

M2 Topic	PMOs as adsorbent for the organic pollutant removal in aqueous phase		
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RESULTATS / ETUDES PRELIMINAIRES

Pesticide adsorption studies in aqueous phase were initiated several years ago in the Zeolite team. The first part of this study has been devoted to the adsorption of non polar organic pollutants. In this case, the hydrophobic properties of micro and mesoporous adsorbents are very important. By contrast, in the case of polar compounds, hydrophobicity is not the essential property for having a selective adsorption of polar pollutant. It is necessary to develop adsorbents with specific adsorption sites which are able to preferentially interact with the pollutant rather than water. The first results obtained in the study of the mesosulfuron adsorption on SBA-15-SO₃H or Ph-PMO-SO₃H were promising results.

RESUME DU PROJET

Synthesized for the first time by three different teams [1-3], MMS (Periodic Mesoporous Organosilica) appeared in 1999. This is a new class of organic-inorganic hybrid nanomaterials mesostructured wherein the organic moieties are totally incorporated in the silica walls. They are obtained by hydrolysis-condensation of a bis-silylated organosilica precursor in presence of a surfactant. PMOs have both an ordered mesostructure and a periodic organic pattern in the silica walls due to alternating Si-R groups (R is the organic part) [4-5]. The presence of organic groups in the mesopore walls makes these materials more hydrophobic and stable in aqueous than pure organized silicas (MCM-41 or SBA-15). In addition, PMOs can be functionalized in order to be used as heterogeneous catalysts for the catalysis in aqueous or aqueous-phase adsorbents. Work of heterogeneous catalysis in aqueous phase in the lab for a few years on the Ph-PMO-SO₃H showed that these materials exhibited considerable water stability [6] and catalytic activities higher than that of mesoporous silica SBA-15-SO₃H [7]. The remarkable catalytic activity of these materials was also observed in the literature on many reactions.

Only a few references were found in the literature concerning the use of adsorptive properties of PMOs for the removal of organic pollutants in aqueous phase. In addition, the molecules studied (BTEX, PAH) are molecules of relatively small size that easily adsorb on zeolite or activated carbon which are efficient adsorbents and less expensive than the PMOs. However, the removal by adsorption of bulky molecules in the aqueous phase is a challenge. Microporous solids do not allow efficient and rapid adsorption. Thus, Mesoporous materials are well adapted for bulky molecule removal. However, the use of conventional silica (MCM-41 or SBA-15) is not recommended because of their high hydrophilicity or their few number of efficient adsorption sites. The grafting of hydrophobic sites and active sites is therefore necessary to use these materials. Some laboratory tests have shown that the performance of adsorption of Ph-PMO were significantly higher than those of a silica MCM-41 and SBA-15 silylated same. The subject of this master 2 deals with PMOs use for the removal of pesticides in aqueous phase. These materials are more stable in aqueous phase and hydrophobic than mesoporous silicas because of their organic groups located within their walls. Different materials will be synthesized, characterized and tested in aqueous phase adsorption (adsorption isotherms). Particular attention will be paid to the nature of the aromatic groups located in the walls in order to highlight the possible effects of $\pi - \pi$ stacking to explain the organophilic

properties of these materials.

[1] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* 1999, 121, 9611 – 9614.

[2] B. J. Melde, B. T. Holland, C. F. Blanford, A. Stein, *Chem. Mater.* 1999, 11, 3302 – 3308.

[3] T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* 1999, 402, 867 – 871.

[4] S. Inagaki, S. Guan, T. Ohsuna and O. Terasaki, *Nature*, 2002, 416, 304-307.

[5] N. Bion, P. Ferreira, A. Valente, I. S. Gonçalves, J. Rocha, *J. Mater. Chem.*, 2003, 13, 1910–1913

[6] A. Karam, J. C. Alonso, T. I. Gerganova, P. Ferreira, N. Bion, J. Barrault, F. Jérôme, *Chem. Commun.*, 2009, 7000–7002.

[7] R. Siegel, E. Domingues, R. De Sousa, F. Jérôme, C. M. Morais, N. Bion, P. Ferreira, L. Mafra, *J. Mater. Chem.*, 2012, 22, 7412-7419.