Metal–organic framework sorbents for the removal of perfluorinated compounds in an aqueous environment

Karima Sini, Damien Bourgeois, Madjid Idouhar, Michaël Carboni, Daniel Meyer

Metal–Organic Frameworks cavity size effect on the extraction of organic pollutants

Karima SINI[ab], Damien BOURGEOIS[a], Madjid IDOUHAR[b], Michaël CARBONI[a]*, Daniel MEYER[a]

[a] *Institut de Chimie Séparative de Marcoule, CEA, CNRS, ENSCM, Univ Montpellier, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France*

[b] *Laboratoire de Chimie Organique Appliquée, USTHB, BP 32, El-Alia, Bab-Ezzouar, 16111 Alger, Algérie*

Abstract

Zirconium Metal−Organic Framework materials (MOF, UiO-66 and UiO-67) have been used for the removal from aqueous solutions of persistent fluorinated pollutants, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). The two isostructural materials differ in cavity size, defined by the ligand, bdc (benzene-dicarboxylic acid) or bpdc (biphenyl-dicarboxylic acid) for UiO-66 and UiO-67 respectively. Both materials enable efficient sorption of both PFOA and PFOS. Sorption kinetics and isotherms have been experimentally determined, and thermodynamic parameters $\Delta H°$, $\Delta S°$ and $\Delta G°$ have been determined. UiO-67 shows higher sorption capacities (up to 743 mg.g^{-1} for PFOA) compared to these of UiO-66 (388 and 160 mg.g^{-1} for the sorption of PFOA and PFOS respectively) with a change in the sorption mechanism.

Keywords: Perfluorinated Pollutants; Hydrophobic interaction; Waste water treatment; Metal-Organic Framework; Porous materials

Corresponding information:

* michael.carboni@cea.fr / tel: (+33) 466 339 204 / ICSM, UMR 5257, Bât 426, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France

Introduction

Fluorosurfactants are composed of very strong C−F bond (116 kcal.mol^{-1}) and lead to very low surface tension in aqueous solutions.[1] Owing to these properties and despite their high costs, fluorocarbons have been used during several decades in many applications, eg cooling agents, fire-fighting foams or in the photolithographic industry.[2] Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) (denoted as PFOX along the manuscript) are very stable and considered as almost non-biodegradable, generating a large pollution in natural environment. Several studies have reported that PFOX are widely present in surface water, in ground, marine or drinking water at mg.L^{-1} to low g.L^{-1} levels.[3] They have received great attention because of their bioaccumulation, and potential health concerns due to their toxicity and carcinogenicity have been largely discussed in the literature.[4] Recently, PFOS has been added to the list of Persistent Organic Pollutants (POPs) under the Stockholm Convention,[5] and the European Food Safety Authority (EFSA) has established a tolerable daily intake (TDI) for both PFOS and PFOA present in food.[6]

Numerous methods have been developed for the degradation of PFOX in aqueous environments, such as sonochemical,[7] irradiation[8] or oxidation methods.[9] However, these techniques have high operating costs, and extraction has also been evaluated with adsorbents such as granular activated carbon (GAC) or resins. But their adsorption capacities remain rather low (112 - 160 and 46 - 41 mg of PFOA and PFOS respectively per gram of GAC and resin).[10]

Hybrid organic-inorganic materials, metal–organic frameworks (MOFs), have attracted considerable interest because of their large specific surface areas and pore volumes.[11] Zirconium-MOFs, UiO-66 and 67 built with bdc (benzene-dicarboxylic acid) and bpdc (biphenyl-dicarboxylic acid) ligands respectively, have shown to possess very high thermal, chemical and water stability,[12] making them suitable as sorbents for environmental purposes.[13,14] Recently, we have shown that Zirconium-MOF UiO-66, with small cavity, can efficiently adsorb PFOX.[15]

In this study, we evaluated the efficiency of UiO-67, with larger cavity, for the removal of PFOX in aqueous solution. Comparison with UiO-66 revealed that the size of the cavity is essential to efficient sorption of pollutants inside the material. Results show that the sorption mechanism is based on a physical process, with very rapid sorption of pollutants in aqueous solution (around 1 hour), but different mechanism according to the cavity size.

Experimental

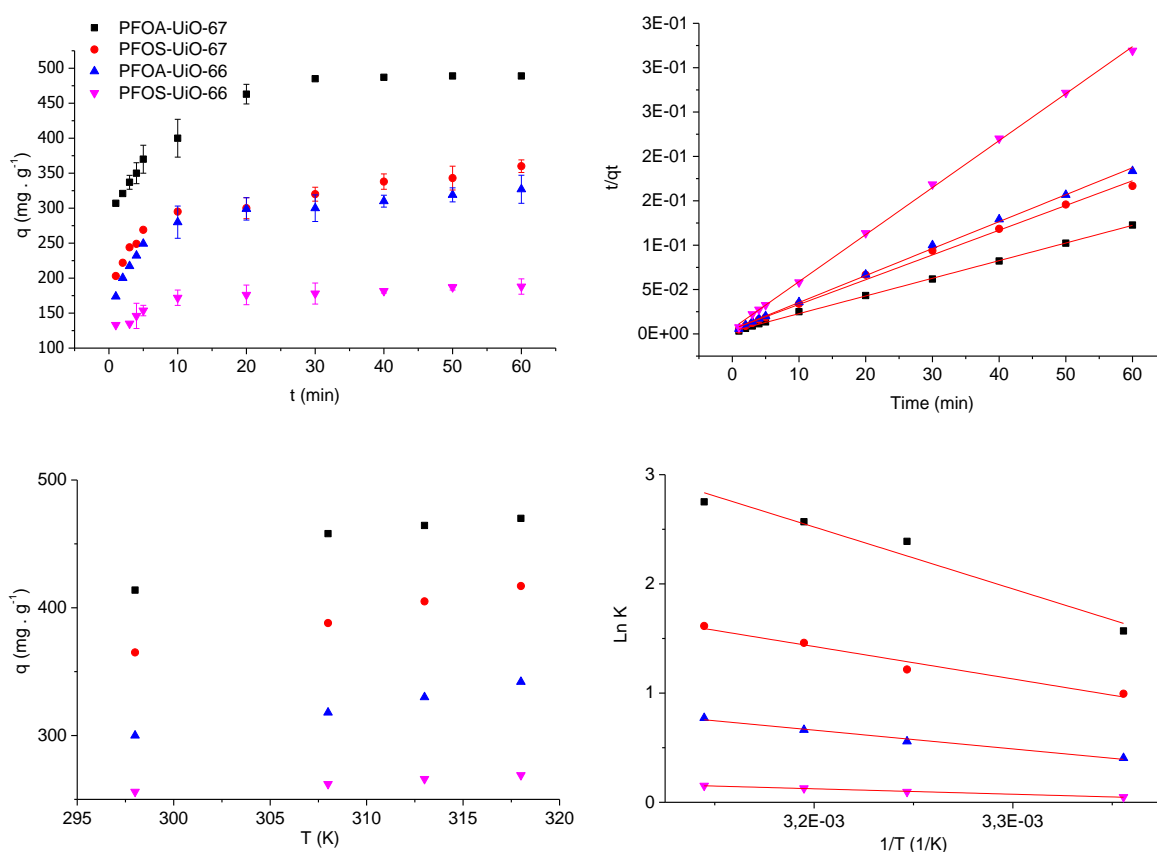*Synthesis and characterizations*

All reagents were purchased from Aldrich and were used without further purification. UiO-66 and UiO-67 were synthesized as reported in the literature[16] and characterized by PXRD and SEM (Supplementary information).

Sorption experiments were performed at 298 K in an aqueous solution at pH 4 with a 1 mg/mL MOF concentration. After centrifugation, the solution was analyzed with ^{19}F NMR (Brucker) with the use of an internal standard (trifluoroethanol), and the concentration of PFOX determined after integration of characteristic peaks as previously reported.[15] All experiments were at least duplicated. Calibration curves were performed for [PFOX] range of 100 to 1000 mg.L^{-1} (**Figure S1**).

Results and discussion

Both materials have been obtained after solvothermal syntheses with the use of HCl as modulator in order to increase the crystallinity of the materials.[16] The UiO phase was confirmed for both materials by SEM and optical microscopy through the formation of discrete octahedral crystals (**Figure S2**), and by diffractograms recorded at high angle peaks (beyond 2θ of 30º) in agreement with the theoretical pattern (**Figure S3**).

Figure 1: Top: (left) Sorption kinetics of PFOX with UiO-66 and UiO-67; (right) Application of the pseudo-second-order kinetic model. Bottom: (left) Evolution of sorption according to temperature; (right) Van't Hoff plot (pH = 4, [PFOX] = 500 mg.L^{-1}, [MOF] = 1 mg/mL, 60 min).

Sorption kinetics of fluorinated pollutants with both MOFs was first studied (**Figure 1, top-left**). A large amount of pollutant is adsorbed in less than 20 minutes and equilibrium is reached within 60 minutes. Pseudo-first order (1) and pseudo-second order (2) equations were used to model the experimental data (q_e and q_t are the sorption capacities at equilibrium and any time t, respectively, and k_1 and k_2 are the pseudo-first- and pseudo-second-order rate constants, respectively). The pseudo-second order model (**Figure 1, top-right**) leads to much better fits in comparison with the pseudo-first order (**Table S1**) with correlation coefficients of 0.999 to 0.996.
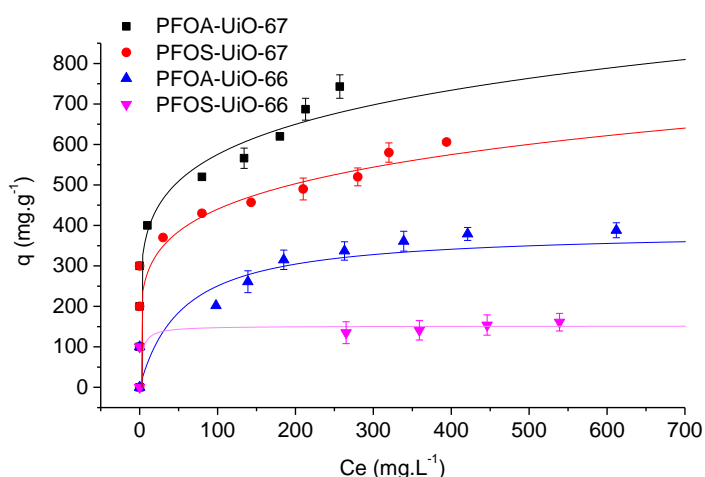
$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Temperature effect on sorption capacities of PFOA and PFOS was studied over a range of 298 K to 318 K. A sorption increase with an increase of the temperature was observed, and is attributed to a higher diffusion of PFOX molecules into the MOFs cavities. The thermodynamic parameters of the sorption including were calculated from the Van't Hoff equation (3) and are summarized in **Table S2**.

$$\text{Ln } K_d = \Delta S° / R - \Delta H° / RT \quad (3)$$

In all cases, ΔG and ΔH values indicate respectively that the sorption process is spontaneous and endothermic, whereas ΔS values suggest that the randomness at the solid-liquid is largely compensated by the release of the freedom in the water phase.

UiO-66 best fit with Langmuir model:

$$\frac{C_e}{q_e} = C_e \times \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} \quad (4)$$

UiO-67 best fit with Freundlich model:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

Figure 2 : Sorption isotherms of PFOA and PFOS by UiO-66 and UiO-67 in water (pH 4) at 298 K. Fits are performed using the Langmuir model for UiO-66 and the Freundlich model for UiO-67.

Sorption isotherms of both PFOX by both MOFs show an increase with the PFOX concentration until saturation (**Figure 2**). Experimental data were then fitted using the linear form of the Langmuir model (Equation 4, **Figure S4**) and the Freundlich model (Equation 5, **Figure S4**). Fitting results are summarized in **Table 1**, where q_e is the sorption capacity at equilibrium, q_m is the saturation sorption capacity, C_e is the PFOX concentration in solution at equilibrium, K_L is the Langmuir constant related to binding site affinity, K_f is the Freundlich constant and n (dimensionless; $0 < n < 10$) is a Freundlich intensity parameter. Complete saturation was observed only for UiO-66. In this case, the Langmuir model seems adequate and supposes that sorption occurs on a homogeneous surface by a monolayer deposition. In the case of UiO-67, the increase of cavity size leads to a change in sorption mechanism, possibly related to a multi-layer process, partially limited by diffusion inside the cavity. Also, higher sorption (up to 743 mg.g^{-1} in the case of PFOA) is observed.

Table 1: Calculated parameters for sorption of PFOA and PFOS by UiO-66 and UiO-67, using Langmuir and Freundlich models.

Adsorbent		Langmuir			Freundlich		
		q_m (mg.g^{-1})	K_L (L.mg^{-1})	R^2	Kf (mg/g)(L/mg)$^{1/n}$	n	R^2
UiO-66	PFOA	388	0.0182	0.9718	1.833	2.150	0.858
	PFOS	160	0.0466	0.9803	1.834	2.597	0.940
UiO-67	PFOA	700	0.1143	0.9740	2.239	5.650	0.912
	PFOS	580	0.0884	0.9805	2.200	5.235	0.883

Conclusion

A Zirconium-MOF based on bpdc (biphenyl-dicarboxylic acid) ligand, UiO-67, has been used for the extraction of fluorinated pollutants from aqueous solutions. It has shown higher capacities than the equivalent MOF based on bdc (benzene-dicarboxylic acid) ligand, UiO-66, which possesses smaller cavities. These results are in full agreement with a sorption mechanism based on hydrophobic interactions between the pollutant and the MOF cavity, instead of coordination of the pollutant on the metal node. The increase of the cavity size also leads to a change in sorption mechanism: this highlights the importance of detailed studies on such materials. MOFs are indeed simple and scalable

materials, and this works demonstrates their potential use for the decontamination of organic pollutants from aqueous solutions.

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