

## NATURAL ZEOLITES FOR PBDEs REMOVAL FROM MUNICIPAL WASTEWATER EFFLUENTS

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### Introduction

Municipal wastewater effluents are of environmental concern because of the various harmful substances that they could still contain, representing a significant source of contamination to the receiving waters. Some of these chemicals may be toxic to aquatic organisms and may pose a risk to human health. Many of these contaminants may also have a long term environmental effects as they are not easily broken down and tend to accumulate in aquatic and /or terrestrial organisms through the food chain. Wastewater treatment plants (WWTP) represent a known source of PBDEs which enter WWTPs from a variety of sources<sup>1</sup>. Three different formulations of PBDE are commercially available, penta-, octa-, and deca-BDE; while penta and octa-mixtures have been phased out in Europe, the deca-BDE environmental release is not regulated and controlled. Because of their high hydrophobicity and low aqueous solubility PBDEs preferentially partition onto sludge during waste water treatment<sup>2</sup>, however their presence in effluents has also been reported. In a recent study we found PBDE congeners both in sludge as well in effluents samples (both in dissolved and particulate phase) collected in a WWTP located in Tuscany (Italy). Mean total PBDE concentrations were 14.4 ng/L and 2.7 ng/L in sewage sludge and treated water samples, respectively. The Directive 2000/60/EC lists PBDE between the priority substances and the Proposal 10790/07 for a Directive of the European Parliament and of the Council on environmental quality standards (EQS), in the field of water policy and amending Directive 2000/60/EC, fixes in 0.2 ng/L the EQS for penta-BDE (BDE-28, BDE-47, BDE-99, BDE-153 and BDE-154) in inland surface waters. Even if this Directive is not applied yet, our data exceeded this guideline value. For this reason, it becomes important to determine the presence of pollutants in effluents in particular when the receiving water is a torrential river, as in this study. One of the most promising approaches to improve the efficiency and increase the capacity to WWTP without increasing size is based upon application of natural zeolites in various processes of the plant. The capacity of zeolites to control odours and gases such as VOC, ammonia and hydrogen sulphide from treatment tanks, reactors, clarifiers and composting operations that exist in a WWTP site has been extensively investigated. The ability of zeolites containing tuffs to remove the most of the dioxin and PAHs contained in a waste water effluent was demonstrated by Manni et al<sup>3,4</sup>, on spiked samples. In this study we test the capacity of natural zeolites to remove PBDEs from a spiked sample and a real effluent sample taking into account the influence of residence time.

### Materials and methods

The investigated WWTP treated municipal (20%) and industrial (80%, mostly textile) wastewater. Water sample was collected at the end of all sewage treatment processes. A grab sample was collected each hour to provide a composite sample over a 8 h period. Sample showed little amount of suspended solids having dimension ( $D_{80}$ ) of 17  $\mu\text{m}$ , determined with laser scattering granulometry (Helos system, Sympatec, Germany) and showing a binomial population with a maximum density population for 2 and 11  $\mu\text{m}$ , as shown in figure 1, and a purple color.

Aliquots of 400 ml of the sample were spiked with internal standard (BDE-77, Wellington Laboratories, Canada) and put in contact with milled zeolitized tuff from the Roman Province, already described in Manni et al.<sup>3</sup>, having a  $D_{80}$ = 170  $\mu\text{m}$ , at different residence time. Liquid/Solid ratio was 15 in order to compare the results obtained to those obtained for PCDD/F's and PAH's<sup>3,4</sup>.

Samples were, then, filtered to remove zeolites. Granulometry was also controlled after the treatment and results are reported in figure 2 and its  $D_{80}$  is still 17  $\mu\text{m}$  even if the particles shown a trinomial population with a maximum density for 2, 7 and 20  $\mu\text{m}$ . The suspension still maintained a purple color.

Liquid-liquid extraction was performed with 3x20 ml of n-hexane. Extracts were reduced in volume to approximately 1 ml using a rotary evaporator. Clean-up was performed through a multilayered silica gel column containing from bottom to top 1 g silica gel, 2.5 g silica gel /sodium hydroxide, 1 g silica gel, 5 g silica gel /sulphuric acid, 1 g silica gel, 2.5 g silica gel/silver nitrate, 5 g sodium sulphate.

Each sample was applied to the column and eluted with 25 ml of cyclohexane followed by 25 ml of cyclohexane-dichloromethane mixture (4:1 v/v)

Extracts were reduced to a final volume of 200  $\mu\text{l}$  and analysed by a HP6890GC (Agilent Technologies) coupled to a HP5973 quadrupole mass spectrometer in NCI mode. An HP-5MS (30 m x 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) containing 5% phenyl methyl siloxane capillary column was used. The temperature program was 50°C for 1 minute, ramped at 20°C  $\text{min}^{-1}$  to 130°C, and further ramped at 5°C  $\text{min}^{-1}$  to 300°C (held for 10 min) and finally ramped at 20°C  $\text{min}^{-1}$  to 251°C and held for 6 min. BDE-209 was analysed on a 15 m DB-5MS column (0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) with the following oven program: 90°C for 1 min, ramped at 30°C  $\text{min}^{-1}$  to 220°C, 10°C  $\text{min}^{-1}$  to 300°C, held for 8 min. The ions  $m/z$  484.7 and 486.7 and 488.7 were used for identification of BDE-209. A short capillary column is necessary to minimise thermal degradation of BDE-209 by long exposures to elevated temperatures in the injector and GC oven. Quality control criteria were adopted to ensure correct analyte identification such as a signal to noise ratio greater than 3 and GC retention times matched ( $\pm 0.1$  min) those of standard compounds. Quantitative determination was performed using an external standard method using eight concentration level calibration curve.

Figure 1 – Density distribution on the effluent pre zeolite treatment

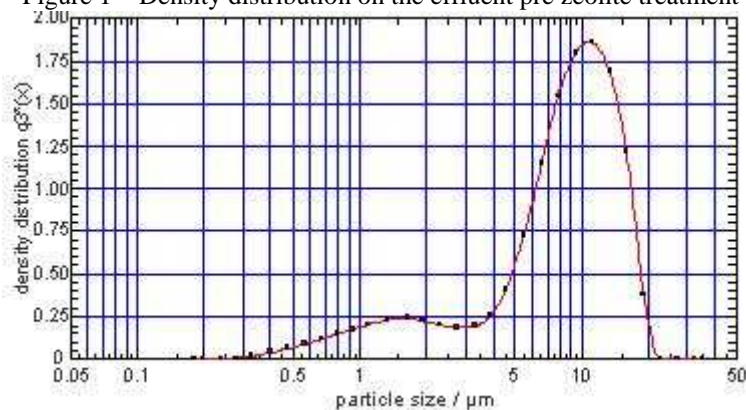
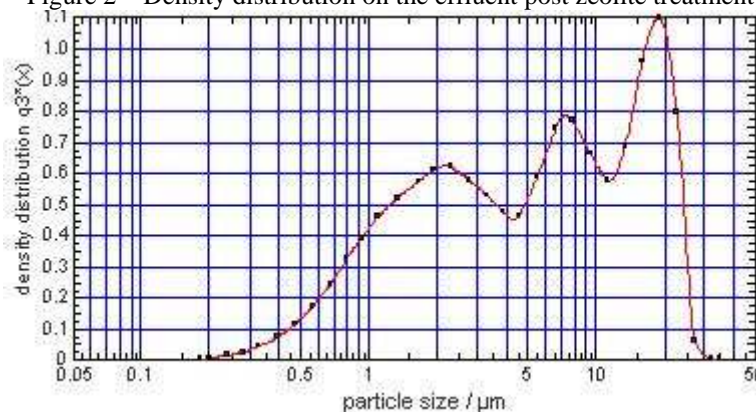


Figure 2 – Density distribution on the effluent post zeolite treatment



## Results and discussion

Penta-BDE concentration (3.8 ng/L) in the WWT effluent sample exceeded the EQS value suggested in the Proposal Directive 10790/07. For this reason a further effluent treatment with zeolitized tuffs was suggested in this study.

In Table 1 are reported the recovery percentages of PBDE in water spiked samples (400 ml of milli-Q water spiked with a native PBDE standard solution) in function of different contact times (4h, 24h and 48 h) with zeolitized tuffs.

The results show that zeolitized tuffs have high potential capability to reduce the PBDE amount present in the effluent already after 4 hours.

In table 2 the extraction percentages of BDE congeners from a real effluent sample at different contact times are reported. L/S ratio was maintained constant at 15, and its influence in the POPs adsorption capacity from water was investigated from Guerriero et al.<sup>5</sup>.

	<b>4h</b>	<b>24h</b>	<b>48h</b>
	<b>%</b>	<b>%</b>	<b>%</b>
<b>Penta-BDE</b>			
<b>BDE28</b>	<b>14.4</b>	<b>16.9</b>	<b>17.2</b>
<b>BDE-47</b>	<b>16.0</b>	<b>18.1</b>	<b>18.5</b>
<b>BDE-99</b>	<b>20.1</b>	<b>21.5</b>	<b>21.8</b>
<b>BDE-100</b>	<b>17.6</b>	<b>18.4</b>	<b>17.4</b>
<b>BDE-153</b>	<b>18.7</b>	<b>21.4</b>	<b>0.8</b>
<b>BDE-154</b>	<b>17.0</b>	<b>18.7</b>	<b>19.2</b>
<b>Octa-BDE</b>			
<b>BDE-183</b>	<b>33.0</b>	<b>32.1</b>	<b>30.5</b>
<b>Deca-BDE</b>			
<b>BDE-209</b>	<b>27.5</b>	<b>25.4</b>	<b>23.6</b>

Table 1 – Residual amount percentage of PBDE in the spiked sample after treatment with zeolitized tuffs at different contact time. % = [(BDE recovered amount/BDE spiked amount )\*100];

	<b>1h</b>	<b>2h</b>	<b>3h</b>	<b>4h</b>	<b>6h</b>
	<b>%</b>	<b>%</b>	<b>%</b>	<b>%</b>	<b>%</b>
<b>Penta-BDE</b>					
<b>BDE28</b>	<b>68.1</b>	<b>65.6</b>	<b>52.1</b>	<b>57.7</b>	<b>48.0</b>
<b>BDE-47</b>	<b>58.5</b>	<b>58.0</b>	<b>54.5</b>	<b>55.4</b>	<b>44.4</b>
<b>BDE-99</b>	<b>35.4</b>	<b>32.5</b>	<b>31.7</b>	<b>32.7</b>	<b>22.6</b>
<b>BDE-100</b>	<b>20.4</b>	<b>26.8</b>	<b>29.3</b>	<b>28.8</b>	<b>19.4</b>
<b>BDE-153</b>	<b>43.0</b>	<b>41.0</b>	<b>36.8</b>	<b>30.9</b>	<b>32.2</b>
<b>BDE-154</b>	<b>42.4</b>	<b>30.3</b>	<b>28.1</b>	<b>26.4</b>	<b>22.8</b>
<b>Octa-BDE</b>					
<b>BDE-183</b>	<b>58.8</b>	<b>48.7</b>	<b>46.2</b>	<b>48.0</b>	<b>42.2</b>
<b>Deca-BDE</b>					
<b>BDE-209</b>	<b>43.6</b>	<b>48.1</b>	<b>38.6</b>	<b>37.1</b>	<b>30.4</b>

Table 2 - Residual amount percentage of PBDE in the effluent sample after treatment with zeolitized tuffs at different contact time % = [(BDE recovered amount/PBDE in the effluent ) \*100]

## Discussion

Zeolitized tuff didn't show high ability to reduce the amount of PBDE in the real effluent as in the spiked samples. This different behaviour is due to the presence of fine suspended particles in the effluent samples, which could not be removed by the adopted filtration system (glass fiber filters), as well suspended particles (i.e. 20  $\mu\text{m}$  particles showed in figure 2) produced from the endogenous milling of zeolitized tuff. In fact, BDE congeners show a strong association with particulate matter as supported by their chemical-physical properties, such as n-octanol/water partition coefficient ( $K_{ow}$ ) values, which increase with the level of congener bromination. Thus, suspended particles play an important role in retaining PBDE.

Moreover the probable presence of surfactants in the effluent sample could saturate the particles porosities inhibiting their absorption capacity.

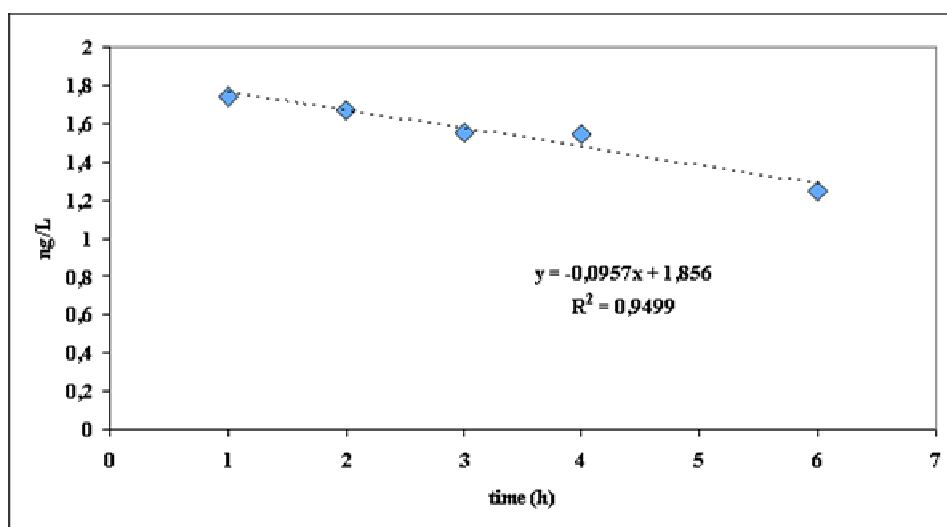


Figure 3 – Penta BDE concentration in the effluent sample vs contact times with zeolitized tuff

Figure 3 shows the strong correlation ( $r^2 = 0,95$ ,  $p=0,005$ ) between penta-BDE concentration in the effluent samples vs contact times. Extrapolating these data, it was possible to estimate a contact time of 17 h to reduce the PBDE amount in the effluent samples below the EQS of 0.2 ng/L.

Taking into account that the increasing of contact time did not increase the zeolitized tuff capacity of retaining PBDE as shown in the spiked samples results, it should be interesting to repeat the experiment testing the influence of a different L/S ratio and zeolitized tuff size distribution.

## References

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