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Selective adsorption of 2,3-DCDD and 1,2,3,4-TCDD on *BEA, EMT, FAU and MFI-type zeolites as alternative adsorbents for on-line dioxin monitoring

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Abstract The aim of this study is to evaluate the capabilities of zeolites as selective sorbents for on-line dioxin monitoring. The adsorption isotherms of 2,3-DCDD and 1,2,3,4-TCDD from isooctane on several zeolites with different pore sizes (*BEA, EMT, FAU and MFI-type zeolites) are determined. Selective adsorption is shown for FAU and EMT-type zeolites. 2,3-DCDD is adsorbed by FAU with the highest adsorption capacity and affinity while 1,2,3,4-TCDD is not adsorbed whatever the zeolites. The adsorption of 2,3-DCDD inside the pores of FAU is qualitatively confirmed by diffuse reflectance UV spectrometry and thermogravimetry measurements.

Keywords Dioxin · Zeolite · Selective adsorption · Adsorption from solution

1 Introduction

Management of solid waste is a major challenge of our society as their amount is still increasing. Today, in combination with waste separation and recycling, incineration is considered to be an effective method for disposing of ultimate residual. However, small amounts of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, collectively known as "dioxins" are released into the atmosphere from 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. Figures 1a and 1b show the generic structures of PCDDs and PCDFs, respectively.

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. 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 one 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 the concentration of the less toxic congeners. Toxic Equivalency Factors (TEFs) are toxicity potency factors that are proposed by the World Health Organization (WHO) (2010) and used by scientists and regulators globally as a consistent method to evaluate the toxicities of a mixture of dioxin (Table 1). 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. In order to determine the toxicity of mixtures of dioxin compounds, Toxic Equivalent Quantity (TEQ) is used. To calculate the TEQ of

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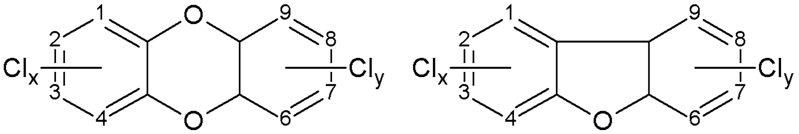


Fig. 1 (**a**) Polyclhorinateddibenzo-*p*-dioxin and (**b**) polychlorinateddibenzo-*p*-furan

Table 1 World health organisation re-evaluation of human and mammalian toxic equivalency factors for dioxins and furans (Pe = penta; Hx = hexa; Hp = hepta; OCDD = octachlorodibenzo *p*-dioxins; OCDF = octachlorodibenzo furans) (World Health Organization 2010)

Compounds	WHO 1998 TEF	WHO 2005 TEF
Chlorinated dibenzo-*p*-dioxins		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	0.0003
Chlorinated dibenzofurans		
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.03
2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	0.0003

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 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 physico-chemical characteristics. All PCDDs and PCDFs are organic solids with high melting temperatures and very low vapour pressures. They are characterised by an extremely low water solubility, and have a tendency to be strongly adsorbed on surfaces of particulate matter. The water solubility of dioxins and furans decreases with the increase of chlorine content. Due to their lipophilicity, low volatility and resistance to degradation properties, the dioxins are adsorbed onto soil and sediment particles. The persistence in the environment leads to a potential health hazard to humans and other organisms.

Worldwide, many countries have introduced stringent standards for dioxins 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 (Kulkarni et al. 2008). This value is an average rate of emission referring to a sampling period from six hours at least to eight hours 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). 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 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 (European Committee for Standardization 2006; Oleszek-Kudlak et al. 2007). 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 (Jay and Stieglitz 1995). 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 be also implemented in an on-line adsorption and thermo-desorption device coupled to a mass spectrometer (MS) for direct dioxin monitoring.

Zeolites 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 (Patarin et al. 2007). Zeolites have already been tested for dioxins. 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 (Neumann and Schmidt 1999). Zeolites with different pore sizes have been chosen to gain a selective adsorption for dioxins (Jäger et al. 2004). Results showed that adsorption takes place according to the pore size and the dynamic size of dioxin molecule. Xi et al. (2003) demonstrated that the nature of the cations trapped in the pores of zeolite could have an influence on the adsorption of dibenzofuran (zeolite framework not specified). Yang et al. (1999) found that dibenzodioxin was thermally desorbed at 241 °C from Y zeolite (FAU-structure type with $Si/Al = 195$), whereas Guan et al. (2005) showed that the desorption temperature of dibenzodioxin adsorbed on NaY zeolite with $Si/Al = 6$ is about 450 °C.

The use of zeolites as adsorbents is related to their high capacity of adsorption and selectivity properties which could lead to isomeric separation of dioxins according to their toxicity and to the exclusion of other compounds of the stack gas. Thus, trapped amount of dioxins will increase according to the selectivity of zeolites.

Because of the low volatility of dioxins, this first study consists in the determination of the liquid-phase adsorption isotherm of dioxin adsorbed onto zeolites in order to select and classify materials according to their affinity. The affinity of a given molecule for a zeolite depends on one side from the accessibility and on the other side from its interaction energy with the pore walls. It is clear that if the accessibility is proven by adsorption from solution, it can be extrapolated to gas adsorption. Concerning the thermodynamic parameter (the adsorption energy or adsorption affinity), the value is different when determined either by gas adsorption or liquid adsorption. Nevertheless we are here interested by a classification between molecules and then we compare their affinity using the same solvent as reference. Indeed, adsorption from solution mechanism is a displacement phenomenon of the solvent by the solute, and it is reasonable to assume that the classification of adsorption energy for gas adsorption will be the same as for liquid adsorption, which can be considered as the difference of adsorption energy of the solute minus that of the solvent. The adsorption properties of several zeolites of different pore sizes are studied for two dioxins: 2,3-dichlorodibenzo-*p*-dioxin and 1,2,3,4-tetrachlorodibenzo-*p*-dioxin.

2 Experimental

2.1 Materials

This study is performed with two non toxic molecules: 2,3-dichlorodibenzo-*p*-dioxin (2,3-DCDD) and 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD). Dioxins are planar molecules (Kim et al. 2003) of different sizes in the xy direction (Table 2). 2,3-DCDD can simulate the 2,3,7,8-TCDD during adsorption process as they have an equivalent dynamic size. Thereby results of this study could be applied to the adsorption behaviours between two position isomers of polychlorinated dibenzo-*p*-dioxin: 1,2,3,4-TCDD and 2,3,7,8-TCDD.

2,3-DCDD and 1,2,3,4-TCDD are purchased from Techlab (Metz, France). Dioxin standards are dissolved in extra dry 2,2,4-trimethylpentane, 99.5%, known as isooctane (Acros Organics, Illkirch, France). Solutions are prepared with isooctane to appropriate levels in a 2-mL auto-sampler vial for GC/MS analysis.

Dibenzo-*p*-dioxin (DD, Techlab, Metz, France) is used as internal standard for GC/MS calibration. Each solution is prepared with 500 µL of sample and 50 µL of a solution at constant concentration of dibenzo-*p*-dioxin (internal standard).

Aluminosilicates NaX (Si/Al molar ratio $= 1.23$) and EMC-2 (Si/Al molar ratio $= 3.5$) zeolites (FAU and EMT structure-types, respectively) and pure silica beta and silicalite-1 zeolites (*BEA and MFI structure-types, respectively) are chosen for their different pore sizes (Table 3) regarding the dynamic size of the two selected dioxins (Table 2). FAU is purchased from Fluka (Lyon, France). EMT, MFI and *BEA are synthesised according to the procedure described in the literature (Soulard et al. 2004; Dougnier et al. 1992). For instance, pure silica MFI and *BEA zeolites are prepared in fluoride medium in the presence of tetrapropylammonium (TPA) and tetraethylammonium (TEA) cations as structure-directing agents, respectively. The reaction gel has the following molar composition:

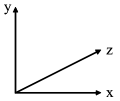
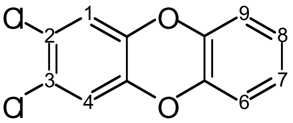
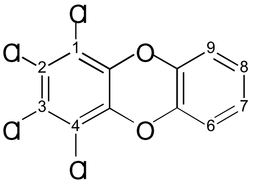
MFI; $1\ SiO_2 : 0.1\ TPABr : 0.2\ NH_4F : 30\ H_2O$,

*BEA; $1\ SiO_2 : 0.7\ TEAOH : 0.7\ HF : 8H_2O$.

In both cases, the mixtures are transferred into PTFE-lined stainless-steel autoclaves and heated at 200 °C for 7 days and at 170 °C for 3 days, for MFI and *BEA zeolites, respectively.

After washing and drying, the as-synthesised EMT, MFI and *BEA samples are calcined at 550 °C during 4 hours under air in order to remove the organic template and to get porous materials.

Table 2 Physical and chemical properties of 2,3-dichlorodibenzo-*p*-dioxin and 1,2,3,4-tetrachlorodibenzo-*p*-dioxin. The molecular size is estimated with the Cerius2 software

Molecule	CAS number	Structure	MW (g·mol^{-1})	Vapour pressure at 298 K (torr) (Chemical Abstract Service 2010)	Size (Å)  x y z
2,3-dichlorodibenzo-*p*-dioxin (2,3-DCDD)	29446-15-9		253	8.33×10^{-5}	12.65 7.4 3.5
1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD)	30746-58-8		322	1.16×10^{-6}	12.65 9.8 3.5

2.2 Characterisation methods

The adsorbents are characterised in terms of structure and phase purity by X-ray powder diffraction. Powder X-ray diffraction (XRD) patterns are obtained from a PANalytical X'pert Pro diffractometer with fixed slits using Cu/Kα radiation ($\lambda = 1.5418$ Å) with θ–2θ mounting. Before analysis samples are finely ground and pressed in a stainless steel sample holder. The patterns are registered in 2θ range of 5–50° with scanning step of 0.1° s^{-1}.

Morphology and size of the different samples are examined by Scanning Electron Microscopy (SEM) using a Phillips XL30 microscope equipped with a field electron gun. Prior to the SEM observations, all samples are coated with gold.

The water content of the zeolite specimen is systematically evaluated by thermogravimetry using a TGA Q500 from Universal Instruments in order to monitor the initial degree of hydration. Experiments are performed with a heating rate of 10 °C·min^{-1} in high resolution mode under argon flow at a flow rate of 40 mL·min^{-1}. The samples (5–20 mg) are heated up to 500 °C.

Nitrogen sorption isotherms are carried out with a Micromeritics ASAP 2010 apparatus at liquid nitrogen temperature (77 K). Equivalent specific surface areas are calculated using the BET equation and micropore volumes are obtained from the *t*-plot method (Rouquerol et al. 1999). Prior to the measurement, the zeolite samples are outgassed under vacuum at 300 °C overnight.

The adsorption of dioxins onto zeolites is qualitatively confirmed by diffuse reflectance/absorbance UV measurements. They are performed in the 200–500 nm range using a Varian 300 spectrophotometer equipped with an integrating sphere DRA-CA-30I. 60 mg of sample are placed in a PTFE sample holder. The surface of the sample is levelled by applying a glass slide. Spectra are displayed in Absorbance units.

Thermogravimetric analysis are performed with a TGA Q 500 apparatus from TA Instruments with a heating rate of 20 °C·min^{-1} under synthetic air flow at a flow rate of 40 mL·min^{-1}. The samples (5–20 mg) are heated up to 900 °C. The TGA curves are used to determine the desorption temperature of dioxins adsorbed onto zeolites.

Before UV and thermogravimetric analyses, the solid samples are separated from the liquid after decantation and then they are dried at room temperature under argon flow for one day in order to remove the liquid remaining between grains.

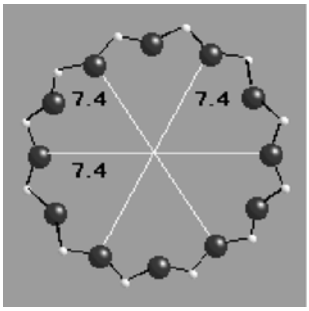
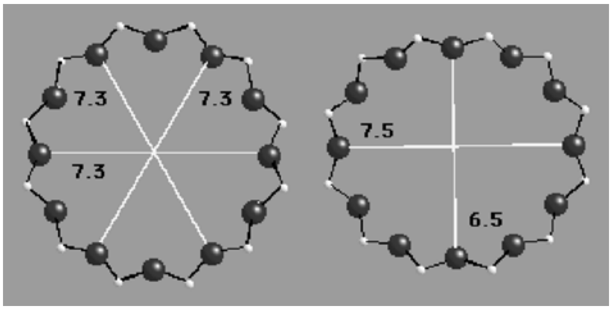
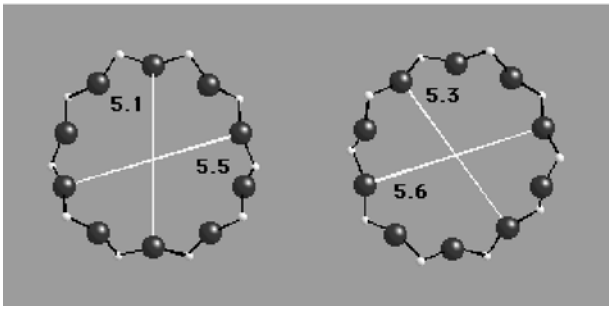
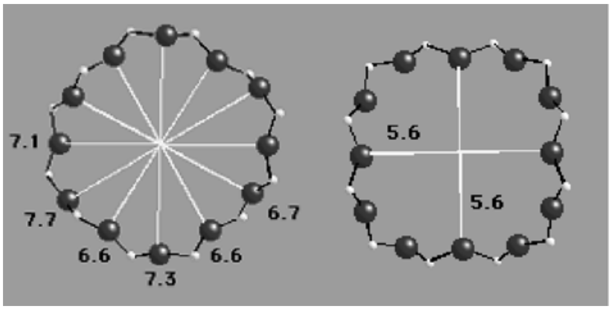
2.3 Adsorption experiments

Adsorption measurements are performed by the solution depletion method: adsorbed amount is derived from the variation of concentration due to adsorption in static conditions. Adsorbed amounts of dioxin are determined for each initial concentration by the following equation:

$$N_a = \frac{(C_i - C_f) \times V}{m_s} \tag{1}$$

where C_i is the initial concentration of dioxin in isooctane (solvent), C_f the final concentration, m_s the solid (zeolite) mass and the volume V of liquid exposed to solid. For the adsorbed amount of dioxin at equilibrium, $C_f = C_e$, the concentration at equilibrium (Denoyel et al. 1990).

Table 3 Size (in Å) of the studied microporous zeolites (Baerlocher et al. 2007)

FAU [NaX]	 ⟨111⟩ 12 7.4 × 7.4
EMT [EMC-2]	 ⟨001⟩12 7.3 × 7.3 ⟨001⟩ 12 6.5 × 7.5
MFI [Silicalite-1]	 ⟨100⟩10 5.1 × 5.5 ⟨010⟩ 10 5.3 × 5.6
*BEA [Pure silica beta] (Polymorph A)	 ⟨100⟩12 6.6 × 6.7⟨001⟩ 12 5.6 × 5.6

The isotherm is a graphic representation of the specific excess adsorbed amount of dioxin versus equilibrium concentration.

In a first operating mode, zeolites are heated at 155 °C under vacuum for six hours. Each sample with a constant liquid/solid ratio (1 mL/5 mg) is stirred at 25 °C until equilibrium is reached. Then, after centrifugation and filtration, 2,3-DCDD or 1,2,3,4-TCDD concentrations in supernatants are determined by GC-MS technique.

In order to evaluate the influence of water content in the pores of zeolites, the adsorption isotherms of 2,3-DCDD on zeolites are determined with a second operating mode. The solid sample is placed into a glass tube that is closed with a septum. The system is heated at 300 °C for six hours under

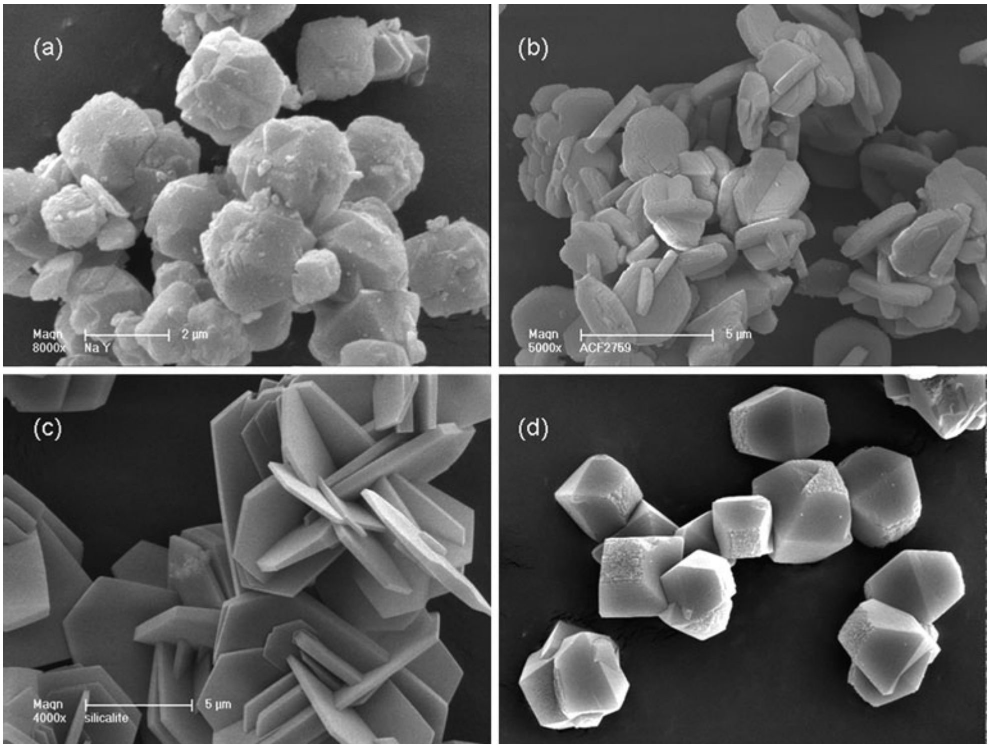


Fig. 2 SEM micrographs of: (**a**) FAU, (**b**) EMT, (**c**) MFI and (**d**) *BEA zeolites

argon flow at flow rate of 5 mL·min^{-1}. After such a treatment the weight loss is calculated from the difference between the final and initial weight of the tube. Around 15 mL of isooctane, previously dried with molecular sieves (5 Å), are added to the zeolites in the tube through the septum by means of a glass syringe. The system is stirred. A stock solution of dioxin, also prepared in isooctane previously dried with molecular sieves (5 Å) under argon flow, is added step by step in the tube. When the equilibrium time is reached after each step, a volume of around 500 µL is taken from the supernatant (stirring is stopped) and filtered for GC-MS analysis thus allowing the measurement of equilibrium concentrations.

Gas chromatography coupled to mass spectrometry (GC-MS) is performed on a Thermo Finnigan Trace GC 2000-Polaris Q ion trap mass spectrometer (Thermo Finnigan, Courtaboeuf, France) operating in the electron impact ionization mode. The CTC CombiPAL auto sampler (Zwingen, Switzerland) is used for the injection of liquid samples. The sample (1 µL) is introduced using the injector in splitless mode, with the split vent being opened 3 min after injection and remaining opened at a split ratio of 30:1 until the next injection, in order to continually flush the injector of any remaining solvent or other contaminants. The injector oven is maintained at 250 °C to ensure volatilisation of the heaviest PCDD. For the same reason, the transfer line from the column oven to the ion trap is kept at 300 °C. The ion trap oven is set to 220 °C, as a compromise between detector efficiency and trap electrode life. The column used is a 30 m × 0.25 mm id ×0.25 µm film thickness TR-5 ms (DB-5 equivalent) while the carrier gas is helium, at a constant flow rate of 1 mL·min^{-1}. For analytical runs, the temperature of the column oven is held constant at 60 °C for 1 min then linearly increased at 20 °C·min^{-1} up to 300 °C and held constant for 10 min.

3 Results and discussion

3.1 Structural and textural characterisations of zeolites

SEM images (Fig. 2a, b, c, d) and powder XRD patterns (Fig. 3a, b, c, d) confirm, respectively, the morphologies and framework types of FAU, EMT, MFI and *BEA zeolites.

The thermogravimetric curves (Fig. 4) show that the two hydrophobic MFI and *BEA zeolites loose about 0.8% of their initial weight before 50 °C, then their weight remains quasi constant until 485 °C. For the hydrophilic FAU and EMT samples, the removal of water occurs before 350 °C. It corresponds to a weight loss of 22.5% for the FAU sample and 22.3% for the EMT sample.

The values of the equivalent specific surface area, micropore volume and external surface area, determined by nitrogen adsorption, are listed in Table 4. For FAU, EMT and MFI zeolites the microporous volumes obtained are in agreement with the other ones reported in the literature (Soulard et al. 2004; Llewellyn et al. 1993; Bellat et al.

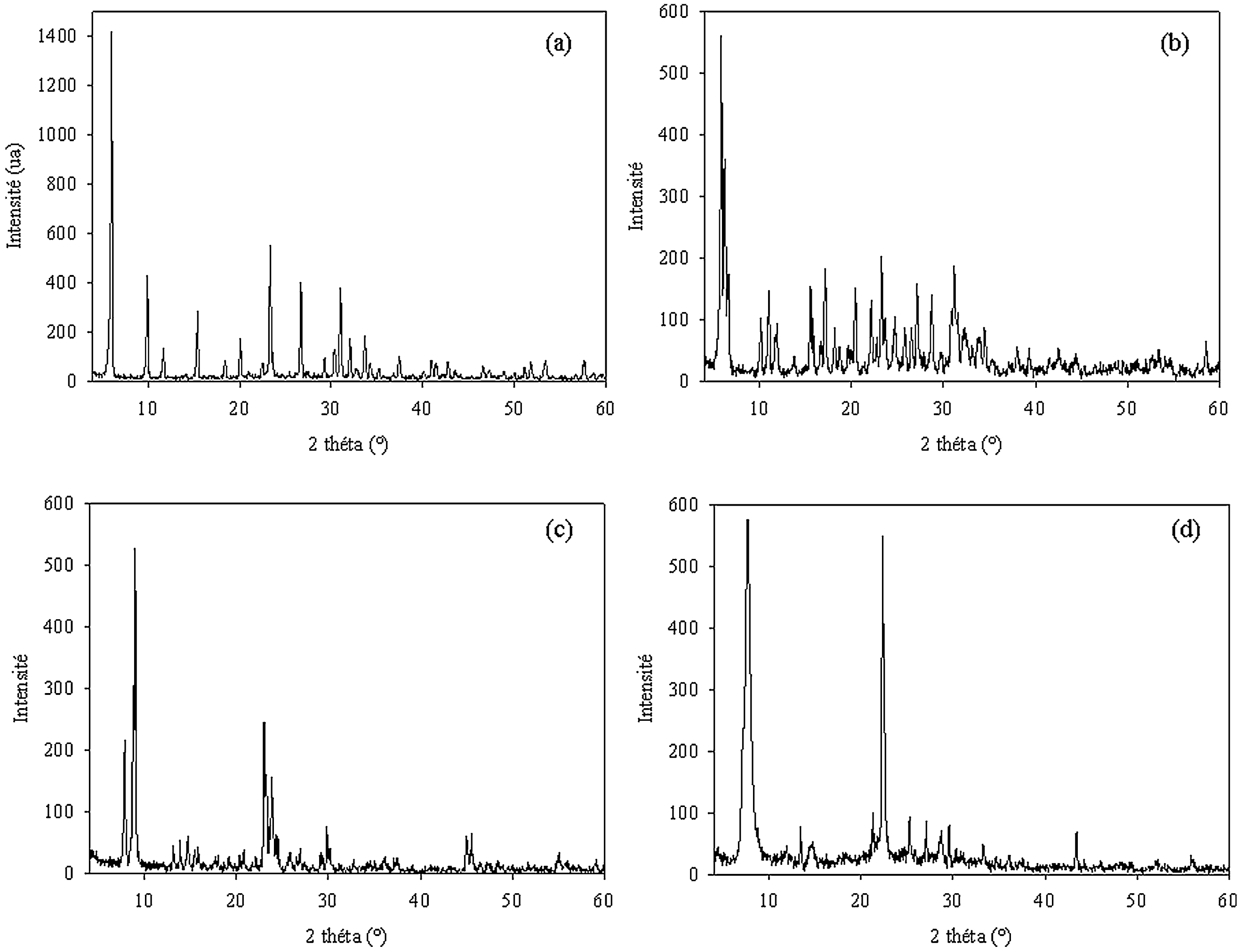


Fig. 3 X-ray powder patterns of: (**a**) FAU, (**b**) EMT, (**c**) MFI and (**d**) *BEA zeolites

2009). It is not the case for the *BEA sample where the experimental value (0.17 $cm^3 \cdot g^{-1}$) is lower than the expected one (0.24 $cm^3 \cdot g^{-1}$) (Soulard et al. 2004). Such a result may be explained either by the fact that zeolite beta is a disordered structure which consists of an intergrowth of at least two polymorphs or by the presence of traces of amorphous materials, not observed on the X-ray powder pattern.

3.2 Kinetic of adsorption of 2,3-DCDD (first operating mode)

Figure 5 shows the amount of 2,3-DCDD adsorbed onto the zeolites as a function of time. The initial concentrations of 2,3-DCDD are 165.6, 262.4, 214.3 and 214.3 $mg \cdot kg^{-1}$ for FAU, EMT, MFI and *BEA, respectively. For FAU and EMT zeolites, this amount increases with time until equilibrium is reached. This adsorption occurs on the external surface or/and on the pore surface. The time necessary to reach the equilibrium onto FAU is about 60 min and 150 min onto EMT.

There is no adsorption of 2,3-DCDD onto MFI and *BEA zeolites during the total time of this experiment that does not exceed 1440 min. The latter result is expected for the medium pore size of the MFI sample (0.55–0.56 nm). For the *BEA-type zeolite, no adsorption is observed despite a pore opening delimited by 12 membered rings as for the FAU and EMT-type zeolites. The pore size seems to be too small for the 2,3-DCDD dioxin (see Tables 2 and 3). Moreover, the pore size reported in Table 3 corresponds to that of polymorph A. Or, as reported above, the experimental sample displays a disordered structure which consists of an intergrowth of a least two polymorphs and that probably reduces again the pore size.

3.3 Kinetic of adsorption of 1,2,3,4-TCDD (first operating mode)

The amount of 1,2,3,4-TCDD adsorbed onto the studied zeolites as a function of time is shown in Fig. 6. The 1,2,3,4-TCDD molecules are weakly adsorbed onto FAU and EMT,

Table 4 Nitrogen sorption results at 77 K

Solid	Surface area (BET) ($m^2 \cdot g^{-1}$)	External area (*t*-plot) ($m^2 \cdot g^{-1}$)	Micropore volume (*t*-plot) ($cm^3 \cdot g^{-1}$)
FAU [NaX]	820	5.1	0.30
EMT [EMC-2]	845	2.4	0.33
MFI [silicalite-1]	365	4.8	0.17
BEA [pure silica beta]	410	16.7	0.17

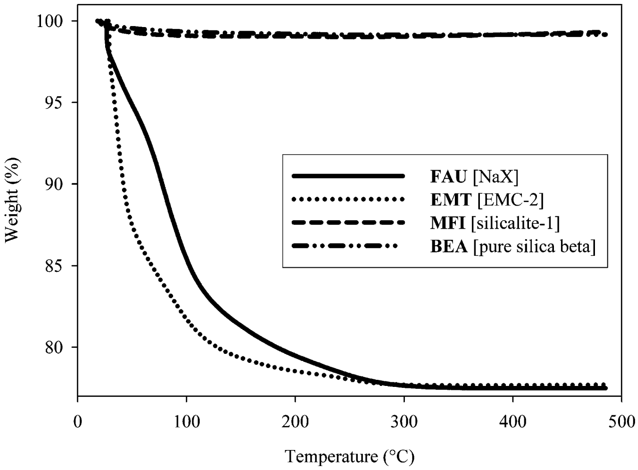


Fig. 4 Thermogravimetric measurements on the studied zeolites

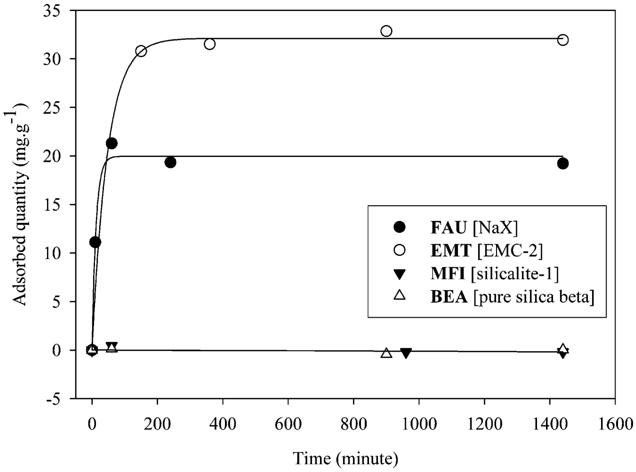


Fig. 5 Adsorption kinetics of 2,3-DCDD onto FAU, EMT, MFI and *BEA zeolites

while there is no adsorption onto MFI and *BEA for the total time of experiment of 1440 min. The adsorption equilibrium onto FAU and EMT are reached after 900 min: these times are longer than those obtained with 2,3-DCDD.

FAU and EMT weakly adsorb 1,2,3,4-TCDD molecules. Since the dynamic size of this dioxin is larger than the pore size of the zeolites, the adsorption occurs probably at the external surface of the zeolite crystals. It has to be noted that with the first operating mode (activation at 155 °C), some water molecules are still present in the pores of these hydrophilic zeolites

With the hydrophobic MFI and *BEA zeolites and with both dioxins (Figs. 5 and 6), it appears negative values for the quantities of adsorbed dioxin. These negative values come from the difference between the initial and final concentrations (see Eq. 1). The solvent (isooctane) can penetrate within the pores, whereas the dioxin cannot, leading to an increase of dioxin concentration in the equilibrium solution.

3.4 Adsorption isotherms of 2,3-DCDD

Adsorption isotherms of 2,3-DCDD from isooctane solutions onto FAU, EMT, MFI and *BEA zeolites are displayed in Fig. 7 for the first operating mode. It appears that 2,3-DCDD is adsorbed more readily onto FAU than onto EMT zeolite, before reaching approximately the same saturation value. The better affinity is obtained for the FAU zeolite in the low-concentration domain (Henry domain). The adsorption capacities are about 32 $mg \cdot g^{-1}$ and 35 $mg \cdot g^{-1}$ for EMT and FAU respectively.

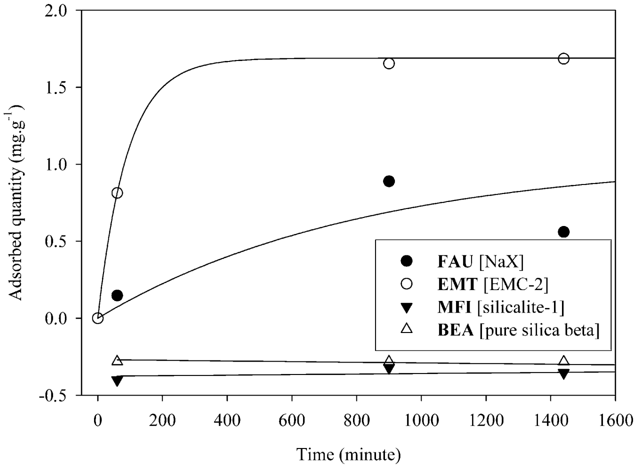


Fig. 6 Adsorption kinetics of 1,2,3,4-TCDD onto FAU, EMT, MFI and *BEA zeolites

Adsorption experiments are conducted for the second operating mode (activation at 300 °C) using the same zeolites, and resulting adsorption isotherms of 2,3-DCDD are illustrated in Fig. 8. According to the TGA curves (Fig. 4), with the first operating mode, the FAU sample looses about

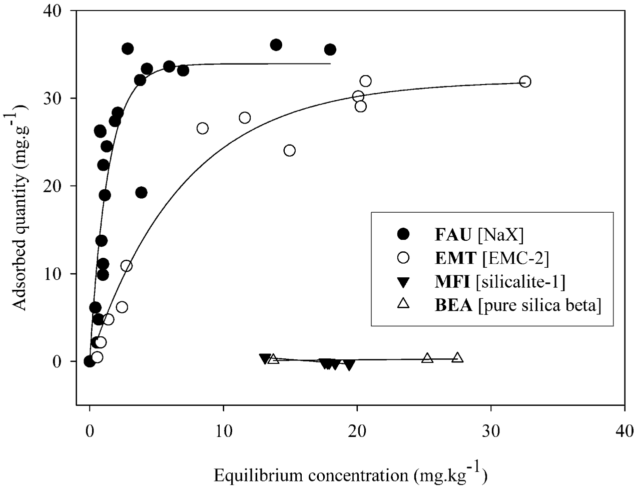


Fig. 7 Adsorption isotherms of 2,3-DCDD onto FAU, EMT, MFI and *BEA zeolites after outgassing at 155 °C under vacuum

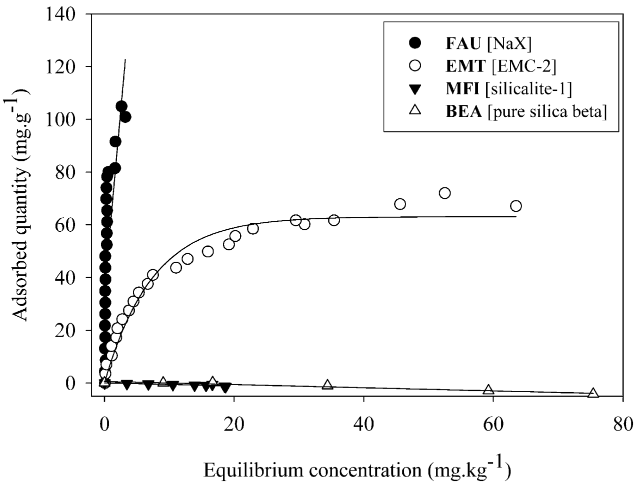


Fig. 8 Adsorption isotherms of 2,3-DCDD onto FAU, EMT, MFI and *BEA zeolites after outgassing at 300 °C under argon gas flow

18 wt% of its initial mass and the EMT one 20 wt%. With the second operating mode, almost the totality of water is eliminated from the zeolite structure.

Consequently, stronger affinities, between 2,3-DCDD and FAU, and between 2,3-DCDD and EMT, are obtained with the second operating mode. In addition, the capacity of adsorption increases. The adsorbed amount of 2,3-DCDD onto EMT is now 75 instead of 32 $mg \cdot g^{-1}$ (Fig. 8). For the FAU sample the saturation of the adsorption sites is not reached in the range of studied concentrations. Adsorbed amount is about 100 $mg \cdot g^{-1}$ instead of 35 $mg \cdot g^{-1}$ for an equilibrium concentration of 3.20 $mg \cdot kg^{-1}$ (Fig. 8).

With the second operating mode, 2,3-DCDD is no more adsorbed onto MFI and *BEA zeolites, while adsorption capacity is improved onto FAU and EMT zeolites in the same equilibrium concentration domain (Fig. 8).

Table 5 Theoretical adsorbed quantity of 2,3 DCDD according to the adsorption mode

Adsorption mode	Theoretical adsorbed quantity on external surface ($mg \cdot g^{-1}$)
Mode 1	8.3
Mode 2	4.8
Mode 3	2.3

As expected, selective adsorption can occur according to the pore size of the zeolites and the dynamic size of the dioxins. 2,3-DCDD is then adsorbed on FAU and EMT zeolites but it is too large for entering into the micropores of MFI zeolite.

For the *BEA-type zeolite, the hypotheses reported above (Sect. 3.2) can also be advanced to explain that no adsorption is observed despite a pore opening delimited by 12 membered rings as for the FAU and EMT-type zeolites.

To locate the adsorption onto the zeolites, either in pores or on the external surface, the theoretical adsorbed amount of 2,3-DCDD on the external surface, calculated from data of nitrogen adsorption at 77 K, is compared to the experimental adsorbed amount.

Knowing the size of the dioxin molecule (Table 2) and the external surface of the zeolite (Table 4), with the assumption that the adsorption phenomenon is limited to one monolayer, it is possible to calculate the theoretical adsorbed amount of 2,3-DCDD onto the external surface of the material using the following equation:

$$N_a = \frac{1}{\sigma \times L} \times M \times A^{ext} \times 1000 \qquad (2)$$

The theoretical adsorbed quantity N_a ($mg \cdot g^{-1}$) is function of the projected surface of the dioxin σ (m^{-2}), the Avogadro constant L (mol^{-1}), the molar mass of the dioxin M ($g \cdot mol^{-1}$) and the external surface area of the zeolite A^{ext} ($m^2 \cdot g^{-1}$). 2,3-DCDD can be adsorbed onto the zeolite surface according to three positions described in Fig. 9. Depending on the position, the theoretical adsorbed quantities on FAU, for example, are ranging from 2.3 to 8.3 $mg \cdot g^{-1}$ (see Table 5). These theoretical adsorbed quantities of 2,3-DCDD onto FAU are much smaller than the experimental ones (35 $mg \cdot g^{-1}$ and 100 $mg \cdot g^{-1}$ for the first and the second operating mode, respectively). Consequently, adsorption of 2,3-DCDD from isooctane solution takes place mainly inside the micropores.

3.5 Competitive adsorption of 2,3-DCDD and 1,2,3,4-TCDD (first operating mode)

FAU and EMT zeolites are put in contact with a solution of 2,3-DCDD and 1,2,3,4-TCDD in isooctane with a 2,3-DCDD/1,2,3,4-TCDD molar ratio equal to about 10 and

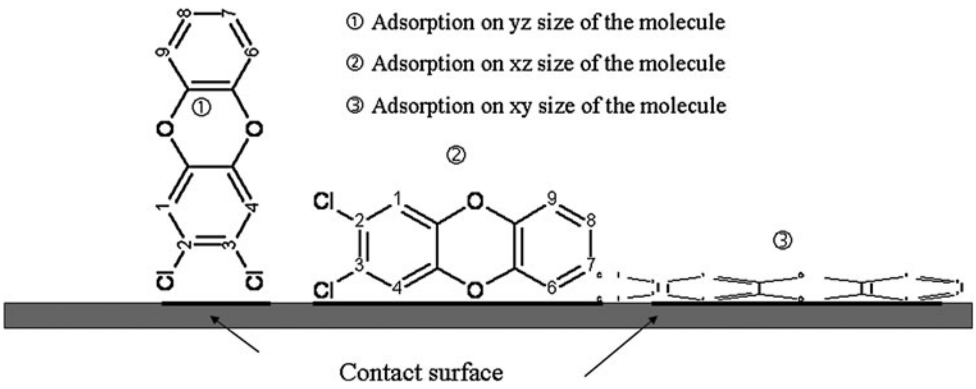


Fig. 9 Some possible positions of adsorbed 2,3-DCDD molecules onto a surface

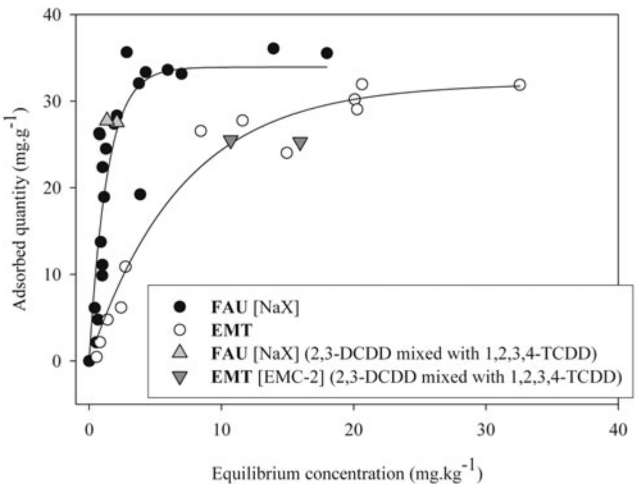


Fig. 10 Adsorption isotherms of 2,3-DCDD onto FAU and EMT zeolites after outgassing at 155 °C under vacuum from a mixture of 2,3-DCDD and 1,2,3,4-TCDD

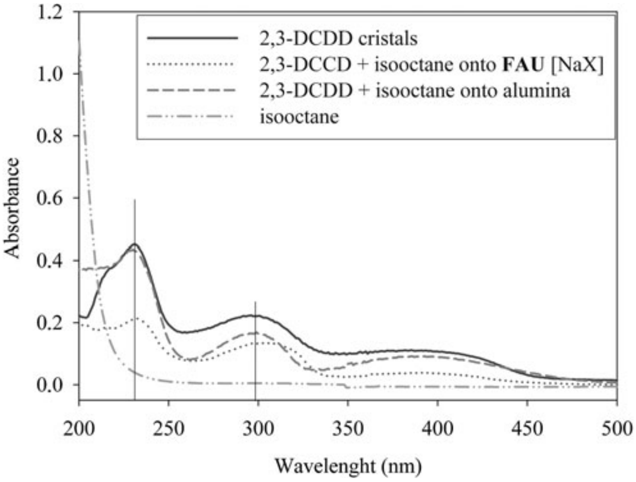


Fig. 11 Comparison of UV spectra of pure solid 2,3-DCDD, isooctane, 2,3-DCDD with isooctane adsorbed onto FAU zeolite and 2,3-DCDD with isooctane adsorbed onto alumina

for the same value of 2,3-DCDD initial concentration. Two identical adsorption experiments are performed for each zeolite. The amounts of 2,3-DCDD adsorbed onto these two zeolites are reported in Fig. 10 together with the adsorption isotherms. These values match those obtained for the adsorption of 2,3-DCDD alone with the same initial concentration. Small amount of 1,2,3,4-TCDD has no influence on the adsorption behaviour of 2,3-DCDD onto FAU and EMT zeolites.

3.6 Characterizations of FAU zeolite after adsorption of 2,3-DCDD

Characterizations by diffuse reflectance UV spectroscopy and thermogravimetry have been carried out in order to confirm the adsorption of the 2,3-DCDD onto FAU zeolites. These analyses are made for the samples issued from adsorption experiments following the second operating mode.

The diffuse reflectance UV spectrum of pure 2,3-DCDD solid presents a high absorption band at 230 nm and a lower at 297 nm while isooctane has only an absorption band at 200 nm (Fig. 11). The UV spectrum of 2,3-DCDD adsorbed from isooctane on FAU zeolite is obtained by subtracting the diffuse reflectance UV spectrum of FAU from the UV spectrum of FAU after immersion in a solution of isooctane containing 2,3-DCDD. It presents a main absorption band at 231 nm and a lower one at 304 nm. For comparison, the UV spectrum of 2,3-DCCD in isooctane in contact with alumina (non porous solid) using the same experimental procedure was registered and it presents the same absorption bands that the pure 2,3-DCDD solid.

These results show that in the case of alumina, where 2,3-DCDD is adsorbed onto the surface of a non porous solid, the same bands as pure 2,3-DCDD solid are obtained, whereas when 2,3-DCDD is adsorbed onto FAU, a red shift of both 230 and 297 nm bands is observed. This bathochromic shift is due to a change in the environment of 2,3-DCDD probably induced by the confinement of the dioxin into the micropores of the zeolite.

Thermogravimetric analysis results are reported in Fig. 12. They show the mass loss of FAU after immersion in isooctane and in a solution of 2,3-DCDD in isooctane.

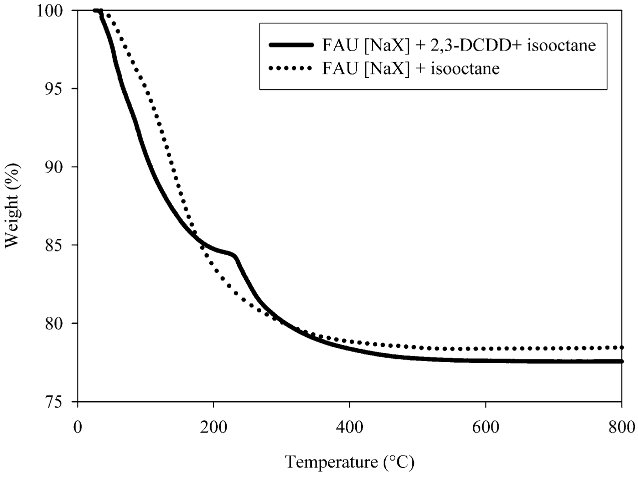


Fig. 12 Thermogravimetric analysis under synthetic air flow of FAU zeolite after adsorption experiments

In both cases, the total weight loss is similar and close to 22 and 25%. However for the dioxin-containing FAU sample, a different behaviour is observed at about 220 °C revealing that two different species are involved in the weight loss. The first step which occurs before 220 °C may be assigned to the removal of isooctane and that after 220 °C to the removal of 2,3-DCDD. This temperature matches the desorption temperature value (241 °C) of dibenzo-dioxin from Y zeolite given by Yang et al. (1999). It appears clearly that both molecules (dioxin and isooctane) are adsorbed onto the zeolite samples. From this thermogravimetric curve, about 6.5 wt% of dioxin is adsorbed on the FAU sample. This value is in quite agreement with the dioxin amount determined by the solution depletion method, about 5.2 wt%.

4 Conclusion

These first results show the selective adsorption of dioxins in isooctane solution onto zeolite according to the position of the chlorine atoms of the pollutant and the pore size of the adsorbent. The confinement effect of pore is the dominant interaction in zeolites with a pore size close to the molecular size of 2,3-DCDD, which results in the strong adsorption of 2,3-DCDD in FAU and EMT zeolites.

However, FAU and EMT zeolites are strongly hydrophilic. We observe that the drying process (associated to the second operating mode) of these zeolites prior to adsorption experiment leads to better adsorption affinity and capacity. Consequently, to use these zeolites in an on-line sampling device, the significant moisture content in the flue gas must be removed by an upstream sorption stage.

Surprisingly, for the hydrophobic *BEA-type zeolite despite a pore opening delimited by 12 membered rings as for the FAU and EMT-type zeolites no adsorption is observed. The pore size seems to be too small for the 2,3-DCDD dioxin. The disordered structure of this zeolite which consists of an intergrowth of at least two polymorphs might explain such a result.

During this work, isooctane appears to not have influence on 2,3-DCDD adsorption then results obtained in liquid phase can be used to select adsorbent/adsorbate couples which will be studied in gas phase. The most efficient adsorbents will be subsequently implemented in the gas adsorption set-up. For instance, current experiments of 2,3-DCDD adsorption in gas phase are performed onto FAU [NaX], zeolite which seems to be the best from liquid phase adsorption results.

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References

Bellat, J.-P., Paulin, C., Jeffroy, M., Boutin, A., Paillaud, J.-L., Patarin, J., Di Lella, A., Fuchs, A.: Unusual hysteresis loop in the adsorption-desorption of water in nay zeolite at very low pressure. J. Phys. Chem. C **113**, 8287–8295 (2009)

Baerlocher, Ch., McCusker, L.B., Olson, D.H.: Atlas of Zeolite Framework Types, 6th rev. edn. Elsevier, Amsterdam (2007)

Chemical Abstracts Service (CAS), a division of the American Chemical Society: http://www.cas.org/index.html. Accessed July 2010

Committee on EPA’s Exposure and Human Health Reassessment of TCDD and Related Compounds: Health Risks from Dioxin and Related Compounds. The National Academies Press, Washington, DC (2006): On-line: http://www.nap.edu/catalog.php?record_id=11688. Accessed July 2010

Denoyel, R., Rouquerol, F., Rouquerol, J.: Thermodynamics of adsorption from solution: experimental and formal assessment of the enthalpies of displacement. J. Colloid Interface Sci. **136**, 375–384 (1990)

Dougnier, F., Patarin, J., Guth, J., Anglerot, D.: Synthesis, characterization, and catalytic properties of silica-rich faujasite-type zeolite (FAU) and its hexagonal analog (EMT) prepared by using crown-ethers as templates. Zeolites **12**, 160–166 (1992)

European Committee for Standardization (ECS). European Standard CEN/TC 264—Air quality. EN 1948-1:2006—Stationary source emissions—Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs—Part 1: Sampling of PCDDs/PCDFs. EN 1948-2:2006—Stationary source emissions—Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs—Part 2: Extraction and clean-up of PCDDs/PCDFs. EN 1948-3:2006—Stationary source emissions—Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs—Part 3: Identification and quantification of PCDDs/PCDFs

European Union, Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste. On-line: http://europa.eu/legislation_summaries/environment/waste_management/l28072_en.htm. Accessed July 2010

French government. Arrêté du 3 août 2010 modifiant l'arrêté du 20 septembre 2002 relatif aux installations d'incinération et de co-incinération de déchets non dangereux et aux installations incinérant des déchets d'activités de soins à risques infectieux JORF no 0193 du 21 août 2010 page 15196 texte no 10 [en ligne]. On-line: http://www.legifrance.gouv.fr/affichTexte.do;jsessionid=86515A7DC338232C60B818FFF5511E81.tpdjo09v_1?cidTexte=JORFTEXT000022727297&categorieLien=id. Accessed September 2010

Guan, Y., Liu, Y., Wu, W., Sun, K., Li, Y., Ying, P., Feng, Z., Li, C.: Dibenzodioxin adsorption on inorganic materials. Langmuir **21**, 3877–3880 (2005)

Jay, K., Stieglitz, L.: Identification and quantification of volatile organic components in emissions of waste incineration plants. Chemosphere **30**, 1249–1260 (1995)

Jäger, R., Schneider, A.M., Behrens, P., Henkelmann, B., Schramm, K.-W., Lenoir, D.: Selective adsorption of polychlorinated dibenzo-p-dioxins and dibenzofurans by the zeosils UTD-1, SSZ-24, and ITQ-4. Chem. Eur. J. **10**, 247–256 (2004)

Kim, S., Kwon, Y., Lee, J.-P., Choi, S.-Y., Choo, J.: A theoretical investigation into the conformational changes of dibenzo-p-dioxin, thianthrene, and selenanthrene. J. Mol. Struct. **655**, 451–458 (2003)

Kulkarni, P.S., Crespo, J.G., Afonso, C.A.M.: Dioxins sources and current remediation technologies—a review. Environ. Int. **34**, 139–153 (2008)

Llewellyn, P., Grillet, Y., Patarin, J., Faust, A.C.: On the physisorption isotherm of the MFI-type zeolites: the high-pressure hysteresis. Microporous Mesoporous Mater. **1**, 247–256 (1993)

Neumann, P., Schmidt, K.G.: Dioxin separation with natural zeolites. Organohalog. Compd. **40**, 543–546 (1999)

Oleszek-Kudlak, S., Shibata, E., Nakamura, T., Li, X.-W., Yu, Y.-M., Dong, X.-D.: Review of the sampling and pretreatment methods for dioxins determination in solids, liquids and gases. J. Chin. Chem. Soc. **54**, 245–262 (2007)

Patarin, J., Spalla, O., Di Renzo, F.: In: Lahami, M., Bréchignac, C., Houdy, P. (eds.) Nanomaterials and Nanochemistry, Part II: Physical and Chemical Properties on the nanoscale, Chapter 11, pp. 303–313. Springer, Berlin (2007)

Rouquerol, J., Rouquerol, F., Sing, K.-S.-W.: Adsorption by Powders and Porous Solids. Principles, Methodology and Applications. Academic Press, Londres (1999) 467 p.

Soulard, M., Patarin, J., Eroshenko, V., Regis, R.: Molecular spring or bumper: a new application for hydrophobic zeolitic materials. In: Van Steen, E., Callanan, L., Claeys, M. (eds.) Studies in Surface Science and Catalysis, Recent Advances in the Science and Technology of Zeolites and Related Materials Part B, Proceedings of the 14th International Zeolite Conference, pp. 1830–1837. Elsevier, Amsterdam (2004)

World Health Organization (WHO)—International Programme on Chemical Safety (IPCS): On-line: http://www.who.int/ipcs/assessment/tef_update/en/index.html. Accessed July 2010

Xi, H., Li, Z., Zhang, H., Li, X., Hu, X.: Estimation of activation energy for desorption of low-volatility dioxins on zeolites by TPD technique. Sep. Purif. Technol. **31**, 41–45 (2003)

Yang, R.T., Long, R.Q., Padin, J., Takahashi, A., Takahashi, T.: Adsorbents for dioxins: a new technique for sorbent screening for low-volatile organics. Ind. Eng. Chem. Res. **38**, 2726–2731 (1999)