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Modified silicates and porous glass as adsorbents for removal of organic pollutants from water and comparison with activated carbons

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Abstract

It is demonstrated that a variety of modified silicate mineral sorbents can be utilized for the removal of organic pollutants from a water suspension or by a filter. Column filters filled with a mixture of quartz sand and organic micelle–montmorillonite (100:1 w/w) or zeolite were constructed. The micelle–clay filter removed 91% of ethylene dibromide (EDB) from an initial solution of 0.2 μg/L and 99.9% of the anionic pollutants sulfosulfuron, imazaquin, sulfentrazone and the neutral bromacil and chlorotoluron from an initial solution of 10 ppm. In contrast a filter filled with activated carbon at the same weight of the organic cation and sand, or without sand removed between 47.6% and 79% of these pollutants. Comparative capacity measurements yielded removal of sulfentrazone (75 ppm initial) at weights corresponding to 18.7% and 5.5% of the weights of the organic cation or activated carbon in the filter, respectively. For the antibiotic trimethoprim the micelle–clay system was not efficient; the clay mineral montmorillonite and the zeolite clinoptilolite yielded respectively 80% and 99.9% removal from its dispersion. A clinoptilolite/sand filter gave 91% removal. We also present varying degrees of efficiencies of removal of isoproturon, benzoic acid, and 1,2 dichlorobenzene by an organo-clay and by silica (controlled pore glass (CPG))-polycation immobilized micelles (SPIM) or without immobilized micelles.
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1. Introduction

Pollution of water by pesticides and industrial wastes has been recognized as a primary health hazard. Consequently standards have been set, prohibiting the use of drinking water when the concentrations of certain chemicals exceed specified values. Thus in the European Community countries the concentration of any herbicide should not exceed 0.1 ppb and the sum of concentrations of all herbicides should be below 0.5 ppb. For ethylene dibromide (EDB), which is an insecticide and a component of certain industrial wastes the limit is set at 0.05 ppb in most developed countries.

Another aspect in water contamination is the presence of antibiotics, because they can increase the proliferation

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of antibiotic resistant pathogens, thus exert a negative effect on human health (Huysman et al., 1993; Halling-Sørensen, 2000).

It has been recognized (Beall, 2003) that chlorination of water in the presence of humic acid produces dangerous levels of trihalomethanes, which are carcinogens. Activated carbon, the most common component in current filters, is not very effective in removing dissolved organic matter (DOM), such as humic acid, and, as demonstrated here, is not efficient in the removal of certain anionic contaminants. In this study we focus on the use of modified silicate mineral surfaces (montmorillonite, zeolites) and glass as alternative adsorbents to activated carbon for water purification from organic contaminants.

Montmorillonite has the advantage of having high surface area, but its use requires a conversion of its surface to a more hydrophobic medium by adsorption of organic cations (Mortland et al., 1986; Boyd et al., 1988; Jaynes and Boyd, 1990; Lagaly, 1994; El-Nahhal et al., 1998; Nir et al., 2000; El-Nahhal et al., 2000). An efficient use of organo-clays in water treatment was presented by Beall (2003).

Our studies on several anionic herbicides such as sulfometuron, sulfosulfuron (Mishael et al., 2002a,b, 2003) and sulfentrazone (Polubesova et al., 2003) indicated that their adsorption by organo-clays was poor, even when the organo-clays were formed by adsorption of organic cations as monomers at loadings which exceeded the cation exchange capacity of the clay mineral, i.e., when the clay mineral was expected to become positively charged. On the other hand a very efficient adsorption of the above anionic herbicides was observed on micelle–clay complexes, where the cationic surfactants were adsorbed as micelles. More recently Polubesova et al. (2005) demonstrated very efficient removal of three anionic pollutants (imazaquin, sulfentrazone, sulfosulfuron) and 4 neutral pollutants (alachlor, acetochlor, chlorotoluron and bromacil) by micelle–clay complexes in aqueous dispersions under two situations: (i) the complexes were introduced into the pollutant solutions, or (ii) the micelles were added to a solution of the pollutants and the clay was added later.

Micelles of octadecyl trimethylammonium (ODTMA) and benzyl dimethyl hexadecylammonium (BDMHDA) were used. The nature of the head group of the organic cation, which forms the micelles, was found to be of importance. Filters made of a mixture of quartz sand and BDMHDA micelle–clay complex (100:1 w/w ratio) removed pollutants very efficiently both in the ppm and ppb ranges.

In the current study we present: (i) the removal of several additional pollutants by the micelle–clay system, e.g., EDB and the antibiotic trimethoprim, and (ii) the efficiency of removal of several pollutants by the micelle–clay filter (described above) in comparison with that of a filter filled with activated carbon. In the case of sulfentrazone the comparison also shows the capacity of both filters for this anionic pollutant. (iii) the ability of other non-modified and modified surfaces to efficiently remove organic pollutants from water.

One theme emphasized in this study is that one should not expect that the above described clay–micelle complexes would exhibit the optimal ability to adsorb any organic contaminant. Hence, a variety of substances may be more effective in certain cases and should be available for an optimized filter composed of a selection of adsorbent layers suitable for different reservoirs. Therefore, we explored the use of a variety of additional modified and non-modified silicate surfaces and demonstrated their efficiency in removing organic pollutants from dispersions or in filters.

We tested the well-known organo-clay and zeolite systems and a relatively new system consisting of silica-polycation immobilized micelles (SPIM) based on controlled pore glass (CPG)-polycations with and without immobilized micelles. Wang et al. (2001) demonstrated the principle of immobilizing anionic micelles to a negatively charged surface via cationic polymers with the aim of removing hydrophobic solutes from an aqueous phase. In particular, poly(dimethyl diallylammonium chloride) was used to bind SDS/TX100 anionic/nonionic mixed micelles to controlled pore glass (a commercially available material with well-characterized surface and pore properties, which is well-known as a chromatographic support). In a latter study (Mishael and Dubin, 2005) we showed that the silica/polyelectrolyte (quaternized polyvinyl pyridine)-immobilized micelle solubilized the model pollutant toluene (40% uptake). In addition we demonstrated simultaneous uptake from solution by SPIM of a mixture of two-dozen halocarbon and aromatic compounds (20–90% uptake). In the current study SPIM was efficiently applied for single neutral polutants and CPG-polycation composites for an anionic pollutant.

2. Materials and methods

2.1. Materials

The clay used was Wyoming Na-montmorillonite SWy-2 obtained from the Source Clays Repository (Clay Minerals Society, Columbia, MO). Quartz sand (grain size 0.8–1.5 mm) was purchased from Negev Industrial Minerals (Israel).

Granular activated carbon was purchased from Chemviron Carbon (Belgium). Analcime was obtained from Barstow; Cal., San Bernardino Co. Mordenite was obtained from Beatty, Nye Co., Nevada. Clinoptilolite was obtained from Horseshoe Dam, Maricopa Co., Ariz. Phillipsite was obtained from Shoshone, Inyo Co., Cal. Controlled pore glass (CPG) (particle size 75–125 μm) with a mean pore diameter of 7.5 nm (±20%) and a surface area of 153 m^2/g was purchased from Millipore (Lincoln Park, NJ).

Octadecyl trimethylammonium (ODTMA) bromide, Poly (dimethyl diallylammonium chloride,PDADMAC-450K MW), sodium dodecylsulfate (SDS), Triton X-100 (TX100), phenyl trimethylammonium chloride (PTMA), trimethoprim (purity 99%) were purchased from Sigma–Aldrich (Sigma Chemical Co., St. Lous, MO). Benzyl dimethyl hexadecylammonium (BDMHDA) chloride was purchased from Fluka Chemie (Buchs, Switzerland). Technical sulfentrazone (purity 91.3%) was obtained from FMC (Princeton, NJ); sulfosulfuron (analytical grade) was obtained from E. I. Du Pont de Nemours and Company (Wilmington, DE). Imazaquin, chlorotoluron, bromacil and isoproturon (all compounds of 98% purity) were supplied by Agan Makhteshim, Israel. EDB (1,2 dibromoethane, purity 99%) was purchased from Aldrich (Steinheim, Germany). Benzoic acid and 1, 2 dichlorobenzene were purchased from Merck (Darmstadt, Germany). Structural formulae of surfactants and pollutants are shown in Fig. 1.

3. Methods

3.1. Substrate preparation and pollutant uptake

3.1.1. Micelle–clay compelexes

ODTMA or BDMHDA were added to pollutant solutions (trimethoprim (10 mg/L), benzoic acid (6.7 mg/L), isoproturon (6.7 mg/L) and 1,2 dichlorobenzene (3.33–33.3 mg/L)). Pollutant–micelle solutions were stirred for 24 h before 10 ml were added to 5 ml clay dispersion (10 g/L final) in polypropylene copolymer or Teflon (for 1,2 dichlorobenzene)

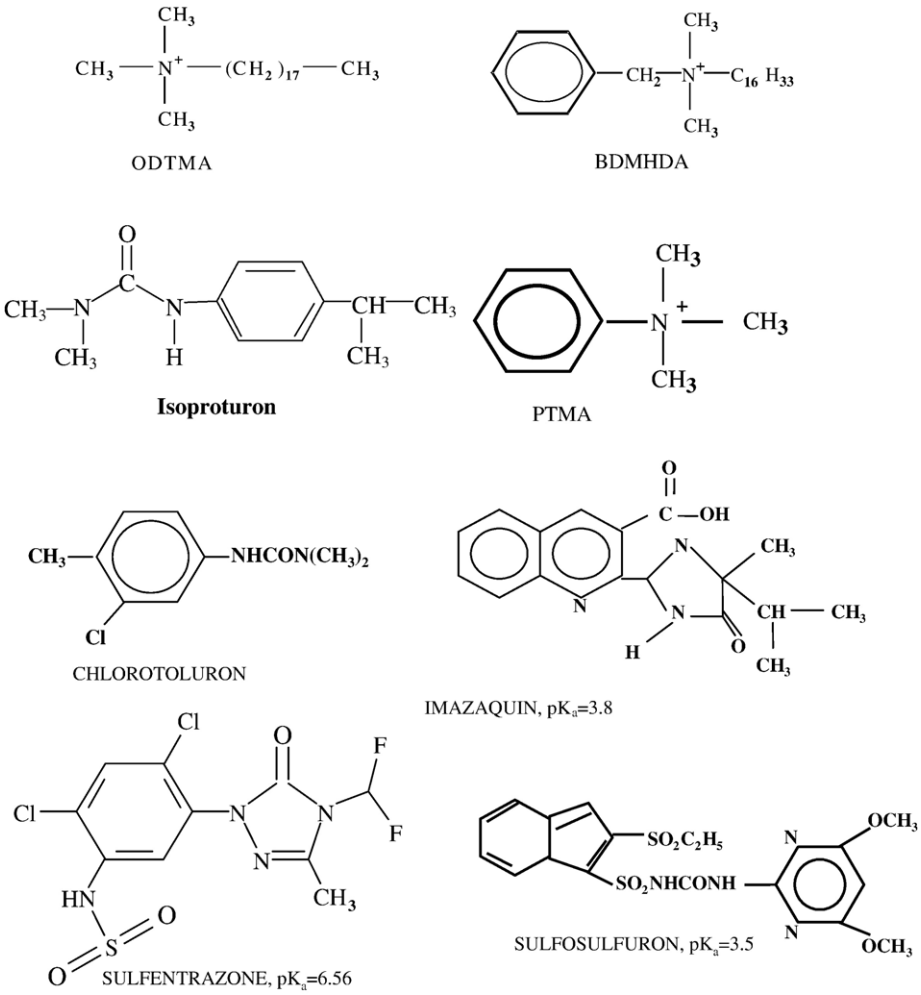

Fig. 1. Molecular structures of surfactants and pollutants.

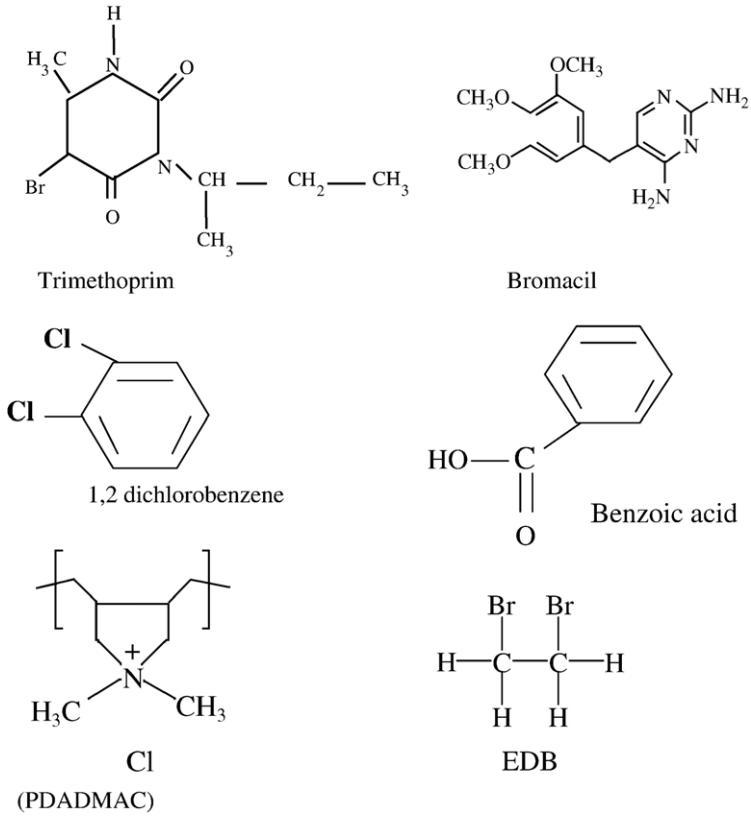

Fig. 1 (*continued*).

centrifuge tubes. Preliminary experiments showed no significant adsorption of pollutants on the tubes. Surfactants concentration (12 mM final) was much higher than their CMC values, which are 0.3 mM and 0.6 mM for ODTMA and BDMHDA, respectively. The samples were kept at 25 ± 1 °C under continuous agitation for 1, 4, 24 or 72 h (reaching equilibrium).

3.1.2. Organo-clay complex

Montmorillonite was pre-loaded by PTMA at 0.5 mmol/g as described by El-Nahhal et al. (2000). Isoproturon solution (15 ml, 6.3 mg/L final) was added to PTMA-clay dispersions (10 g/L final) and was kept at 25 ± 1 °C under continuous agitation for 72 h (reaching equilibrium).

3.1.3. Zeolites

Mordenite, phillpsite, clinoptilolite and analcime (10 g/L) were grinded manually to a powder and added to 15 ml trimethoprim (10 mg/L). The samples were kept at 25 ± 1 °C under continuous agitation for 72 h (reaching equilibrium).

3.1.4. Activated carbon

Granular activated carbon (10 g/L) was added to 15 ml of 1,2 dichlorobenzene (3.33–33.33 mg/L). The samples were kept at 25 ± 1 °C under continuous agitation for 1, 4 or 24 h (reaching equilibrium).

3.1.5. CPG-PDADMAC-micelles

PDADMAC (4 ml of 10 g/L) in NaCl (0.5 M) adjusted to pH 9.5 were added to 0.3 g of CPG in glass tubes. The samples were shaken for 4 days to reach equilibrium (Mishael and Dubin, 2005). After centrifugation (20 min at 8000 *g*), the supernatant was separated and the concentration of PDADMAC was determined using the Carbon analyzer, Carlo-Erba. Four ml of TX100/SDS (Y = [SDS] / ([SDS] + [TX100]) = 0.35, 20 mM total surfactant concentration, NaCl = 0.5 M, pH 9.5) were added to the CPG preloaded with PDADMAC. The samples were shaken overnight to ensure equilibration. After centrifugation (20 min at 8000 *g*), the supernatant was separated and TX100 concentration was measured using a UV calibration curve at 224 nm. The resultant amounts of bound TX100 were calculated, and then used to calculate the total mass of micelle bound. Eight ml of sulfentrazone (50 mg/L), 1, 2 dichlorobenzene (50 mg/L) and isoproturon (25 mg/L) were added to the SPIM composite and shaken for 3 days.

Following agitation all samples (duplicates) were centrifuged for 20 min at 15,000 *g*, supernatants were filtered using Teflon filters (ISI, Israel) of 0.2 μm pore diameter and analyzed by HPLC.

3.2. Column filter experiments

3.2.1. Micelle–clay complexes

A layer of 23 cm composed of a mixture of quartz sand (700 g) and micelle–clay complex (7 g) was placed in a column of 25 cm length and of 5 cm diameter. The bottom of the column was covered by a 2 cm layer of quartz sand. The quartz sand was thoroughly washed with distilled water and dried at 105 °C for 24 h. The micelle–clay complex was prepared by stirring 2.5 mM of BDMHDA with 2 g/L clay for 72 h. The dispersions were centrifuged for 20 min at 15,000 *g*, supernatants were discarded, and the complex was lyophilized. Non-woven polypropylene geotextile filters (Markham Culverts Ltd., Papua New Guinea) were placed on both ends of the column. The column was connected to a peristaltic pump and saturated with distilled water from the bottom (flow 5 ml/min). A liter of 10 mg/L of each pollutant excluding EDB whose concentration was 0.2 μg/L was passed through the column. The eluant was collected from the bottom of the column and measured by HPLC or in the case of EDB by GC–MS. The experiments were performed in duplicate.

3.2.2. Activated carbon

A layer of 23 cm composed of a mixture of quartz sand (700 g) and granular activated carbon (2 g which is equal to the weight of the surfactant in the 7 g micelle–clay complex) was placed in the column and the pollutants were passed through the column as described above.

3.2.3. Zeolite

The experiment was performed in two different columns. The first column was prepared as described above with Clinoptilolite (7 g). The second column contained a mixture of quartz sand (50 g) and Clinoptilolite (7 g) in a column of 20 cm length and of 1.8 cm diameter. The column was connected to a peristaltic pump and saturated by distilled water from the bottom (flow 5 ml/min for the first column and 1.3 ml/min for the second). The pollutants were passed through the column as described above.

Table 1
Percent of removal and capacity of the micelle–clay filter and the activated carbon filter as percent (w/w) of sulfentrazone (75 ppm) relative to the organic cation or activated carbon

Successive volumes of pollutant solution passing through the filter (liter)	BDMHDA-clay filter (% of removal)	Activated carbon filter (% of removal)
1	100	47.6
2	100	34
3	99.9	23.4
4	99.8	18
5	99	23
6	40	–
7	29	–
[a]Total removal (g)	0.374	0.11
[a]Percent captured (w/w)	18.7	5.5

[a] Total removal and percent capture were taken for first 5 L.

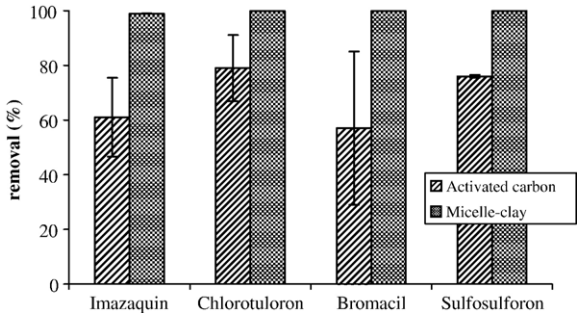

Fig. 2. Removal of herbicides (10 mg/L) from water by micelle–clay and activated carbon filters for the passage of one-liter pollutant solution.

Filter capacity was measured for the micelle–clay filter and for the activated carbon filter. Seven liters of 75 mg/L of sulfentrazone solution were passed through the columns (flow 5 ml/min). Each liter of eluant was collected and measured by HPLC.

3.2.4. Analysis of pollutants

The solutions were analyzed by HPLC (Merck Hitachi 6200) equipped with a diode array detector. In the experiment with concentration of 0.2 μg/L of EDB the concentration was measured by GC–MS.

The HPLC column was LiChrospher^{R} 100 RP–18 (5 μm) and the flow rate was 1.0 mL min^{-1}. Measurements were carried out isocratically; calibration curves were constructed as peak areas versus concentrations of pollutants. For the anionic pollutants the binary mobile phases were acetonitrile or methanol with acidified water (trifluoroacetic acid adjusted to pH 2.95 ± 0.09). The ratios used were; acetonitrile/water (50/50) for sulfentrazone; acetonitrile/water (70/30) for sulfosulfuron; methanol/water (60/40) for imazaquin and benzoic acid. For neutral pollutants the following mobile phases were used: methanol/water (75/25) for chlorotoluron; methanol/water (65/35) for bromacil; acetonitrile/methanol/water (30/35/35) for isoproturon and acetonitrile/water (80/20) for 1,2-dichlorobenzene. The concentrations of pollutants were measured at the following wavelengths: sulfentrazone at 220 nm, sulfosulfuron at 216 nm, imazaquin at 242 nm, benzoic acid at 228 nm, chlorotoluron at 248 nm, isoproturon at 240 nm, 1,2-dichlorobenzene at 210 nm and bromacil at 280 nm.

For trimethoprim the mobile phases consisted of 10 mmol/l ammonium acetate in water-acetonitrile (method ANT) as described by Hirsch et al. (1998).

EDB was analyzed by GC–MS. Purge- and -trap Concentrator with Cryofocusing Module (Tekmar, Ohio, USA) was used. GC–MS measurements were performed with Saturn 2000 GC–MS (Varian, Walnut Creek, USA) equipped with fused silica capillary column, 60 m, × 0.25 mm ID, × 1.4 μm film thickness from Supelco (Bellefonte, USA). The carrier gas was helium. The oven temperature was raised from 40 °C to 150 °C at 4 °C/min. The transfer line temperature was 210 °C.

4. Results and discussion

4.1. Column filter efficiency and capacity: comparison with activated carbon

The efficacy of column filters containing a mixture of quartz sand and the micelle–clay, or activated carbon is shown in Table 1 and Fig. 2. More than 99% of sulfosulfuron, imazaquin, sulfentrazone, bromacil and chlorotoluron were removed from solutions of 10 mg/L by a BDMHDA micelle–clay filter as reported in (Polubesova et al., 2005). Filters containing activated carbon mixed with quartz were less efficient than micelle–clay–quartz systems, removing 47.6–79% of the above pollutants from their initial solutions containing 10 mg/L (Fig. 2, Table 1). The presence of the quartz sand had no effect on pollutant removal by the activated carbon filter (results not shown).

It should be emphasized that the difference in efficiency of pollutant removal between the micelle–clay and activated carbon filter is very significant. Assume that it is required to reduce pollutant concentration in water by two orders of magnitude. Whereas the micelle–clay filter reduced the pollutants' concentrations by more than two orders of magnitude (Fig. 2 and Table 1) with a 23 cm long filter, 60% removal by the activated carbon filter implies that its length should be 5-fold larger for achieving an efficiency of 99% removal. For such elongation of the corresponding micelle–clay filter, it can be expected that the emerging pollutant concentration will be reduced by at least five orders of magnitude.

4.1.1. Filter capacity

Percent of removal and capacity of the micelle–clay filter and the activated carbon filter are presented in Table 1. The micelle–clay filter removed more than 99% of sulfentrazone (75 ppm) for the first 5 L. The activated carbon filter removed only 47.6% in the first liter and significantly less in the next 4 L. The capacity is expressed as percent (w/w) of the total captured pollutant relative to the weight of the surfactant, or activated carbon, which is included in the filter (containing 2 g). When limiting the capacity of the filter to the first 5 L, the capacities of the micelle–clay and activated carbon filters are 18.7% and 5.5%, respectively, yielding a ratio of 3.4.

4.2. Other methods

Table 2 presents the removal of several pollutants from a water dispersion applying the following adsorbents: (1) Micelle–clay complexes formed from the interactions of the organic cations ODTMA or BDMHDA with montmorillonite. (2) PTMA-montmorillonite or unmodified montmorillonite (3) A polycation adsorbed on controlled pore glass with and without immobilized negatively charged mixed micelles (4) Zeolites (mordenite, phillipsite, clinoptilolite, analcime). The results of trimethoprim and EDB removal by a filter are shown in the last two rows of Table 2.

Table 2
Removal of pollutants (6–50 mg/L) from water by several modified substrates

Pollutant	Substrate	% Removed
Isoproturon	ODTMA-clay	67
	BDMHDA-clay	85
	PTMA-clay	99
	CPG-polycation-micelles	65
Benzoic acid	ODTMA-clay	61
	BDMHDA-clay	91
1,2 Dichlorobenzene	BDMHDA-clay	99.9
	CPG-polycation	40
	CPG-polycation-micelles	99.9
	Activated carbon	99.7
Trimethoprim	BDMHDA-clay	10
	Montmorillonite	80
	Mordenite	95
	Phillipsite	2.5
	Clinoptilolite	99.9
	Analcime	0
Sulfentrazone	ODTMA-clay*	99.9
	BDMHDA-clay*	99.9
	CPG-polycation	94
Trimethoprim (10 mg/L)	Clinoptilolite filter	91
EDB (0.2 μg/L)	ODTMA-clay filter	91

* Polubesova et al. (2005).

4.2.1. Benzoic acid

Removal of benzoic acid by BDMHDA-clay was 91% versus 61% by ODTMA-clay (Table 1), which indicates that the nature of the surfactant head group which forms the micelle may be critical; compatibility of the aromatic head group of BDMHDA with the aromatic structure of pollutant molecules led to a significant increase in the adsorption of this compound.

4.2.2. Isoproturon

Removal of isoproturon from water was most efficient by PTMA-montmorillonite at a loading of 0.5 mmol/g clay (Table 2). This efficiency of isoproturon removal can probably be explained by the proper alignment of the herbicide molecules on the surface, which enables efficient interactions of isoproturon molecules with adsorbed PTMA cations. Removal of isoproturon by BDMHDA-clay was more efficient than by ODTMA-clay, which confirms the importance of the compatibility

of the structure of the surfactant head group and the molecular structure of pollutant (Polubesova et al., 2005).

Trimethoprim. Removal of the antibiotic trimethoprim from water by micelle–clay complexes was rather poor (results not shown). Trimethoprim is a weak base with a pK_a of 7.4; 85% of this compound is in cationic form at pH 6.7 of the mixed trimethoprim–micelle solution. Therefore the adsorption of trimethoprim to the positively charged micelle–clay complex was negligible as expected. Unmodified montmorillonite removed 80% of this antibiotic. The pH of trimethoprim — clay dispersion is 9.3, indicating that a very small fraction is cationic. The efficient removal of trimethoprim by montmorillonite could be explained by the cooperative adsorption of clusters composed of cations and neutral molecules similarly to a report on aniline adsorption to montmorillonite (Homenauth and McBride, 1994). However, it is also possible that at the montmorillonite surface the pH is about two units lower (Nir et al., 1986), which would imply that a significant degree of positive charge is associated with trimethoprim.

The zeolites differed in the efficiency for trimethoprim adsorption. The most efficient removal was by the clinoptilolite (Table 2). The removal of trimethoprim from water by mordenite was also high, in contrast to phillipsite and analcime. These results can be explained by the differences in channel sizes of the zeolites (Boettinger and Ming, 2002). Apparently, the smaller channels of analcime and phillipsite (0.26×0.26 and 0.33×0.33 nm, respectively) reduced the adsorption of trimethoprim molecules by these zeolites, whereas the larger channels of clinoptilolite and mordenite (0.41×0.47 and 0.67×0.70 nm, respectively) promoted their adsorption. The removal of trimethoprim by the clinoptilolite filter (7 g zeolite and 50 g sand) was 91% (Table 2). In using zeolite filters (see Methods) we had to discard the case where 7 g of clinoptilolite were mixed with 700 g sand due to low efficiency. In contrast to the general trend of improved removal by the filter in comparison with that in dispersion, we found higher removal of trimethoprim in dispersion in the case of the zeolite. We attribute this result to a kinetic effect, since the batch experiments lasted 72 h in comparison to a few minutes of the filter experiments. Adsorption in small channels is expected to be slower than on flat surfaces (Mishael and Dubin, 2005). Indeed reducing the flow rate in the zeolite filter improved the removal of the antibiotic.

4.2.3. 1,2 Dichlorobenzene

The removal of 1,2 dichlorobenzene from water by the micelle–clay complex, the CPG-PDADMAC-micelle substrate and by activated carbon was very high for all the concentrations (3.33–50 ppm) and times of adsorption (1, 4 and 24 h) that were examined (Table 2). The removal by the CPG-PDADMAC alone was poor since it is positively charged and designed to effectively remove negatively charged pollutants, as was demonstrated for sulfentrazone. However, there was some degree of affinity between the polymer and 1,2 dichlorobenzene, which resulted in a 40% removal. Immobilizing the negatively charged mixed micelles to the CPG-PDADMAC substrate enabled efficient removal of hydrophobic neutral pollutants such as 1,2 dichlorobenzene (94% removal, Table 2). This principle of solubilizing neutral pollutants in CPG-polycation immobilized micelles (SPIM) was demonstrated by the simultaneous removal (20–90%) of two-dozen halocarbon and aromatic compounds (Mishael and Dubin, 2005).

4.2.4. Sulfentrazone

The results (Table 2) indicate a very efficient removal from dispersion by both types of micelle–clay (99.9%) and by CPG-PDADMAC (94%).

4.2.5. EDB

The result (Table 2) indicates 91% removal by the ODTMA-clay complex in a filter. It should be pointed out that this yield is in the ppb range, and that the emerging pollutant was at a concentration of 0.018 ppb, which is well below the allowed limit of 0.05 ppb.

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