Development of a silica-based cryogel for the adsorption of perfluorooctanoic acid (PFOA) in water

POSTER

(Innovative Materials)

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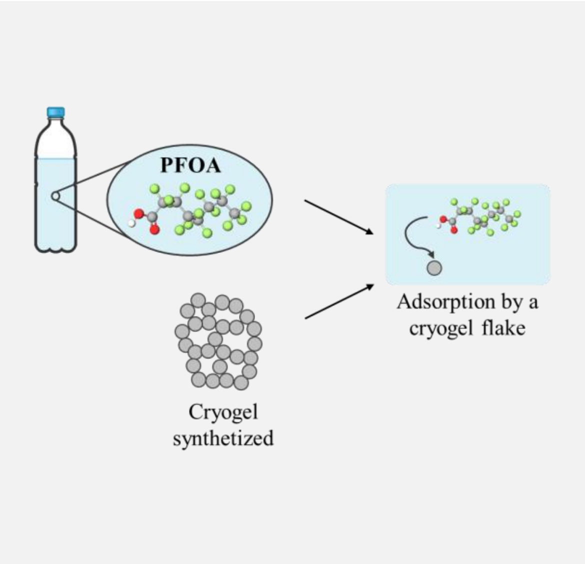

Water quality has been a major concern in recent years, given the increase of industrialization and globalization. The presence of per- and polyfluoroalkyl substances (PFAS) in water is an increasing concern. This work aimed at developing a silica-based material, by the sol-gel process, with an affinity for the perfluorooctanoic acid (PFOA), to remove it from water. The synthetized material was characterized by SEM, and by its water contact angle and zeta potential. The adsorption capacity of the synthetized material to adsorb the PFOA was analyzed and, from this test, removal rates from 69.4% to 91.7% were obtained, depending on the initial concentration of the pollutant. In this sense, this material shows to be a suitable candidate for the removal of PFOA present in water. Furthermore, the adsorption isotherm proved to be better described by the Freundlich model.

Introduction

The increase of industrialization and globalization over the past years has taken a toll on the water quality. The consequent presence of several water pollutants has led to more careful water quality analysis and the imposition of stricter water quality regulations, including the creation of regulatory limits for new substances. The presence of PFAS in water has been a concern as they are toxic, persistent and are accumulating in the organisms [1].
Silica-based materials have shown to be good adsorbents aiding in water pollutant removal, as a result of their porous structure and easy characteristics' tailoring, by making several changes to the sol-gel method (*e.g.*, surface modification, drying method, *etc.*) [2].

Objectives

The objective of this work is to synthetize a silica-based adsorbent with affinity for one PFAS, the PFOA, so to remove efficiently this pollutant from water.

Methods

A silica-based adsorbent was synthetized by the sol-gel method, using tetraethyl orthosilicate, methyltrimethoxysilane and 3-aminopropyltriethoxysilane (25:70:5 (mol%), respectively) as the reaction precursors. Ethanol was used as the solvent. For this process, oxalic acid and ammonium hydroxide were used as sol-gel catalysts. The drying method employed in the synthesis of the material was freeze drying.
The quantification of the PFOA was performed according to the METTLER TOLEDO© procedure which relies on a colorimetric method for the extraction of the PFAS-methylene blue complex, onto chloroform, which can then be analyzed by a UV-Vis spectrophotometer.

Results

The cryogel synthetized by the sol-gel process was characterized by the determination of its water contact angle, zeta potential and by analysis of its surface by means of scanning electron microscopy (SEM).
The analysis of the water contact angle showed the material to be slightly hydrophobic, according to Anderson et al., as it presented a water contact angle of 91º [3]. It was also verified how this characteristic changed over time, and by day two the water contact angle could no longer be measured, which in turn is beneficial for the purpose of this work, as the contact with water improves. Furthermore, it was also verified if this characteristic did not lead to a degradation of the material over time. To this end, the behavior of this material in water was analyzed over 3 weeks. This test showed that the material could be maintained in water during this time.
To assess the possibility of the synthetized material's ability to be used to adsorb the PFOA, an analysis of its surface charge was performed. This analysis showed that the material is positively charged, having a zeta potential of 25.9 mV.
A SEM study was also performed, to evaluate the structure of the material (Figure 1), showing the presence of an aerogel-like ramified and porous structure, being the very high porosity crucial for the extensive adsorption of the pollutant.

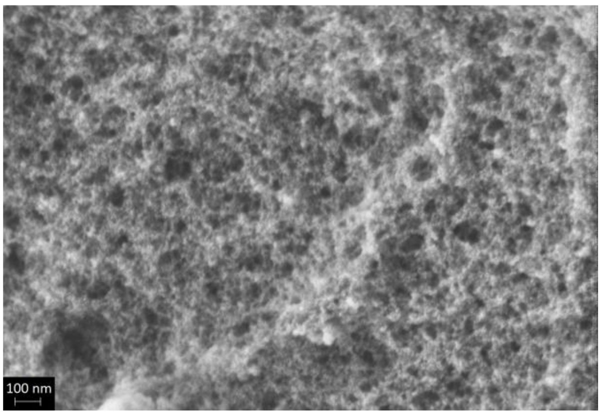

Figure 1. SEM performed to the synthetized adsorption material.

A calibration curve for the PFOA was created by measuring the absorbance of solutions with different pollutant concentrations (from 2.07 mg/L to 30 mg/L), at 650 nm (Figure 2).

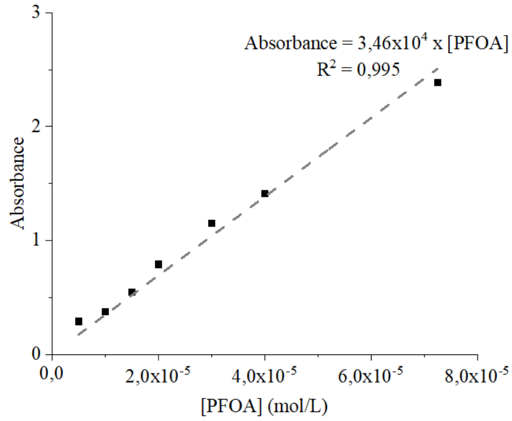

Figure 2. Calibration curve for the PFOA.

For the adsorption isotherm, 15 mL of different PFOA solutions with various concentrations were placed in contact with 0.03 g of the cryogel, over 24 h. After, the extraction of the PFOA was performed and its quantification was conducted by UV-Vis spectrophotometry. The equilibrium capacity (q_e) (mg/g) was then obtained by Equation 1, where C_i is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), m is the mass of the adsorbent (g) and V the volume of the solution (L) [4]. The C_i, C_e, and q_e values obtained for the PFOA adsorption by the cryogel are present in Table 1.

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

The removal of the pollutant by the cryogel was obtained by Equation 2 [4]. The results for this removal are also represented in Table 1.

$$R\ (\%) = \frac{100(C_i - C_e)}{C_i} \quad (2)$$

Table 1. Equilibrium capacity, initial and equilibrium concentrations, and removal achieved by the adsorption of the PFOA by the cryogel.

C_i (mg/L)	C_e (mg/L)	q_e (mg/g)	Removal (%)
5	1.53	1.74	69.4
10	2.60	3.70	74.0
15	4.17	5.41	72.2
20	5.15	7.43	74.3
30	7.81	11.1	74.0
50	10.3	19.8	79.4
100	12.2	43.9	87.8
200	16.7	91.7	91.7

From the previous results it is possible to observe that a considerable removal of the PFOA pollutant was achieved and that for higher initial PFOA concentrations, higher removal rates were also obtained.

The experimental results were then compared with the Langmuir and Freundlich models, Equations (3) and (4), respectively (Figure 3). In the Langmuir model, q_m represents the maximum adsorption capacity (mg/g) and K_L is the adsorption model constant (L/mg); in the Freundlich model, K_F is the adsorption model constant (mg/g), and n is the adsorption strength [4].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

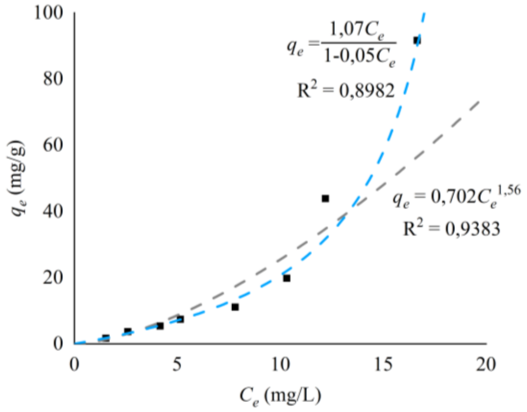

Figure 3. Experimental data adjusted by the Langmuir (blue) and Freundlich (gray) models.

From Figure 3 it is possible to verify that the experimental results are better described by the Freundlich model isotherm. According to Pourhakkak et al., this is an indicative of a non-uniform adsorbent surface with exponentially expanding adsorption energy and interactions between active sites and soluble molecules [5]. The SEM analysis, previously performed, confirmed the ramified, porous structure with many active sites, favoring the PFOA adsorption.

Conclusion

With this work, a silica-based material, with a potential for the adsorption of PFOA, was developed. The adsorption of the pollutant by the cryogel was evaluated by the analysis of the adsorption isotherm, which can be described by the Freundlich model. The removal values obtained ranged from 69.4% to 91.7%, proving to be a viable alternative for the adsorption of PFOA from water.

Acknowledgements

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