

REMOVAL OF ANIONIC CONTAMINANTS USING SURFACTANT-MODIFIED PALYGORSKITE AND SEPIOLITE

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Abstract—In this study, the feasibility of using surfactant-modified palygorskite (PFI-1) and sepiolite (SepSp-1) for removal of anionic contaminants from water was evaluated from batch experiments. The results showed that both minerals had strong affinity for hexadecyltrimethylammonium (HDTMA), a cationic surfactant used for surface modification. The HDTMA sorption capacities were 520 and 260 mmol/kg for PFI-1 and SepSp-1, respectively. Accompanying HDTMA sorption, the sorption of counterion bromide reached 380, and 210 mmol/kg, for PFI-1 and SepSp-1, respectively, indicating that the sorbed surfactant molecules form admicelles on the minerals' surfaces. After modification by HDTMA to sorption maxima, these clays showed strong affinity for anionic contaminants such as chromate and nitrate. The chromate sorption capacities were 42 and 34 mmol/kg for HDTMA-modified PFI-1 and SepSp-1, respectively. Desorption of counterion bromide due to sorption of chromate followed a straight-line relationship, suggesting that the sorption of chromate on surfactant-modified palygorskite and sepiolite was also due to anion exchange as with other surfactant-modified clay minerals and zeolites.

Key Words—Chromate, Hexadecyltrimethylammonium, Palygorskite, Sepiolite, Sorption, Surfactant.

INTRODUCTION

Studies of sorption of cationic surfactants on clay minerals and the potential application of such modified clays in environmental remediation were mainly focused on platy clay minerals such as smectite, vermiculite, illite and kaolinite (Boyd *et al.*, 1988a, 1988b; Jaynes and Boyd, 1991; Smith and Jaffe, 1994; Xu and Boyd, 1995; Sheng *et al.*, 1998). One of the exceptional properties of cationic surfactant-modified clays is their enhanced ability to sorb non-ionic organic compounds from aqueous solution (Boyd *et al.*, 1988a, 1988b; Jaynes and Boyd, 1991; Smith and Jaffe, 1994; Sheng *et al.*, 1998). Recently, it has been shown that sorption of cationic surfactants on negatively charged clay minerals and zeolite may result in an organoclay or organozeolite that has affinity for different anions such as chromate, nitrate, sulfate (Li and Bowman, 1997, 1998, 2001; Li, 1999; Li *et al.*, 2002), and iodide (Bors *et al.*, 1997). At low loading levels, surfactant monomers are retained by ion exchange and eventually form a monolayer. As the amount of available surfactant increases, interactions among hydrocarbon tails of the surfactant molecules result in the formation of a bilayer or patchy bilayer (Xu and Boyd, 1995; Li and Bowman, 1997). At the surfactant bilayer surface coverage, the clay minerals will develop positive charges on their outermost surfaces, resulting in a great affinity for anionic contaminants (Li and Bowman, 1998, 2001; Li, 1999; Li *et al.*, 2002). Column transport studies showed that the chromate retardation factor of an illite increased by two orders of magnitude after modification by hexade-

cytrimethylammonium (HDTMA) bromide, a cationic surfactant (Li *et al.*, 2002).

Palygorskite and sepiolite are fibrous clay minerals. The basic structure of palygorskite and sepiolite can be described as being composed of 2:1 ribbons that are linked to each other laterally by single basal oxygens. The structure of palygorskite is similar to that of sepiolite except that a shorter *b* dimension incorporates only two linked pyroxene-like chains in the ribbon width, instead of three for sepiolite (Bailey, 1980). Such a structural arrangement results in a larger specific surface area (SSA) for these minerals (Rytwo *et al.*, 1998), suitable as sorbents for sorption of various organic compounds. Natural sepiolite was found to remove atrazine, isoproturon and imidacloprid from water with their sorption capacities of 2.7 and 4.0 mmol/kg for isoproturon and atrazine, respectively (Pradas *et al.*, 1999). Sorption of monobutyltin on sepiolite showed two steps with the first step corresponding to cation exchange and the second step to hydrophobic bonding (Hermosin *et al.*, 1993). Modification of sepiolite with 3-mercaptopropyltrimethoxysilane to the surface =Si-OH groups of the clay resulted in an increase in the Hg sorption capacity by a factor of three, while the Pb sorption capacity decreased by a factor of three (Celis *et al.*, 2000). The sorption of quaternary amine surfactants on sepiolites revealed two distinct sorption regions, with the first stage governed by an ion-exchange process between NH_4^+ ions and Mg^{2+} ions in the octahedral sheet and the second attributed to a combination of chain-chain interaction through van der Waals forces and ion-exchange processes (Sabah and Celik, 2002; Sabah *et al.*, 2002). However, whether these fibrous clay minerals will be able to sorb anionic contaminants after surfactant

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DOI: 10.1346/CCMN.2003.0510411

modification has not been studied. If such a property for anion sorption is demonstrated, the applications of these fibrous clay minerals could be extended.

The primary objectives of this study were (1) to study the sorption of cationic surfactants on palygorskite and sepiolite; (2) to modify these fibrous clay minerals with cationic surfactants to their sorption plateau and to use the modified clay minerals to remove anionic contaminants from water; and (3) to investigate the mechanisms that govern the surfactant sorption on these clays minerals and anion sorption after surfactant modification.

MATERIALS AND METHODS

Clay minerals

The clay minerals used were palygorskite (PFI-1) and sepiolite (SepSp-1); both are reference clays from The Clay Minerals Society Source Clay Minerals Repository, Purdue University, West Lafayette, Indiana. The palygorskite was used as received, while the sepiolite was purified by dispersing it in water and having the granular minerals removed by sedimentation. X-ray powder diffraction showed that PFI-1 had trace amounts of smectite while SepSp-1 was almost pure after removal of granular minerals. Scanning electron microscopy (SEM) showed short fibers for palygorskite (~0.1 μm wide and 1–2 μm long) and long fibers for sepiolite (~0.1 μm wide and 2–5 μm long). Their chemical compositions were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) calibrated using a standard basalt sample (BHVO-1) recommended by the USGS. The reported cation exchange capacity (CEC) for PFI-1 was 175 meq/kg measured by an ammonia electrode method (Borden and Giese, 2001). Using the same method, the CEC measured in this study was 165 and 15 meq/kg for PFI-1 and SepSp-1, respectively. The surface areas measured by single point BET were 126 and 250 m^2/g for PFI-1 and SepSp-1, respectively.

Surfactant sorption

HDTMA-Br (from Aldrich) and dodecyltrimethylammonium bromide (DDTMA, from Acros) were used for batch sorption experiments. The critical micelle concentrations (CMCs) are 9×10^{-4} M and 2.5×10^{-2} M for HDTMA-Br and DDTMA-Br, respectively (Rosen, 1989). The initial HDTMA concentrations were 5–70 mM with 5 mM increments for the PFI-1 sorption study, and 0.25–10 mM with 1 mM increments and 10–40 mM with 5 mM increments for the SepSp-1 sorption study. The initial DDTMA concentrations were 5–50 mM with 5 mM increments for the PFI-1 sorption study. To each 50 mL centrifuge tube, 2.0 g of clay minerals and 20 mL of surfactant solution were mixed and shaken on a shaker table at 150 rpm and 22°C for 24 h. The mixture was centrifuged at 4000 rpm for 30 min and the supernatant liquid was filtered through a 25 mm 0.22 μm syringe filter before analysis by an

HPLC method for equilibrium surfactant concentration (Li and Bowman, 1997).

Surfactant modification

To ensure maximum anion sorption, the clay minerals were modified with HDTMA and DDTMA to their sorption maxima. For PFI-1, 20 g of solid and 200 mL of 50 mM HDTMA solution or 30 mM DDTMA solution were used to target at 500 mmol/kg surface coverage for HDTMA or 200 mmol/kg surface coverage for DDTMA; for SepSp-1, 20 g of solid and 200 mL of 25 mmol/L HDTMA solution were used to target at 250 mmol/kg surface coverage. The mixtures were shaken at 150 rpm and 22°C for 24 h. After centrifugation the supernatant liquid was removed and the clay minerals were washed with two portions of distilled water, and then air dried. The final HDTMA and bromide loadings were 485 and 293 mmol/kg on PFI-1 and 235 and 187 mmol/kg on SepSp-1, while the final DDTMA and bromide loadings on PFI-1 were 178 and 54 mmol/kg.

Anion sorption

Mixtures of 2.00 g of surfactant-modified clay minerals and 20.0 mL of chromate solution (K_2CrO_4) at concentrations of 50–500 mg/L, or nitrate (KNO_3) solution at concentrations of 100–1200 mg/L were placed in 50 mL centrifuge tubes. The mixtures were shaken at 150 rpm and 22°C for 24 h. After centrifugation, the supernatant liquids were filtered through 25 mm 0.22 μm syringe filters and then analyzed for equilibrium chromate concentration by a modified EPA 7196A method (Li and Zou, 1999). Nitrate and bromide concentrations were analyzed using ion-selective electrode methods (Orion).

For chemical analyses, all calibrations were based on four to six standards over the range of sample concentrations. Coefficients of determination (r^2) for the standard curves were no less than 0.995. The amount of solute sorbed was calculated from the difference between the initial and equilibrium concentrations. All sorption experiments were performed in duplicate.

RESULTS

Sorption of cationic surfactants from solution onto solid surfaces can be described by the Langmuir isotherm, even though the assumptions of Langmuir sorption may not be completely satisfied (Rosen, 1989). The Langmuir sorption isotherm has the form

$$C_S = \frac{K_L S_m C_L}{1 + K_L C_L} \quad (1)$$

where C_S is the amount sorbed on solid at equilibrium (mmol/kg), C_L the equilibrium liquid concentration (mmol/L), S_m the sorption capacity or sorption maximum (mmol/kg), and K_L is the Langmuir coefficient (L/mmol).

Sorption of HDTMA on these clay minerals is well described by the Langmuir isotherm, with r^2 exceeding 0.99 (Figure 1). The HDTMA sorption maxima are 520 and 260 mmol/kg for PFI-1 and SepSp-1, respectively (Table 1). The amount of counterion bromide sorbed at HDTMA sorption maxima, an indication of surface configuration of sorbed surfactant molecules on these clay minerals, are 380 ± 20 and 210 ± 10 mmol/kg for PFI-1 and SepSp-1, respectively. The DDTMA and bromide sorption on PFI-1 was 260 and 140 ± 10 mmol/kg, respectively (Figure 1). The difference between the amount of surfactant sorbed and counterion sorbed determines the amount of surfactant sorbed via cation exchange and the rest of the sorbed surfactants are

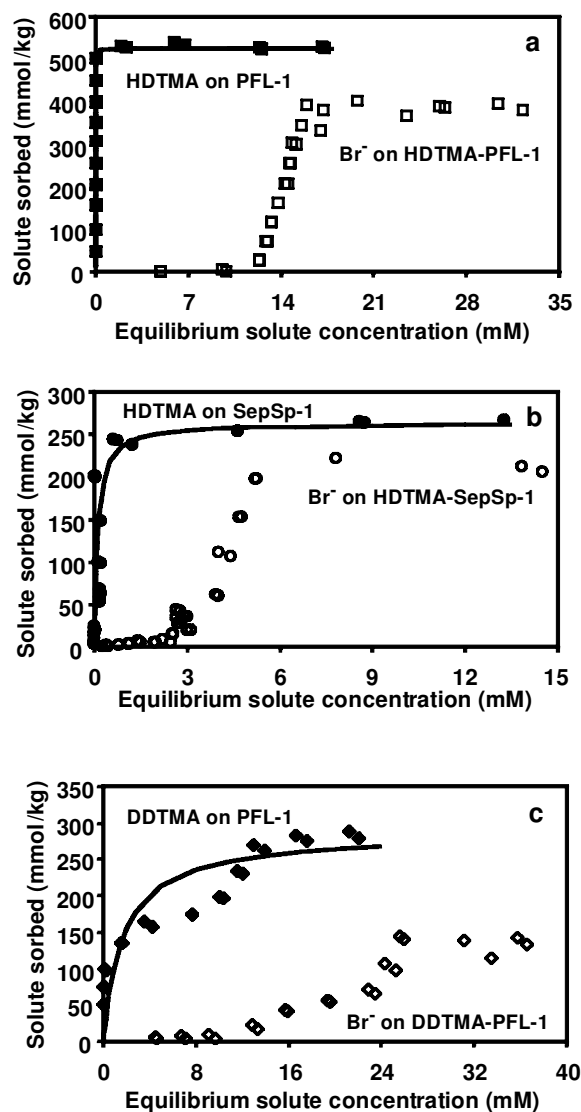


Figure 1. Sorption of HDTMA and counterion bromide on palygorskite (a) and sepiolite (b) and sorption of DDTMA and counterion bromide on palygorskite (c). Lines are Langmuir fits to the observed data.

due to hydrophobic bonding (Li and Bowman, 1997). For PFI-1, the amount of HDTMA sorbed due to cation exchange was 140 mmol/kg, in accord with its CEC of 165 mmol/kg, as determined by the ammonia electrode method (Borden and Giese, 2001). The amount of DDTMA sorbed on PFI-1 was 280 mmol/kg, while the amount of counterion bromide sorbed was 140 mmol/kg. The difference (140 mmol/kg) relates to the DDTMA sorption due to cation exchange, in accord with that obtained from HDTMA sorption. For SepSp-1, the amount of HDTMA sorbed due to cation exchange was 50 mmol/kg. This value is larger than its CEC of 15 mmol/kg as determined by the ammonia electrode method. The amount of HDTMA sorbed due to hydrophobic bonding accounted for 80% of the total HDTMA sorption. As observed by Sabah and Celik (2002), sepiolite is highly receptive to sorption of cationic surfactants and adsorption of cationic surfactants on sepiolite exhibits two distinct regions with the first characterized by low rate and governed by an ion-exchange process between NH_4^+ ions and Mg^{2+} ions in the octahedral sheet and the second ascribed to a combination of chain-chain interactions through van der Waals forces and an ion-exchange process. The results from this study showed that the amount of HDTMA sorbed via hydrophobic bonding is significantly larger than that via cation exchange.

To increase their affinity for anions, these two minerals were modified by HDTMA to their sorption maxima. Similar to other surfactant-modified clay minerals, the organo-palygorskite and organo-sepiolite showed strong affinity for chromate and the sorption was well described by the Langmuir isotherm (Figure 2). The chromate sorption capacities were 42 and 34 mmol/kg, for HDTMA-modified PFI-1 and SepSp-1, respectively (Table 2), similar to that of surfactant-modified zeolite, surfactant-modified kaolinite, illite and smectite (Li and Bowman, 1997, 1998, 2001; Li *et al.*, 2002). Since the CECs of these two minerals are much lower than that of smectite, the similar chromate sorption capacity may indicate that comparable numbers of positive charges exist on the outermost surface of PFI-1 and SepSp-1 as with smectite, which is in accord with that obtained from counterion sorption (Figure 1).

Desorption of counterion bromide due to sorption of chromate followed a straight-line relationship (Figure 3a) and the slope of the straight lines was 1.4,

Table 1. Langmuir sorption parameters for surfactant sorption onto PFI-1 and SepSp-1.

Sample	K_L (L/mmol)	S_m (mmol/kg)	r^2
HDTMA on PFI-1	245	520	0.999
HDTMA on SepSp-1	10	260	0.999
DDTMA on PFI-1	3	260	0.990

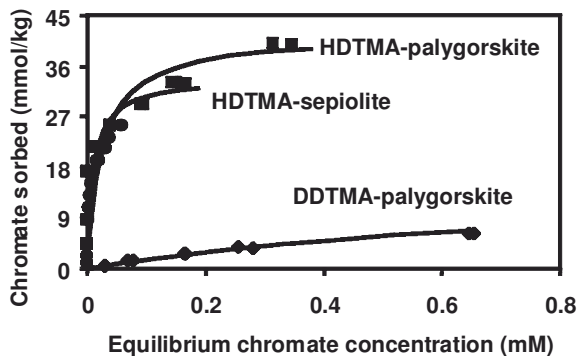


Figure 2. Sorption of chromate by surfactant-modified PFI-1 and SepSp-1. The lines are Langmuir fits to the observed data.

similar to the results from previous studies (Li and Bowman, 1997, 1998, 2001; Li, 1999). In theory, if one CrO_4^{2-} replaces two Br^- anions on external surfaces, the slope should be 2, while an HCrO_4^- substituting one Br^- will result in a slope of 1. A slope of 1.4 might indicate that equal amounts of chromate and hydrogen chromate were sorbed on the modified surface. Since the $\text{p}K_a$ of hydrogen chromate dissociating to chromate is 5.9, a slope of 1.4 may indicate that the surface pH is ~ 6 , in agreement with the results observed for chromate sorption on surfactant-modified zeolite and kaolinite

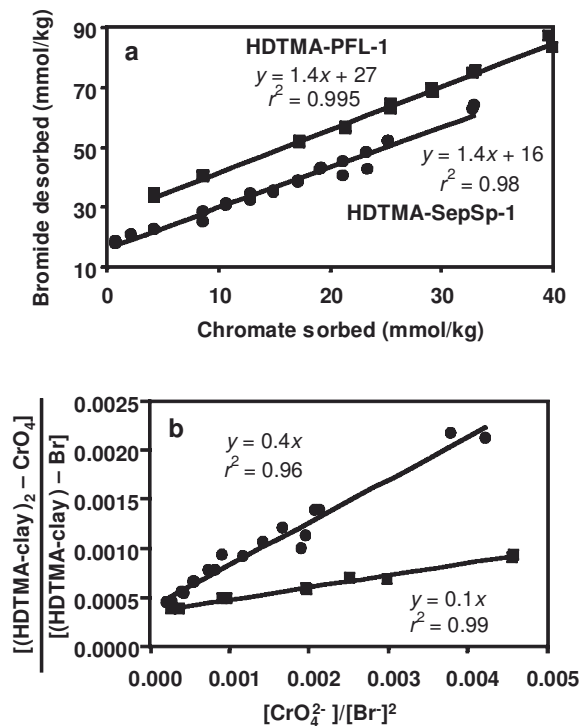


Figure 3. Desorption of counterion bromide as a function of the amount of chromate sorbed on surfactant-modified PFI-1 and SepSp-1. Lines are linear fits to the observed data and the non-zero intercepts indicate an excess of counterion bromide that over balanced the surfactant admicelles (a). Plot of data using equation 4 further verified the anion exchange mechanism (b).

Table 2. Langmuir sorption parameters for chromate sorption onto surfactant-modified PFI-1 and SepSp-1 and other surfactant-modified clay minerals.

Sample	HDTMA loading (mmol/kg)	K_L (L/mmol)	S_m (mmol/kg)	r^2
HDTMA-PFI-1	520	38	42	0.98
HDTMA-SepSp-1	260	90	34	0.98
DDTMA-PFI-1	260	1	17	0.98
HDTMA-kaolinite ¹	60	20	13	0.99
HDTMA-illite ²	160	31	18	0.98
HDTMA-zeolite ³	200	31	11	0.99
HDTMA-smectite ⁴	3000	10	53	–

¹ From Li and Bowman (2000)

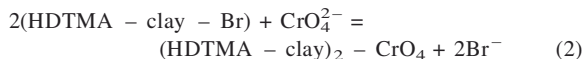
² From Li *et al.* (2002)

³ From Li and Bowman (1997)

⁴ From Li and Bowman (1998)

(Li and Bowman, 1997, 2001). The straight-line relationship between chromate sorbed and bromide desorbed revealed that the sorption of chromate on surfactant-modified palygorskite and sepiolite surfaces was also due to anion exchange as with other surfactant-modified clay minerals and zeolites (Bors *et al.*, 1997; Li, 1999). From Figure 3a it can be seen that a non-zero intercept exists between chromate sorption and bromide desorption, which was attributed to surface over-balance of counterions during the initial modification stage (Li and Bowman, 2001; Li *et al.*, 2002).

Surface anion exchange of chromate for counterion bromide on modified clay minerals can be written as (Li, 1999):



with a selectivity coefficient, K_S , defined as

$$K_S = \frac{[(\text{HDTMA} - \text{clay})_2 - \text{CrO}_4][\text{Br}^-]^2}{[\text{HDTMA} - \text{clay} - \text{Br}]^2[\text{CrO}_4^{2-}]} \quad (3)$$

The square brackets denote concentrations in mmol/L for the solution phase and mmol/kg for the sorbed phase. Equation 3 can be rearranged to

$$\frac{[(\text{HDTMA} - \text{clay})_2 - \text{CrO}_4]}{[\text{HDTMA} - \text{clay} - \text{Br}]^2} = \frac{[\text{CrO}_4^{2-}]}{[\text{Br}^-]^2} K_S \quad (4)$$

so that K_S can be calculated using linear regression. Using the initial $[\text{HDTMA-clay-Br}]$ of 293 and 187 mmol/kg for PFI-1 and SepSp-1 determined during the surfactant modification stage. The equilibrium $[\text{HDTMA-clay-Br}]$ could be determined from the amount of Br^- released after sorption of CrO_4^{2-} . Equilibrium $[(\text{HDTMA-clay})_2 - \text{CrO}_4]$ can be calculated from the difference between the initial and equilibrium solution $[\text{CrO}_4^{2-}]$. These results also followed a straight line, further verifying the anion-exchange mechanism for chromate sorption (Figure 3b).

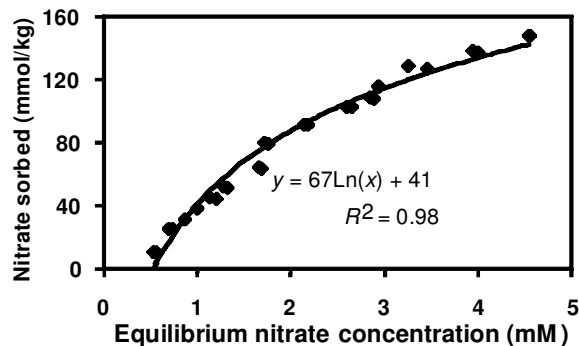


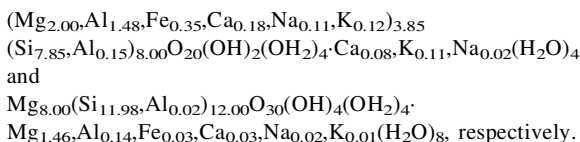
Figure 4. Sorption of nitrate on HDTMA-PFI-1. The line is the Freundlich fit to the observed data.

In addition to chromate sorption, HDTMA-PFI-1 has a larger sorption capacity for nitrate (Figure 4). However, a Freundlich sorption isotherm fitted the observed data better.

DISCUSSION

Compared to surfactant-modified platy clay minerals and granular zeolite, the sorption of HDTMA on fibrous clay minerals is slightly different. Measurements of the exchangeable cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) released due to the sorption of HDTMA on zeolite surfaces indicated that the external CEC (ECEC) equalled half of the HDTMA sorption plateau, and thus, the HDTMA sorption plateau could be used as an indicator of the ECEC (Li and Bowman, 1997). In the case of HDTMA sorption on regular non-expandable clays and zeolites, the amount of counterion bromide sorbed is primarily on the external surfaces and is close to half of the amount of surfactant sorbed, indicating that the sorbed surfactant form bilayer formations on mineral surfaces (Li and Bowman, 1997, 1998). In this study, the CECs of PFI-1 and SepSp-1 are 165 and 15 mmol/kg, respectively. However, their HDTMA sorption maxima were 520 and 260 mmol/kg (about 3 to 17 times the amount of their CECs). In addition, the amounts of counterion sorbed were much more than half of the HDTMA sorbed (Figure 1). Thus, flat surfactant bilayer formation cannot be used to explain the differences between surfactant and counterion sorption and CEC. Similar results were found in a study of the sorption of the organic cations methylene blue and crystal violet onto sepiolite, in which the largest amount of organic cation sorption was about four times the CEC of sepiolite (Rytwo *et al.*, 1998).

The chemical formulae of PFI-1 and SepSp-1, based on their chemical analysis, can be written as:



The substitution in tetrahedral sites is small (Bailey, 1980). For sepiolite, the substitution in octahedral sites is also limited. Figure 5 depicts the structures of palygorskite and sepiolite along the [100] projection. The elongation of the fibers is parallel to the *a* crystallographic axis. The channel size of these minerals is similar to that of the head group of HDTMA molecules. In addition, these minerals have relatively large SSAs. The charge densities based on CEC and SSA measurements are $e^-/127 \text{ \AA}^2$ and $e^-/280 \text{ \AA}^2$ for PFI-1 and SepSp-1, respectively, while the HDTMA head group is 25 \AA^2 (Sabah *et al.*, 2002). Assuming all sorbed surfactant molecules form monolayer surfactant coverage (which is incorrect due to the counterion sorption), the surface area occupied per HDTMA molecule would be 55 \AA^2 for PFI-1 and 167 \AA^2 for SepSp-1, much larger than the surface area of the surfactant head group. In addition, the ratio of sorbed counterion to sorbed HDTMA was 4:5, indicating that multiple HDTMA molecules in the upper layer of the bilayer formation may attach to a single HDTMA molecule in the lower layer via hydrophobic bonding, forming tree-like admicelles as depicted by Rupprecht and Gu (1991) or cylindrical admicelles on the minerals' surfaces (Manne and Gaub, 1995). In contrast to surfactant bilayer formation on platy minerals, the cylindrical admicelles will require more counterions to balance the positive charges created by the head groups of the surfactants. Due to the similar size of the channel and HDTMA head group, it may suggest that the cylindrical admicelles are parallel to the direction of elongation of the minerals (Figure 6). Sorption of HDTMA in the channel or inside the grooves if the channels are on the external surface may account for the enhanced HDTMA sorption even at relatively low surface-charge density. Rytwo *et al.* (1998) attributed the excess organic cation uptake by sepiolites to sorption on neutral sorption sites (in the order of 600 mmol/kg) originating from silanol (Si-OH) groups, while the sorption on the charged sites due to cation exchange was of the order of 100–150 mmol/kg. The net ratio of sorption on neutral sites to that on charged sites is 4–6, similar to this study. Thus, the surfactant sorption on these minerals may be governed, to a large extent, by hydrophobic bonding, whereas cation exchange was the main mechanism for other clay minerals and zeolites.

Higher chromate sorption capacity and Langmuir sorption coefficients were observed for HDTMA-PFI-1 and HDTMA-SepSp-1 compared to other clay minerals and zeolites except HDTMA-smectite (Table 2). The enhanced chromate sorption may be attributed to the overbalance of counterions on the minerals' surface. In other words, the total surface anion exchange capacities as determined by the counterion sorption could be 380 and 210 mmol/kg for HDTMA-modified PFI-1 and SepSp-1, respectively. These values are much higher than that for HDTMA-modified zeolites (100 mmol/kg,

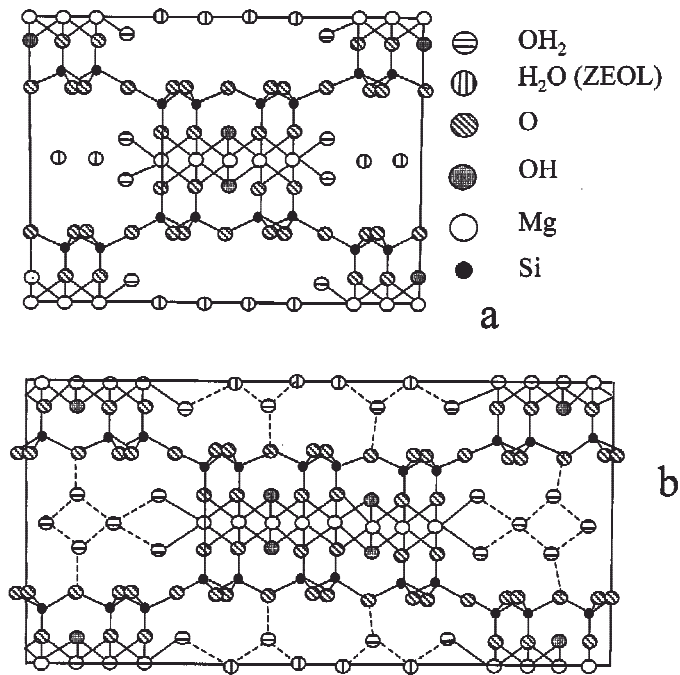


Figure 5. Crystal structure of palygorskite (a) and sepiolite (b) (after Bailey, 1980).

Li and Bowman, 1997), kaolinite (30 mmol/kg, Li and Bowman, 2001), and illite (120 mmol/kg, Li *et al.*, 2002). Compared to an HDTMA-modified smectite with 3000 mmol/kg, whose chromate sorption capacity was only 53 mmol/kg (Li and Bowman, 1998), the PFI-1 was modified to 500 mmol/kg and the chromate sorption

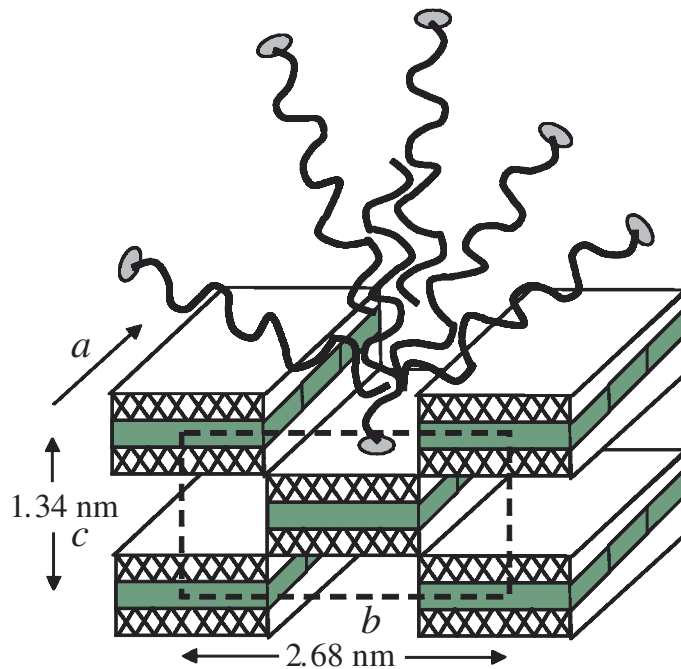


Figure 6. Hypothesized surfactant admicelles on fibrous clay mineral surfaces such as sepiolite.

capacity was 42 mmol/kg. One explanation was that much of the sorbed HDTMA on smectite was in the interlayer space and the positive charge of the surfactant head groups was balanced in the interlayer space. Thus, higher HDTMA sorption capacity may not necessarily have higher anion sorption capacity.

Although previous results showed that HDTMA sorbed via hydrophobic bonding was not as stable as those sorbed via cation exchange and was subject to slow desorption (Xu and Boyd, 1995; Li and Bowman, 2001; Li *et al.*, 2002), the sorbed chromate on surfactant-modified zeolite was stable under various conditions (Li, 1998). Due to different surfactant surface configurations, further study on the stability of sorbed chromate on surfactant-modified fibrous minerals is needed.

CONCLUSIONS

From this research it is concluded that HDTMA-modified fibrous clay minerals, like HDTMA-modified platy clay minerals and zeolites, are effective sorbents for anionic inorganic contaminants. At the sorption maximum, the sorbed HDTMA molecules form micelles on the external surface of the clay minerals, resulting in a positively charged surface, and are responsible for chromate sorption. Quantitative counterion desorption and chromate sorption data indicate that surface anion exchange is the major mechanism that governs chromate sorption.

ACKNOWLEDGMENTS

This research was partially sponsored by the State of Wisconsin Groundwater Coordinating Council. Funding from Creative Research Activity, Professional Opportunity Fund, and the Collaborative Undergraduate Research Project of University of Wisconsin–Parkside is greatly appreciated. We thank Dr M. Celik Karakaya and another anonymous reviewer for their constructive comments and suggestions for ways of improving the quality of this manuscript.

REFERENCES

- Bailey, S.W. (1980) Structure of layer silicates. Pp. 1–123 in *Crystal Structures of Clay Minerals and their X-ray Identification* (G.W. Brindley and G. Brown, editors). Monograph 5, Mineralogical Society, London.
- Borden, D. and Giese, R.F. (2001) Baseline studies of The Clay Minerals Society source clays: cation exchange capacity measurements by the ammonia-electrode method. *Clays and Clay Minerals*, **49**, 444–445.
- Bors, J., Gorny, A. and Dultz, S. (1997) Iodide, cesium and strontium adsorption by organophilic vermiculite. *Clay Minerals*, **32**, 21–28.
- Boyd, S.A., Mortland, M.M. and Chiou, C.T. (1988a) Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite. *Soil Science Society of America Journal*, **52**, 652–657.
- Boyd, S.A., Sun, S., Lee, J.F. and Mortland, M.M. (1988b) Pentachlorophenol sorption by organo-clays. *Clays and Clay Minerals*, **36**, 125–130.
- Celis, R., Hermosin, M.C. and Cornejo, J. (2000) Heavy metal adsorption by functionalized clays. *Environmental Science and Technology*, **34**, 4593–4599.
- Hermosin, M.C., Martin, P. and Cornejo, J. (1993) Adsorption mechanisms of monobutyltin in clay minerals. *Environmental Science and Technology*, **27**, 2606–2611.
- Jaynes, W.F. and Boyd, S.A. (1991) Clay mineral type and organic compound sorption by hexadecyltrimethylammonium clays. *Soil Science Society of America Journal*, **55**, 43–48.
- Li, Z. (1998) Chromate extraction from surfactant-modified zeolite surfaces. *Journal of Environmental Quality*, **27**, 240–242.
- Li, Z. (1999) Sorption of oxyanions and surface anion exchange by surfactant-modified clay minerals. *Journal of Environmental Quality*, **28**, 1457–1463.
- Li, Z. and Bowman, R.S. (1997) Counterion effects on the sorption of cationic surfactant and chromate on natural clinoptilolite. *Environmental Science and Technology*, **31**, 2407–2412.
- Li, Z. and Bowman, R.S. (1998) Sorption of chromate and PCE by surfactant-modified clay minerals. *Environmental Engineering Science*, **15**, 237–245.
- Li, Z. and Bowman, R.S. (2001) Retention of inorganic oxyanions by organo-kaolinite. *Water Research*, **35**, 3771–3776.
- Li, Z. and Zou, Y. (1999) A comparison of chromate analyses by AA, UV-Vis spectrophotometric, and HPLC methods. *Advance in Environmental Research*, **3**, 125–131.
- Li, Z., Alessi, D., Zhang, P. and Bowman, R.S. (2002) Organoillite as a low permeability sorbent to retard migration of anionic contaminants. *Journal of Environmental Engineering*, **128**, 583–587.
- Manne, S. and Gaub, H.E. (1995) Molecular organization of surfactants at solid-liquid interfaces. *Science*, **270**, 1480–1482.
- Pradas, E.G., Villafranca-Sánchez, M., Socías-Viciana, M., Fernández-Pérez, M.D. and Ureña-Amate, M.D. (1999) Preliminary studies in removing atrazine, isoproturon and imidacloprid from water by natural sepiolite. *Journal of Chemical Technology and Biotechnology*, **74**, 417–422.
- Rosen, M.J. (1989) *Surfactants and Interfacial Phenomena*, 2nd edition. John Wiley & Sons, New York, 431 pp.
- Rupprecht, H. and Gu, T. (1991) Structure of adsorption layers of ionic surfactants in the solid/liquid interface. *Colloid and Polymer Science*, **269**, 506–522.
- Rytwo, G., Nir, S., Margulies, L., Casal, B., Merino, J., Ruiz-Hitzky, E. and Serratos, J.M. (1998) Adsorption of monovalent organic cations on sepiolite: experimental results and model calculations. *Clays and Clay Minerals*, **46**, 340–348.
- Sabah, E. and Celik, M.S. (2002) Adsorption mechanism of quaternary amines by sepiolite. *Separation Science and Technology*, **37**, 3081–3097.
- Sabah, E., Turan, M. and Celik, M.S. (2002) Adsorption mechanism of cationic surfactants onto acid- and heat-activated sepiolites. *Water Research*, **36**, 3957–3964.
- Sheng, G., Wang, X., Wu, S. and Boyd, S.A. (1998) Enhanced sorption of organic contaminants by smectitic soils modified with a cationic surfactant. *Journal of Environmental Quality*, **27**, 806–814.
- Smith J.A. and Jaffe, P.R. (1994) Benzene transport through landfill liners containing organophilic bentonite. *Journal of Environmental Engineering*, **120**, 1559–1577.
- Xu, S. and Boyd, S.A. (1995) Cationic surfactant sorption to a vermiculitic subsoil via hydrophobic bonding. *Environmental Science and Technology*, **29**, 312–320.

(Received 19 November 2002; revised 17 March 2003; Ms. 741)