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## Uranium extraction from sulfuric acid media with Zr-Metal-Organic Frameworks

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### Abstract

A Zr based metal-organic framework functionalized with an amidophosphonate ligand has been synthesized, characterized and tested toward the uranium extraction in sulfuric acid conditions (representative of uranium leaching from ores). A synthetic method has been developed to obtain the material by an efficient post-synthetic modification technique that allows 95 % functionalization of active sites of the precursor material (UiO-68-NH<sub>2</sub>). This material has revealed to be stable in aggressive conditions ([SO<sub>4</sub><sup>2-</sup>] = 1 M, pH = 2) and to extract uranium up to 25 mg.g<sup>-1</sup>, thus showing for the first time the possibility to use these hybrid materials for such an application.

**Keywords :** Metal-Organic Frameworks; Uranium mine extraction; Water treatment; Solid/Liquid extraction; Environmental decontamination

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## Introduction

The increase of world energy production, consequence of a growing population and demand, will *de facto* intensify global warming and the pollution.[1] Nuclear energy may need to be accepted as a valid alternative to fossil fuels for short or even long term, as it can provide a powerful and efficient energy source with a competitive cost and with no greenhouse gas emissions, compatible with a sustainable development.[2]

Some technological advances are still necessary to increase the efficiency of raw material supply, to reduce nuclear wastes and to optimize their recycling and long-term storage.[3] In the mining industry, uranium is extracted from the raw ore by reacting the mineral with an acid or a base. Acid leaching with sulfuric acid is a convenient method due to its low cost and its efficiency for different types of uranium ores.[4] There is an increasing effort to find alternative, innovating and more efficient techniques for uranium recovery from the sulfuric leaching solution. Methods such as precipitation, solvent extraction or adsorption have been widely developed.[5] Compared to these techniques, the solid/liquid extraction has the undeniable advantage of reducing liquid wastes and solvent-associated hazards.[6] Current innovations focus on developing materials with high affinity for uranium compared to the other competitor species (cationic or anionic), enough stable in the particularly difficult conditions of the acidic leaching solution.

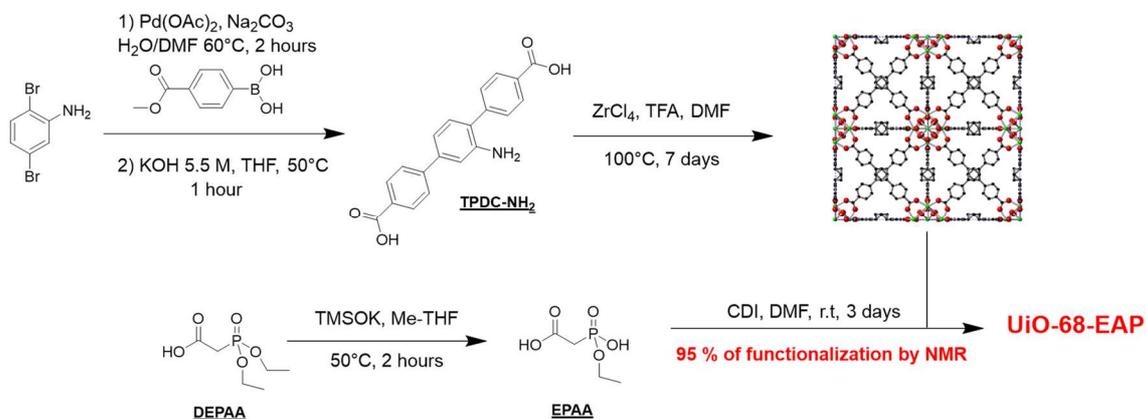
A recent class of organic-inorganic materials, called Metal-Organic Frameworks (MOFs), has shown promising results for many applications.[7] In particular, these materials have exhibited interesting results for the extraction of metals in aqueous solutions, as for the uranium extraction,[8] due to their specific properties such as high porosity, easy tunability[9] or crystalline structure[10] that confer to this class of materials a very high thermal and chemical stability. UiO-type MOFs obtained by the condensation of zirconium chloride and carboxylic acid ligands[11] are particularly relevant for an application in aqueous solution.[12]

The uranium extraction from ores is primarily affected by the acidic and complexing conditions of the leaching solution, making the use of MOFs delicate for such an application, and therefore such materials have not yet been studied in conditions representative of a uranium mining process. In this study, we propose the use of a UiO MOF functionalized with an amidophosphonate ligand known for its ability to extract uranium from sulfuric acid solution.[13,14] This material has shown extraction capacities for uranium up to 25 mg.g<sup>-1</sup>.

## Experimental

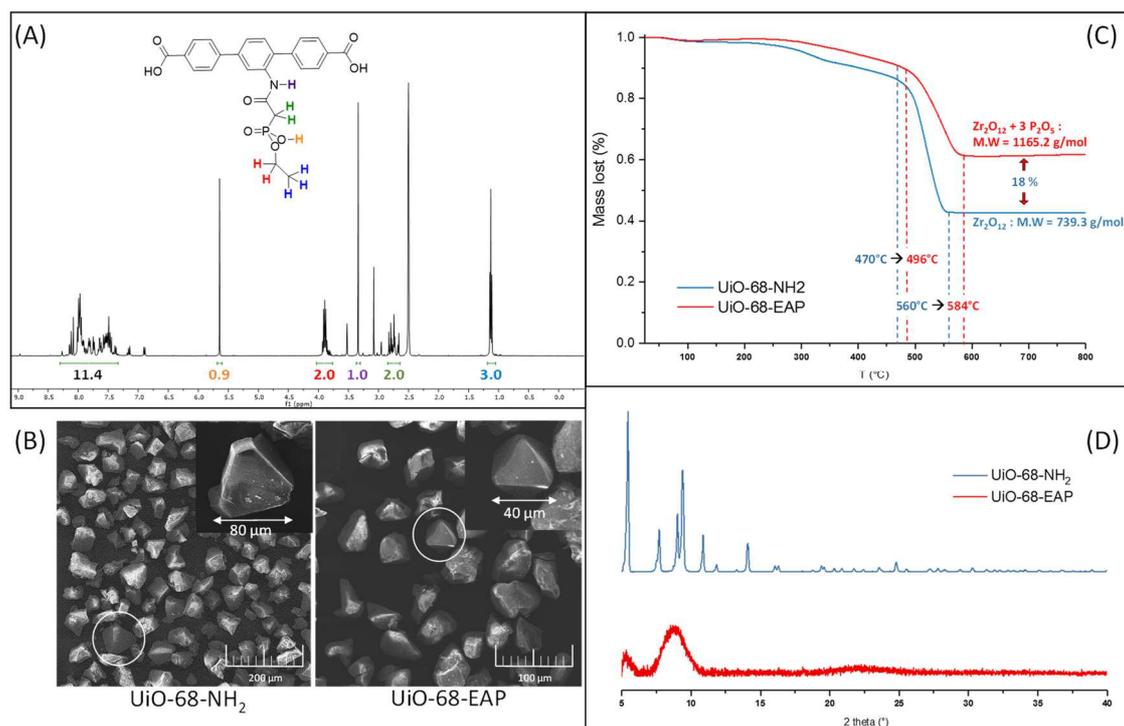
### Synthesis and characterization

The synthetic strategy used to obtain UiO-68-EAP is presented in **Figure 1**.



**Figure 1** : Schematic synthesis pathway for UiO-68-EAP

The linker precursor TPDC-NH<sub>2</sub> was synthesized in two step by a Suzuki coupling reaction adapted from [15] (yield 79 %). Crystalline UiO-68-NH<sub>2</sub> MOF has been obtained by solvothermal synthesis at 100 °C in a Parr® Teflon-lined reactor using the trifluoroacetic acid as modulator. Finally, UiO-68-NH<sub>2</sub> was functionalized by amide coupling using an excess of carbonyldiimidazole and 2-(ethoxy(hydroxy)phosphoryl)acetic acid (EPAA) grafting synthon to give UiO-68-EAP by a post-synthetic modification process. The percentage of the NH<sub>2</sub> functions converted to amidophosphonate was determined by <sup>1</sup>H NMR after acid digestion (95 %, **Figure 2-A, S1 and S2**).

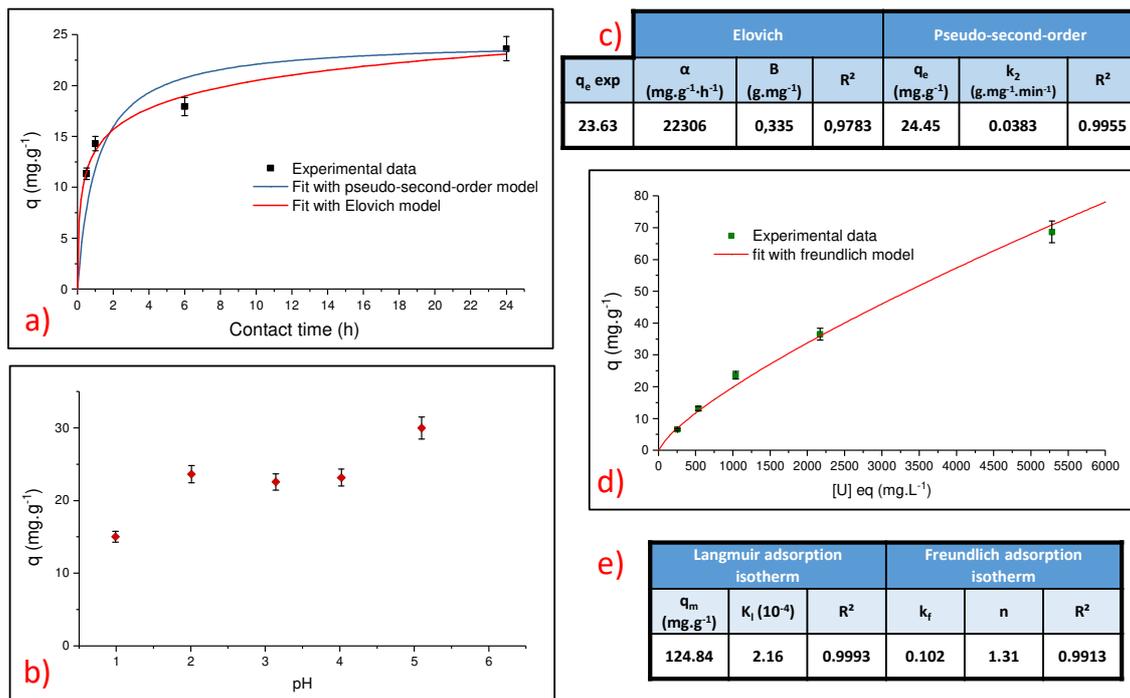


**Figure 2:**  $^1\text{H}$  NMR analysis of the digested UiO-68-EAP (A); Characterization of UiO-68-EAP and UiO-68-NH<sub>2</sub> by SEM (B), TGA (C), and PXRD (D)

SEM analyses confirm the conservation of the UiO-68-NH<sub>2</sub> morphology with a reduction of the particle size from 80 to 40  $\mu\text{m}$  after the functionalization (**Figure 2-B**). TGA analyses reveal the very high thermal stability of both materials (**Figure 2-C**). It was observed an increase of the organic part for UiO-68-EAP in accordance with the addition of the amidophosphonate on the linker (**Table S1**). XRD pattern of UiO-68-NH<sub>2</sub> is not conserved after the functionalization with the broadening of principal diffraction peaks at 5° and 9° (**Figure 2-D**).

#### *Sorption experiments*

Uranyl(VI) sorption experiments were performed at room temperature (293 K) with a 1 M sulfate concentration to simulate the conventional uranium ores leachate. In a typical procedure 5 mg of MOF was added to 5 mL of uranyl solution at the desired concentration in 1 M sulfate in a plastic vessel ( $m/V = 1$ ).



**Figure 3** : Uranium adsorption study : a) Adsorption kinetics ( $[U] = 1000 \text{ mg.L}^{-1}$ ,  $[\text{SO}_4^{2-}] = 1 \text{ M}$ ,  $\text{pH} = 2$ ), b) Influence of the pH ( $[U] = 1000 \text{ mg.L}^{-1}$ ,  $[\text{SO}_4^{2-}] = 1 \text{ M}$ ,  $t = 24 \text{ h}$ ), c) Adsorption isotherm ( $[\text{SO}_4^{2-}] = 1 \text{ M}$ ,  $\text{pH} = 2$ ,  $t = 24 \text{ h}$ ), d) Kinetic fits and e) Isotherm adsorption fits

The suspension was agitated during the required time followed by filtration onto a polyethersulfone membrane filter under vacuum. Finally, for analytical purposes the material was mineralized in a nitric acid/hydrogen peroxide mixture in order to measure by ICP-AES the adsorbed uranium concentration in the material.

### Results and discussion

The extraction efficiency as a function of the solution acidity has been studied in a range of pH from 1 to 5 at uranium concentration of 1000 ppm in 1 M sulfate solution (**Figure 3-b**). At pH 6, uranyl precipitation has been observed in these conditions. The capacity of UiO-68-EAP to extract uranium generally increases with increasing pH while a plateau is observed between pH 2 to 4. It is interesting to note that in these conditions the material is not highly influenced by the pH variation, unlike MIL-101(Cr) [16] or UiO-66-NH<sub>2</sub> where the extraction efficiency at pH 5 is four times higher than at pH 2.[17] The higher extraction rate observed at pH 5 could be induced by the modification of the surface potential of the MOF which tends to attract anionic uranyl species, while the lower performance at pH 1 is probably due to a lower stability of the material.

Adsorption kinetics has been studied in a range of 0.5 to 24 hours and the results are presented in **Figure 3-a**. The material stability in our conditions has been verified up to 24 hours (**Figure S3**). The uranium adsorption quickly increases during the first 6 hours followed by a plateau to reach the equilibrium after 24 hours. The adsorption data were fitted with Elovich (1) and pseudo-second order models (2) and kinetic parameters are presented in **Figure 3-d** ( $q_e$  and  $q_t$  are the sorption capacities at equilibrium and at time  $t$ , respectively,  $k_2$  are the pseudo-second-order rate constant,  $\alpha$  is the initial sorption rate and  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption).

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (1)$$

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

According to the regression parameter, U(VI) sorption onto UiO-68-EAP was better simulated by the pseudo-second-order model however the kinetic profile is in better accordance with Elovich model which indicated that adsorption is dominated by chemical multilayer adsorption. [18]

In order to evaluate the uranium adsorption mechanisms, the equilibrium adsorption isotherms were obtained with uranium concentrations from 250 to 5000 mg.L<sup>-1</sup> (**Figure 3-c**). The extraction capacity  $q$  increases function of the uranium concentration and the adsorption equilibrium was not reached even at 5000 mg.L<sup>-1</sup> of U(VI). The sorption isotherm has been simulated by the Langmuir, and Freundlich models (supporting information).[19] which describe respectively an homogeneous monolayer adsorption of metals in a material and adsorption onto heterogeneous surfaces.[19] Results suggest that the Freundlich model is more relevant to describe the adsorption, because the equilibrium is not reached even at high uranium concentrations (**Figure 3-e**), which is indicative of adsorption onto heterogeneous surfaces or surface supporting sites of varied affinities. The correlation with Elovich kinetic model suggested strong interaction at the surface of the material and Freundlich model indicates different sites on the surface maybe due to a slow diffusion of uranyl inside cavities (8.1 Å for the tetrahedral cavity and 11.4 Å for the octahedral cavity). Uranium adsorption experiment with UiO-68-NH<sub>2</sub>, in representative condition, shows lower extraction efficiency (13.2 mg.g<sup>-1</sup>). The results are comparable to other materials based on amidophosphonate functionalized silica (**Table S2**) but for a similar extraction capacity, UiO-68-EAP MOF shows higher affinity for uranyl(VI).

Finally, the uranium desorption has been evaluated with 3 different eluents: water, a sodium hydrogenocarbonate solution 1 M at pH 9 and a sulfuric acid solution containing 1 M sulfate at pH 1. The uranium was fully desorbed with sulfuric acid and 93% with water, while in the presence of the hydrogenocarbonate solution, the material was fully dissolved.

## Conclusion

A new material has been synthesized by the quantitative functionalization of a zirconium MOF (UiO-68-NH<sub>2</sub>) with an amidophosphonate extractant unit, known for its ability to complex uranium in sulfuric acid conditions. The material has been shown to be stable in the representative acid conditions for uranium extraction from conventional ores. This material has shown the possibility to extract uranium (at 1 g.L<sup>-1</sup>) with an efficiency up to 25 mg.g<sup>-1</sup>. These results open the field of research of these materials for the uranium extraction from high sulfate-loaded acid solutions often encountered in the mining applications.

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**Graphical Abstract :**

