

## 5- Membranes and materials for depollution (VOCs, EDCs, radioactive effluents...)

### *Environmental mineralization of caffeine micro-pollutant by Fe-MFI zeolite*

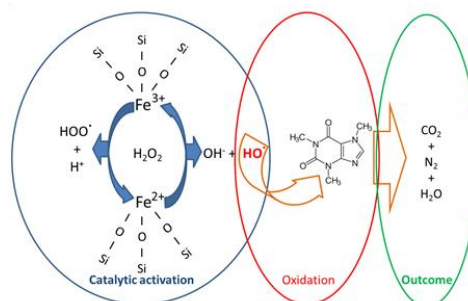
*Environmental Science and Pollution Research 25 (2018) 3628-3635*

Collaboration: The Univ. of Queensland- Brisbane, Australia

Involved MCP researchers: Martin Drobek, Anne Julbe

*This work investigates the effect of iron in the structural formation of Fe-MFI zeolites and the catalytic effect in the degradation of a micro-pollutant caffeine. The iron was isomorphically incorporated into the zeolite structure forming a Fe-silicalite-1. The FEMFI was characterized by crystal structures where the cell volume decreased as the amount of iron to silica ratio increased from 0 to 2.33 %. The addition of iron resulted in smaller zeolite particles, packed with aggregated crystal and resembling a cauliflower formation. The microporous pure MFI zeolite*

*(i.e. no iron) was unable to degrade caffeine in a heterogeneous Fenton-like reaction in the presence of peroxide. However, Fe-MFI zeolites performed well and the zeolites containing 2.33% of Fe reached 96% degradation based on total organic carbon measurements. This significant improvement in reaction was attributed to the increase of Fe content which favored the formation of  $Fe(O)_4$  sites within the MFI structure and likewise increased the degradation of caffeine. In addition, the mesopore formation facilitated caffeine access and transport to the MFI zeolite structure, otherwise not available in free iron microporous MFI.*



### *PVDF-MFI Mixed Matrix Membranes for VOCs removal*

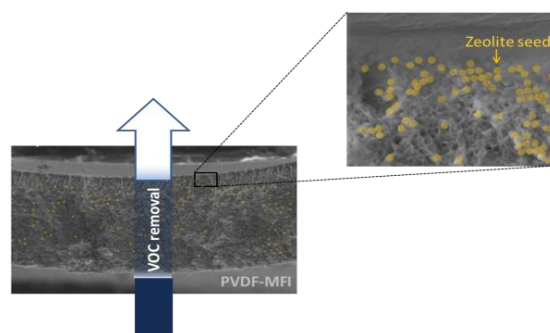
*Microporous and Mesoporous Materials 207 (2015) 126-133*

Collaborations: Univ. of Calabria- Italy ; Univ. of Zaragoza-Spain

Involved MCP researchers: Martin Drobek, Anne Julbe

*This work focuses on the preparation of porous Mixed Matrix Membranes (MMMs) by non-solvent induced phase inversion (NIPS) using poly(vinylidene fluoride) (PVDF) as polymer and nano-sized silicalite-1 (S-1) and Ti-silicalite-1 (TS-1) seeds of MFI zeolite structure as inorganic fillers. These MMMs have been used as VOCs adsorbers. Different zeolite seed concentrations (up to 22*

*wt.%) were homogeneously dispersed into the polymeric matrix to evaluate the influence of the amount of zeolites on the membrane characteristics. In all cases, asymmetric porous membranes, made up of two layers were obtained: the bottom side exhibited spherulitic structure; whereas, at the top side, a smooth layer was observed. With respect to the neat PVDF membranes, the hydrophobic character was found to be improved by the zeolite addition; in particular S-1 nano-seeds. The mechanical properties of the membranes were reduced by the addition of the filler, although the mechanical resistance of the MMMs was still sufficiently preserved. Experiments of hexane adsorption were carried out in order to evaluate the performance of the adsorbers in Volatile Organic Compounds (VOCs) removal. The as-prepared composite porous membranes revealed high adsorption capacity, confirming their potential as adsorbers for removing VOCs traces from waste air environment.*



## Functionalization of 3D printed ABS filters with MOF for toxic gas removal

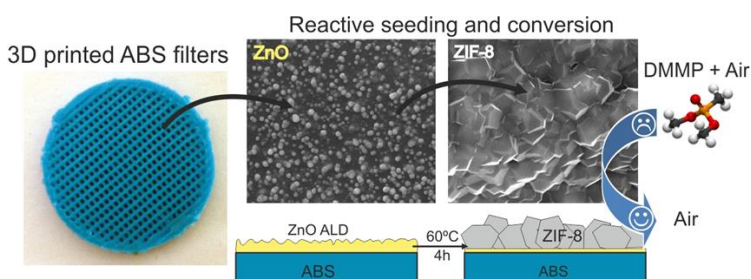
Journal of Industrial and Engineering Chemistry 89 (2020) 194–203.

Collaborations: Public Univ. of Navarra-Spain ; Univ. of Zaragoza-Spain ; Centro Universitario de la Defensa-Spain.

Involved MCP researchers: Martin Drobek, Anne Julbe,

Acrylonitrile butadiene styrene (ABS) is one of the most extensively used polymer in 3D printing manufacturing due to its competitive thermal and mechanical properties. Recently, a special attention has been devoted to novel ABS composites featuring

extra functionalities e.g. in the area of VOC removal. Herein, we report on a facile protocol for the functionalization of 3D printed ABS filters with a Metal-Organic Framework material (ZIF-8) targeting the conception of attractive gas filters. The proposed synthesis strategy consists in low temperature ALD of ZnO on the ABS grid followed by the hydrothermal conversion of ZnO to ZIF-8, both steps being conducted at 60 °C. In such way, the method enables an effective growth of ZIF-8 without altering the stability of the polymeric ABS support. The as-fabricated ABS/ZIF-8 filters offer a promising adsorption behaviour for dimethyl methylphosphonate (~20.4 mg of DMMP per gram of ZIF-8), thus proving their potential for toxic gas filtration applications.



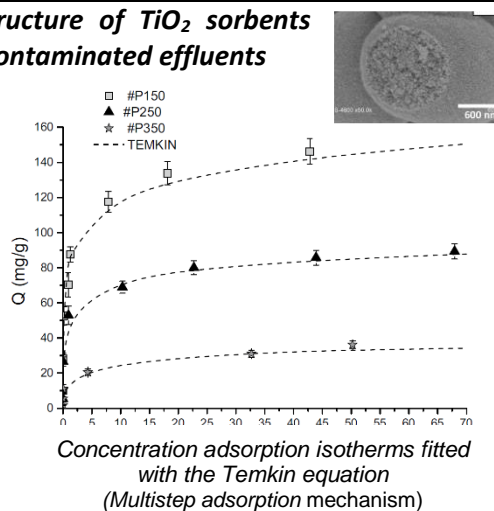
## Investigation of the surface properties and microstructure of TiO<sub>2</sub> sorbents prepared in supercritical CO<sub>2</sub> for the treatment of Sr<sup>2+</sup> contaminated effluents

SN Applied Sciences 2 (2020) 641

Collaborations: CEA-Marcoule, France

Involved MCP researchers: Anne Julbe

Nuclear facilities generate contaminated effluents containing radionuclides (such as Cs, Sr, Co...) that need to be removed for human health and environment protection reasons. Inorganic sorbents are attractive candidate materials because of their high thermochemical and radiation stability. Furthermore, their microstructural and surface properties can be adjusted to increase the radionuclide extraction efficiency. In this study, nanostructured sorbents consisting of aggregated TiO<sub>2</sub> nanocrystals with different surface properties and microstructures were prepared in supercritical CO<sub>2</sub> by varying the synthesis temperature. The Sr<sup>2+</sup> sorption process was characterized by measuring the surface properties and extraction capacity of the samples as a function of pH. In basic effluents, the Sr sorption capacity of these materials is directly linked to their specific surface area and sorption site density through a classic physisorption mechanism. Sr<sup>2+</sup> diffusion into the mesopores leads to rapid initial sorption, which is followed by a slower process driven by a proposed multistep mechanism. This mechanism involves the initial adsorption of partially hydrated Sr<sup>2+</sup> ions up to complete TiO<sub>2</sub> surface coverage, which implies slower Sr ion diffusion due to steric hindrance in small mesopores thus limiting access to additional secondary sites with lower adsorption energies



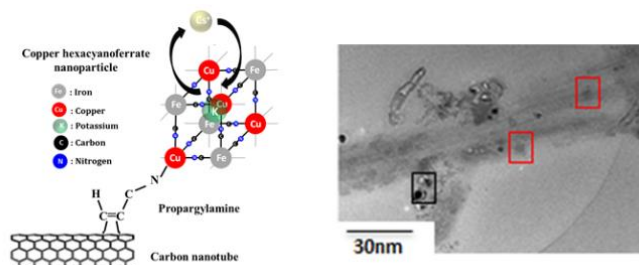
## **Copper hexacyanoferrate functionalized single-walled carbon nanotubes for selective cesium extraction**

New J. Chem. 41(15) (2017) 7705-7713.

Collaborations: Institut de Chimie Séparative de Marcoule, Labo. Charles Coulomb, Univ. de Tunis, ENSIT - Tunisie.

Involved MCP researchers: Julien Cambedouzou

*Single-walled carbon nanotubes (SWCNTs) are functionalized with copper hexacyanoferrate (CuHCF) nanoparticles to prepare solid substrates for sorption of cesium ions ( $\text{Cs}^+$ ) from liquid outflows. The high mechanical resistance and large electrical conductivity of SWCNTs are*



*associated with the ability of CuHCF nanoparticles to selectively complex  $\text{Cs}^+$  ions in order to achieve membrane-like buckypapers presenting high loading capacity of cesium. The materials are thoroughly characterized using electron microscopy, Raman scattering, X-ray photoelectron spectroscopy and thermogravimetric analyses. Cs sorption isotherms are plotted after having measured the  $\text{Cs}^+$  concentration by liquid phase ionic chromatography in the solution before and after exposure to the materials. It is found that the total sorption capacity of the material reaches  $230 \text{ mg g}^{-1}$ , and that about one third of the sorbed Cs ( $80 \text{ mg g}^{-1}$ ) is selectively complexed in the CuHCF nanoparticles grafted on SWCNTs. The quantification of  $\text{Cs}^+$  ions on different sorption sites is made for the first time, and the high sorption rates open interesting outlooks in the integration of such materials in devices for the controlled sorption and desorption of these ions.*