In the chemical regeneration experiments, a high regeneration efficiency of the adsorbent was observed in all performed cycles by using HCl as eluting agent.

Acknowledgements

Work developed under the project “CleanOilGel - Functionalization of silica based aerogels for treatment of wastewater with phenolic compounds” by the consortium Active Aerogels/UC/Ventilaqua, funded by ADI, through the Promotion of Research and Technological Development System of QREN.

References

- [1] J. Michałowicz, W. Duda, Pol. J. Environ. Stud. **16**, 347 (2007).
- [2] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, J. Hazard. Mater. **160**, 265 (2008).
- [3] A. Dabrowski, P. Podkościelny, Z. Hubicki, M. Barczak, Chemosphere **58**, 1049 (2005).
- [4] F. An, B. Gao, X. Feng, Chem. Eng. J. **153**, 108 (2009).
- [5] M. N. Perdigoto, R. C. Martins, N. Rocha, M.J. Quina, L. Gando-Ferreira, R. Patrício, L. Durães, J. Colloid Interface Sci. **380**, 134 (2012).
- [6] S. Šandekar, Z. Novak, Ž. Knez, J. Colloid Interface Sci. **310**, 362 (2007).
- [7] G. Qin, Y. Yao, W. Wei, T. Zhang, Appl. Surf. Sci. **280**, 806 (2013).
- [8] T. Matias, J. Marques, M. Quina, L. Gando-Ferreira, A. J. M. Valente, A. Portugal, L. Durães, Colloids Surf. A **480**, 260 (2015).
- [9] M. Kilic, E. Apaydin-Varol, A. Pütün, J. Hazard. Mater. **189**, 397 (2011).