

## ORGANIC AND INORGANIC MATERIALS AS PERMEABLE REACTIVE BARRIERS FOR GROUNDWATER REMEDIATION FROM TOXIC METALS AND BTEX – CONTINUOUS FLOW STUDY

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### ABSTRACT

The main goal of this study is the evaluation of an organic material (compost) in comparison to an inorganic one (zeolite) as potential reactive barriers in order to deal with multi pollutant groundwater contamination. The reactive barriers technology achieves groundwater remediation utilizing the physical flow.

The present study focuses on the comparison of compost from municipal solid waste and natural zeolites for the simultaneous removal of petroleum hydrocarbons (benzene, toluene, ethylbenzene, and xylenes - BTEX) and toxic metals (Cd, Zn) from groundwater. Experiments in small scale tanks were conducted simulating the real field conditions. Basic hydraulic parameters such as hydraulic conductivity and porosity of each material were determined. The effect of the initial concentration of the pollutants were also studied. Finally, the contaminants flow was simulated through the use of simulation software.

The results indicate that the mature compost achieve 80% removal of heavy metals and 90% removal of BTEX when the zeolite had 75% and 80% respectively. The real groundwater was not polluted in the same level as the experimentally prepared dilutes so under the same conditions the removal was almost 98% and the exhaustion time of the barrier was expanded. The selectivity of zeolites follows the order Cd > Zn & toluene > m- & p-xylene > ethylbenzene > o-xylene > benzene, while the selectivity of compost follows the order Cd > Zn & toluene > ethylbenzene > m- & p-xylene > o-xylene > benzene.

The utilisation of the Princeton Transport Code (PTC), which is a simulation program for groundwater flow, enables the accurate and efficient design of the reactive barriers technology eliminating the need of time consuming and expensive laboratory tests. In conclusion, compost has many advantages, when applied as a reactive material, and achieves high removal percentages both for organic and inorganic pollutants.

**Keywords:** compost, zeolite, hydrocarbons, metals, barriers

### 1. Introduction

Many researchers have focused on various technologies and numerous processes that can achieve the highest removal of inorganic and/or organic pollutants from industrial wastewater (Fua and Wang, 2011). The adsorption process of these pollutants has proven to be highly efficient, even for low concentrations (Yeh *et al.* 2010). During the last decade, the use of cheap and easily available materials for metals in toxic concentrations and BTEX adsorption, has been studied more intensively. According to the relative literature the most commonly used reactive materials are granular activated carbon, zeolites, zerovalent iron, and oxygen release compounds, compost and peat (Scherer *et al.* 2000). The present work compares the adsorption efficiency of compost and zeolite for BTEX, Cd and Zn removal, in column mode. The use of compost and/or zeolite may prove to be efficient in the

simple, efficient and low cost technology of the reactive barriers, as they do not produce any toxic by-products and have minimal construction and operational costs (Vignola *et al.* 2011).

## 2. Materials and methods

### 2.1. Materials and chemicals

In this study two materials were studied the compost, produced from the Chania Prefecture solid waste plant and the Greek natural zeolite. The compost was produced from the organic matter of the municipal solid waste, under aerobic digestion. Afterwards, the fresh compost was placed in an appropriate area for 8 month maturation. Zeolite was obtained from the S&B Industrial Minerals S.A from Aspropyrgos, Greece. The parameters pH, Cation Exchange Capacity (CEC) and Brunner-Emmett-Teller Surface Area (BET) were defined for both materials. The D 4972-01 method was used for both adsorbents with their leachates being measured for their pH value. The pH value was monitored directly using a Crison, PH25. The cation exchange capacity (CEC) of both materials was defined according to the EPA 9080 method, the surface area was determined using the Brunner-Emmett-Teller (BET) by isotherm nitrogen gas (N<sub>2</sub>) adsorption procedure. The hydraulic parameters porosity and hydraulic conductivity were determined for both materials and both types of sand used in the experiments according to standard methods. The organic chemicals, which were used for the preparation of water solutions were benzene (Riedel-de Haen, purity 99.7%), toluene (Riedel-de Haen, purity 99.7%), ethyl benzene (Fluka purity 99%), p-xylene (Fluka, purity 99%) and o-xylene (Fluka, 99%) respectively. The stock solutions of cadmium and zinc were prepared by the solid salts CdN<sub>2</sub>O<sub>6</sub>·4H<sub>2</sub>O and N<sub>2</sub>O<sub>6</sub>Zn·6H<sub>2</sub>O which were analytical-grade reagents and were supplied by Fluka.

### 2.2. Experimental procedure

Experiments in laboratory tanks were conducted in this study (Figure 1). The tank had 22 cm active length and 14 cm active height and was packed with 3 or 4 materials. The sequence of the materials in the tank is coarse sand, fine sand (1 kg each), compost (500 g) or/and zeolite (600 g). All the materials had 10 cm depth and 6 cm width. The tanks were maintained at 20-21 °C room temperature and were tapped in order to avoid BTEX volatilization. The inflow rate was stable at 0.45 mL/min and the solution was instilled from the storage tank onto the first sand layer by a peristaltic pump. Afterward, the effluent samples were taken in different time intervals and were filtered, acidified and measured. The samples were analyzed for BTEX concentrations, on GC-2010 Shimadzu gas chromatographer coupled to a QP-2010 Plus mass spectrometer, using Headspace Solid Phase Micro Extraction method (Aivalioti *et al.* 2012). The metal concentrations were measured by the means of the Atomic Adsorption Spectrophotometer (AAS) Perkin-Elmer AA analyst, 100A using the air-acetylene flame.

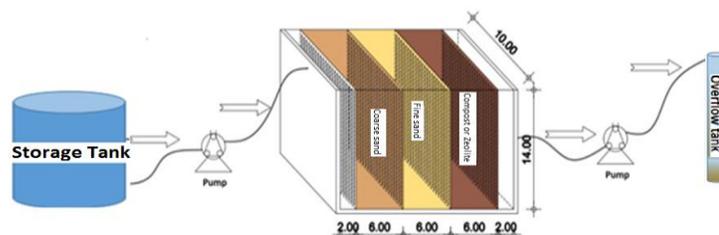


Figure 1: Experimental set up.

## 3. Results and discussion

### 3.1. Properties of the materials

The quality analysis of both materials indicates that the compost has higher moisture and cation-exchange capacity than the zeolite. However, both materials have characteristics that enhance sorption and ion exchange.

**Table 1:** Physicochemical properties of compost and zeolite

Material	pH	Moisture (%)	BET (m <sup>2</sup> /g)	CEC (meq/100g Na)
Compost	8.2	21.7	3.2	5000
Zeolite	8.0	5.8	26	200

For a proper understanding of streaming experiments is necessary to determine the basic hydraulic properties of the materials such as porosity and hydraulic conductivity (Table 2).

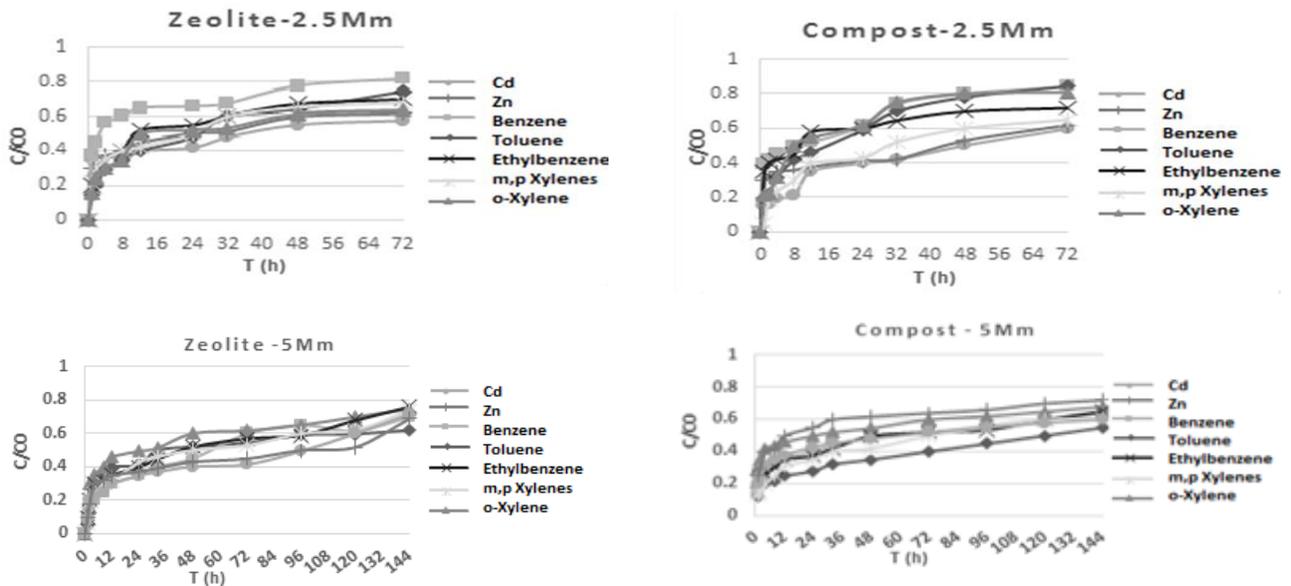
**Table 2:** Hydraulic properties of compost, zeolite and sands

Material	Porosity n	k (cm/s)
Fine sand	0.32	$2.77 \times 10^{-6}$
Coarse sand	0.43	$4.51 \times 10^{-6}$
Compost	0.63	$6.36 \times 10^{-6}$
Zeolite	0.37	$4.86 \times 10^{-6}$

The hydraulic conductivity of both compost and zeolite is greater than the two types of sand thus favoring the groundwater flow through them. This is the desired goal when designing a system reactive barriers.

### 3.2 Effect of the initial concentration

The breakthrough curves present the ratio  $C_{effluent}/C_{influent}$  versus time, for both materials and initial concentrations equal to 2.5 mM and 5mM (Figure 2).



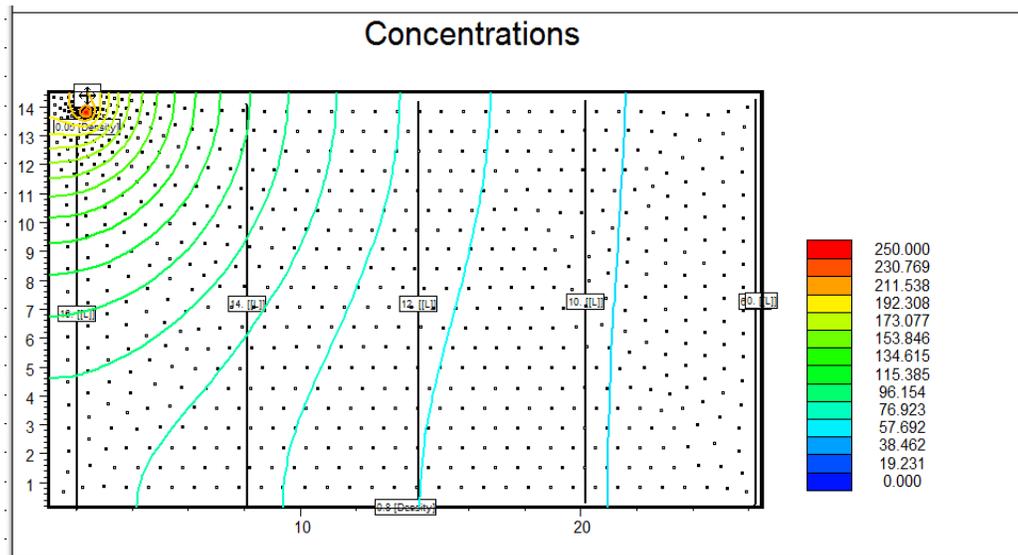
**Figure 2:** Effect of the initial concentration ( $C_0$ : 2.5mM and 5mM)

The results indicate that an increase in the initial concentration was inversely related to the pollutants removal (%) and in accordance with other published works (Plassard *et al.*, 2000) the saturation was earlier attained. The removal decrease for both organic and inorganic pollutants is attributed to the decrease in the free adsorption sites which are filled faster and in a less strongly way. Also, as the initial concentration increases, the pH value decreases and this leads to a higher concentration of  $H^+$ , which compete with the metal cations for the available sites. The maximum levels of pollutants'

sorption from the compost for 5 mM initial concentration, ranging from 30 to 65% and 40-80% for the zeolite respectively. The above remarks leads to the conclusion that compost has better adsorption capacity than zeolite and the decrease rate of removal vs initial concentration is lower.

### 3.3. Simulation of the contaminants' flow with software application

The software ARGUS ONE Student Version 4.2.0.q in combination with the Princeton Transport Code PTC were applied for the simulation of the contaminants' flow into the tank. The software was used for the simultaneous use of compost and zeolite in series. The layers' order is : fine sand-coarse sand- compost - zeolite. Firstly, the essential data were inserted in PTC model in order to represent the flow into the laboratory tank. Initial concentration, materials' porosity and hydraulic conductivity, bottom and surface elevation, experimental duration and boundary conditions were taken as input. The contaminants' plume is presented in Figure 3.



**Figure 3:** Contaminants plume for  $C_0 = 250$  mg/L

According to Figure 3, the concentrations' contours are presented for a time period of six days. The contaminants' concentration at the outlet of the tank estimated to be less than 20 mg / L. This means that the time required for the exhaustion of the reactive barriers, so as the concentration of the pollutants in the effluent, to be equal to the initial concentration (250 mg / L) is greater than 6 days.

### 3.4. Remediation of real groundwater sample

The aim of this research is to study the utilization of the compost and the zeolite in actual groundwater sample contaminated with organic (BTEX) and inorganic (Cd, Zn) pollutants. Therefore, groundwater derived from the outlet to the marine field of an industrial area was analyzed in order to determine the initial concentrations of BTEX and metals. Afterwards, the sample was applied to the continuous flow system with simultaneous use of both materials. The initial concentrations of the pollutants and their comparison with the maximum permissible limits are presented in Table 3.

According to Table 3 the concentration of cadmium exceeds the threshold of the New Netherlands List. Also, the concentrations of benzene, ethyl benzene and toluene determined beyond the US EPA and the New Dutch List while the concentrations of xylenes exceed the strictest limits of the same list. As expected, up to 98% sorption of pollutants of both materials was achieved over a period of 6 days.

**Table 3.** Initial concentrations of real sample and comparison with legislation limits

Contaminant	Concentration in the real sample (mg/L)	Maximum Contaminant Limits in groundwater US EPA (BTEX) (mg/L)	Maximum Contaminant Limits in groundwater New Dutch list (mg/L)
<b>Cd</b>	0.46	-	0.006
<b>Zn</b>	9.56	-	0.80
<b>Benzene</b>	2.54	0.005	0.03
<b>Toluene</b>	3.67	1	0.15
<b>Ethylbenzene</b>	1.48	0.7	1
<b>m.p Xylenes</b>	1.42	10	0.07
<b>o-Xylene</b>	1.12	10	0.07

#### 4. Conclusions

The results, derived from the continuous flow experiments, confirm the higher efficiency of the compost especially for the metals. Metal removal efficiencies of between 89% and 85% were achieved for compost and between 83% and 80% for zeolites. The maximum removal was achieved at lower initial concentration. The selectivity of both materials with slight differences follows the order Cd > Zn & toluene > m-p xylenes > ethylbenzene > oxylene > benzene. The laboratory system was efficient for the real contaminated groundwater and the contaminants' flow is well simulated by the selected software. Compost is capable for the simultaneous removal of both organic and inorganic pollutants from wastewater and its performance is superior to zeolites.

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