

SIZE CONTROLLED SEPARATION OF DIOXINS BY ADSORPTION ONTO ZEOLITES

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Introduction

Incineration is the most common way to reduce solid waste volumes, reaching about 75%. However, gases from the incinerator stacks contain pollutants such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, both known as "dioxins". Although the amounts of dioxins in incineration gases are quite low, some are very toxic.

Many countries have introduced standards for dioxins emission. The European Directive 2000/76/EC sets emission low-threshold values for dioxin at 0.1 ng I-TEQ.m⁻³ with 11% of O₂ content for waste incineration and co-incineration plants¹ referring to a sampling period from six to eight hours (European Union 2010)².

In France, legislation on waste-incineration emission monitoring was recently modified. Semi-continuous dioxin measurements based on monthly sampling for instance are used³. Even if this approach provides more information about dioxin emission, continuous on-line measurements will probably be needed in the future.

Therefore, the main objective of the study on hand is to participate developing a method to detect dioxins at ppb to ppm levels in real time. For this we use a procedure of pre-concentration by selective adsorption onto zeolites prior to controlled thermal-desorption and mass spectrometry analysis.

We established a method for size-selective dioxin adsorption in non-aqueous solution (iso-octane) with activated (completely dehydrated) zeolites as adsorbents.

Zeolites are crystalline, essentially aluminosilicate based microporous solids. Their mineral framework (Si-O-Al) can be described as a construction of tetrahedra TO₄ where T stands for silicon or aluminium, and O for oxygen atoms; each oxygen atom is shared by two tetrahedra. Al in the silica framework induces a negative charge, to be compensated by extra-framework cations such as Na⁺, K⁺, Ca²⁺, and others. Furthermore, water molecules are present in the zeolite pore system forming hydration spheres on the cations (zeolitic water).

The use of zeolites as adsorbents is related to their high capacity of adsorption (up to 1.2 mmol of dioxin per gram, theoretically) together with their size and shape selectivity which could lead to the separation of dioxins according to their toxicity (related to their Cl-symmetry) and the exclusion of other compounds of the stack gas. Affinity and capacity depend on the intrinsic properties of the respective zeolite structure type, residual water content and the type of charge compensating cations.

Zeolites have already been tested for dioxin adsorption. Some have been used for the adsorption of dioxin and furan emissions from a municipal solid waste incinerator⁴ and zeolites with different pore sizes have been chosen to gain a selective adsorption for dioxins⁵. The results showed that adsorption takes place according to the pore size and the dynamic size of dioxin molecule. Also, in another study⁶, results showed that the nature of the charge compensating cations present in the zeolite pores could have an influence on the adsorption of dibenzofuran (zeolite framework not specified).

In this paper we show that the zeolite with the highest affinity towards adsorption of a given dioxin (FAU13X) can be modified by ion exchange in order to adsorb other dioxins to separate 2,3-dichlorodibenzo-p-dioxin (2,3-DCDD), 1,2,3-trichlorodibenzo-p-dioxin (1,2,3-TrCDD) and 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TeCDD), which is size equivalent to the biggest existing dioxin. Furthermore, dioxins with a large number of chlorine are the most interesting because of their concentration in incineration gases.

Charge-compensating cations have different sites in zeolites. Some positions of cation sites can prevent the access of dioxins to pores, such as site III for FAU zeolites [Fig 1].

In order to adsorb these types of dioxins, ion exchange of FAU13XNa zeolites' respective charge-compensating cation vs Ce^{3+} , La^{3+} and Y^{3+} was done, as ion exchange can liberate access to pores: each Ce^{3+} , La^{3+} and Y^{3+} cation will theoretically replace three Na^+ cations on the same site.

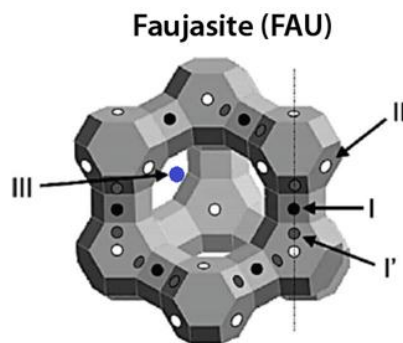


Fig 1: Different cation sites of FAU zeolites⁷.

Materials and methods

The study on hand is performed with 2,3-DCDD and 1,2,3,4-TeCDD. Dioxins are purchased from Techlab (Metz, France). Solutions for analyses are prepared in extra dry 2,2,4-trimethylpentane, 99,5%, better known as isooctane (SDS, France).

Two zeolites structure types with different morphologies were tested: FAU13X (Si/Al=1.3, Na^+ , grain size 2 μm , Sigma-Aldrich, USA) and, alternatively zeolite BEA* (Si/Al = 300, H^+ , medium grain size 400 nm, Zeolyst, USA).

Cation exchanges of FAU13X were carried out in aqueous solutions of $Ce(NO_3)_3$, $Y(NO_3)_3$ and $La(NO_3)_3$ (Sigma Aldrich). With the exception of Y^{3+} , solutions of 1 M were used for cation-exchange with a liquid/solid ratio of 100 ml/ gram of zeolite. The procedure was repeated once a 50°C and each exchange lasted about 12 h. The product was filtered and washed with distilled water each time. A total of 2 g of each zeolite was prepared for each batch.

For $Y(NO_3)_3$, a solution of 0.05 M was used instead of 1 M because of its high acidity as very acidic solutions can damage the structure of zeolites.

Adsorption measurements were established by the depletion method using an Agilent HPLC System. The adsorbed amount is derived from the variation of concentration due to adsorption under agitation at 50°C. The equation (1) is used to determine the amount of adsorbed dioxin onto zeolite at equilibrium (N_{eq}):

$$N_{eq} = \frac{(C_i - C_{eq}) \times V}{m_s} \quad (1)$$

where C_i is the initial concentration of dioxin in isooctane, C_{eq} the equilibrium concentration, m_s the zeolite mass and V the volume of solution exposed to zeolite adsorbents.

The zeolites were previously heated at 350°C over a period of about seven hours to eliminate any adsorbed water as far as possible (activation). Then they were ready for dioxin adsorption.

For each experiment, 20 mg of activated zeolite were placed into a vial in contact with 1ml solution of dioxin. Standard solutions of dioxins are prepared with dry isooctane. Vials are heated at 50°C for two hours. Early studies have shown that equilibrium is achieved under these conditions.

A volume of ca. 0.5 ml was taken from the supernatant and filtered for HPLC analysis, thus allowing the measurement of equilibrium concentrations. The analyses were carried out using an UV detector. They are performed at 294 nm with isooctane as the solvent at a constant flow rate of 0.5 ml/min.

As we always had only one type of dioxin to be analysed, there was no need to use a separation column. The injection system was connected directly to the UV detector. During analysis, the temperature was held constant at 25°C.

Results and discussion

Our focus laid on the affinity between zeolites and dioxins. Earlier studies found the highest affinity of 2,3-DCDD towards FAU13XNa from all tested zeolites (FAU and BEA*- structure type)⁸ [Fig 2].

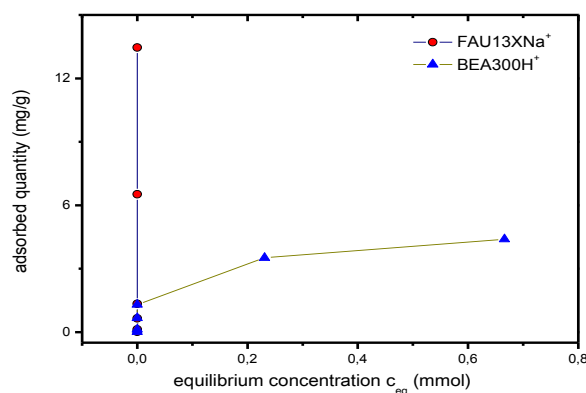


Fig 2: Adsorption isotherms of 2,3-DCDD on FAU and BEA*- structure type.

These results also showed the bad adsorption performance of FAU zeolite structure type for the biggest dioxin molecules such as 1,2,3,4 TeCDD, probably due to blocking Na⁺ ions in every site III position (see fig.1). Based on these results, FAU13XNa was selected for ion exchange for trivalent cations in order to partially liberate the passage and to potentially adsorb 1,2,3,4-TeCDD. Results show that ion exchange was established up to 80% [Fig 3].

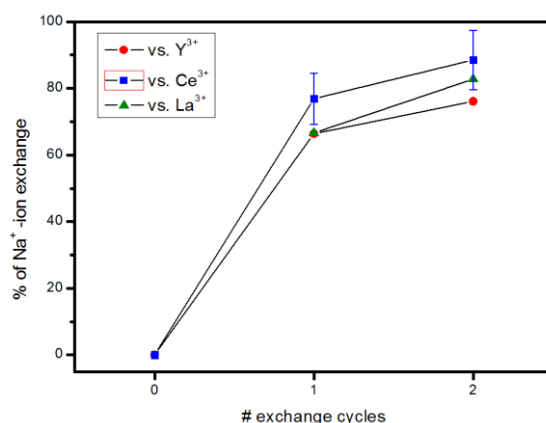


Fig 3: Ion exchange of FAU13XNa zeolites' respective charge-compensating cation vs Ce³⁺, La³⁺ and Y³⁺.

We can show that 1,2,3,4-TeCDD is adsorbed on all FAU13XMe³⁺ zeolites with different affinities and quantities. Figure 4 shows the results of adsorption behaviour between the most performant FAU13XMe³⁺, which is FAU13XLa³⁺, compared to standard FAU13XNa⁺:

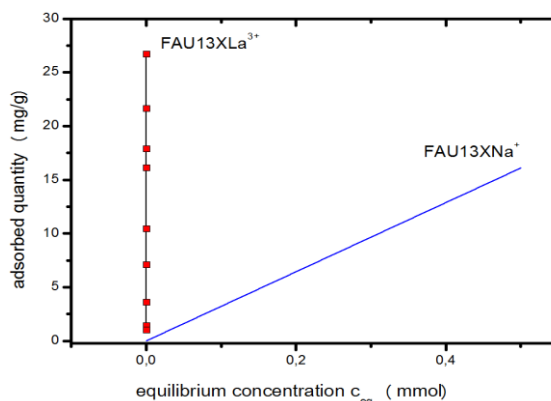


Fig 4: Adsorption isotherms of 1,2,3,4-TeCDD on FAU13XLa³⁺ and FAU13XNa⁺, respectively.

Due to the very high affinity of 1,2,3,4 TeCDD towards FAU13XLa³⁺ the reversibility of the dioxin-zeolite interaction has to be questioned. Current investigations by solid state MAS-NMR have to clarify if the dioxin molecules adsorbed on the zeolite remain unaltered compared to those in solution.

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