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Ion exchange effect on asymmetric dioxins adsorption onto FAU-type X-zeolites

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ABSTRACT

The effect of trivalent cation exchange on fully dehydrated (activated) FAU-type X-zeolites with respect to the adsorption of the sterically biggest, asymmetric dioxin-molecules (1,2,3,4 TeCDD) in iso-octane solvent was investigated. FAU 13X Na zeolites were selected due to their pore openings, close to the diameter of the 2,3-DCDD (0.74 nm) as well as their high adsorption affinity for this dioxin molecule. This zeolite also adsorbed 1,4 DCDD, but with significantly lower affinity.

With the aim to eventually liberate the channel's access for the sterically biggest dioxin molecule 1,2,3,4 TeCDD, Na^+ cations were replaced by trivalent cation species Y^{3+}, Ce^{3+} and La^{3+}. Symmetric dioxins were not tested in this study due to their high toxicity.

Analyses performed indicate that cation exchange reaches 80% on the zeolite, while the zeolite structure is preserved during the process. La^{3+}- FAU-type X-zeolites showed the same extreme affinity towards 1,2,3,4 TeCDD as Na^+ – FAU-type X-zeolites did for 2,3-DCDD. At the same time it could be shown that both dioxins could be separated by adsorption, while 1,2,3,4 TeCDD only interacts with the external surface of Na^+-FAU-type X-zeolite, not entering the zeolite pores.

1. Introduction

Management of solid waste is a major challenge of today's society. Due to its increasing quantity, nowadays, in combination with waste separation and recycling, incineration is considered to be an efficient way for waste disposal such as municipal waste, medical waste and hazardous waste [1]. In fact, this process reduces the waste volume to 20–30%, however, small amounts of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, collectively known as “dioxins” are released into the atmosphere as a result of such combustion processes.

Dioxins are chemicals known as Persistent Organic Pollutants (POPs). They are composed of two benzene rings interconnected by two oxygen atoms for polychlorinated dibenzo-p-dioxins (PCDDs) or by one oxygen atom for polychlorinated dibenzofurans (PCDFs). These molecules can have from zero to eight chlorine atoms on the benzene rings, which make a total of 75 congeners of chlorinated dibenzo-p-dioxins and 135 of chlorinated dibenzofurans [2].

A report released by the US Environmental Protection Agency (Committee on EPA's Exposure and Human Health Reassessment of TCDD and Related Compounds 2006) clearly describes dioxins as carcinogenic substances to humans [3]. In addition, dioxins also adversely affect the immune and endocrine systems and constant exposure can cause severe reproductive and developmental problems.

Dioxins and related compounds are members of a class of polyhalogenated hydrocarbons and their harmfulness is well known. However, the toxicity of dioxins varies with the substitution pattern and the number of the chlorine atoms. Only 17 of the 210 congeners of dioxins are considered as toxic molecules. The most toxic is the 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) known as Seveso dioxin. Typically, its concentration is much lower than that of the less toxic congeners. Toxic Equivalency Factors (TEFs) are toxicity potency factors that are proposed by the World Health Organization (WHO – 2010 [4]) and used globally by scientists and regulators as a consistent method to evaluate the toxicities of a mixture of dioxin. 2,3,7,8-TCDD is assigned a TEF of 1 and the remaining compounds (i.e., those with chlorine substitution in the 2,3,7, and 8 positions) are typically assigned values lower than 1.

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In order to determine the toxicity of mixtures of dioxin compounds, Toxic Equivalent Quantity (TEQ) is used. To calculate the TEQ of a mixture, the concentration (or mass) of an individual congener is multiplied by its respective TEF, or weighting factor, to obtain the congener specific TEQ concentration (or mass). The sum of the TEQ concentrations for the individual congeners is the TEQ concentration for the mixture of the concentration of the 17 most toxic dioxins.

Among Semi-Volatile Organic Compounds (SVOCs), dioxins are ubiquitous in all environmental compartments. Moreover, much of the environmental behaviour of dioxins can be related to their physical and chemical characteristics. All PCDDs and PCDFs are organic solids with high melting temperatures and very low vapour pressures. They are characterised by a low water solubility, and have a tendency to be strongly adsorbed on highly dispersed surfaces. The water solubility of dioxins and furans decreases with the increase of chlorine content. Due to their lipophilic character, low volatility and resistance to degradation properties, the dioxins are adsorbed onto soil and sediment particles. The persistence in environment leads to a potential health hazard, to humans and other organisms.

Worldwide, many countries have introduced stringent standards for dioxin emission because of their adverse health effects. The European Directive 2000/76/EC sets emission limit values for dioxin at 0.1 ng I-TEQ.m^{-3} with 11% of O_2 content for waste incineration and co-incineration plants [5,6]. This value is an average rate of emission referring to a sampling period from 6 h at least to 8 h at maximum (European Union 2010). In France, there are still strong concerns regarding dioxin emissions from waste incineration plants. Hence, in August 2010, the French legislation on waste incineration was modified in order to require dioxin semi-continuous measurements based on a monthly sampling for instance (French government 2010 [7]). However, although they will provide a more comprehensive information, such semi-continuous measurements will not be sufficient if on-line measurements are needed in the future.

According to the European standard three manual sampling methods can be performed: the filter/condenser method, the dilution method and the cooled probe method. Stack gas is sampled isokinetically by using a probe; it passes through a glass fiber filter and a packed column of adsorbent material, such as XAD-2 resin or polyurethane foam. The most interesting method is the filter/condenser method as the sample gas is cooled to below 5 °C before it passes through the adsorbent. Hence most condensable compounds in large amounts such as moisture could be removed before by trapping. Then, sampling supports and materials are sent to accredited laboratories, where a solid–liquid extraction (Soxhlet) is performed for adsorbent and filter. Highly selective sampling purification techniques as well as very specific and sensitive analytical methods are required: high resolution gas chromatography (GC) combined with high resolution mass detection [8] (European Committee for Standardisation 2006). Consequently, pollution levels are available three weeks later at least. This long period is mainly due to the extraction and clean-up steps. Indeed, most of the stack-gas compounds are trapped on these universal adsorbents [9]. This long period could be reduced by the use of specific materials, such as zeolites or related materials, which could trap selectively dioxin congeners from the stack gas. Zeolites could also be implemented in an on-line adsorption and thermo-desorption device coupled to a mass spectrometer (MS) for direct dioxin monitoring.

Zeolites used are crystalline aluminosilicate microporous solids. Their mineral framework (Si–O–Al) can be described as an assembly of tetrahedra TO_4 where T stands for silicon or aluminium, in which the vertices are occupied by oxygen atoms and each oxygen atom is shared by two tetrahedra. These assemblies determine channels and cavities of molecular dimensions, with precisely defined sizes [10]. Zeolites have already been tested for dioxins. A phonolite containing 45% zeolite (zeolite framework not specified) has been used for the adsorption of dioxin and furan emissions from a municipal solid waste incinerator [11]. Also, zeolites with different pore sizes have been chosen to gain a selective adsorption for dioxins [12].

Results showed that adsorption takes place according to the pore size and the dynamic size of dioxin molecule [13]. Furthermore, it was demonstrated that the nature of the cations trapped in the pores of zeolite could have an influence on the adsorption of dibenzofuran [14].

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 with the aim to separate 2,3-dichlorodibenzo-p-dioxin (2,3-DCDD), 1,4-trichlorodibenzo-p-dioxin (1,4-DCDD) 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.

2. Experimental

2.1. Materials

This study was performed with 2,3-dichlorodibenzo-p-dioxin (2,3-DCDD), 1,4-dichlorodibenzo-p-dioxin (1,4-DCDD) and 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD). Dioxins were purchased from Techlab (Metz, France). The dioxins are, according to Techlab, Metz, France, 100% pure. According to our GC analyses, no impurities could be detected, which means that eventually present impurities are lower than 10e^{-9}g.

2,3-DCDD has the same dynamic static size as 2,3,7,8-TeCDD (about 0.74 nm). Therefore, size selective adsorption of 2,3,7,8-TeCDD can be simulated by 2,3-DCDD adsorption. The adsorption of 1,4-DCDD compared to 2,3-DCDD allows us to study the influence of position isomers of polychlorinated dibenzo-p-dioxin. The static sizes of 1,4-DCDD and 1,2,3,4-TeCDD are about 0.99 nm.

Solutions for analysis were prepared in extra dry 2,2,4-Trimethylpentane, 99,5%, better known as isooctane (SDS, France).

FAU 13X Na zeolite was selected due to its dynamic size (about 0.74 nm) and was purchased from Sigma–Aldrich, USA (Si/Al = 1,3; Na^+ as charge compensating cation; grain size 2 μm).

Cation exchanges of FAU 13X Na were carried out in aqueous solutions of $Ce(NO_3)_3$, $Y(NO_3)_3$ and $La(NO_3)_3$ (Sigma Aldrich). Modified zeolites should have the same pore size as FAU 13X Na (about 0.74 nm).

2.2. Characterisation methods

Water content of the zeolite was evaluated by thermogravimetry using TGA Q500 from TA Instruments, USA, in order to determinate the activation temperature before and after ion exchange. Analyses were performed in high resolution mode under argon with a heating rate of lower than 5 °C/min. Samples were heated up to 400 °C. Morphology, grain size of zeolites and chemical composition before and after ion exchange were examined by Scanning Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy (SEM/EDS) using a Philips SEM XL30Sfeg FEI, The Netherlands, equipped with an Oxford EDX Inca 300, United Kingdom, EDS system.

The FAU 13X Na used was characterised in terms of structure and phase purity by X-ray powder diffraction before and after ion