ZEOLITES AS SELECTIVE ADSORBENTS FOR EMISSION CONTROL OF DIOXINS – GAS FLOW IN ZEOLITIC POROUS MEDIA, GENERATION AND ADSORPTION

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Introduction:
Worldwide, incineration is used as waste treatment. The incomplete combustion of organic and chlorinated compounds generates polychlorinated dibenzo-p-dioxins (PCDD). Because of their adverse heath effects, many countries have established stringent standards for dioxin emissions. Only 17 congeners are toxic. Their toxicity is due to the chlorine atoms located in the 2,3,7,8 positions. The 2,3,7,8-TCDD, known as Seveso dioxin, is the most toxic PCDD. The European Directive 2000/76/EC sets emission limit values for the toxic dioxins at 0.1 ng I-TEQ.m^{-3} for waste incineration and co-incineration plants[1]**.** The International Toxic Equivalent Quantity (I-TEQ) is calculated by multiplying the concentration of each 2,3,7,8-chlorine substituted PCDD/F (i.e17 congeners.) by its respective Toxic Equivalent Factor.

In this work, we develop a new laboratory prototype of an analytic device coupling an adsorption, a thermal desorption, a gas chromatography and a mass spectrometry stages. This prototype could be added to the filter /condenser sampling method in order to carry out in-line and real time toxicity detection and quantification.

Indeed, from the three manual sampling methods detailed by the European standard[2], the filter/condenser method is the most suitable for our application, as the gas is cooled to below 5 °C before it passes through the adsorbent (XAD-2 resin or polyurethane foam). Thus, condensable compounds like water (moisture) are removed from the gas before passing through the adsorbent. The adsorbent and all the sampling system are cleaned to collect and then to extract and analyse dioxins. Analyses are carried out by sample purification and by high resolution gas chromatography coupled with high resolution mass spectrometry. The laboratories in charge of these analyses have to be accredited. Carrying out this process is quite long; results are obtained after a minimum of three weeks. Using a selective adsorbent instead of resins might reduce this delay.

The process will have to be selective, due to the complex nature of flue gas. Stack emission contains interfering chemicals, at much higher concentrations than the trace amounts of dioxins. To obtain the selective property, we have chosen to use zeolites as adsorbent instead of the resin adsorbent described in the standard process. Zeolites have a lot of interesting characteristics. For instance their pore size can be readily controlled allowing dioxins to be trapped according to their dynamic dimension and consequently to their toxicity. Consequently the most toxic TCDD (2,3,7,8-TCDD) with a lower dynamic dimension than the non toxic TCDD (1,2,3,4-TCDD) will be selectively adsorbed on a zeolite with the appropriate pore size.

Several works are carried out to complete this project. The first one was focused on liquid phase adsorption of dioxin on several media, such as XAD-2 resin, or several zeolites: **EMT**, **FAU** [NaX], **MFI** [Silicalite-1], to perform a preliminary choice of a suitable adsorbent[3]. It concluded that **FAU** [NaX] is the most accurate; it presents the best adsorption affinity, capacity and selectivity of adsorption between 2,3-DCDD and 1,2,3,4-TCDD.

The second work, concerning the gas phase study, is composed of two steps which are carried out at the same time. One is the characterisation of gas flow in a bed of porous medium, (more precisely **FAU** [NaX]) in order to obtain the best experimental parameters to ultimately optimize the dynamic adsorption. The other is the gaseous dioxin generation in an inert gas flow for the two non toxic molecules 1,2,3,4-TCDD and 2,3-DCDD. Once this stage will be achieved, the dynamic adsorption will be studied (breakthrough, kinetic, isotherm) for the **FAU** [NaX] and compared with the XAD-2 adsorbent.
In this paper, the flow characterisation and the dioxin generation will be presented.

Materials and methods:
To characterise the flow, the porous medium is set in an instrumented tube. This tube is made of Plexiglas [see Fig. 1-a] and equipped with five pressure gauges which are almost in contact with the porous bed. This device is located in an experimental setup composed of a mass flowmeter [Fig.1-b], a regulation valve [Fig.1-c], and pressure sensors (absolute [Fig.1-d] and differential [Fig.1-e]). A homemade LabVIEW program is used to control the flow and acquire pressure data.

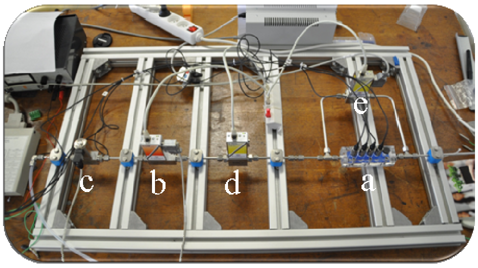

Figure 1: Experimental set up dedicated to flow studies

Thanks to this setup, the energy loss induced by selected porous media is determined. The pressure gradient along the cylindrical porous tube is calculated from the different pressure measurements by plotting the modified pressure (taking into account the compressibility effect) versus the location [Figure 2]. The permeability, the inertial coefficient, the Ergun coefficients [4,5] can be determined.

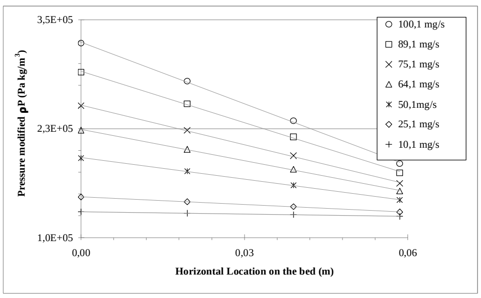

Figure 2: Modified pressures along the porous bed

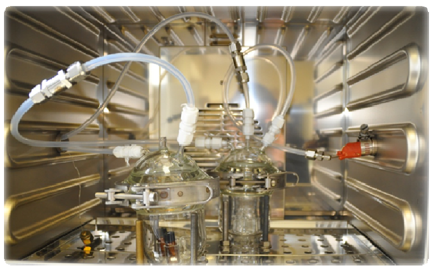
Figure 3: Gaseous dioxin generation

For dioxin gaseous phase generation, solid dioxin is set in a vial with a permeable membrane. The vial is placed in a pressurized glass vessel [see Figure 3], heated in an oven. Nitrogen passes through the vessel, driving out the gaseous dioxin. Both the nitrogen flow used for the dioxin generation and a dilution nitrogen flow are controlled. The dioxin concentration is set by varying the generation and dilution flows. The dioxin generation is determined by weighting the mass loss inside the vial. The polluted flow can be analysed by gas chromatography coupled with mass spectrometry.

Results and discussion:

Flow study

The lineic pressure drop is determined for each porous bed. It is important to reduce the energy loss induced by the porous filter in order to increase for instance either the flow velocity to improve the adsorption kinetics, or the bed length to improve the adsorption capacity. The influence of various parameters was tested such as flow rate, shape (beads or pellets), bed length, porosity and granulometry. Figure 4 gives an example of the lineic pressure drop versus the gas velocity for two kinds of zeolite without binder. As expected, the smaller the particles, the greater the lineic pressure drop. Nevertheless, even for the same particle size, huge differences are observed depending of the zeolite type. This behaviour is due to the irregular shape and the surface roughness of the zeolites obtained after compression and grinding.

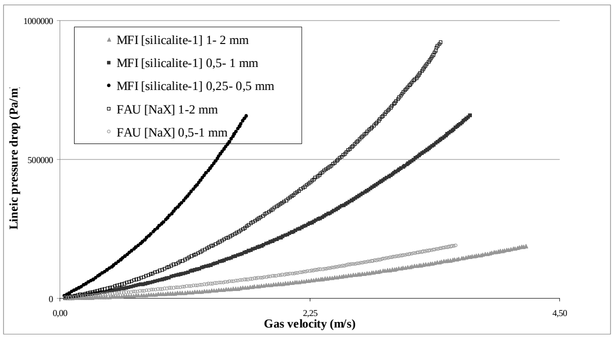

Figure 4: Lineic pressure drop for **MFI** [silicalite-1] and **FAU** [NaX]

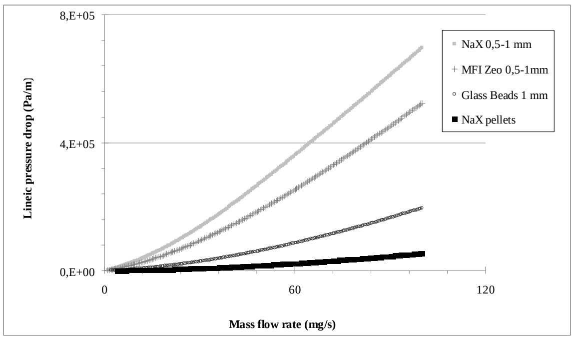

Figure 5: Lineic pressure drop for **MFI** [silicalite-1], **FAU** [NaX], glass beads and XAD-2

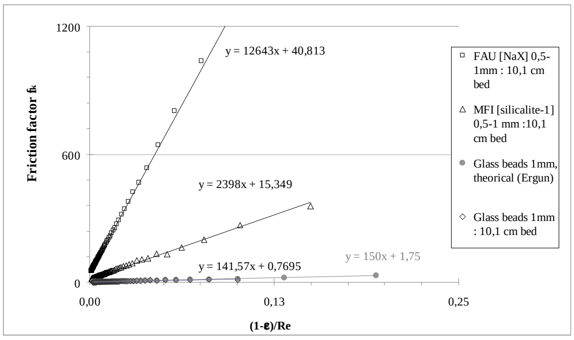

Figure 6: Modified Friction Coefficient versus modified Reynolds number

Figure 5 compares the results obtained with glass beads, **FAU** [NaX] zeolite pellets with binder, XAD-2 resin and two sizes of **FAU** [NaX] (1-2 mm B, 0.5-1 mm C). We can see that the energy loss induced by the **FAU** [NaX] is similar to the one induced by the XAD-2 used at present for the normalized sampling. An analysis of these kinds of results can lead to the determination of the friction coefficient law versus the modified Reynolds number [see Figure 6]. The Ergun model does not fit in the zeolite case, the model will have to be modified to take into account factors such as the shape.

Generation study

A parametric study of the generation of gaseous dioxin versus the temperature of the oven and of the flow rate has been performed. Figure 7 shows the results obtained for the 2,3-DCDD by varying the temperature and keeping the inert gas flow constant (200 mL/min). For a given temperature we can observe that the mass generated is linear versus time, consequently we obtain a constant rate of generation. The generated mass rate

increases with the oven temperature. Then, the oven temperature is kept stable (95°C), but the generation and the dilution flows vary [see Fig. 8]. The sum of these two flows equals 200 mL/min.
It seems that the generation mass rate is not dependant on the inert flow rate. This behavior is due to the fact that the more significant phenomenon in the dioxin vial and through the permeable membrane is diffusion. This hypothesis will be confirmed

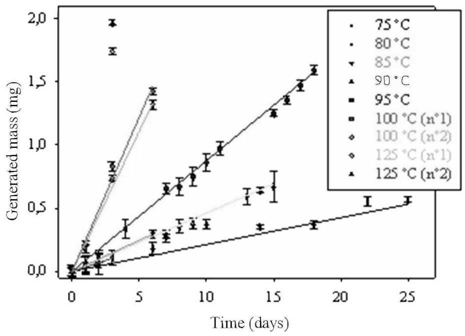

Figure 7: Generated mass of dioxin for different oven temperatures

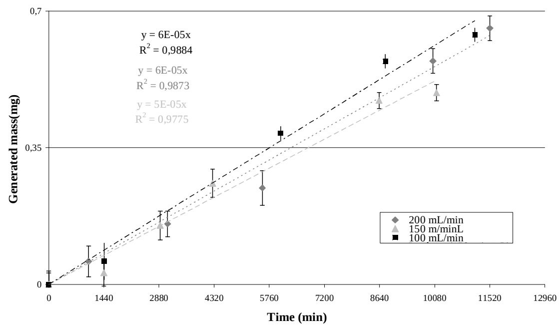

Figure 8: Generated mass of dioxin for different flow rates

Conclusion:
The flow study shows the importance of the zeolite shape. Zeolite coarse grains lead to an important lineic pressure drop. Moreover it induces a non homogenous bed, so the porosity is not equals all along the bed, which can affect the dioxin adsorption. Spheres of **FAU**[NaX] can be synthesized, without binder to maximize the adsorption. Thus a regular particle pilling will be obtained.
The gaseous dioxin generation is not related to the flow rate, it only depends on the oven temperature. So the concentration of gaseous dioxin can be controlled by adjusting the temperature and the two kinds of flow.
The adsorption efficiency of **FAU**[NaX] and XAD-2 resin will be compared during a field sampling campaign scheduled in May 2011 and in our laboratory using the generation of 2,3-DCDD at a constant rate.

Acknowledgements:
These studies have been undertaken thanks to financial support from the French Agency for Environment and Energy Management (ADEME), the French National Research Agency within the scope of the Environmental Technologies Programme and Sustainable Development (ANR PRECODD 2007 – METERDIOX).
These works are supported by NOVERGIE subsidiary of SITA France specialist in waste treatment and recovery within the Suez Environnement group.
The French Competitiveness Clusters on Risk Management (Pôle de compétitivité Gestion des risques, vulnérabilité des territoires) have given the "METERDIOX" project their seal of approval.

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