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# Influence of the synthesis conditions on the characteristics and metal adsorption properties of the 3-(1,4-phenylenediamine)propylsilica xerogel

*J. C. P. Vaghetti, J. L. Brasil, T. M. H. Costa, E. C. Lima, E.V. Benvenutti **
*Instituto de Química, UFRGS, CP 15003, 91501-970, Porto Alegre, RS, Brazil.*
** Corresponding author: e-mail: benvenutti@iq.ufrgs.br*

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**Abstract:** The hybrid 3-(1,4-phenylenediamine)propylsilica xerogel was obtained starting from two different organic precursor quantity (5 and 8 mmol) to 22 mmol of TEOS, in the synthesis. The xerogel samples were characterized by using CHN elemental analysis, $N_2$ adsorption-desorption isotherms, infrared thermal analysis. The xerogel was used as metal sorbent for $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ in aqueous solution with concentration range of $10^{-3}$ to $10^{-5}$ mmol $l^{-1}$. The quantity of organic precursor added in the synthesis influences the characteristics of the xerogel as morphology and thermal stability, as well as the metal adsorption capacity.

*Keywords:* sol-gel; hybrid powders; pore distribution; morphology; metal adsorbent.

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## Introduction

Silica is an inorganic support widely used in many chemical processes aiming several scientific and technical applications [1-5]. This support has been increasingly used because it offers many advantages due for example, its high thermal and chemical stability. In addition, its surface can be easily modified with several organic or inorganic groups. In the last two decades the chemical modification of silica surfaces with organic groups was studied, mainly by using the grafting reactions [6-8]. More recently, hybrid silica based materials, obtained by using sol-gel reactions, have been also studied [9-11]. This synthesis method is attractive due to the possibility to change the physical properties, such porosity, surface area, particle size, etc, by choosing the synthesis conditions [11,12]. The sol-gel reactions used to obtain hybrid silica based materials, consist in the hydrolysis and polycondensation of appropriated silicon alkoxides such tetraethylorthosilicate (TEOS) simultaneously with organosilicon derivatives as $R\text{-}Si(OR')_3$ where R is the desired organic group. The mild reaction conditions afford an opportunity to incorporate several organic species by choosing the appropriated reagent. If the organic species present chelating groups, the resulting materials can act as metal chelating sorbents. The possibility of prepare sorbent materials with controlled physical properties, as surface area and pore diameter, allows their use for selective trace metal evaluation in analytical measurements [13-16]. Even so, this method was not extensively explored to obtain metal sorbent materials.

In this work, the 3-(1,4-phenylenediamine)propylsilica was obtained by the sol-gel reaction. Changes in the physical properties were attained by varying the organic/inorganic precursor ratio, in the synthesis. The organic grade incorporation, the thermal stability and the resulting porosity of the hybrid xerogels were studied by using infrared thermal analysis and $N_2$ adsorption desorption isotherms. The hybrid xerogels were used as metal adsorbents for divalent copper, cadmium and lead ions in aqueous medium. The metal determination was carried out by visible spectrophotometry.

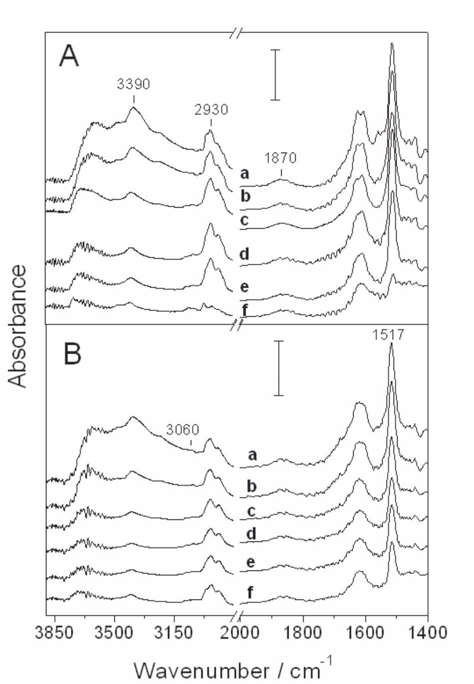


**Figure 1:** FTIR absorbance spectra for xerogel samples A and B, obtained at room temperature, after heating in vacuum, for 1 hours at: a) 100, b) 200, c) 300, d) 350, e) 400 and f) 450 °C. The bar value is 0.2 for both samples.

## Experimental

### *Sol-gel synthesis*

The 1,4-phenylenediamine was activated with sodium hydride (Acros) in 10 ml of aprotic solvents mixture (toluene:thf) (1:1) (Merck) for 30 minutes, and 3-chloropropyltrimethoxysilane (CPTMS, Merck,) was added. The quantities used were stoichiometric, 5 and 8 mmol for the synthesis A and B, respectively. The mixtures were stirred under argon at solvent-reflux temperature for a period of 5 hours. The solutions were then centrifuged, and the supernatants that contain the 3-(1,4-phenylenediamine)propyl trimethoxysilane were used as sol-gel organic precursors in the gelation process. Afterwards, tetraethylorthosilicate (TEOS, Acros) (5 ml), ethyl alcohol (5 ml, Merck), HF 40 % (0.1 ml, Synth) and water in stoichiometric ratio with Si r=4/1 (1.6 ml), were added to each organic precursor solutions, under stirring. The gelation occurs by a fluoride nucleofilic catalytic process, at pH between 8 and 9. The mixtures were stored for a week, just covered without sealing, for gelation and solvent evaporation. The obtained materials were extensively washed using the solvents: toluene, thf, dichloromethane, ethyl alcohol, distilled water and ethyl ether. The xerogel materials were finally dried for 30 minutes in an oven at 100 °C. The resulting xerogel powders were designated as samples A and B.

### *Elemental Analysis*

The organic phase contents were obtained using a CHN Perkin Elmer M CHNS/O Analyzer, model 2400. The analyses were made in triplicate, after heating the materials at 100 °C, under vacuum, for 1 hour.

### *Pore size distribution*

The pore size distribution was obtained by the $N_2$ adsorption-desorption isotherms, determined at liquid nitrogen boiling point, using a homemade volumetric apparatus, connected to turbo molecular Edwards vacuum line system, employing a Hg capillary barometer for the pressure measurements. The apparatus is frequently checked with alumina standard reference. The hybrid materials were previously degassed at 150 °C, in vacuum, for 2 h.

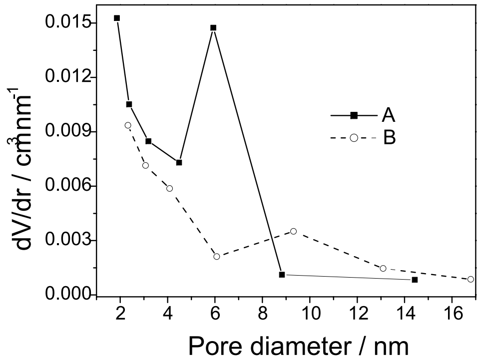


**Figure 2:** Pore size distribution of xerogel samples A and B, obtained by using BJH method.

| Sample | Organic precursor added mmol | Elemental analysis mmol $g^{-1\ a}$ | BET Surface área $m^2\ g^{-1}$ |
|---|---|---|---|
| A | 5 | 0.6 | 180 |
| B | 8 | 0.5 | 150 |

[a] mmol de organic groups per gram of xerogel, obtained from CHN analysis.

**Table 1:** Elemental analysis and surface area of the obtained xerogels.

*Surface Area*

The specific surface area of the previous degassed solid at 150 °C, under vacuum, was determined by the BET multipoint technique in the volumetric apparatus, cited above, using nitrogen as probe.

*Infrared measurements*

Self-supporting disks of the xerogels, with an area of 5 $cm^2$, weighing *ca.* 100 mg, were prepared. The disks were heated for 1 hour to temperature ranging from 100 to 450 °C, under vacuum ($10^{-2}$ Torr), using an IR cell [17]. The disks were analyzed in the infrared region using a Shimadzu FTIR, model 8300. The spectra were obtained with a resolution of 4 $cm^{-1}$, with 100 scans.

The infrared thermal analysis is a very effective tool to investigate the presence and the distribution of the organic phase in hybrid xerogel materials with covalent organic-inorganic interface. The analysis is based on the evolution of the infrared band areas of the organics in relation to the thermal treatment [17]. The organics dispersed in opened pores are completely desorbed when heat treated up to 450 °C, in vacuum. However, the remaining organic bands, that not vanish, are attributed to trapped organics in closed pores. Thus, it is possible to calculate the relative organic coverage *ie.* organic groups that are really on the surface, in opened pores. This is obtained subtracting the band area corresponding to the organic trapped groups from band areas of the organic total content. The organic band area values are obtained by using the overtone silica band at *ca.* 1870 $cm^{-1}$ as a reference band. This normalization was necessary, considering the heterogeneity in the disks thickness and taking into account the position changes of the infrared beam.

*Pre-concentration procedure*

A 5.00 ml of solution containing individually $Cd^{2+}$ ($8.90\ 10^{-6} - 3.11\ 10^{-3}$ mol $l^{-1}$), $Cu^{2+}$ ($1.57.10^{-5} - 1.57.10^{-2}$ mol $l^{-1}$), and $Pb^{2+}$ ($4.83.10^{-6} - 4.83.10^{-3}$ mol $l^{-1}$) solution plus 20.0 ml of $NaCH_3CO_2$-$HCH_3CO_2$ buffer solution (pH 5.1) were transferred to a 50 ml conical polyethylene flask containing 20.00 ± 0.09 mg of hybrid xerogel sorbent. The system was putted in a horizontal shaker (360 min) in order to concentrate the analytes. Subsequently, the solid phase was separated from aqueous phase by filtration, being the aqueous phase retained for analysis.

The elements, which were not retained in the xerogel sorbent, were spectrophotometrically determined. The elements $Cd^{2+}$ and $Pb^{2+}$ were determined using 4-(2-pyridylazo)-resorcinol (PAR, $2.0.10^{-4}$ mol $l^{-1}$) at $\lambda$= 510 and 540 nm [18], respectively, and $Cu^{2+}$ was determined using sodium diethyldithiocarbamate (DDTC, $8.9.10^{-3}$ mol $l^{-1}$) [19] using an FEMTO 600 S spectrophotometer, according to the following procedure: an aliquot of 500 µl of aqueous phase and/or analyte standard

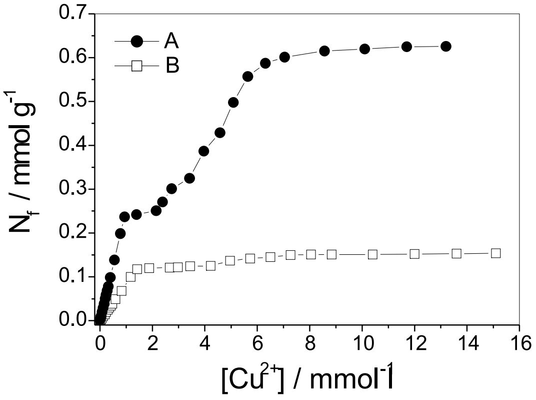


**Figure 3**: Metal ion adsorption isotherms of xerogel samples A and B, obtained at 25 °C, in aqueous solution for $Cu^{2+}$.

| Sample | Organic coverage / % | Available sites mmol $g^{-1}$ | Cu (II) mmol $g^{-1\ a}$ | Cd (II) mmol $g^{-1\ a}$ | Pb (II) mmol $g^{-1\ a}$ |
|---|---|---|---|---|---|
| A | 89 | 0.53 | 0.62 | 0.31 | 0.40 |
| B | 65 | 0.33 | 0.15 | 0.11 | 0.17 |

a = mmol of metal adsorbed per gram of xerogel.

**Table 2:** Metal adsorption capacities ($N_f$) of the xerogel samples.

solution plus 1000 µl of 0.25 mol $l^{-1}$ $Na_2B_4O_7$- 0.07 mol $l^{-1}$ $HNO_3$ (pH 9.1) plus 500 µl of chromogenic reagent were added to a Hellma glass curvette (10 mm of optical path). The analyte solutions with concentration higher than those cited above were properly diluted with distilled water. The metal ion adsorption capacity of the solid phase ($N_f$), obtained in the saturation plateau, was calculated by applying the equation $N_f = (N_a - N_s) / m$, where $N_a$ is the initial metal quantity added, $N_s$ is the metal quantity present in the solution, in equilibrium with the solid phase, and m is the weight of the solid phase.

## Results

Two samples of hybrid xerogels were obtained and their CHN elemental analysis and the surface area results are showed in Table 1. The presence of the organic component of the hybrid materials can be by confirmed by the elemental CHN analysis, which showed 0.6 and 0.5 mmol of organic groups per gram of xerogel for samples A and B respectively. The sample A presented the higher value for surface area, 180 $m^2g^{-1}$.

The immobilization of the 3-(1,4-phenylenediamine)propylsilica groups on the matrix surface was also confirmed by the infrared analysis showed in the Figure 1. It can be observed the typical spectra of hybrid material, with both organic and inorganic moieties. The inorganic component can be identified from the typical silica overtone bands at *ca.* 1870 $cm^{-1}$ and the silanol stretching bands above 3500 $cm^{-1}$. The organic phase is clearly identified by the bands at 1517 $cm^{-1}$ corresponding to the aromatic ring modes, bands at 3060 and 2930 $cm^{-1}$, are attributed to aromatic and aliphatic C-H stretching modes, respectively, and also the N-H stretching at *ca.* 3390 $cm^{-1}$ [20]. The presence of the organics in the samples even after heat treated at 300 °C, in vacuum, is an evidence of the high thermal stability of the organic moieties, bonded in the covalent form [17].

The pore size distribution of the xerogel samples are showed in the Figure 2. It can be seen that the sample A presented a large fraction of pores with diameter higher than 4 nm, while in the sample B the pores presented diameter values lower than 4 nm.

The metal adsorption results for the samples A and B are presented in the Figures 3, 4 and 5, respectively for $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$. The xerogel sample A showed higher adsorption capacity than xerogel B, for the three studied metals (Table 2), and the best adsorption capacity was attained for copper 0.62 mmol $g^{-1}$.

## Discussion

Although the organic quantity added during the synthesis was lower for the sample A in relation to the sample B, the final organic content expressed in mmol per gram of xerogel, was 0.6 for A and 0.5 for B. In previous works, it was observed that the organic grade in the final hybrid xerogel was not linear with the organics/TEOS ratio used in the synthesis, and saturation in organic grade was attained [21]. Additionally, the quantity of oligomers formed increases with the organics/TEOS ratio increasing [22], which causes a major leaching process during the washing with different solvents after the synthesis [23].

In the infrared spectra of the Figure 1 it can be seen that the organic component present thermal stability even after heat treatment in vacuum at 400 °C. Further thermal treatment at 450 °C causes a decreasing in the organic content mainly visible for sample A. In the Figure 6 is showed a more complete interpretation of these results. Considering that the characteristic band area of the organics is related to the organic content of the

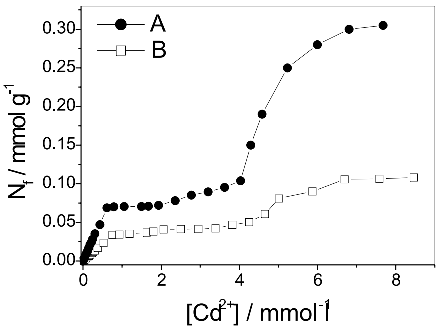


**Figure 4:** Metal ion adsorption isotherms of xerogel samples A and B, obtained at 25 °C, in aqueous solution for $Cd^{2+}$.

sample, it can be seen that samples A and B present a similar organic content, after thermal treatment up to 100 °C, according to CHN results showed in Table 1. The better thermal stability was achieved for the sample A, since their remaining organic contents decreased near 25%, after heat treatment up to 400 °C, while for sample B the decreasing was 49%. The marked reduction in the remaining organic grade for the sample B was interpreted taking into account the formation a large quantity of oligomeric species during the synthesis, as above proposed. Further thermal treatment up to 450 °C produces desorption of all the organic groups from the surface, as observed by the sharp reduction of the remaining organic content for the sample A (Figure 6). After thermal treatment up to 450 °C the organic groups which cover the surface were completely desorbed, and the remaining band area are due to the organics trapped in closed pores [17]. The trapped organic amount was 11 and 35 %, for samples A and B, respectively. Thus, considering the surface organic coverage, the best sample is the A, that has 89 % of the total organics (0.6 mmol g$^{-1}$, Table 1), in opened pores, corresponding to 0.53 mmol of available organic groups per gram of xerogel, while sample B presents only 65 % of total organics (0.5 mmol g$^{-1}$, Table 1) in opened pores, corresponding to only 0.33 mmol of available organic groups per gram of xerogel (Table 2). The larger amount of organics in opened pores for sample A is in accordance with the pore size distribution analysis presented in Figure 2, which shows a higher porosity for this sample.

The adsorption capacity behavior showed in Table 2 can be explained by the samples features discussed above. The sample A really presents the best characteristics to be used as metal adsorbent since it presents a higher surface area, a proper pore size distribution and a larger surface organic coverage.

The isotherm curves (Figures 3-5) present some characteristics that deserve to be discussed. In a general way the isotherms were similar to the subgroup 4-L type [24], where the sorbent presents a second surface that can be formed during the adsorption process. In present situation, the organic moiety has two chelating sites per pendant group with different steric availability, as represented in the scheme 1. Additionally we have to consider the morphological effects since the samples present a large fraction of small pores with diameter lower than 3 nm, which could make important diffusion effects for both sites, mainly in the low metal ion concentration. All these features can explain the differences between the isotherm plateaus, *i.e.* the value of the adsorption capacity for the second isotherm plateau was not twice the first one.

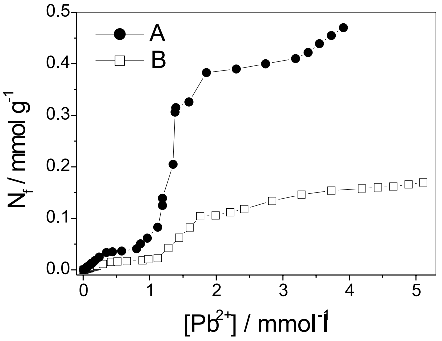


**Figure 5:** Metal ion adsorption isotherms of xerogel samples A and B, obtained at 25 °C, in aqueous solution for $Pb^{2+}$.

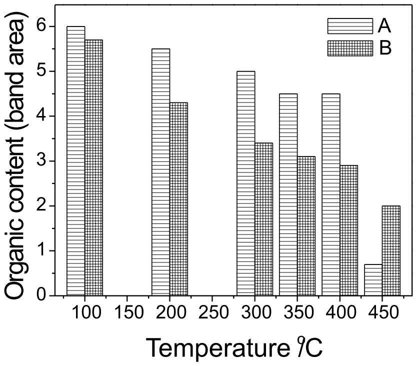
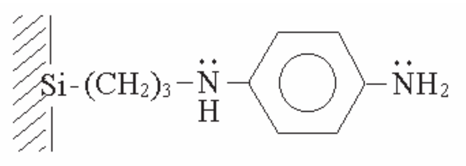


**Figure 6:** Relative remaining organic content of the xerogel samples A and B calculated from the band areas of the infrared ring mode at 1517 cm$^{-1}$, after thermal treatment at each temperature.



## Conclusions

The hybrid 3-(1,4-phenylenediamine)propylsilica xerogel was prepared adding two different quantities of organic precursor, 5 and 8 mmol per 22 mmol of TEOS, samples A and B, respectively. However the final organic content was similar for both, 0.6 (A) and 0.5 (B) mmol $g^{-1}$ of xerogel. The sample A presented a higher thermal stability, surface area and porosity. On the other hand, the lower final organic content and lower thermal stability of the sample B was interpreted considering the formation of oligomeric species during the synthesis. The sample A showed a lower fraction of organics occluded in closed pores, and consequently high organic coverage, *i.e.* organics in the surface. These characteristics influenced markedly the metal adsorption capacity, making the sample A better metal adsorbent.

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J. C. P. Vaghetti, J. L. Brasil, T. M. H. Costa, E. C. Lima, E. V. Benvenutti. Influência das condições de síntese nas características e nas propriedades de adsorção de metais do xerogel 3-(1,4-fenilenodiamina)propilsílica**.**

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**Resumo:** O xerogel híbrido 3-(1,4-fenilenodiamina)propilsílica foi obtido partindo-se de duas quantidades de precursor orgânico (5 e 8 mmol) para 22 mmol de TEOS, na síntese. As amostras dos xerogéis foram caracterizadas usando-se análise elementar CHN, isotermas de adsorção e dessorção de $N_2$ e termoanálise no infravermelho. Os xerogéis foram usados como adsorventes metálicos para $Cu^{2+}$, $Cd^{2+}$ e $Pb^{2+}$ em meio aquoso, na faixa de concentração de $10^{-3}$ até $10^{-5}$ mmol $l^{-1}$. A quantidade de precursor orgânico adicionado na síntese influencia nas características do xerogel como morfologia e estabilidade térmica, como também na sua capacidade de adsorção de metais.

*Palavras-chave***:** sol-gel; pós híbridos; distribuição de poros; morfologia; adsorvente metálico.

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