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ADSORPTION OF DIOXINS AND 1,2-DICHLOROBENZENE ISSUED FROM WASTE INCINERATION INTO ZEOLITES AND METAL-ORGANIC FRAMEWORKS (MOFS) MATERIALS

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Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans can be emitted from different industrial sources. In the case of waste incineration plants, the European Directive 2010/75/UE has set a dioxin emission limit value (ELV) at 0.1 ng I-TEQ.m⁻³ (International-Toxic Equivalents) with 11% of O₂ content. In order to meet such ELVs, adsorption is often considered to be the easiest to implement and the cheapest option. In this study, zeolite- and Metal-Organic Framework-types adsorbents were employed.

Zeolites are crystalline microporous solids with crystalline aluminosilicate or pure silica frameworks. They are constituted of channels and cavities of molecular dimensions. These materials have already been tested for dioxin removal.^{1,2} Metal-Organic Frameworks (MOFs) are based on the assembly of organic linkers and inorganic entities (metal ions) to form crystalline networks with high pore volumes and surface areas. Some MOFs have already been used for gas storage or pollutants adsorption.³ But to our knowledge, none has been investigated for the dioxin adsorption.

Because of their toxicity and their very low volatility, the handling in laboratory of dioxin compounds is delicate. Polychlorobenzenes were often used as probe molecules to mimic dioxins. In addition, this type of molecules constitutes precursors in the formation of dioxin compounds and thereby is also present in waste treatment gases.^{4,5}

Materials and methods

FAU-type zeolite powder with crystal sizes of 3-5 μm (Si/Al = 1.1, NaX Sigma-Aldrich®) and MOF MIL-101(Cr) powder with crystal sizes of 1-2 μm synthesized according to Hong et al.⁶ were used. FAU-type zeolite beads were made using an Eirich® shearer/mixer as described by Rioland et al.⁷ They were prepared with 5 wt. % (in the final beads) of inorganic binder (Na₂SiO₃).

1,2-dichlorobenzene adsorption kinetics in FAU-type zeolite powder and beads (with different diameters: 0.25 < Øbeads < 0.4 mm and 0.5 < Øbeads < 0.8 mm) and MOF MIL-101(Cr) powder were carried out using a Setaram® TGA 92 thermobalance under dynamic conditions. The adsorption of 1,2-dichlorobenzene was performed at 25°C with a relative pressure $p/p^\circ = 0.5$ (p is the vapor pressure and p° is the saturation vapor pressure of 1,2-dichlorobenzene at 25°C ($p^\circ = 1.36$ mmHg)).

These adsorbents have also been tested in a waste incinerator for toxic dioxin congeners adsorption (during two different site measurement campaigns).

Results and discussion

The adsorption kinetics of 1,2-dichlorobenzene in FAU-type zeolite powder and beads are shown in Figure 1.

The presence of binder in beads slightly affects the adsorption capacity of FAU-type zeolite. Indeed, the adsorption capacity of beads is close to 25 molecules per unit-cell instead of 29 for the powder. Moreover, it is worthy to observe that the kinetic adsorption of the 1,2-dichlorobenzene is much faster (x1.5) in beads than in powder. This might be explained by closer micropores in small beads and therefore a faster diffusion of 1,2-dichlorobenzene molecules.

The adsorption capacity of MOF MIL-101(Cr) is multiplied by 5 compared to FAU-type zeolite (see Figure 1). This is explained by a micropore volume 5 times greater for the MOF material (1.44 versus 0.30 cm³/g). Additionally, the adsorption appears faster in MOF MIL-101(Cr) than in the FAU-type zeolite powder. This kinetic difference could be explained by the presence of larger pores and by some preferential adsorption sites such as the aromatic linkers and the Lewis acidic sites in the MOF structure.

The distribution of toxic dioxin congeners in FAU-type zeolite small (0.25 < Øbeads < 0.4 mm) and bigger (0.5 < Øbeads < 0.8 mm) beads obtained in the first campaign is reported in Figure 2 (a) and (b). In Figure 2 (c) and (d) is given the distribution of dioxin congeners obtained in the second campaign for a mixture of 5 g of MOF MIL-101(Cr) powder dispersed in 25 g of FAU-type zeolite small beads and for 30 g of FAU-type zeolite small beads.

The analytical results show a slightly higher concentration of dioxin congeners in small bead adsorbents (Figure 2, (a)) than in the bigger ones (Figure 2, (b)). This might be explained by a better diffusion of 1,2-dichlorobenzene molecules in the core of the small beads and therefore a greater adsorption capacity than in the bigger ones.

The second campaign (Figure 2 (c) and (d)) confirms the previous results obtained for the MOF material. Assuming that the MOF powder is homogeneously dispersed among the small FAU-type zeolite beads, the results show that MIL-101(Cr) material is more efficient than the FAU-type zeolite for dioxin adsorption.

The noteworthy sorption properties of the MOF material make it very promising for environmental applications.

Acknowledgements

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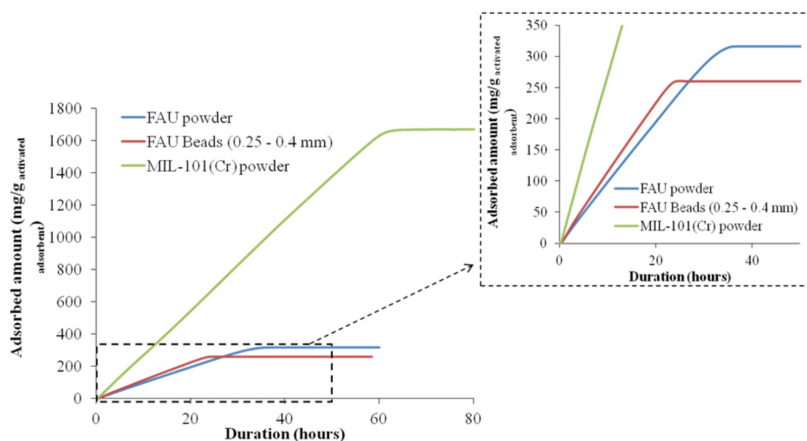


Figure 1: Adsorption kinetics of 1,2-dichlorobenzene in FAU-type zeolite powder (blue curve), small beads with $0.25 < \phi_{\text{beads}} < 0.4\text{mm}$ (red curve) and MOF MIL-101(Cr) (green curve)

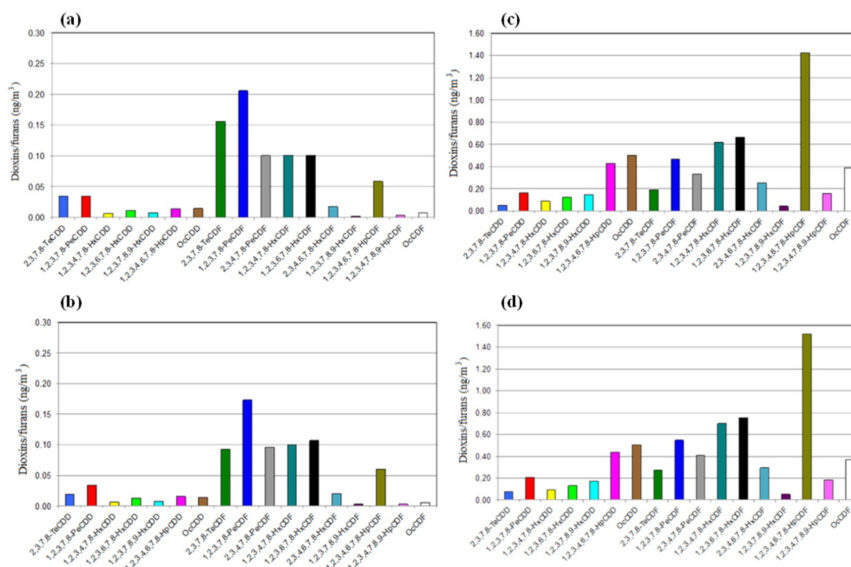


Figure 2: Distribution of dioxins and furans in adsorption cartridges used in the first measurement campaign ((a) for FAU-type zeolite small beads ($0.25 < \phi_{\text{beads}} < 0.4\text{mm}$), (b) for FAU-type zeolite big beads ($0.5 < \phi_{\text{beads}} < 0.8\text{mm}$)) and in the second measurement campaign ((c) for FAU-type zeolite small beads ($0.25 < \phi_{\text{beads}} < 0.4\text{mm}$) and (d) for MIL-101(Cr) (5 g) dispersed among 25 g of small FAU-type zeolite beads ($0.25 < \phi_{\text{beads}} < 0.4\text{mm}$))