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Zeolites in a permeable reactive barrier (PRB): One-year of field experience in a refinery groundwater. Part 2: Zeolite characterization

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ABSTRACT

Zeolite filters composed by ZSM-5 and Mordenite extrudated with 20 wt% of clay and alumina, respectively, were used in a long term tests of decontamination of groundwater containing a variety of hydrocarbons and significant concentrations of dissolved inorganic salts. Extensive physical–chemical characterization of the samples taken after 6 and 12 months of tests confirmed that zeolites did not undergo any modification, the original microporous volume being restored by thermal treatment. Deposition of gypsum and iron sulphide occurred without altering the sorption capacity of the adsorbents. The only macroscopic effect of the long permanence in groundwater was identified in the modification of the textural properties of the extrudates, with the increase of the mesopore volume, probably associated with the reconstruction of the binders due to the loss of Al in the case of ZSM-5 and to its deposition in Mordenite samples.

1. Introduction

The zeolite advantages concerning with organic contaminant selectivity, rapid kinetics and no salt and humic substances interference (also at concentration of tens grams per liter) and mainly, the effective capacity in the removal of almost all the organic compounds present in groundwater of petrochemical and refinery sites, were demonstrated in previous laboratory works [1–3]. Specific zeolites were identified for efficient removal of methyl-tertbutylether (MTBE), 1,2-dichloroethane (1,2-DCA) and vinyl chloride (VC). In particular, ZSM-5 zeolites turned out suitable for aliphatic, halo-aliphatic and mono-aromatic molecules, such as benzene, toluene, ethylbenzene and xylenes (BTEX) and halo-benzene derivatives, while Mordenite was more appropriate for aromatic molecules with two or more aromatic rings, halo- and alkyl-substituted ones, and ethers such as MTBE. Furthermore, these microporous adsorbents have been proposed for the decontamination of groundwater with the use of permeable reactive barriers (PRB), as described in the first part of this study [4]. In such case, the system of one or two zeolites placed in series forms the active medium of the barrier, situated *in situ* perpendicular to the groundwater flow. In fact, the decontamination of the polluted stream passing through it occurs by immobilizing the contaminating species. Generally, in literature and practical PRB application, the selection of the reactive medium is based on the targeted contaminants and on the hydro-geological assessment of the site. Zero-valent iron (ZVI) is the most common medium used in PRBs, followed by granulated activated carbon (GAC). Examples of other reactive media include micro-organisms, natural zeolites, peat, phosphate, limestone, and amorphous ferric oxide. The treatment processes that occur within the trench consist into degradation, adsorption, and/or precipitation of the contaminant. ZVI, used in PRB since the nineties, appears to be ineffective on irreducible compounds such as 1,2-DCA and chlorobenzenes as well as hydrocarbons [5]. Further efforts have been placed on finding innovative reactive systems either following the reductive approach by introducing other metals (*e.g.* Pd, Ni) or using more effective adsorbents (*e.g.* ion-exchange polymers of Amberlite^{TM} family). On the other hand, the use of the GAC was encouraged by economics and by the possibility of removing a wide range of contaminants, such as chlorinated solvents and hydrocarbons. However, GAC presents several disadvantages due to the physical–chemical characteristics of its surface: pore plugging, interactions with humic substances and inorganic ions, adverse effect of pH on the adsorption of organics. Additionally, GAC has been shown to be slightly effective in treatment of water containing very soluble compounds, such as

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Table 1
Main characteristics of zeolites.

Characteristics	ZSM-5	Mordenite
SiO_2/Al_2O_3 (mol/mol)	2100	230
Na_2O (wt%)	<0.01	<0.05
Binder (wt%)	Clay (20)	Alumina (20)
Pellets size (diameter × length (mm))	1.5 × 3	1.5 × 3

oxygenated organics, or low molecular weight compounds, such as VC [6–8].

This paper discusses the use of hydrophobic zeolites as an innovative adsorbent material suitable for the *in situ* abatement of contaminants in groundwater through PRB and mainly evidences its use in an industrial site situated on the coast. The field treatment, with the duration of one-year, was divided into two operational phases different for water flow, the first one to verify the material performance and the second one to verify the system limits.

The main aim of present work is to show that channels of zeolite adsorbents are not affected by fouling occurred during working time. In this respect, physical–chemical characterization of aged materials was performed: X-ray powder diffraction (XRD) to determine any structural changes, scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) to detect the presence of compounds adhering to the external surface, thermo-gravimetric (TG) and gas-chromatographic (GC–MS) analyses to verify the immobilization of contaminants within the channels.

2. Experimental

2.1. Samples

Zeolites were supplied by Tosoh Corp. as extrudated cylinders; the characteristics are reported in Table 1.

The field tests were performed as previously described [4]. Two working phases, six months long each, were conducted with different set of filters:

Phase A: 120 kg ZSM-5 filter (*Z*) followed by 150 kg Mordenite filter (*M*) in a *Z* + *M* sequence.

Phase B: new filters of 120 kg ZSM-5 (*Z*′) and 150 kg Mordenite (*M*′) were added so each previous filter was followed by a new one in a sequence *Z* + *Z*′ + *M* + *M*′. Groundwater went through filters from bottom to top (up flow).

At the end of the test, samples were taken from the top and from the bottom of each filter and opportunely treated for the analyses.

3. Methods

Structural analysis was carried out on powdered sample by XRD; a Philips X'PERT™ vertical diffractometer equipped with a scintillator detector and a secondary mono-chromator was used. Data were collected stepwise in the $5 \leq 2\theta \leq 50^\circ$ angular region, with a step size of 0.02° 2θ and 7 s/step accumulation time, using the Cu Kα (λ = 1.54178 Å) radiation.

Textual analyses were performed through adsorption/desorption cycles of N_2 at 77 K with a ThermoQuest Sorptomatic 1990™ porosimeter. Samples were analyzed in form of pellets previously treated at 383 K for 2 h under vacuum.

Morphological and compositional characterization of the samples was carried out by means of SEM) equipped with an EDS detector. A Jeol JSM 7600F™ with "in lens" thermal field emission gun emitter (FEG) was used. SEM had an accelerating voltage from 0.1 kV to 30 kV, a SEI resolution of 1.0 nm at 15 kV, upper and lower (semi-in lens) detectors for secondary electrons, retractable and low angle backscattered electron detectors (RBE and LABE). The EDS spectrometer, from Oxford Instruments, has a resolution of 130 eV and a crystal area detector of 20 mm.

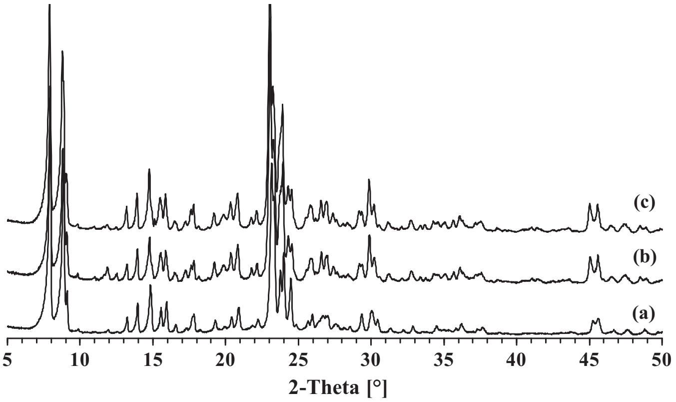

Fig. 1. XRD patterns of ZSM-5 samples: (a) fresh, (b) filter *Z* bottom and (c) filter *Z* top.

The samples, previously treated at 343 K for 4 h under vacuum to eliminate the volatile components, were analyzed in different forms:

- *pellets*: the samples were milled and the powder pelletized in an infra-red spectroscopy press to obtain pellets suitable for the determination of the average chemical composition. For each pellet, 5 different areas were analyzed by EDS at relatively low magnifications (500×) and the results averaged;
- *as made*: the extrudates were analyzed without any manipulation in order to inspect the surface morphology and composition;
- *embedded*: the extrudates were embedded, either in vertical and horizontal positions, in epoxy resin then polished with abrasive papers of decreasing size; in this way, it was possible to obtain transversal and longitudinal sections which allowed the inspection of the surface and the internal morphology as well as the distribution of the main elements through the acquisition of X-ray maps and profiles.

4. Results and discussion

In order to verify the stability of the zeolite adsorbents left for long time (from 6 to 12 months) in groundwater contaminated by organic species and with a significant amount of dissolved inorganic ions, samples of zeolites recovered from the top and the bottom of the filters were subjected to an extensive physical–chemical characterization.

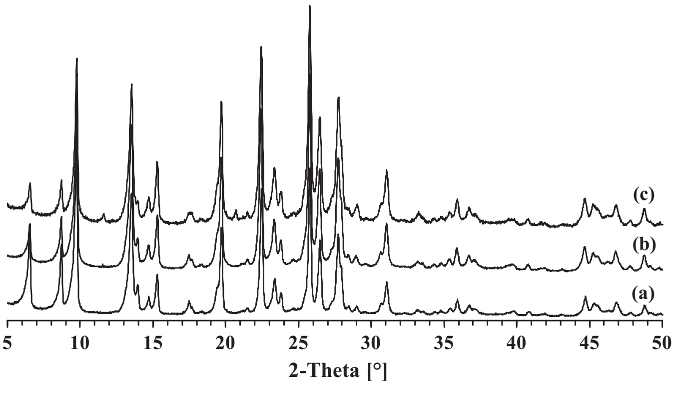

Fig. 2. XRD patterns of Mordenite samples: (a) fresh, (b) filter *Z*′ bottom and (c) filter *Z*′ top.