

Determination of release of organic cations from micelle–clay complexes and their re-adsorption in sand/clay columns

D. Zadaka^a, T. Polubesova^a, Y. Mishael^a, A. Spitzzy^b, H. Koehler^b,
E. Wakshal^a, O. Rabinovitz^a, S. Nir^{a,*}

^a*Hebrew University of Jerusalem, Faculty of Agricultural, Food and Environmental Quality Sciences,
Seagram Center for Soil and Water Sciences, Rehovot 76100, Israel*

^b*University of Hamburg, Institute of Biogeochemistry and Marine Chemistry, Hamburg 20146, Germany*

Received 28 April 2004; received in revised form 17 January 2005; accepted 24 January 2005

Available online 7 April 2005

Abstract

Release of organic cations from cationic micelle–clay complexes in slow release herbicide formulations or in column-filters for water purification may pose a problem. In this study we determined the release of octadecyltrimethylammonium (ODTMA) or benzyldimethylhexadecylammonium (BDMHDA) from micelle–clay complexes, and devised a method to retain the released cations by using a column filled with sand/clay mixtures. The adsorption of 5 mM ODTMA or BDMHDA on montmorillonite added at 5 g/l clay was complete. The release was examined at different times and complex concentrations. The percents of release of ODTMA after 24 h were 13.2, 3.8 and 0 for 0.1, 1 and 5 g/L, respectively, whereas for BDMHDA the corresponding values were 31.2, 19.4 and 7.2. Measurements of dissolved organic carbon (DOC) yielded the amount of the released organic cation from micelle–clay complexes in column-filters for water purification after adding a layer (13 cm) of quartz mixed with clay (150:1 w/w ratio) at the bottom of the column. The amount of the released organic cation from columns including the micelle–clay complexes was less (or equal within the experimental error) than the amount released from those including quartz alone or a quartz–clay mixture. Hence, the carbon analysis showed that in the ppm range all the released cations (ODTMA or BDTMA) were retained by the column-filter. The water passing through a 25 cm column filled with quartz mixed with micelle–clay was also passed sequentially through three columns filled with quartz–clay (150:1) and was concentrated 1000-fold. Measurements by GC-MS showed no traces of the organic cations. The conclusion is that the released organic cations from micelle–clay complexes can be completely retained by adding quartz–clay layers.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Micelles–organic cations; Organo-clays; Cation adsorption and release

1. Introduction

The presence of pollutants in underground water and wells, due to intensive application of pesticides in

* Corresponding author. Fax: +972 8 9475181.

E-mail address: Nir1@agri.huji.ac.il (S. Nir).

agriculture, raises the importance of the control and protection of drinking water quality (Carter, 2000; Pasquarell and Boyer, 1996; Potter and Carpenter, 1995). A study elucidated that herbicides that were introduced to Israeli agriculture since 1970, such as atrazine, bromacil, diuron and simazine, had polluted groundwater in some regions during a time span of 25–30 years (Wakshal et al., 2001).

Common treatment technologies for drinking water are coagulation, ultra-filtration, lime softening, ion exchange, reverse osmosis and nanofiltration (Agenson et al., 2003), aeration and chlorination (Berne and Richard, 1991; Driscoll, 1989). Activated carbon, which is efficient in removing certain organic molecules from water, performs poorly in the removal of humic acids (Beall, 2003). Few studies have reported modified silica as a surface which can remove pollutants. Trichloroethane was decomposed on ozone adsorbed high silica zeolites (Fujita et al., 2004). Removal of humic acids and the potential to remove organic and inorganic pollutants by montmorillonite preadsorbed with polymeric Al/Fe has been recently reported (Jiang and Cooper, 2004). Organo-clays, which are prepared by adsorption of organic cations on negatively charged surface, are suitable for the removal of organic pollutants from water due to enhancing the affinity of their modified surfaces to the hydrophobic organic molecules (Jaynes and Boyd, 1991; Lagaly, 1995; Xu et al., 1997; El-Nahhal et al., 2000; Beall, 2003). Long-chain organic cations such as octadecyl-trimethylammonium (ODTMA) and hexadecyl-trimethylammonium (HDTMA), can form micelles strongly adsorbed on montmorillonite. The binding coefficients for ODTMA and HDTMA adsorption on montmorillonite are about three orders of magnitude above that of Na^+ (Mishael et al., 2002a).

Recently, we introduced the micelle–clay system for the design of slow release formulations of anionic herbicides, such as sulfometuron (Mishael et al., 2002a, b), sulfosulfuron (Mishael et al., 2003), and sulfentrazone (Polubesova et al., 2003). The micelles were formed of organic cations with long alkyl chains, such as ODTMA, or benzyltrimethylhexadecylammonium (BDMHDA), which have low critical micelle concentrations (cmc), 0.3 and 0.6 mM, respectively. The slow release formulations of the above herbicides yielded significantly reduced leaching, and also

enhanced biological activity. Hence, these micelle–clay formulations have a potential of reducing significantly ground water contamination and are also promising from the economic point of view.

In Mishael et al. (2003), it was shown that the order of addition of components, i.e., sulfosulfuron (0.25 mM), ODTMA (5 mM) and clay (5 g/l) yielded the same large fraction of adsorbed herbicide (98%). The implication is that the micelle–clay system has a potential for purification of water from organic pollutants. Indeed, our preliminary results (Polubesova et al., 2005) demonstrate that the micelle–clay system is efficient in removing anionic and neutral organic contaminants from water.

The current study addresses the issue of the release of organic cations from the micelle–clay complexes, which is essential in the use of herbicide formulations, and is even more critical in planned water purification procedures based on the micelle–clay system. As will be shown, a column filter which includes a quartz–clay layer can capture essentially all the organic cations released from the micelle–clay complexes.

2. Materials and methods

The clay mineral used was Wyoming Na-montmorillonite Swy-2 obtained from the Source Clays Repository (Clay Minerals Society, Columbia, MO). ODTMA was purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO). BDMHDA was purchased from Fluka Chemie (Buchs, Switzerland). The quartz sand used (grain size 0.8–1.5 mm) was purchased from Negev Industrial Minerals (Israel). The quartz sand was thoroughly washed by distilled water and dried at 500 °C for 24 h. Non-woven polypropylene geotextile filters were from Markham Culverts Ltd. (Papua New Guinea).

2.1. Adsorption, release and re-adsorption of organic cations from micelle–clay complexes in aqueous suspensions

The adsorption of ODTMA and BDMHDA on montmorillonite added at 5 g/l clay was measured at added concentration of 5 mM by using polycarbonate centrifuge tubes; 5 ml of 15 g/l clay (final 5 g/l) was added to 10 ml of 7.5 mM organic cation solutions (final 5 mM). The suspensions were kept under continuous agitation, using a shaker, for 3 days to reach equilibration. Supernatants were separated by centrifugation at 15 000 g rpm for 20 min. The precipitates were

freeze-dried. The percent of carbon in the precipitates, indicating the amount of cation adsorbed, was measured by using a CHNSO analyzer, Carlo-Erba 1108. Six replicates were performed.

The release of ODTMA and BDMHDA was measured by adding 15 ml of distilled water to the freeze-dried precipitates. The release was measured at different times (1, 4 and 24 h) and concentrations of clay in the system (0.1, 1 and 5 g/l). The procedure of measurement was the same as described in the previous paragraph.

The re-adsorption of ODTMA and BDMHDA was measured by adding 5 g/l clay to the supernatants. The suspensions were kept under continuous agitation, using a shaker, for times varying from 1 h to 1 day. Since there was no release of ODTMA at clay concentration of 5 g/l the re-adsorption of released ODTMA was examined only for 0.1 and 1 g/l. Two replicates were used.

2.2. Removal of organic cations from water by quartz–clay layers in a column

The removal of organic cations from water by quartz–clay layers was measured by passing distilled water through a column (25 cm long, diameter 5 cm) filled with a layer (13 cm) of quartz mixed with micelle–clay (100:1 w/w) followed by a layer (10 cm) of quartz mixed with clay (150:1 w/w), and a third layer of quartz (2 cm) at the bottom of the column. Non-woven polypropylene geo-textile filters were placed on both sides of the column. The water (1200 ml, corresponding to 6.7 pore volumes) was collected at the bottom of the column for analysis of the concentration of the carbon released from the column. Similarly the carbon released from a column filled with quartz (750 g), or with a mixture of quartz–clay (100:1 w/w) or (150:1 w/w) was determined. Due to the swelling of the clay a granular substance was necessary to enable the flow through the column. A ratio of 100:1 w/w quartz–clay resulted in a very slow water flow. Therefore a quartz–clay ratio of 150:1 was chosen. The water was pumped through the column by a peristaltic pump; the flow rate was 2 ml/min. Dissolved organic carbon (DOC) was determined by continuous-flow-oxidation of GF/F-filtered water samples using a UV-thin-film-reactor (Gräntzel, Karlsruhe, Germany) according to the method described by Huber and Frimmel (1991). The carbon dioxide resulting from the oxidation of the DOC was monitored by a non-dispersive IR-detector (LICOR LI-6262), whose signals were quantified with an AZUR chromatographic software. The detection limit of the system is 0.1 mg C/l. Two replicates were performed.

To reach complete removal of organic cation from water which passed through a column filled with quartz mixed with a complex of an organic cation with clay, the eluate

from the column was pumped sequentially through three columns filled with 150/1 quartz/clay mixture. The eluate from the third column was analyzed by GC-MS.

For GC-MS analysis the eluate was filtered through Whatman GF/C filter followed by ME 25 filters with 0.45- μ m pore diameter (Schleicher & Schull, Dassel, Germany). Then the organic cation was extracted by ENVI™ extraction disks, 47 mm with C₁₈ phase from Supelco (Bellefonte, PA) and eluted by methylene chloride or acetone. Then the extracts were evaporated to a volume of 1 ml with gentle stream of nitrogen. GC-MS measurements were performed with Saturn 2000 GC-MS (Varian, Walnut Creek CA) equipped with SPB™-5 capillary column, 30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness from Supelco (Bellefonte, PA). The carrier gas was helium; linear velocity was 50 cm/s. Injector temperature was 280 °C. The oven temperature was held at 50 °C for 2 min, and then raised at 5 °C/min to 260 °C. The transfer line temperature was 300 °C. Biphenyl was used as internal standard.

3. Results and discussion

3.1. Adsorption, release and re-adsorption of organic cations from micelle–clay complexes in aqueous suspensions

The adsorption of 5 mM of ODTMA or BDMHDA on montmorillonite added at 5 g/l clay was complete. We examined the release at different times (1, 4 and 24 h) and at complex concentrations of 0.1, 1 and 5 g clay/l. The percents of release of ODTMA and BDMHDA are presented in Table 1.

The results indicate that for ODTMA–montmorillonite complex at 5 g/l, or 0.5% there was no release of ODTMA, whereas in a 50-fold more dilute suspension 13.2% of the cation were released after 24 h. For BDMHDA whose alkyl chain is shorter by two carbon atoms than that of ODTMA, and its CMC is twice that of ODTMA the corresponding fractions of release after 24 h were 7.2% and 31.2% for 5 and 0.1 g/l. A comparison of the adsorption results of these cations on montmorillonite (Mishael et al., 2002a; Polubesova et al., 2004) also indicates that ODTMA exhibits higher affinity of adsorption on the clay than BDMHDA. In several cases studied (Polubesova et al., 2005) micelle (BDMHDA)–clay exhibited higher percentage of removal from water of anionic and neutral organic molecules than ODTMA–clay micelles. However, the current results may

indicate that further tests are required in deciding which organic cation is preferred when cation release is also a factor.

When we added 5 g/l clay to the supernatant all the organic cations re-adsorbed within 1 h. Hence, within the experimental uncertainty (about 1%) the released organic cations from micelle–clay complexes can be completely retained by adding clay to the system.

The clay content of sandy soils is usually above 0.5% (5 g/l). Hence, when employing micelle–clay formulations of herbicides at typical rates of organic cations below 0.1 g/m² all the released organic cations will be adsorbed by the clay particles within a few cm of the soil layer. The implication is also that we can anticipate complete adsorption of organic cations released from micelle–clay complexes in a column filter, if the water passes through a layer of quartz mixed with clay at a weight ratio of 200. Such a test is described in the next subsection.

3.2. Removal of organic cations from water by quartz–clay layers in a column

We measured by carbon analysis the amount of the released organic cation from micelle–clay complexes in column-filters for water purification after adding a layer (10 cm) of quartz mixed with clay (150:1 w/w) at the bottom of the column. Separate measurements which determined the carbon released from columns filled with quartz or with quartz/clay mixtures are presented in Table 2. The measurements of dissolved organic carbon (DOC) showed that the carbon concentration in the filtered water due to the organic cation released from the micelle–clay complexes (0.2

Table 2

Carbon analysis of water after passage through a 25 cm column

DOC (mg C/l)	Column compositions ^a (w/w)
0.29 ± 0.1	Quartz
0.5 ± 0.1	Quartz+clay 1:100
0.49 ± 0.1	Quartz+clay 1:150
0.2 ± 0.14	(i) Quartz+BDMHDA/Clay 1:100 (13 cm) (ii) Quartz+clay 1:150 (10 cm)
0.18 ± 0.11	(i) Quartz+ODTMA/Clay 1:100 (13 cm) (ii) Quartz+clay 1:150 (10 cm)

^a At the bottom of the column was a 2 cm layer of quartz.

ppm) was less than (or equal within the experimental error) the carbon concentration in the water filtered through the quartz or the quartz–clay mixture. Hence, the carbon analysis showed that in the ppm range all the released cations (ODTMA or BDMHDA) were retained by the column-filter, i.e., by the 10 cm layer of quartz mixed with clay.

The water which eluted or passed through a column filled with quartz mixed with micelle–clay (BDMHDA) was also passed three times through a 25 cm column filled with quartz–clay (150:1 w/w) and then was concentrated 1000-fold. Measurements with GC-MS showed that the concentration of organic cation in the eluate was less than 1 ppb. No difference between elution of compound by methylene chloride or acetone was found.

The conclusion is that the released organic cations from micelle–clay complexes can be completely retained by placing quartz–clay layers below the micelle–clay layer, in which the particular organic pollutants will be captured.

4. Concluding remarks

Both the organic cations studied, ODTMA and BDMHDA, which have a long alkyl chain, i.e., a large hydrophobic part are characterized by large affinities of adsorption by montmorillonite and by small CMC values. The results demonstrate that existing or released monomers of these cations are expected to be tightly adsorbed by the clay particles in the soil, and do not pose a threat of contaminating ground water by the application of micelle–clay formulations of herbicides. In the case of filters, which include mixtures of micelle–clay particles with a granular material to avoid the problem of clay swelling, the

Table 1

Release of organic cations from micelle–clay complexes in aqueous suspensions

BDMHDA release (%)	ODTMA release (%)	Clay concentration (g/l)	Time (h)
24.3 ± 0.6	8.8 ± 0.12	0.1	1
18.8 ± 0.3	4.8 ± 0.04	1	
8 ± 0.1	0 ± 0.07	5	
28.8 ± 0.2	7.8 ± 0.05	0.1	4
20.4 ± 0.2	3.8 ± 0.01	1	
8.3 ± 0.1	0 ± 0.02	5	
31.2 ± 0.3	13.2 ± 0.12	0.1	24
19.4 ± 0.2	3.8 ± 0.02	1	
7.2 ± 0.1	0 ± 0.01	5	

organic cations dissolved in the water passing through the micelle–clay layer can be completely trapped by a layer which includes a mixture of a granular substance with clay.

References

- Agenson, K.O., Oh, J., Urase, T., 2003. Retention of a wide variety of organic pollutants by different nanofiltration/reverse osmosis membranes: controlling parameters of process. *J. Membr. Sci.* 225, 91–103.
- Beall, G.W., 2003. The use of organo-clays in water treatment. *Appl. Clay Sci.* 24, 11–20.
- Berne, F., Richard, Y. (Eds.), 1991. *The Water Treatment Handbook*, 6th edition. Degremont Water and the Environment, France. Two volumes.
- Carter, A.D., 2000. Herbicide movement in soil: principles, pathways and processes. *Weed Res.* 40, 113–122.
- Driscoll, F.G., 1989. *Groundwater and Wells*, 2nd edition. Johnson Filtration Systems Inc., USA.
- El-Nahhal, Y., Nir, S., Serban, C., Rabinovitz, O., Rubin, B., 2000. Montmorillonite-phenyltrimethylammonium yields environmentally improved formulations of hydrophobic herbicides. *J. Agric. Food Chem.* 48, 4791–4801.
- Fujita, H., Izumi, J., Sagehashi, M., Fujii, T., Sakoda, A., 2004. Decomposition of trichloroethene on ozone-adsorbed high silica zeolites. *Water Res.* 38, 166–172.
- Huber, S.A., Frimmel, F.H., 1991. Flow injection analysis of organic and inorganic carbon in the low-ppb range. *Anal. Chem.* 63, 2122–2130.
- Jaynes, W.F., Boyd, S.A., 1991. Clay mineral type and organic compound sorption by hexadecyltrimethylammonium-exchanged clays. *Soil Sci. Soc. Am. J.* 55, 43–48.
- Jiang, J.Q., Cooper, C., 2004. Preparation of modified clay adsorption for the removal of humic acids. *Environ. Eng. Sci.* 20, 581–586.
- Lagaly, G., 1995. Surface and interlayer reactions. In: Churchman, G.J., Fitzpatrick, R.W., Eggleton, R.A. (Eds.), *Proc. of the 10th International Clay Conference*. CSIRO Publishing, Melbourne, Australia, pp. 137–144.
- Mishael, Y.G., Undabeytia, T., Rytwo, G., Papahadjopoulos-Sternberg, B., Rubin, B., Nir, S., 2002a. Sulfometuron adsorption via alkylammonium cations adsorption as monomers and micelles on montmorillonite. *J. Agric. Food Chem.* 50, 2856–2863.
- Mishael, Y.G., Undabeytia, T., Rabinovitz, O., Rubin, B., Nir, S., 2002b. Slow release formulations of sulfometuron incorporated in micelles adsorbed on montmorillonite. *J. Agric. Food Chem.* 50, 2864–2869.
- Mishael, Y.G., Undabeytia, T., Rabinovitz, O., Rubin, B., Nir, S., 2003. Sulfosulfuron incorporation in micelles adsorbed on montmorillonite for slow release formulations. *J. Agric. Food Chem.* 51, 2553–2559.
- Pasquarell, G.C., Boyer, D.C., 1996. Herbicides in karst groundwater in Southeast West Virginia. *J. Environ. Qual.* 25, 755–765.
- Polubesova, T., Nir, S., Rabinovitz, O., Borisover, M., Rubin, B., 2003. Sulfentrazone adsorbed on micelle–montmorillonite complexes for slow release in soil. *J. Agric. Food Chem.* 51, 3410–3414.
- Polubesova, T., Epstein, M., Yariv, S., Lapidés, I., Nir, S., 2004. Adsorption of alizarinate–micelle complexes on Na-montmorillonite. *Appl. Clay Sci.* 24, 177–183.
- Polubesova, T., Nir, S., Zadaka, D., Rabinovitz, O., Serban, C., Groissman, L., Rubin, B., 2005. Water purification by optimized micelle–clay and organo-clay systems. *Environ. Sci. Technol.*, in press.
- Potter, T.L., Carpenter, T.L., 1995. Occurrence of alachlor environmental degradation products in groundwater. *Environ. Sci. Technol.* 29, 1557–1563.
- Wakshal, E., Tzivon, H., Rubin, B., 2001. Characterization of salinization processes and Herbicides content within groundwater of Hatzor Area, Israel. Report submitted to Mekorot National Water Company, Tel Aviv (in Hebrew with English summary). 98 pp. with appendixes.
- Xu, S., Sheng, G., Boyd, S.A., 1997. Use of organo-clays in pollution abatement. *Adv. Agron.* 59, 25–62.