

## ORGANIC MICROPOLLUTANTS ADSORPTION CAPACITY FOR A KAOLINIC ORE: A PRELIMINARY ASSESSMENT

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### Introduction

Kaolin ball clays with a sedimentary origin, industrially used as binder and anticaking agent feed additives, are very often contaminated by PCDD/Fs up to 520.000 pg/g; they show a typical pattern with the contamination being concentrated in the most chlorinated congeners (especially OCDD)<sup>1</sup>.

Primary kaolin ore deposits, mainly due to the alteration of feldspars contained into igneous formations by acid epithermal and mesothermal fluids, show much smaller or no contaminations<sup>2,3</sup>. An Italian primary kaolin ore deposit has been previously studied and its PCDD/Fs contamination has been determined<sup>4</sup>.

The aim of the study was to evaluate the PCDD/Fs adsorption capacity from a wastewater stream for the above mentioned Italian kaolinic ore showing a negligible initial micropollutants contamination. The obtained result is also adding data to the question if the presence of PCDD/Fs in kaolin has an anthropogenic or a natural origin.

### Materials and methods

#### Sample preparation and Size distribution

Kaolin was separated from the siliceous gangue simulating the action of an attrition cell in a 3-dimensional shaker/mixer (Turbula 2TF, Willy A. Bachofen AG Maschinenfabrik, Switzerland) for fast (60 rotations/minute) and homogeneous mixing of powder substances of different weights, and particle sizes in combination with liquids (liquid/solid ratio =4). The instrument was working with the Schatz geometry theory (<http://www.paul-schatz.ch/en/news/>). During the above procedure a natural enrichment in kaolin was obtained in smaller size fraction while a silica gangue mainly remained in the +75  $\mu\text{m}$  fraction. After wet sieving, the -75  $\mu\text{m}$  fraction has overcome a laser diffraction particle analysis (Bettersize, China. Model BT-2003, with range lens 0,040-0,600 mm). Results are shown in figure 1.

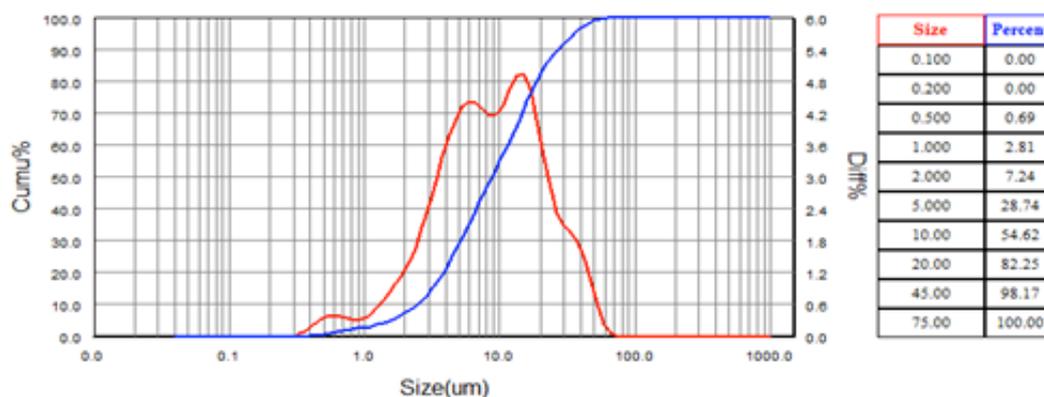


Figure 1 –75  $\mu\text{m}$  Kaolin's particle size distribution,  $D_{50}= 8,80 \mu\text{m}$ ;  $D_{90}=27,22 \mu\text{m}$

#### Chemical Analysis

Kaolin ore's chemical inorganic composition was performed, in triplicate, by XRF (Expert Mobile, INAM, USA) and shown on Table 1. Kaolin ore's PCDD/Fs concentration was determined using EPA8280B as reference method. Analytical conditions are reported below. Results can be seen on table 2.

Table 1 – Sample inorganic chemical composition by XRF

Sample	Fe <sub>2</sub> O <sub>3</sub> (%)	K <sub>2</sub> O (%)	TiO <sub>2</sub> (%)	CaO (%)	Sn (ppm)	SiO <sub>2</sub> (%)	V (ppm)	Pb (ppm)	Al <sub>2</sub> O <sub>3</sub> (%)	As (ppm)
Kaolin	0,56	0,22	0,16	0,05	421	78,11	69	60	14,81	61

Table 2- Kaolin ore's PCDD/F contamination, by GC-MS/MS.

PCDD	Concentration (pg/g)	PCDF	Concentration (pg/g)
2,3,7,8-TCDD	< LOQ	2,3,7,8-TCDF	0,05
1,2,3,7,8-PeCDD	< LOQ	1,2,3,7,8-PeCDF	< LOQ
		2,3,4,7,8-PeCDF	0,05
1,2,3,4,7,8-HxCDD	< LOQ	1,2,3,4,7,8-HxCDF	0,05
1,2,3,6,7,8-HxCDD	0,16	1,2,3,6,7,8-HxCDF	0,05
1,2,3,7,8,9-HxCDD	< LOQ	2,3,4,6,7,8-HxCDF	< LOQ
		1,2,3,7,8,9-HxCDF	< LOQ
1,2,3,4,6,7,8-HpCDD	0,21	1,2,3,4,6,7,8-HpCDF	< LOQ
		1,2,3,4,7,8,9-HpCDF	0,06
OCDD	2,04	OCDF	0,37

### Leaching test

Artificial wastewater (AW) was prepared by adding 4-8 ng of native PCDD/Fs standard (NK-ST-A, Wellington Laboratories, Canada) diluted in 20 mL of Acetone to 3 liters of distilled water. Kaolin samples have been added to 150 mL of AW, keeping the L/S ratio to 10. The slurry was kept in a shaking water bath at 303K for 1h, 6h and 24h, then it was filtered/centrifuged in order to separate solids from AW.

### Automated clean-up

The samples were ground and dried at 50 ° C for 48 hours and 30 g of sample was then spiked with <sup>13</sup>C<sub>12</sub>-labelled PCDD/Fs standard EPA1613-LCS (Wellington Laboratories, Canada) and extracted by soxhlet using toluene for 36 hours. The extract was evaporated to 1 mL using a Rotavapor (Büchi) and then in a thermostatic bath set at 40 ° C under a stream of nitrogen. The samples were diluted to 5 mL with methylene chloride and then purified with an automated system based on size exclusion chromatography and described elsewhere. The automated clean-up system (Accuprep, J2 Scientific Llc, USA) consists of a 2.5 cm x 45 cm glass column packed with BioBeads SX-3 resin in 100% methylene chloride, a pump, an auto sampler and an "in line" evaporating chamber. The whole system is computer controlled and can be programmed as required (i.e. volume, flow-rates, direction of solvent flow, etc.). The system used a 5-mL sample loop and a flow rate of 5 mL/min with methylene chloride as the mobile phase. Briefly, the sample is loaded on the GPC column and after the elution, is concentrated in the AccuVap module up to a final volume of 0.5 mL. Then it is loaded on the SPE alumina column in n-hexane and the collected fraction is sent again to the AccuVap module, where it is concentrated up to a volume of 1.5 mL. The sample is manually dried under a gentle stream of nitrogen and after addition of <sup>13</sup>C<sub>12</sub>-labelled PCDD/Fs internal standards (EPA1613-IS), the samples were analyzed.

Waters were extracted in a separatory funnel with methylene chloride for 3 times. The extracts were then concentrated and dried under a gentle stream of nitrogen. After the addition of EPA1613-LCS standard, the samples were analyzed.

### Analysis

Purified extracts were analyzed by a Trace GC Ultra high resolution gas chromatograph equipped with an TriPlus autosampler and coupled by a heated transfer line to a TSQ Quantum Triple Quadrupole spectrometer (Thermo Scientific, USA). Chromatographic separation was achieved with a TG-XLB (Thermo, USA) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 µm film thickness) with hydrogen as carrier gas in splitless injection mode.

### Results and discussion:

PCA is a classical statistical approach to reduce the dimension of the original dataset by transforming it to a new set of variables (called "principal components") to summarize the features of the above mentioned original variables. Principal components are uncorrelated and ordered such that the  $k^{\text{th}}$  PC has the  $k^{\text{th}}$  largest variance

among all PCs. So, the first component has maximum variance. Successive components progressively explain smaller portions of the variance and are all uncorrelated with each other. The PCA's data set used in the present study is the combination of the ones from the present and past<sup>5</sup> works. Principal component analysis (PCA) has been used to perform clustering. Results are shown in figure 2, where 3 clusters of original variables are clearly separated. It shows that in the kaolinic ore the heavy PCDDs have similar patterns to the concentration of iron oxide and silica, as these variables are homogeneous with respect to their properties. This result is in accordance to other references showing that the iron oxide's presence is the residue of the oxygen reaction with iron chloride and that the latter one can promote the formation of high chlorinated PCDD/Fs<sup>6</sup>. The PCs were calculated from the variance matrix. Table 3 lists the loading coefficients for the first 2 PCs. PC1 accounted for 54% of the variance and PC2 accounted for 33% of the variance. Therefore, the two PCs together accounted for 87% of the variance.

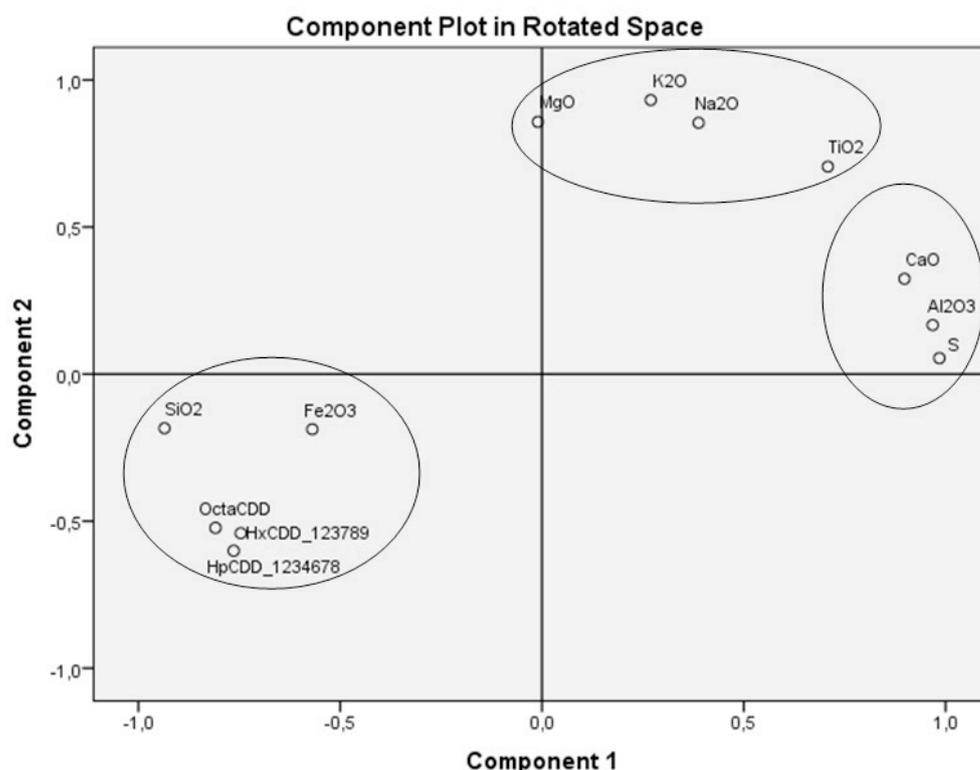


Figure 2 – PCA for inorganic constituent of the kaolinic ore and its PCDDs contamination. This latter has similar patterns to the silica and iron oxide concentration

Tab.3 – PCA loading matrix of kaolinic ore inorganic content and main PCDDs congeners; variance explained.

Variables	Comp. 1	Comp. 2	Variables	Comp. 1	Comp.2
1,2,3,7,8,9-HxCDD	-,746	-,541	TiO <sub>2</sub>	,708	,706
1,2,3,4,6,7,8-HpCDD	-,764	-,601	SiO <sub>2</sub>	-,935	-,184
OctaCDD	-,809	-,523	CaO	,898	,324
MgO	-,010	,858	K <sub>2</sub> O	,269	,932
Na <sub>2</sub> O	,388	,854	Al <sub>2</sub> O <sub>3</sub>	,968	,167
Fe <sub>2</sub> O <sub>3</sub>	-,569	-,188	S	,985	,054
% variance	54	33	Cumulative % variance	54	87

Rotation method: Varimax with Kaiser Normalization

During the leaching tests PCDD/Fs concentration in AW follow up a similar trend among all the congeners. As an example, figure 3 shows the percentage initial concentration of 2,3,7,8-TCDD and OCDD remaining into AW after 1.5, 6 and 24 h. After 1,5 h the concentrations are reduced of about 90% and after 6 h a plateau of concentration under the limits of quantification is reached. The same trend is observed for all the other

congeners. The adsorption is not affected by the grade of chlorination and all PCDD/Fs congeners are totally removed from WA after 6 h.

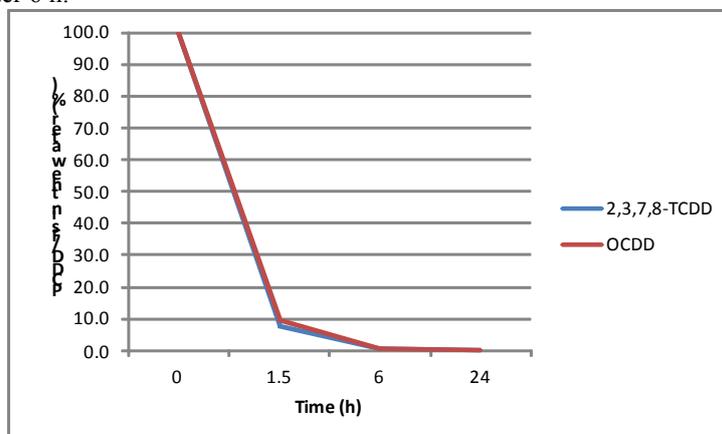


Figure 3 – Concentration of 2,3,7,8-TCDD and OCDD (%) in WA during the leaching tests.

### Conclusions:

The leaching tests demonstrate that the kaolin ore is able to remove all the dioxins and furans from the water at the same time. The PCA displays how the concentration of highly chlorinated congeners has similar properties to the silica and iron oxide in the matrix. Its role may be important in the “De Novo Synthesis” of PCDD/Fs during the formation of the ore itself. As the kaolin is usually contaminated by high chlorinated congeners, their presence can be only of natural origin. In the presence of an external (anthropogenic) source of contamination, the kaolin can indiscriminately adsorb all the congeners. This fact demonstrates that the presence of low chlorinated PCDD/Fs can be only a consequence of the anthropogenic contamination. Otherwise the co-existence of the other congeners can derive from the sum of their natural and anthropogenic origins.

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