RECOVERY OF WASTES FROM THE QUARRYING OF BUILDING MATERIALS IN THE ROMAN PROVINCE AS PRODUCTS FOR ORGANIC POLLUTANTS REMOVAL FROM LIQUID WASTES

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Introduction

From a geological point of view, between 561K and 541K years ago, the Roman province has been subjected to extended pyroclastic lava flows, so called “tuffs”, that quite often has been zeolitized (hydrothermally diagenized through the action of the high temperature fluids entrapped inside the mass of the pyroclastic material). These rocks has been used as building material since the roman age.[1,2] Nowadays the quarrying activity does produce a large amount of wastes, mainly consisting in small particles having a size distribution -4000 +38 μm. They have a very high volume, higher then the mined rocks and they create a big environmental impact.

These rocks has been characterized from a mineralogical and petrografic point of view[3].

The aim of the present work was to demonstrate the possible use of this wastes as substrate for the removal of organic pollutant from liquid wastes.

Materials and methods

10 kg of zeolitized tuffs, wastes of the mining activity on the geological formation of the “yellow tuff of Tiberina Valley”, has been collected in 3 different quarries. They have been homogenized and sampled down to 1 kg then sieved at 2000 μm. The over fraction has been milled and than added to the under fraction. Each 1 kg sample has been re-sampled down to 10 g by the means of an automatic sampler (Retsch, USA) in order to ensure a good representativity of each sample for the following experiments. Moreover some experiments has been carried out after a further screening and elimination of the fines (250 μm).

Quantity and quality of the zeolite components of the tuff has been determined by X-Ray diffraction by a Philips PW 1830 diffractometer at the following experimental conditions:

- kV 40
- mA 20
- Rad CuKα
- Range 2θ 15°-120°
- Step scan (2θ) 0.02
- Time per step (s) 12

Scanning electron microscopy has been performed by SEM Hitachi S2500 equipped with a EDS Kevex Quantum microanalysis.

Analysis methods

The zeolites have been added to tap water (150 ml) spiked with 600 pg of native dioxin standard EPA 1613 [4] (Wellington Laboratories - Canada). Adsorption test has been carried out in batch reactors, in a shacking water bath, at the controlled temperature of 20 °C (293 K). One experiment has been performed for each contact time. This procedure has been adopted in order to avoid that multiple sampling could affect the rapresentativity of the solid sample and/or the sensitivity of the analysis. Contact time was extended up to 96h. At the end of each experiment a solid-liquid separation has been performed by the means of paper filtering and centrifuge.

Extraction standards LCS were added both to the water and to the zeolites, according to EPA 1613 B method.

The pollutants was recovered by liquid-liquid extraction from the water and by solid-liquid (i.e. toluene) extraction with Soxhlet [5] from zeolites. After the concentration with AccuVap™ (J2 Scientific) the samples were cleaned-up by a Gel Permeation Chromatography (GPC) [6]. The divinylbenzene copolymer resin column packing material separates high molecular size matrix co-extractives and low molecular size interferents from the dioxins and furans. For this purpose a AccuPrep MPS™ GPC Cleanup System automates (J2 Scientific) was employed. After another automatic concentration the extract was finally analysed by HRGC/HRMS. A gas chromatograph

Fisons 8000 coupled with a selective mass detector VG Autospec was used, operating in SIM mode [6]. Data were acquired in SIM mode. The concentrations were calculated considering half of the detection limit for those compounds not detected.

Results and Discussion

The major oxides constituents of the waste of the quarrying activity of the “Yellow tuff of the Tiberina Valley” has been chemically analised; results are reported on table 1. As major trace elements can be reported Ba (1980 ppm), Sr (1830 ppm), Zr (330 ppm), Ce (171 ppm) and La (113 ppm).

	SiO_2	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**LOI**	**Total**
.DL	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,005	0,01	0,01	
Waste	43.52	14.13	3.75	0,10	1.66	12.99	1.96	3.54	0.45	0.19	17.20	99.50

Table 1: major constituents of the waste of the quarrying activity. Results expressed in %.

From a mineralogical point of view , Rx diffraction has show that the major constituent are the following (in order of importance): K-feldspate (17%), calcite (14%), plagioclase (12%), quartz, augite, analcime, and magnetite. Zeolite minerals are present in the form of Chabazite (38%) and Philipsite (14%).

SEM analysis has shown that zeolites are in the form of tiny crystals of few microns in lenght has shown on figure 1 and 2 reported below.

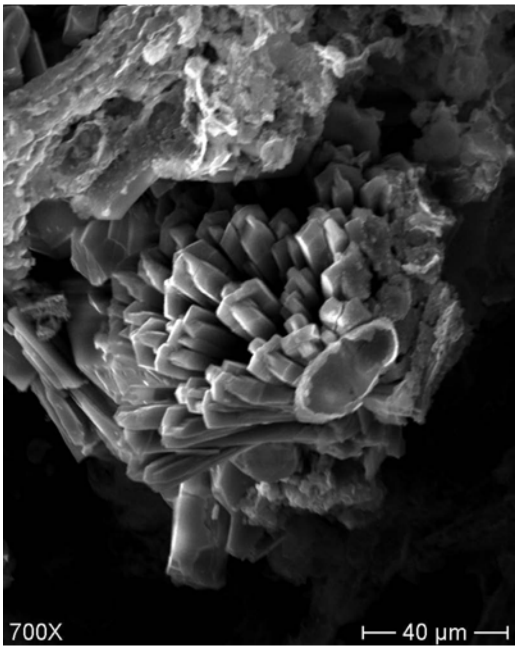

Figure 1 – Philipsite by secondary electrons at 25 KV

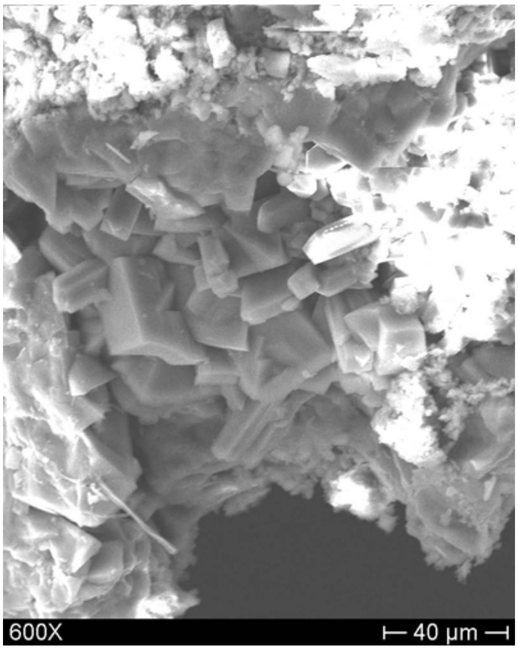

Figure 2 – Chabazite by secondary electrons at 25 kV

Size distribution of the waste and of the different samples used as removing agent of organic pollutants in liquid wastes has been shown in figure 3 reported below.

Figure 3 – Size distribution of the samples: the waste has been grinded and sieved in order to remove fines.

Following are reported the recovery percentage in water in function of different contact times at two different zeolitized tuff size distribution.

	Size distribution: -2000 µm				**Size distribution: -2000 +250 µm**		
Contact time	**24 h**	**48 h**	**72 h**	**144 h**	**24 h**	**48 h**	**120 h**
Congener	% (a)	% (a)	% (a)	% (a)	% (a)	% (a)	% (a)
TetraCDD	2.3	2.3	1.6	1.1	0.8	0.8	0.6
PentaCDD	2.3	2.5	1.9	3.9	2.0	1.8	1.9
Esa-CDD	4.3	4.1	2.3	0.8	1.8	2.1	1.2
HeptaCDD	3.1	2.9	3.0	3.6	3.2	4.3	0.8
OctaCDD	8.1	8.3	6.6	9.8	6.0	3.9	1.7
Tetra CDF	4.0	1.4	5.3	2.1	0.8	0.2	0.2
Penta CDF	6.4	6.7	5.1	5.6	3.7	3.5	1.5
EsaCDF	3.5	3.8	3.8	1.8	3.3	5.7	2.5
HeptaCDF	4.5	6.1	2.2	5.7	3.5	2.9	2.3
OctaCDF	26.6	25.3	17.2	11.1	7.5	5.6	5.5

(a) % = [PCDD/F recovered amount/PCDD/F spiked amount]*100

Table 2 – Recovery percentage of PCDD/F in water vs contact time and size distribution

How results in Table 2 the PCDD/F residual amount in the water is really low already after 24 hours. In some case the observed values are near to detectable limits of method.

Only for the OCDF a concentration decrease is observed in function of the contact time because the absorption reaction is slower.

The size distribution affect the results inversely than expected: this is due to the presence in the water samples of some colloidal fines, that did contain some PCDD/F, and that was not possible to remove from the sample even

after centrifugation. These fines were in higher amount when the sample was not sieved (-2000 μm) than for the sieved one (-2000 +250 μm).
A next target of the experiment will be therefore to verify the adsorption with shorter contact time and evaluate the zeolites capability to adsorb other micropollutants as PCBs and PAHs.

References

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