## Metal Organic Framework advanced adsorbents for metal ions recovery from polluted water sources.

<sup>1</sup>Fernández de Luis, R., <sup>2,3</sup>Copello, G., <sup>4</sup>García, A., <sup>1</sup>G-Sainz, P.; <sup>2,3</sup>Tovar, G.; <sup>2,3</sup>Torres, D.; <sup>1</sup>Valverde, A.; <sup>4</sup>Quintero Y.; <sup>4</sup>M. Rosales, <sup>4</sup>B. Gonzalez, <sup>1,5</sup>Larrea, E. S.; <sup>1</sup>Fidalgo-Marijuan, A.; <sup>5</sup>Lezama, L.; <sup>1,5</sup>Arriortua, M. I.

<sup>1</sup>Basque Center for Materials, Applications & Nanostructures, Leioa, Spain.
<sup>2</sup> Fac. de Farmacia, Dpto. de Química Analítica. Universidad de Buenos Aires (UBA).
Buenos Aires, Argentina. <sup>3</sup>Inst. de Química y Metabolismo del Fármaco (IQUIMEFA-UBA-CONICET), Buenos Aires, Argentina. <sup>4</sup>Advanced Mining Technology Center (AMTC), Universidad de Chile, Chile. <sup>5</sup>Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Leioa, Spain.

email: <a href="mailto:roberto.fernandez@bcmaterials.net">roberto.fernandez@bcmaterials.net</a>

Metal Organic Frameworks (MOFs) have emerged as high surface area chemical versatile adsorbents with ordered crystalline structures able to overcome the performances of classic adsorbent over organic and inorganic pollutants capture [1]. Recently, giving a step further, the MOF scientific community have performed several works where the modified MOF materials have been applied successfully to recover low concentrated metal ions/radioactive isotopes from complex multi-element solutions, or to use them as Rare Earth Elements separation systems, even in the presence of competing ions at high concentration [2].

We have explored the potentials of zirconium MOF materials to capture different metal ion cationic and anionic species following two different approaches, ligand and metal functionalization paths. In the first approach, a group of Zr-therepthalate (UiO-66) [3] based materials has been synthesised and deeply characterized, varying the ligand functionalization and defect density of the framework. Their performance as both Cr(VI) adsorbents and reducers has been assessed, studying the chromium speciation after the process. In the second approach, a cluster functionalization of zirconium trimesate material (MOF-808) [4] has been applied, anchoring amino acids and natural carboxylic acids to the framework that varies the metal specificity of the initial adsorbent.

Despite the promising initial results obtained in slight acid solutions, the low chemical stability of the natural amino-acids groups at acid conditions (pH< 4) induce their release from the porous framework, and hence, the loss of the metal-ion specificity of the designed adsorbent. To close the current ongoing strategy, the future trends that will be applied to overcome this structural instability will be briefly summarized; aiming to unlock the applicability of MOF materials to more challenging scenarios, such as mining/industrial acid water sources, or metal ion recovery from sea-water and sea-water brines.

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[1] Mon. et. al. (2018) J. Mater. Chem. A, 6, 4912 [2] Li et. al. (2018) Chem. Soc. Rev., 47, 2322 [3] V. V. Butova et. al. (2017) Cryst. Growth Des., 17, 5422, [3] J. Jiang et. al. (2014), J. Am. Chem. Soc., 136, 12844