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# DEVELOPMENT OF A SILICA-BASED CRYOGEL FOR THE ADSORPTION OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

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## ABSTRACT

Recently, there has been a greater focus in ensuring the distribution of safe water, as a result of the increase in industrialization and globalization. Per- and polyfluoroalkyl substances (PFAS) are starting to be in the center of attention, due to their recurrent presence in water. This work aimed at developing a silica-based material, by the sol-gel process, with an affinity for the perfluorooctanoic acid (PFOA), nonafluorobutane-1-sulfonic acid (NFSA) and perfluorooctanesulfonic acid (PFOS), to remove them from water. The silica-based material was characterized and its adsorption capacity to remove these pollutants was analyzed, through the adsorption isotherms determination. Removal rates from 69.4% to 91.7% were obtained for the PFOA, from 68.5% to 90.7% for the NFSA and of 100% for the PFOS. Additionally, the adsorption isotherms for the PFOA and the NFSA showed to be better described by the Freundlich model.

**Keywords:** per- and polyfluoroalkyl substances; silica-based cryogel; adsorption; water treatment

## INTRODUCTION

The water quality has been affected in recent years as a result of the industrialization and globalization, throughout the world. As a result, stricter regulations have been imposed to prevent the development of several diseases associated with different water-present pollutants. One type of pollutants that has recently been included in these new regulations are the PFAS, given their toxicity persistence and accumulating ability in different organisms [1].

Nanomaterials, and specially silica-based materials, have gained ground for water pollutant removal, given their porous structure and easy adaptation of their characteristics for the end-purpose. This is achieved by changing parameters in the sol-gel method used for the production of these materials (e.g., surface modification, drying method, etc.) [2].

## OBJECTIVES

The objective of this work is to synthetize a silica-based cryogel, by the sol-gel method, with an ability to remove different PFAS from water, with a main focus on the PFOA ($C_8HF_{15}O_2$), NFSA ($C_4HF_9O_3S$) and PFOS ($C_8HF_{17}O_3S$). Furthermore, it also aims at comparing the cryogel adsorption removal efficiency for the different PFAS and analyze their adsorption isotherms behavior.

## METHODS

Tetraethyl orthosilicate, methyltrimethoxysilane and 3-aminopropyltriethoxysilane (25:70:5 (mol%), respectively), ethanol, oxalic acid and ammonium hydroxide were used to synthetize the silica-based adsorbent, by the sol-gel method. The synthetized material was dried by freeze drying.

For the PFAS' quantification, the METTLER TOLEDO© procedure was used. This method is a colorimetric method, were the PFAS-methylene blue complex is extracted onto chloroform and can then be measured by UV-Vis spectrophotometry.

## RESULTS

### Material Characterization

The cryogel obtained by the sol-gel method was characterized by the measurement of its water contact angle and zeta potential. The surface of this material was also analyzed through scanning electron microscopy (SEM).

The water contact test lead to a resulting water contact angle of 91º which, according to Anderson et al., leads to conclude that the cryogel has intermediate hydrophilic-hydrophobic character [3]. However, this characteristic was analyzed over time to verify if there was any variation of the water contact angle and, on the day after the drying process, this angle decreased significantly and could no longer be measured due to the fast absorption of water. This difference in behavior is beneficial for the application of this adsorbent material in water treatment. Furthermore, it was also analyzed if there would be any degradation of the material by an extended water contact, and, within 4 weeks the material remained unchanged. To verify if the material could be used to remove the PFOA, NFSA and PFOS from water, the zeta potential test was performed, which showed a surface charge of 25.9 mV. Furthermore, it is important that the material presents a structure that favors the adsorption of pollutants. In this sense, a SEM study was performed, showing an aerogel-like ramified porous structure, essential for pollutant adsorption.

### Calibration Curve and Adsorption Isotherm

The construction of the calibration curve was based on the relationship between the concentration of the solutions ($C$) and their absorbance ($A$), described by the Beer-Lambert law, i.e. $A=\varepsilon\, C\, l$, where $\varepsilon$ is the absorptivity and $l$ is the length of the absorbing medium [4]. The absorptivity for each pollutant is presented in Fig. 1. For the PFOA, the concentration of the solutions was varied from 2.07 mg.L$^{-1}$ to 30 mg.L$^{-1}$, for the NFSA from 1.15 mg.L$^{-1}$ to 20 mg.L$^{-1}$, and for the PFOS, from 2.50 mg/L to 100 mg.L$^{-1}$. The absorbance was analyzed at 650 nm, for all the samples of the different pollutants.

For the adsorption isotherm (Fig. 2), 15 mL of different PFAS solutions, with initial concentrations ranging from 5 mg.L$^{-1}$ to 200 mg.L$^{-1}$, were placed in contact with 30 mg of the synthetized cryogel, over 24 h. After, the extraction of the PFAS and their quantification by UV-Vis spectrophotometry were performed. The equilibrium capacity ($q_e$) (mg.L$^{-1}$) was obtained by Eq. 1, where $C_i$ is the initial concentration of the solution (mg.L$^{-1}$), $C_e$ is the concentration of the solution at the equilibrium (mg.L$^{-1}$), $m$ is the mass of the adsorbent (g), and $V$ is the volume of the solution (L) [5]. The removal of pollutants ($R$) was also determined.

$$q_\mathrm{e}=\frac{(C_i - C_\mathrm{e})V}{m} \quad , \quad R\,(\%)=\frac{100(C_i - C_e)}{C_i} \qquad (1)$$

The pollutants removal varied from 69.4% to 91.7% for the PFOA, and from 68.5% to 90.7% for the NFSA. For the PFOS the removal was 100% for all the initial concentrations.

The experimental results were compared to the Langmuir and Freundlich models, represented in Eq. 2, where $q_m$ represents the maximum adsorption capacity (mg.g$^{-1}$), $n$ the adsorption strength and $K_L$ (L.mg$^{-1}$) and $K_F$ (mg.g$^{-1}$) the adsorption model constants for the Langmuir and Freundlich equations, respectively [5].

$$\frac{C_\mathrm{e}}{q_\mathrm{e}}=\frac{1}{q_\mathrm{m}K_\mathrm{L}}+\frac{C_\mathrm{e}}{q_\mathrm{m}} \quad , \quad \ln q_\mathrm{e}=\ln K_\mathrm{F}+\frac{1}{n}\ln C_\mathrm{e} \qquad (2)$$

In Fig. 2 the best model that describes the adsorption behavior for the PFOA and the NFSA is represented, which is the Freundlich model. According to Pourhakkak et al., this leads to conclude that the adsorbent surface is non-uniform and has an exponentially expanding adsorption energy, having an interaction between its active sites and the soluble molecules [6]. For the PFOS, the pollutant is completely adsorbed by the cryogel, as a result of the large affinity between the two.

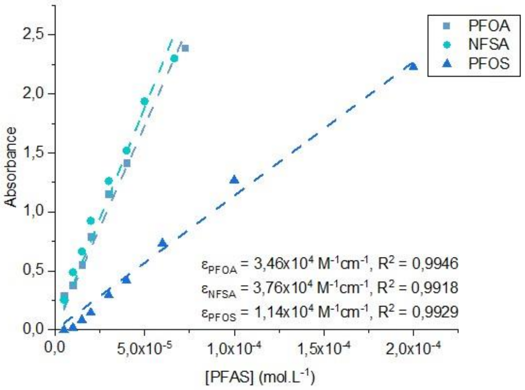

Figure 1. Calibration curve for PFOA, NFSA and PFOS.

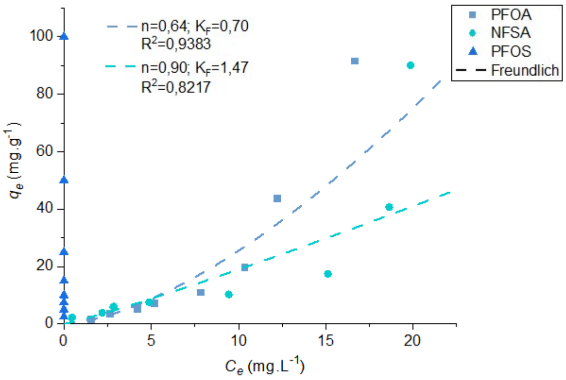

Figure 2. Experimental data for the PFOA, NFSA and PFOS and Freundlich model fitting, for PFOA and NFSA

## Conclusion

In this work, a silica-based cryogel was developed and its applicability for the adsorption of PFAS (PFOA, NFSA and PFOS) was tested. The material was characterized by SEM, by its water contact angle and zeta potential, showing a great potential for the adsorption of the PFAS. The adsorption of the PFOA, NFSA and PFOS by the cryogel was assessed through the construction of the adsorption isotherms, which can be described by the Freundlich model for the PFOA and NFSA. The material proved to be a good alternative to remove all of these pollutants from water, as removals above ca. 70% were obtained for all pollutants, reaching 100% for PFOS.

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