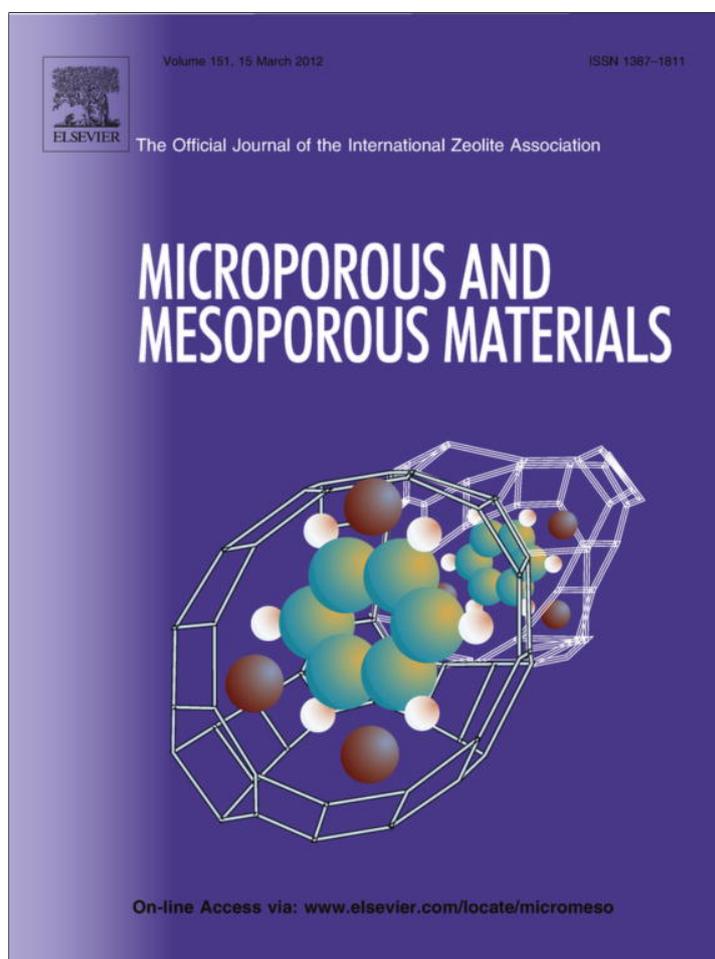


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Removal of methyl *tertiary*-butyl ether (MTBE) from water by polymer–zeolite composites

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ABSTRACT

Methyl *tertiary*-butyl ether (MTBE), a semi volatile organic compound used as a gasoline additive, has been extensively detected in surface and groundwater and therefore became a major issue as an environmental pollutant. The removal of methyl *tertiary*-butyl ether (MTBE) from water by high-silica zeolite, high-silica zeolite composites, and by granular activated carbon (GAC) was investigated in suspension and by filtration. The Langmuir model yielded good simulation and prediction of MTBE removal. The removal of MTBE from water was more efficient by composites of polyacrylamide (PAM)-zeolite designed in this study than by untreated zeolite or GAC. Even in the presence of BTEX (benzene, toluene, ethyl-benzene and xylene) MTBE removal was very efficient by the PAM-zeolite composites, in comparison to its removal by the zeolite or GAC, reaching 2.5- and 75-fold higher removal, respectively. Filtration of MTBE solution through columns filled with GAC mixed with a PAM-zeolite composite (5:1 w/w ratio) demonstrated several-fold enhanced removal relative to a control which included only GAC. We suggest that the enhanced removal by the PAM-zeolite composite is attributed to (a) the displacement of water from the zeolite surface upon PAM adsorption, which promotes MTBE adsorption and (b) hydrogen binding between the polymer and MTBE.

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1. Introduction

Methyl *tertiary*-butyl ether (MTBE), a semi volatile organic compound, has been extensively used as a gasoline additive for improved oxidation. In the last decade, its distribution in the aquatic environment and its occurrence in drinking water resources has become a major issue in the United States and in Europe [1–4]. The main sources of MTBE contamination in the environment are leaking underground storage tanks, exhausts from recreational watercrafts, urban runoff and air deposition [4–6].

MTBE has a high vapor pressure which predicts volatilization from soil surfaces [7]. However, its high water solubility, small molecular size and relatively low Henry's law constant imply that its solution predominates its volatilization [8]. In addition, MTBE is very mobile in the soil solution and hardly sorbs to soil particles. Consequently, MTBE migrates rapidly to the groundwater. In the US, more than 1500 drinking water supply systems in 28 states have reported detectable levels of MTBE [9]. MTBE is a potential human carcinogen, which can adversely affect the taste and odor quality of water. In 1997, EPA issued a drinking water advisory limit of 20–40 ppb based on taste and odor [7].

Due to the characteristics of MTBE its removal from contaminated water is difficult. Adsorption processes have relatively low efficiency, which makes them costly; for example, activated carbon requires high sorbent usage rates [4,10–12]. Air stripping can be effective for MTBE removal. However, low mass transfer coefficients are observed for these systems due to the high water solubility of MTBE [12]. MTBE is fairly resistant to biodegradation and chemical oxidation. Furthermore, these processes may result in the formation of undesirable metabolites, or oxidation byproducts, such as *tertiary*-butyl alcohol (TBA) or bromate [13,14].

Recently nano-sized zeolites, inorganic porous minerals, with good mechanical and hydrothermal stability, have received attention as adsorbents for the removal of MTBE [4,15–19]. Erdem-Senatalar et al. [18] who studied four zeolites with high silica content (silicalite-1, mordenite, zeolite beta and Y) for the sorption of MTBE from water concluded that silicalite-1 is the most effective adsorbent due to its higher hydrophobicity. High-silica zeolites exhibit considerably larger single-solute MTBE adsorption capacities than granular activated carbon (GAC) [4,16,17]. Few studies have quantified MTBE adsorption on activated carbon and alternative adsorbents; however, reports on the effects of the presence of other organic pollutants on MTBE uptake are scarce. The organic pollutants BTEX (benzene, toluene, ethyl-benzene and xylene) are typically present in MTBE contaminated water [7,20,5], but to

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the best of our knowledge the employment of high-silica zeolites for MTBE removal from such water has not been reported.

The overall objective of the current research was to design high-silica zeolite composites for improved MTBE removal from water. Previously, we have demonstrated enhanced removal of several organic pollutants by specifically designed polymer–clay composites [21–23]. We hypothesized that the enhanced removal was due to molecular compatibility between the polymer and the pollutant. Specific objectives of this study were: (1) to compare MTBE removal by polymer–high-silica zeolite composites to its removal by the untreated zeolite and by GAC, (2) determine parameters that describe the adsorption of MTBE on the high-silica zeolite composites from water, (3) examine MTBE removal by column filters composed of the sorbents (composite, zeolite and GAC), (4) study the effect of BTEX on MTBE removal.

2. Experimental

2.1. Materials

Silicalite zeolite HiSiv 3000 (denoted in this paper as zeolite) was received from UOP, Mount Laurel, NJ, USA. Quartz sand (grain size 0.8–1.5 mm) was purchased from Shoshani & Weinstein (Israel). Methyl tertiary-butyl ether (MTBE; purity 98%), a solution of benzene, toluene, ethyl-benzene and xylene (BTEX; purity 99.9%), polydiallyldimethylammonium chloride (PDADMAC; MW 400–500 K), polyacrylamide (PAM; MW 10 K), octadecyltrimethylammonium bromide (ODTMA), and CsCl (purity 99.5%) were supplied by Sigma–Aldrich (Steinheim, Germany). Granular activated carbon Hydrarffin 30 N and Hydrarffin CC 8 × 30 were purchased from Benchmark Ltd. (Israel). Physical characteristics of adsorbents are given in Table S1 (Supporting information (SI)). Structural formulas of the polymers, organic cation and MTBE are shown in Fig. 1.

2.2. Methods

2.2.1. Composite preparation: modifier adsorption on zeolite

The composites were prepared by applying batch experiments using 300 mL polycarbonate Oak Ridge centrifuge tubes. Polymer,

surfactant or cesium solutions were prepared (0.5–15 mM). The zeolite was added to the solutions at a concentration of 10 g/L. The suspensions were agitated for 24 h using a shaker; the precipitates were separated by centrifugation (10,000g for 20 min) and freeze-dried. The percentage of carbon in the precipitates, indicating the amount of organic cation or polymer adsorbed, was measured using a CHNSO analyzer (Fisons, EA 1108, Waltham, MA, USA).

2.2.2. Zeta-potential

The mobilities (converted to zeta potentials by Smoluchowski equation) of the zeolite and zeolite composites were measured in distilled water (pH ≈ 6.5) using a Zetasizer Nanosystem (Malvern Instruments, Southborough, MA). The samples were let to settle for a couple minutes and only the top of the suspension was sampled. The mobilities of zeolite and zeolite composites were measured in a dilute suspension (~0.05%).

2.2.3. MTBE adsorption on GAC, zeolite and zeolite composites (batch experiments)

A solution of MTBE (2.3 mg/L) was added to Teflon centrifuge tubes (no headspace) containing the zeolite, PDADMAC-zeolite, PAM-zeolite, ODTMA-zeolite or cesium-zeolite composites (1 g/L). The tubes were agitated for 1–24 h in which equilibrium was reached [4,18]. Measurements were also taken after 1, 2 and 4 h and no significant increase in adsorption was obtained after 2 h. Supernatants were separated by centrifugation (10,000g for 10 min) and analyzed by GC/MS headspace to determine MTBE concentrations. Tests indicated that there was no sorption of MTBE on the Teflon centrifuge tubes and no volatilization of MTBE. The experiments were performed in triplicate.

2.2.3.1. Adsorption isotherm of MTBE on polymer–zeolite composite. For the equilibrium experiments a freeze-dried polymer PAM-zeolite composite (0.0175 g polymer/g zeolite) was employed (prepared as described above). The experiments were performed at MTBE concentrations of 0.12–8.5 mg/L. MTBE solutions (42 mL) were mixed with polymer–zeolite composite (reaching 1 or 0.25 g composite/L) in Teflon centrifuge tubes (no headspace) and kept at 25 ± 1 °C under continuous agitation for 24 h. MTBE concentrations were determined as described above.

2.2.3.2. Modeling MTBE adsorption on the composites. The Langmuir equation was employed as in [24].

$$(L_0 - L)/L = R_0 \cdot k/(1 + k \cdot L), \quad (1)$$

in which L_0 and L denote the molar concentration of total and free MTBE molecules, respectively. R_0 is the molar concentration of sorbing surface sites, and k , whose unit is M^{-1} , is the binding coefficient. The adsorption was analyzed as described in [22]. Eq. (1) was used to determine k -values for assumed values of R_0 for given experimental values of adsorbed amounts. The value chosen for R_0 was the one which gave the smallest variation in k . Then in the next stage the value of k was fixed according to the best fit to the experimental data.

2.2.3.3. MTBE adsorption on GAC, zeolite and polymer–zeolite composite in the presence of BTEX. A solution of MTBE (0.93 mg/L), MTBE and BTEX (0.9 mg/L for each component) or MTBE (8.3 mg/L) and BTEX (1.5 mg/L for each component) were added to 40 mL Teflon centrifuge tubes (no headspace) containing GAC, zeolite or polymer–zeolite composite (1 g/L). The tubes were agitated for 60 min. MTBE concentrations were determined as described above.

2.2.4. Column filters experiments

Column filter experiments were performed at MTBE concentrations of 0.23 and 1 mg/L, in glass columns of 20 cm length and

Structures	Materials
<p>ODTMA</p>	Surfactant (organic cation)
<p>PAM</p> <p>PDADMAC</p>	Polymers
<p>MTBE</p>	Pollutant

Fig. 1. Molecular structures of the materials.

1.6 cm diameter. To enable a flow of 5 mL/min through the column the zeolite or zeolite composites were mixed with quartz sand at ratio of 1:18.3. Quartz sand was thoroughly washed in distilled water and dried at 105 °C for 24 h. Preliminary experiments showed no adsorption of MTBE by the quartz sand and the glass columns. The MTBE solution was stored in and pumped from polypropylene sample bags of 10 L with Teflon tubing (SKC, USA) to avoid MTBE volatilization. The columns were filled with 44 g of sand mixed with 2.4 g of zeolite, zeolite composites, or with a layer of 2.4 g of GAC in the middle of the column and the rest of the column filled with 44 g sand. The bottom of the columns was covered by 2 cm layer of quartz sand. Non woven polypropylene geo textile filters (Markham Culverts Ltd., Papua New Guinea) were placed on both ends of the column to prevent exit of the sand and the composites from the column. Prior to filtration the column was connected to a peristaltic pump and saturated by distilled water from the bottom (2 mL/min). A MTBE solution (1500 mL) was passed through the silicalite zeolite, zeolite composites and GAC columns at a rate of 5 mL/min. The eluting water was collected for analysis. One pore volume was 10 or 14 mL for zeolite and zeolite composites, or GAC columns, respectively.

2.2.4.1. Effect of BTEX on MTBE removal by GAC, zeolite and polymer-zeolite composite column filters. Column filter experiments were performed at MTBE and BTEX concentrations of approximately 0.3 mg/L (of each component), as described above.

2.2.4.2. Removal of MTBE by column filter of polymer-zeolite composite mixed with activated carbon. The experiment was performed at MTBE concentrations of 0.4 mg/L, in glass columns of 25 cm length and 5 cm diameter. The column was filled with a mixture of 39 g of zeolite composite and 180 g of granular activated carbon. For comparison, a column filled with 220 g of granular activated carbon was also prepared. A MTBE solution (150 L) was passed through the zeolite composite + GAC and GAC columns at a flow rate of 50 mL/min. In the experiments above the MTBE solution was kept in polypropylene sample bags to avoid MTBE volatilization. However, volatilization occurs when employing large volumes. In the current experiment MTBE volatilization was monitored and the calculations of MTBE removal at each pore volume took into account this volatilization.

2.2.5. MTBE and BTEX analysis

Water samples retrieved from the experiment were collected in headspace-free 40 mL vials and refrigerated at 4 °C for no more than 14 days before analysis. Aliquots from the vials were placed in 10 mL head space vials, which were incubated at 90 °C for 10 min in a CombiPal autosampler (CTC analytics AG, Switzerland) and then analyzed by gas chromatograph (6890N, Agilent Technologies) coupled to a mass spectrometric detector (5973, Agilent Technologies). The GC separation was performed on a Varian column (VF-5 ms; 30 m × 0.25 mm × 0.25 μm). The column oven temperature was the following: 5 min at 35 °C, then a ramp at 2 °C/min until 41 °C and finally at 30 °C/min until 200 °C. Compounds were identified by comparison of the mass spectra with those of the NIST (USA) 92 library. Quantification of the analyses was performed in the selected ion monitoring mode (SIM), using the compound-specific ions given in Table S2 (Supporting information (SI)).

3. Results and discussion

3.1. MTBE removal by zeolite composites in suspension

Four zeolite composites, ODTMA-, PDADMAC-, PAM- and Cs-zeolite were designed. In all cases complete adsorption of 0.15 mM

modifier/g zeolite was achieved reaching 0.058, 0.02, 0.017 and 0.02 g/g, respectively. Zeta potentials of the composites were determined. The removal of MTBE from water by these composites, untreated zeolite and GAC was examined (Table 1). High MTBE adsorption (98 ± 1.4%) by the untreated zeolite was obtained similar to results reported in previous studies (ref). In comparison, the adsorption of MTBE from water to two GACs was low (83–88%).

We hypothesized that by modifying the zeolite surfaces its affinity towards MTBE would enhance as has been demonstrated with several organo-clays (higher affinity of an organic pollutant to the complex than to the untreated clay). For example, the high efficiency of ODTMA micelle-clay complexes to purify water from organic contaminants in comparison to the low affinity of the untreated clay [25–27]. However, MTBE adsorption on the micelle-clay (43%) and micelle-zeolite (91–92%) composites was relatively low. And modifying the zeolite with PDADMAC (also an environmental friendly polymer [30,31]) also did not enhance MTBE adsorption (93%). In contrast, the PAM-zeolite composite (an environmental friendly polymer [28,29]) showed the highest MTBE adsorption (>99%) even after only 1 h (Table 1).

The design of the PAM-zeolite composites for MTBE removal from water was based on the hypothesis that the nonionic polymer PAM (unlike ODTMA and PDADMAC) has the ability to displace water molecules from the zeolite surface upon adsorption. Based on a rough estimation of the polymer width (~5 Å) and the zeolite pore sizes (5.3 × 5.5 and 5.5 × 5.6 Å) [18] we suggest that the polymer may partially enter the framework channels. Previous studies demonstrated the penetration of polymers in pores of the same size as polymer width, i.e. polymer minimum width/pore diameter ≈ 1 [32]. It is known that the presence of water in zeolite pores can interfere with MTBE adsorption [18]. The high adsorption of MTBE to the nonionic polymer PAM composites in comparison to its adsorption on the composites of the polycation PDADMAC (Table 1) supports our hypothesis, since PDADMAC adsorbs with a larger hydration shell. To further test this hypothesis the adsorption of MTBE by a Cs-zeolite composite was examined. Cs has a large bare ionic radius with a small hydration shell, which reduces the number of water molecules on the zeolite surfaces. Indeed high MTBE adsorption was obtained by the Cs-zeolite composite (98.6%).

This high adsorption of MTBE to the PAM composite can be also explained by the contribution of hydrogen bonds between the two.

The adsorption of low amounts of Cs or PAM on the zeolite reduced its zeta potential (less negative) (Table 1). In contrast, the adsorption of such small amount of PDADMAC and ODTMA resulted in charge reversal (positive values) which may suggest that these large molecules block the zeolite pores [33].

3.2. PAM-zeolite composite characterization

Adsorption isotherm measurements indicated interactions of the polymer with the zeolite reaching 100–20% adsorption (Fig. 2). However, zeta potential measurements indicate that the composites were not neutralized even at the highest polymer loadings. The measured zeta potential of the zeolite was –76 mV and was reduced to ~–20 mV at the highest polymer loading of 0.023 g/g. The zeolite's zeta potential decreased as the loading of the PAM increased and reached a plateau at a loading of 0.0175 g polymer/g zeolite (Fig. 2). At a loading of 0.0175 g polymer/g zeolite which was employed in the current study zeta potential of the composite was –40 mV.

3.3. MTBE removal by PAM-zeolite composite in suspension

3.3.1. Adsorption isotherm of MTBE on PAM-zeolite composite

The adsorption isotherm of MTBE on the PAM-zeolite composite (1 g/L) was in good agreement ($R^2 = 0.99$) with the Freundlich equa-

Table 1
MTBE (1 mg/L) adsorption on GACs, zeolite and zeolite composites (1 g/L) in water.

MTBE adsorption (%) after 24 h	MTBE adsorption (%) after 1 h	Zeta potential (mV)	Modifier	Adsorbent
92.7 ± 1.1 ^b	83.4 ± 6.4 ^b	N.D. ^a	–	GAC (Hydrffin 30 N)
92 ± 1	88.6 ± 1.9	N.D. ^a	–	GAC (Hydrffin CC 8 × 30)
99.8 ± 0.1	98 ± 1.4	–76.3	–	Zeolite (HiSiv 3000)
91 ± 2.1	92.6 ± 0.8	7.3	ODTMA	Zeolite composites
99.4 ± 0.2	93.1 ± 2.8	19.6	PDADMAC	
99.8 ± 0.1	98.6 ± 0.4	–61.6	Cs	
99.8 ± 0.1	99.1 ± 0.3	–40.2	PAM	

^a Not determined.

^b ± represents standard deviation.

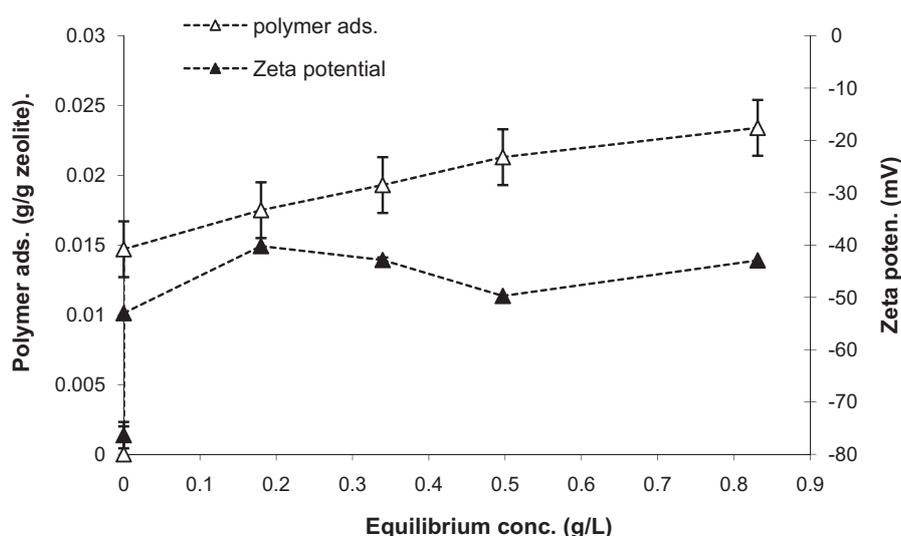


Fig. 2. Adsorption isotherm (after 24 h) of PAM (0–1.065 g/L) on zeolite (10 g/L) and zeta potentials of the composites. The error bars represent standard deviation.

tion. The Freundlich isotherm calculated parameter k was 70 (mg/g) (L/mg)^{1/n} and $1/n = 0.84$. However, this equation was inadequate in explaining the adsorption results at a lower composite concentration of 0.25 g/L.

3.3.2. Modeling MTBE adsorption on PAM-zeolite composites by the Langmuir equation

For a large range of MTBE/composite ratios the Langmuir model (Table S3) could yield a reasonably good simulation and prediction of the results. The results of the fit of calculations to the experimental values in Table S3 are summarized by $R^2 = 0.93$ and RMSE (root mean square error) of 3.8, which is well within the experimental errors. The parameters describing MTBE adsorption were $R_0 = 2.7 \times 10^{-4}$ mol/g composite and $k = 130,000 \text{ M}^{-1}$. The value of the binding coefficient, k is rather large in comparison with binding of neutral molecules to organo-clay or micelle-clay composites (e.g., for bromacil the value determined for k was $10,000 \text{ M}^{-1}$; [25]), but a much larger value was recorded for the adsorption of several anionic herbicides by a liposome-clay composite [34]. The value of R_0 is related to the number of pores which can favorably capture MTBE. It is about 1/8 of the CEC of the zeolite ZSM-5 [35].

3.3.3. MTBE adsorption on GAC, zeolite and PAM-zeolite composite in the presence of BTEX

Contamination of groundwater by MTBE is frequently accompanied by the contamination of aromatic components, such as BTEX. In the presence of these contaminants MTBE adsorption on GAC and synthetic resins is reduced significantly [36,37]. The uptake of MTBE in the presence of BTEX by the PAM-zeolite composite (Fig. 3), was

similar to the uptake without BTEX, especially at the lower MTBE and BTEX concentrations (~ 1 mg/L). In contrast, MTBE uptake by the zeolite was significantly reduced in the presence of BTEX in both cases tested (Fig. 3). The adsorption of MTBE to GAC was low in all cases examined (results not shown). BTEX adsorption was high for all adsorbents tested ($>90\%$) emphasizing the selectivity of the composite towards MTBE. These results suggest that in complex MTBE contaminations the PAM-zeolite composite will be more effective in adsorbing MTBE than the untreated zeolite and obviously more effective than GAC.

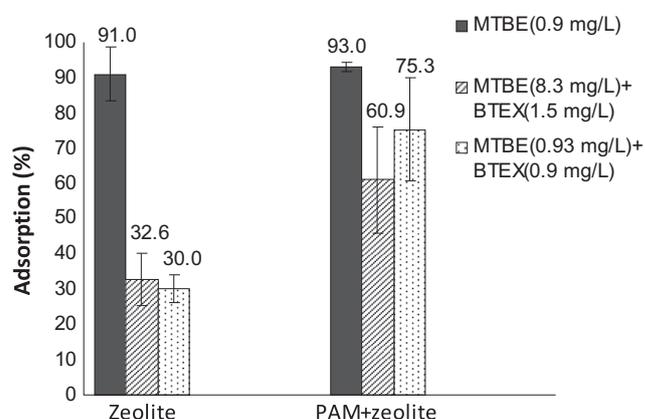


Fig. 3. MTBE adsorption (after 1 h) on PAM-zeolite composite or zeolite (1 g/L) in suspension (BTEX concentrations are for each of its components). The error bars represent standard deviation.

3.4. MTBE removal by filtration columns

3.4.1. Removal of MTBE by column filters which included GAC, zeolite and zeolite composites

The removal of MTBE was studied by employing column filters (25 cm) including equal amounts of PAM-zeolite composite, zeolite or GAC (2.4 g) mixed with inert sand. The filtration experiments demonstrate that the PAM-zeolite composite filter is the most efficient among the four adsorbents examined in removing MTBE (0.23–1 mg/L) from water (Fig. 4). After 120 pore volumes (corresponding to 1200 mL) the PAM-zeolite composite filter removed 95% of MTBE (Fig. 4a), whereas the Cs-zeolite composite filter removed 91.7%, the zeolite filter removed 86% and the GAC filter removed only 68%. When comparing the PAM-zeolite composite filter with the zeolite filter (Fig. 4b) after 300 pore volumes of the MTBE solution were passed, the advantage of the PAM-zeolite composite filter was even more pronounced with 91% removal of MTBE by the PAM-zeolite filter (reaching a concentrations below the EPA recommended limit) and only 65% by the zeolite filter.

3.4.2. Effect of BTEX on MTBE removal by GAC, zeolite and polymer-zeolite composite column filters

In the presence of BTEX the efficiency of the silicalite-zeolite filter to remove MTBE from water decreased significantly (from 98–84% to 93–54% removal for 1500 mL); whereas, the corresponding

efficiency of the PAM-zeolite composite filter was only slightly influenced by the presence of BTEX (from 99–93% to 99–89% removal) (Fig. 5). Consistently the GAC filter showed the lowest removal efficiency. Under these conditions the eluting MTBE concentrations from the PAM-zeolite filter were below the recommended limit, whereas, the concentrations eluting from the zeolite filter exceeded the limit. BTEX removal was efficient by filters of the composite, zeolite and GAC. On average benzene removal reached 97.5%, 93% and 95% removal by composite, zeolite and GAC filters, respectively. Toluene removal was 95%, 96% and 95% by composite, zeolite and GAC filters, respectively. Ethyl-benzene removal was 99%, 98.8% and 96% by composite, zeolite and GAC filters, respectively and xylene removal reached 90.5%, 73.5% and 95.3% by composite, zeolite and GAC filters, respectively. The high efficiency of MTBE removal by the PAM-zeolite composite filter in the presence of BTEX presents another advantage of the composite versus the untreated zeolite and GAC.

3.4.3. Removal of MTBE by column filter of polymer-zeolite composite mixed with activated carbon

The zeolite, or the PAM-zeolite column filters included excess sand in order to enable unperturbed flow. However, the sand is inert and does not contribute to MTBE removal. An approach of applying a granular component that is also active could be optimal. Following this approach the PAM-zeolite composite was mixed

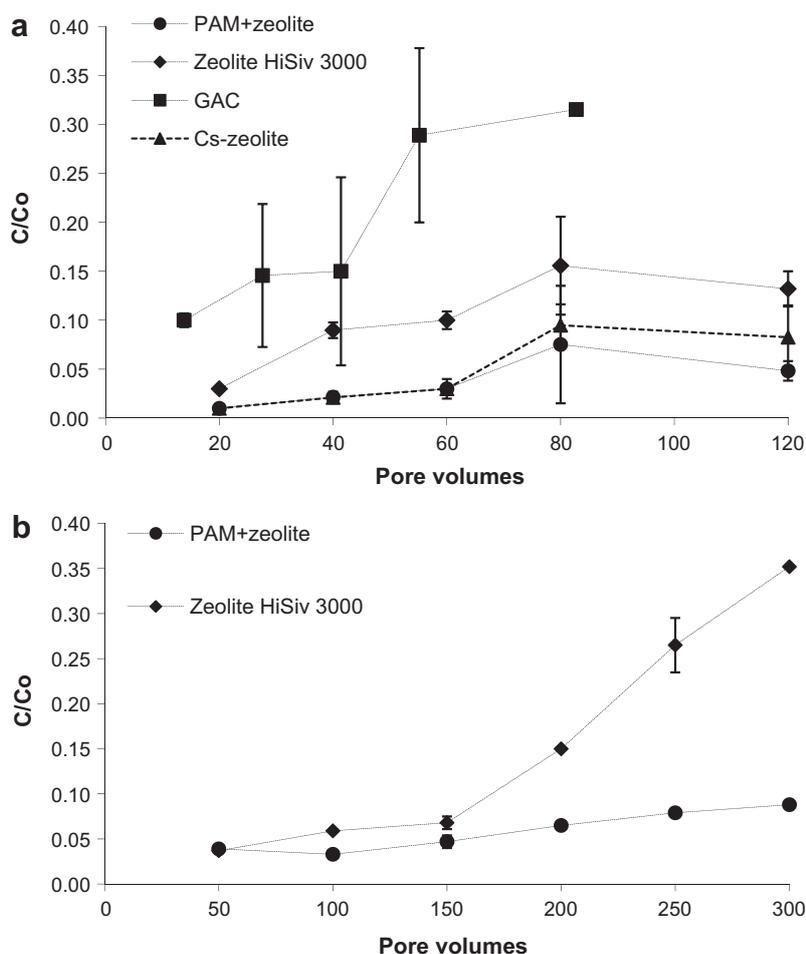


Fig. 4. (a) MTBE (0.23 ± 0.064 mg/L) removal by filters including PAM-zeolite composite, Cs-zeolite composite, zeolite or GAC (for GAC filter 80 pore volumes corresponds to 1200 mL, for zeolite and zeolite composites filters 120 pore volumes corresponds to 1200 mL). (b) MTBE (1 ± 0.168 mg/L) removal by filters including PAM-zeolite composite or zeolite. The error bars represent standard deviation.

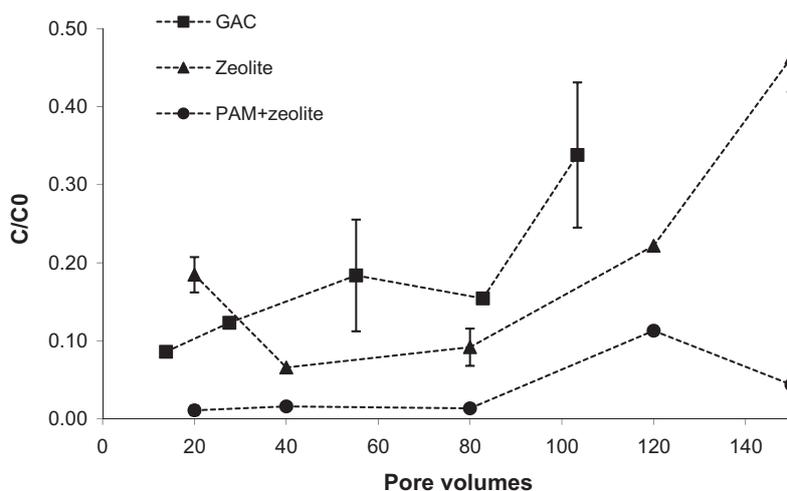


Fig. 5. MTBE (0.333 ± 0.084 mg/L) removal in the presence of BTEX (0.303 ± 0.028 mg/L for each component) by filters which included PAM-zeolite composite, Zeolite, or GAC (1500 mL corresponds to 110 pore volumes in the GAC filter and 150 pore volumes in the zeolite or zeolite composite filters). The error bars represent standard deviation.

Table 2

MTBE removal from water by filters which included GAC or a mixture of PAM-zeolite composite with GAC.

Initial MTBE conc. ($\mu\text{g/L}$)	Volumes (L)	Removal (%)		Ratio between emerging MTBE concentrations from filters: GAC/GAC + composite
		GAC filter	GAC + composite filter	
499	10	99.8	99.8	1
433	30	75	94	4.2
239	50	72	90	2.8
136	70	68	81	1.7
60	90	52	53	1.0
39	130	31	50	1.4
20	150	5	43	1.7

Experimental errors obtained for adsorption ranged between 1% and 5%.

with GAC (1:5 w/w). The filtered volume of MTBE solution in this experiment (Table 2), (150 L) was significantly larger than in the previous ones (Figs. 4 and 5).

Mixing PAM-zeolite composites in the GAC filter notably improved MTBE removal efficiency and the filter's capacity. The improved performance of the mixed column is emphasized by looking at the ratio between the emerging MTBE concentrations from the GAC filter and those emerging from the composite-GAC filter (Table 2). This improvement reached up to more than four-fold. In addition, the results indicate that the filter which included the PAM-zeolite composite yielded an average MTBE concentration below the EPA recommendation limit in drinking water, for a filtered volume of 50 L. In contrast, MTBE concentration above this limit emerged from the pure GAC filter at filtered volumes less than 20 L.

Clearly, more results are needed before reliable economical estimation for MTBE removal can be given, but the results of Table 2 may suggest that mixing PAM-zeolite composite with GAC is a promising solution. Rossner and Knappe [4] estimated that the cost associated with purification of MTBE from water by the zeolite was 84% larger than by using GAC, on account of sevenfold larger price of the zeolite (\$7 vs. \$1 per lb). The addition of PAM to the zeolite does not make it more expensive since very low loadings are required and PAM is extremely cheap. Hence, using a 5:1, w/w mixture between GAC and the composite makes the price of the material in the filter $5/6 + 7 \times 1/6$, i.e., twofold of the corresponding price of a GAC filter. On the other hand the results in Table 2 suggest a larger gain in the capacity by using the mixture. As noted [7] the limit on MTBE concentrations in drinking water varies

between 0.02 and 0.04 mg/L. For the GAC filter the emerging MTBE concentrations exceed 0.04 mg/L already after 30 L (0.108 mg/L), whereas for the GAC + composite filter the corresponding values after 30 and 70 L are 0.026 mg/L. Therefore, it may be beneficial to further explore the removal of MTBE by the composite on a larger scale.

4. Conclusions

The removal of MTBE by the PAM-zeolite composite was: (1) Higher than its removal by all other adsorbents examined in batch and in column filtration experiments. (2) Hardly influenced by the presence of BTEX, unlike the reduction in MTBE removal by the untreated zeolite. In addition, the column filter experiments emphasize the higher efficiency and capacity of the PAM-zeolite filter, than that of the zeolite, or GAC one, particularly in the presence of BTEX. We suggest that the enhanced removal by the PAM-zeolite composite is attributed to (a) the displacement of water from the zeolite surface upon PAM adsorption, which promotes MTBE adsorption and (b) hydrogen binding between the polymer and MTBE. An employment of a mixture of a PAM-zeolite with GAC in filtration columns may be a promising step for reducing the cost of MTBE removal from water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2011.10.033.

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