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From phosphate rocks to uranium raw materials: hybrid materials designed for selective separation of uranium from phosphoric acid.

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Innovative hybrid materials with high and selective extraction capacity of uranium ions from phosphoric media was developed by grafting phosphorous-based ligands within the porosity of mesoporous silica (SBA15) or mesoporous carbon (CMK3).

Phosphate rocks represent a non-conventional source for uranium production and could be exploited as a by-product.[1-4] Several processes based on solvent extraction have already been developed to extract uranium from phosphoric acid.[5-11] In spite of recycling processes, they suffer from significant drawbacks as the use of important volume of organic solvent or a possible loss of extracting complexes[5, 6, 12] and the use of a large amount of water which does not fit with arid and dry country where are phosphate industries. Thus, to avoid these difficulties, the solid phase extraction could be a smart alternative process. Since the 1980's, some researchers have proposed the used of Ionic Exchange Resin as efficient solid support for extraction of uranium ions from phosphoric acid.[13-15] The principal benefit of the solid phase extraction is the absence of any organic solutions. Despite their high extraction capacities[14] (between 100 and 200 g.kg^{-1}) the main drawbacks are that such resins are limited for the extraction of tetravalent uranium U(IV) and require the addition of Fe(0) to reduce U(VI) (predominant form of uranium in phosphoric acid) to U(IV). Also their selectivity is generally low in regards to the other common impurities presents in the phosphate rocks (mainly iron) some adsorption are irreversible leading to a weak possibility of regeneration[12] and only limited number of extraction cycle can be performed due to fouling issues.[13, 16] Moreover, they tend to swell[16] which result in trouble for implementation of processes. To get around most of these drawbacks, inorganic framework with selective extracting part is a promising alternative option. Mesoporous inorganic supports are distinguished by high available surfaces, but also chemical, thermal and mechanical inertia, hence their high potential in adsorption applications. Recent results[17] demonstrates that effects of phosphoric acid damage depend strongly on the wall thickness and the pore diameter of silica used. SBA15 appeared to be phosphoric acid resistant even after 96h of 5M phosphoric acid exposure.

Functionalization of mesoporous silica[18-22] or carbon supports[23, 24] by specific organic complexes has been proposed in numerous papers for decontamination of uranium ions from aqueous effluents[25, 26] from dilute nitric acid.[27, 28] Nevertheless, to our knowledge, this approach has still not been used for selective extraction of uranium from phosphoric acid. This study is an attempt at applying the general concept of functionalization of mesoporous silica (SBA15) or mesoporous carbon (CMK3) by an extracting agent designed for the selective extraction of uranium ions from phosphoric acid media.

Uranium (VI) in phosphoric acid has been reported to exist in many forms (charged and uncharged) depending on phosphoric acid concentration.[29-31] Recently it has been reported that the speciation of uranium (VI) in aqueous solutions of 0.73-7.08 mol/L^{-1} phosphoric acid exists likely as $UO_2(H_2PO_4)_n(H_3PO_4)_m^{(2-m)}$ (where n+m=3).[32] Then to extract uranium from phosphoric acid, it is necessary to choose organic ligands showing a higher affinity to uranyl ions than phosphate ions. In case of phosphorous-based ligands, this affinity is linked to the functional group bonded to the phosphoryl group (P=O). To enhance the affinity of the functionalized solid we have chosen to introduce an amido function to the phosphoryl group as selective molecule. Such multifunctional molecules, a combination of an amido and a phosphonate groups which can be assimilated to carbamoylphosphonate ligands, have shown their potential to extract actinides either in the form of bidentate[33] or tridentate[34] ligands. Only few examples of mesoporous supports designed for sequester actinides have been developed based on carbamoylphosphonate.[35] From these statements and from the recent performances obtained for the selective extraction and quantitative recovery of uranium (VI) from phosphoric acid with carbamoylphosphonate ligands[9, 10] we designed and synthesized two ligands: a bidentate ligand BP and a tridentate ligand TR which are able to be introduce on a solid state matrix.
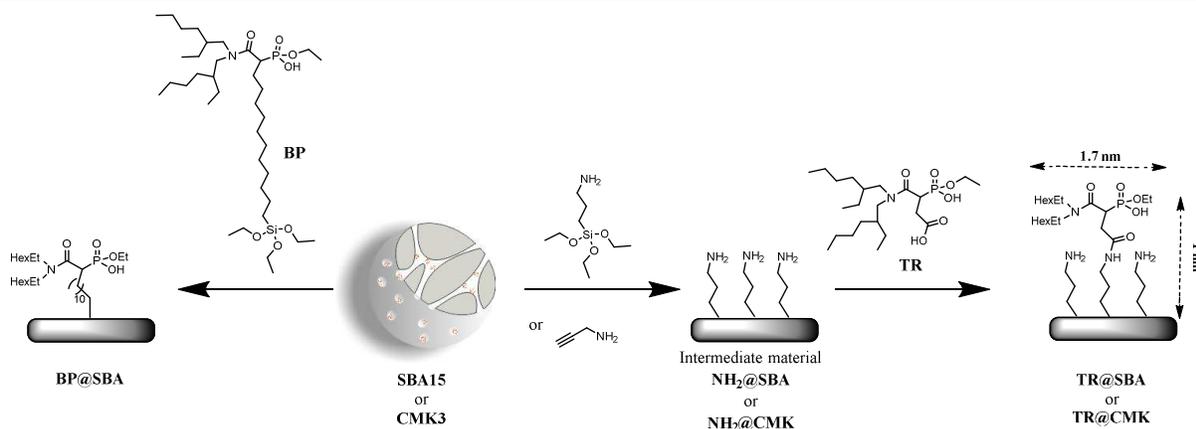
Figure 1: hybrid materials used: BP@SBA (right) and TR@SBA or TR@CMK (left)

Thanks to these molecules three kinds of materials were then synthetized (*Fig. 1*): BP@SBA from the bidentate ligand (BP) which is post grafted onto mesoporous silica (SBA15) by silanisation; TR@SBA and TR@CMK obtained after an amidation reaction between tridentate ligand (TR) and an intermediate functionalized support containing amino group (NH2@SBA or NH2@CMK[36-38]) (see ESI). In case of silica support, the grafting efficiency was followed and confirmed by CP-MAS NMR (^{29}Si, ^{13}C, ^{31}P), whereas in case of CMK support it was followed using Raman spectroscopy, using the ratio between the D-band intensity and the G-band intensity (see ESI).[36, 37] Chemical stability of the intermediate material have been followed and confirmed by Total Organic Carbone measurement. Indeed, less than 10% is leaching after 96 hours in a phosphoric acid solution (5M). After silanisation of APTES and amidation reaction with TR the pore size diameter clearly decreases which testifies a filling of the pores with the organic species (**table S1, ESI**). This hybrid material could be seen as functionalized monolayer on mesoporous supports (FMMS) as describe in the literature.[39] Combining SAXS data (**Fig. S1**) and adsorption experiment gives an easy method for the determination of the "wall thickness" [40] **(Fig. S2)** as well as the size of the grafted molecule by comparison with the initial material (SBA15). These calculated sizes were compared to the empiric Tanford formula assuming only hydrocarbon chain.[41] In regards to the value obtained, these two ways of evaluation are consistent. So it is reasonable to admit that the TR grafted molecule has a length of around 1nm.

TGA experiments, as well as elementary analysis, allow the determination of the grafting ratio at each step (**table 1**). For the intermediate material, NH2@SBA and NH2@CMK, the amount of amino group grafted within the porosity is higher for silica support compared with carbon support, even if the available surface is lower. For the amidation step, around 30% of the amino groups present within the porosity of amorphous carbon (CMK3) react with TR ligand, compared to only 16% by using NH2@SBA. The most likely hypothesis to explain this low reaction yield comes from the high density of amino group that covers the surface of the solid and the large size of the TR molecule to react with these free amino groups. Thus, during the amidation reaction, the TR molecule should cover several amino groups avoiding further reaction, as schematically shown on **figure 1**. This phenomenon is less important in case of carbon-based materials due to a lowest density of amino group in NH2@CMK3, but also due to the fact that CMK3 has a mesostructure more open than SBA15, without micropores. Using the same Tanford assumption, the width of this molecule could be estimated to be equal to 1.7nm. Consequently one TR-grafted molecule should recover about 2.3 nm^2 of the available surface. According to the graft ratio evaluated by elemental analysis or TGA, these grafted molecules should wrap 290 m²/g of the SBA which matches with the specific area (286 m².g^{-1}). As a result, we argue that the rate of TR grafting onto SBA15 is limited by the steric hindrance of this organic compound. The graft ratio of BP@SBA is lower and this molecule does not recover the entire available surface. This behavior should come from its high volume which could block the entrance of the pores during the grafting step.

The extraction capacity ($Q_{Uext} =([U]_i-[U]_f)*V/m$) of the hybrid material TR@SBA was investigated by mixing 250 mg (*m*) of the solid with 10mL (*V*) of three different synthetic solutions containing different concentration of U(VI) and 1 mol.L^{-1} of H$_3$PO$_4$ during 24hours, at room temperature and under vigorous stirring. Some experimental kinetics using hybrids SBA15 have shown that equilibrium is reached after a few hours for uranium extraction from acidic media.[42, 43]

Table 1: Graft Ratio (GR) evaluated by TGA and elemental analysis.

| | Sample | Elemental Analysis | | | TGA | |
		%C	%N	GR mmol.g^{-1}	Δm (%)	GR mmol.g^{-1}
SBA15	SBA15	-	-	-	-	-
	NH2@SBA	5.1	1.7	1.4	9.4	1.6
	TR@SBA	12.2	1.9	0.21	20.5	0.23
	BP@SBA	4.9		0.17	6	0.13
CMK3	NH2@CMK		1.1	0.79		
	TR@CMK		1.3	0.26		

[Texte]
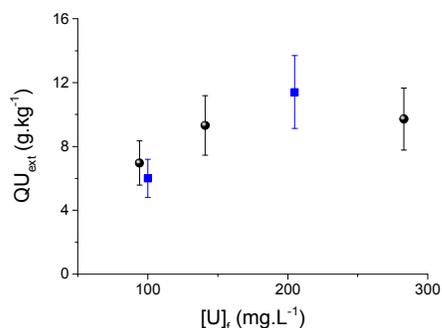
Figure 2: Extraction isotherm of TR@SBA material (black circle) and TR@CMK material (blue square)

Figure 3: Logarithm of solid extraction coefficient $E_s(U)$ versus log([H_3PO_4]) (feed solution 500 mg.L^{-1} of U(VI); volume to solid-mass ratio: 40 mL.g^{-1} (10mL of the feed solution and 250mg of solid). Black circle TR@SBA; blue square TR@CMK and red open circle BP@SBA.

24 hours shaking-time was used in the experiments and meant thermodynamic equilibrium was ensured.

The uranium concentration from each solution, before and after contact with the solid was analyzed using X- Ray Fluorescence spectroscopy. An increase of the initial U amount in solution leads to a rise of extraction capacity up to a maximum, close to 10 g.kg^{-1} (equal to 0.042mmol.g^{-1}) for both TR containing materials (**Fig. 2**). Thus amount of TR complex grafted onto the SBA and CMK solid evaluated previously and the determination of the uranium extraction capacity lead to the ratio [U]$_{extracted}$:[TR] which are similar in each case (TR@SBA and TR@CMK) roughly 1:5. The extraction capacity of BP@SBA in the same experimental conditions was evaluated to be much lower, close to 0.2g.kg^{-1}. It was demonstrated that remaining free amino groups[43] or silanol groups[42] do not interact with uranyl cation under pH 3. Therefore we argue that the efficiency of this kind of hybrid solid comes essentially from the TR or BP molecule grafted onto the available surface rather than from the nature of the support or for free amino or silanol surface groups.

Comparable performance were reported for different ionic exchange resins under reasonable similar conditions with an extraction capacity in the range 5 to 20g.kg^{-1} for aminophosphonic resin,[13] and much higher than those obtained with biopolymeric microcapsules containing DEHPA - TOPO molecule (2 g.kg^{-1}).[15] The extraction capacities obtained for our materials are 10 times lower than those of Kabay *et al* [14] but in this case such resin containing phosphonic acid are non-selective resin against especially iron.

Uranium elution from TR@CMK was broached by nitric acid (1M) and KOH solution (0.5M) respectively for the SBA and carbon materials. Results show a recovery up to 40% of the uranium previously uptake with a single contact.

To complete this study, both TR@SBA and BP@SBA were evaluated to extract selectively uranium (VI) towards iron (III) competitive ion, in phosphoric acid. Experimental results were evaluated in term of selectivity coefficient ($S_{U/Fe}$=Kd$_U$/Kd$_{Fe}$, with Kd$_i$=Q$_{iext}$/[i]$_f$ dissociation coefficient).

The silica support loaded with TR was able to extract uranium selectively ($S_{U/Fe}$ = 100) towards iron, in a range of H_3PO_4 concentration below or equal to 1mol.L^{-1}. In the case BP, the selectivity is only 3. Beyond the amount of grafted ligand, this difference can be explained through the extraction mechanism involved for each ligand. Therefore this can be related to the structure differences of BP and TRF or both
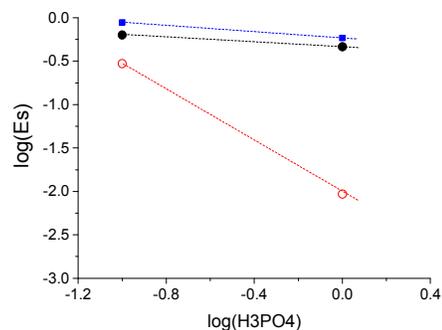
functionalized material with TR ligand (TR@SBA and TR@CMK); 5 groups could be involved in the mechanism of extraction of U: two amido group (N-C=O), a phosphoryl group (P=O) for complexation mechanism and phosphonate group (P-OH) and an amino group (NH) for ionic exchange (**Fig. 1**). In the case of the hybrid solid loaded with an organosilane (BP), 3 groups could be involved in the extraction of U: amido group, phosphoryl group and phosphonate group.

To approach extraction mechanisms, H_3PO_4 dependence of U(VI) extraction was performed for the three different materials: BP@SBA, TR@CMK, TR@SBA (**Fig. 3**) .In each case, the extraction of uranium decreases gradually as the H_3PO_4 concentration increases, as already observed with impregnated resin.[13] The effect of acid concentration onto the extraction of uranium were evaluated in terms of solid extraction coefficient ($E_s(U)$=[U]$_{extracted}$/[U]$_{remaining in solution}$) and slope analysis (**Fig. 3**). For BP@SBA materials, a variation between Log($E_s(U)$) and Log(H_3PO_4) with a slope of 1.3 was observed and could be interpreted in a cation exchange mechanism with the release of about mainly 1 mole of H_3PO_4. Considering BP@SBA material, only the phosphonate group could be involved in this cation exchange mechanism. Thus, the following reaction could be proposed:

$UO_2(H_2PO_4)_2.H_3PO_4$ + HBP@SBA $\Leftrightarrow$ $UO_2(H_2PO_4).H_3PO_4$- BP@SBA + H_3PO_4
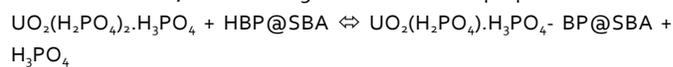
For TR@SBA and TR@CMK materials, the behavior of the solid extraction coefficient as a function of H_3PO_4 concentration is far different, where the extraction is not affected by the acidity of the solution. A slope of -0.1 is obtained here; we suggest a uranium extraction through a solvatation mechanism without releasing any H_3PO_4. A chelation would occur through coordination with the oxygens of the phosphoryl group and the amido group.

These results demonstrate the promising interest of using phosphorous based grafted materials to extract uranium ions in phosphoric media, event in the presence of iron ions. The grafting efficiency is limited by the steric hindrance of this organic compound. Extraction mechanisms depends on the H_3PO_4 concentration, with complexation or ionic exchange mechanisms according to a di or tridentate ligand.

Notes and references

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† Electronic Supplementary Information (ESI) available: [synthesis details, SAXS data, selectivity data, pores properties].

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Graphical abstract