

## Development of Metal-Organic Frameworks-Type Hybrid Functionalized Materials for Selective Uranium Extraction

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**Abstract :** Different types of materials have been developed for the solid/liquid uranium extraction processes, such as functionalized organic polymers, hybrid silica or inorganic adsorbents. In general, these materials exhibit a moderate affinity for uranyl ions and poor selectivity against impurities like iron, vanadium or molybdenum. Moreover, the structural organization deficiency of these materials generates ion diffusion issues inside the material. Therefore, the aim of our study is to develop efficient and organized materials, stable in the acid media encountered in uranium extraction processes. Metal organic frameworks (MOFs) are hybrid crystalline materials consisting of an inorganic part (cluster or metal ions) and tailored organic linkers connected via coordination bonds. These hierarchical materials have exceptional surface area, thermal stability and a large variety of tunable structures. However, due to the reversibility of constitutive coordination bonds, MOFs have moderate stability in strongly complexing or acidic media. Only few of them are known to be stable in aqueous media and only one example is described in strong acidic media. However, these conditions are very often encountered in the environmental pollution remediation of mine wastewaters. To tackle the challenge of developing MOFs adapted for uranium extraction from acid mine waters, we have investigated the stability of several materials. To ensure a good stability we have synthesized and characterized different materials based on highly coordinated metal clusters, such as LnOFs and Zirconium based materials. Among the latter, the UiO family shows a great stability in sulfuric acid media even in the presence of 1.4 M sodium sulfate at pH 2. However, the stability in phosphoric media is reduced due to the high affinity between zirconium and phosphate ligand. Based on these results, we have developed a tertiary amine functionalized MOF denoted UiO-68-NMe<sub>2</sub> particularly adapted for the extraction of anionic uranyl (VI) sulfate complexes mainly present in the acid mine solutions. The adsorption capacity of the material has been determined upon varying total sulfate concentration, contact time and uranium concentration. The extraction tests put in evidence different phenomena due to the complexity of the extraction media and the interaction between the MOF and sulfate anion. Finally, the extraction mechanisms and the interaction between uranyl and the MOF structure have been investigated. The functionalized material UiO-68-NMe<sub>2</sub> has been characterized in the presence and absence of uranium by FT-IR, UV and Raman techniques. Moreover, the stability of the protonated amino functionalized MOF has been evaluated. The synthesis, characterization and evaluation of this type of hybrid material, particularly adapted for uranium extraction in sulfuric acid media by an anionic exchange mechanism, paved the way for the development of metal organic frameworks functionalized by different other chelating motifs, such as bifunctional ligands showing an enhanced affinity and selectivity for uranium in acid and complexing media. Work in this direction is currently in progress.

**Keywords :** extraction, MOF, ligand, uranium

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