

## Adsorption of benzene and naphthalene to modified montmorillonite

Yasser El-Nahhal<sup>1,2\*</sup> and Jamal Safi<sup>2,3</sup>

<sup>1</sup>Institut für Anorganische Chemie, Christian-Albrechts-Universität, Olshausenstr. 40, D-24118 Kiel, Germany, <sup>2</sup>Environmental Protection and Research Institute P. O. Box 1175 (EPRI) Gaza, Palestinian National Authority (PNA), <sup>3</sup>Faculty of Agriculture and Environment, Al-Azher University-Gaza, Palestinian National Authority (PNA). \*e-mail: y\_el\_nahhal@hotmail.com

Received 29 December 2004, accepted 16 March 2005.

### Abstract

This study aims to characterize the adsorption pattern of benzene and naphthalene on montmorillonite modified with hexadecyltrimethylammonium (HDTMA), tetramethylammonium (TMA), tetraethylammonium (TEA), tetrabutylammonium (TBA) or benzyltrimethylammonium (BTMA). Adsorption isotherms of benzene and naphthalene from water followed Langmuir and Freundlich models respectively. The Langmuir form of the isotherms suggests that benzene and naphthalene adsorbed to the surfaces as a monolayer. Binding coefficient of naphthalene increased as the molecular weight of the pre-adsorbed surfactant increased. Adsorption of benzene and naphthalene follows the sequence: montmorillonite-benzyltrimethylammonium > montmorillonite-hexadecyltrimethylammonium > montmorillonite-tetrabutylammonium > montmorillonite-tetraethylammonium > montmorillonite-tetramethylammonium. The results indicate that using those complexes can be useful in removing pollutants from water.

**Key words:** Benzene, naphthalene, adsorption, montmorillonite.

### Introduction

The increasing use of organic compounds and petroleum products poses a serious impact to human health and the environment. Such environmental problems must be controlled in order to minimize the harmful effects of these products. One problem frequently encountered with these compounds is contamination of ground water<sup>31</sup>. Montmorillonite in soil determines the fate of many organic compounds which reach the soil. The hydrophilic montmorillonite is an ineffective sorbent for poorly water-soluble compounds such as aromatic hydrocarbons that frequently move from contaminated sites (agricultural and/or industrial sites) into the subsurface environment and groundwater. The adsorption of non-ionic organic compounds (NOCs) on hydrophilic montmorillonite is suppressed in the presence of water because non-polar or less polar organic compounds cannot effectively compete with water for adsorption sites on the montmorillonite surfaces. Adsorption of NOCs on montmorillonite can be enhanced by replacing the inorganic cations by larger cationic surfactants<sup>2, 3, 5, 13, 20</sup>. Earlier studies indicated that exchanging quaternary alkylammonium organic cation for metal ions on montmorillonite greatly modified the sorptive characteristics for organic vapors<sup>4, 18, 20, 24, 28</sup>. Sorbed surfactants to sediments or soils retarded the migration of NOCs in subsurface environment and can provide an effective transport barrier in soils<sup>8, 12, 32</sup>. Shen<sup>26</sup> studied the sorption of benzene and naphthol by bentonites exchanged with short-chain quaternary ammonium surfactants. Here we report the adsorption of benzene and naphthalene on different types of alkylated montmorillonites.

### Materials and Methods

**Material:** The sodium montmorillonite SWy-1 was obtained from the Source Clays Repository (Clay Minerals Society, Columbia, MO). The cation exchange capacity (CEC) is 0.8 mol/kg montmorillonite<sup>23</sup>.

The cationic surfactants: hexadecyltrimethylammonium (HDTMA), tetramethylammonium (TMA), tetraethylammonium (TEA), tetrabutylammonium (TBA), and benzyltrimethylammonium (BTMA), were received as chloride or bromide salts from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO, USA; Aldrich Chem. Co., Milwaukee, WI, USA). Analytical grade naphthalene and benzene were obtained from Sigma Chemical Co, USA. Some physical properties and the chemical structures are shown in Table 1 and Fig. 1 respectively.

**Interaction of cationic surfactants with montmorillonite surfaces:** The adsorption isotherms of TMA, TEA and TBA were measured in the range of 0.1-5.0 mol surfactant/kg montmorillonite as described in El-Nahhal et al.<sup>5</sup>. Appropriate aliquots of the surfactant were diluted and added to 25 mg montmorillonite suspension in 40 ml glass centrifuge tube. The total volume was 25 ml. The tubes were kept under continuous agitation for 48 h using a rotary shaker. The supernatants were separated by centrifugation at 6,000 rpm at 20°C for 25 min. The final concentration of clay was 1 g/l. The amount of surfactant adsorbed was derived from the carbon content (CHNSO analyzer, Carlo-Erba 1108) as described previously<sup>5</sup>.

**Preparation of the organo-clay minerals:** Montmorillonite-TMA, -TEA, -TBA, -HDTMA and -BTMA complexes were prepared at a full saturation capacity (0.8 mmol/g montmorillonite) by dropwise addition of aliquots of a 10 mM aqueous solution of the organic salt to a 1% (w/v) aqueous dispersion of montmorillonite under continuous stirring for 48 hours as described previously<sup>5, 17</sup>.

**Density of the organo-montmorillonites:** Organo-montmorillonite was filled in a 10 ml glass cylinder and pressed manually several

times up to reach a final volume of 10 ml. The mass of the surfactant-montmorillonite was weighed with a digital balance. The density was calculated from the mass-volume ratio. All samples were made in triplicate. The results were accurate and reproducible. Statistical analysis does not discriminate significant difference among measurements.

**Adsorption of benzene and naphthalene:** Adsorption isotherms of benzene and naphthalene were measured in a range of 0-200  $\mu\text{mol}$  benzene or naphthalene per gram organo-montmorillonite at room temperature ( $25 \pm 1^\circ\text{C}$ ). A stock solution of benzene was prepared by dissolving 15.6 mg benzene in 1 litre of distilled water. The stock solution of naphthalene was prepared by dissolving 25.6 mg naphthalene in 3.5 ml methanol and diluting to 1 litre with distilled water.

Appropriate aliquots of aqueous solutions of benzene or naphthalene were diluted with water to give a volume of 25 ml and were added under continuous stirring to 5 ml of the 0.5% (w/w) organic-montmorillonite dispersion in 30 ml centrifuge tubes. The final concentration of the montmorillonite was 0.83 g/l. The samples were kept under continuous horizontal agitation for 24 h. The supernatant was separated by centrifugation at 6,000 g for 0.5 h.

After centrifugation, 10 ml aliquots of the supernatant were extracted with 10 ml carbon disulphide ( $\text{CS}_2$ ) in glass vials and analyzed by gas chromatography (Hewlett-Packard Model 5890, flame ionization detector, an automatic sample holder)<sup>7</sup>. To monitor volatilization losses, blank samples were measured without montmorillonite or its hydrophobic complexes. The blank recoveries were 75 and 85% for benzene and naphthalene respectively. The relatively low recoveries may probably be due to the very hot conditions outside the laboratory during the experiment. The data measured were not adjusted to the losses.

**Data analysis:** Adsorption data were fit to multiple regression analysis. Binding coefficient,  $K_d$  is a measure of interaction between the compound and the organo-clay complex. For better comparison, the organic carbon based sorption coefficients ( $K_{oc}$ ) of benzene and naphthalene were obtained by normalizing the slope of the isotherms ( $K_d$ ) to the organic fraction ( $f_{oc}$ ) of montmorillonite complex ( $K_{oc} = (K_d/f_{oc}) * 100$  as described in Kile et al.<sup>10</sup>). The free energy of the adsorption was calculated by equation (1)<sup>11</sup>.

$$\Delta G^\circ = -RT \ln (C_i/C_e) \quad (1)$$

where  $\Delta G^\circ$  is the molar free energy change (Joule/mol),  $R$  is the gas constant (8.3143 Joules/mole/K),  $T$  is the absolute temperature and  $C_i/C_e$  are the initial and equilibrium concentration respectively.

## Results and Discussion

**Organo-montmorillonite:** The amounts of surfactant adsorbed followed the sequence TMA > TEA > TBA but the overall pattern is similar for adsorption by montmorillonite up to the CEC.

According to Rosen<sup>22</sup>, adsorption of cationic surfactants from solution to solid surfaces can be described by Langmuir isotherms even though the assumptions of Langmuir adsorption may not be completely satisfied:

$$S = K_1 S_m C_e / (1 + K_1 C_e) \quad (2)$$

where  $S$  is the adsorbed at equilibrium (mmol/g),  $C_e$  equilibrium

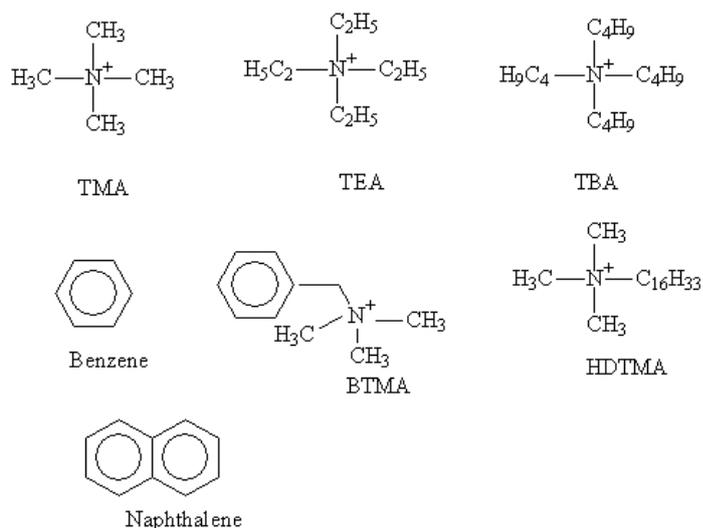


Figure 1. Chemical structure of the used materials.

concentration adsorption, (mmol/l),  $S_m$  adsorption capacity (mmol/g) and  $K_1$  is the Langmuir coefficient (l/mmol). Thus  $K_1$  and  $S_m$  are obtained from the linear regression by plotting  $C_e/S$  versus  $C_e$ .

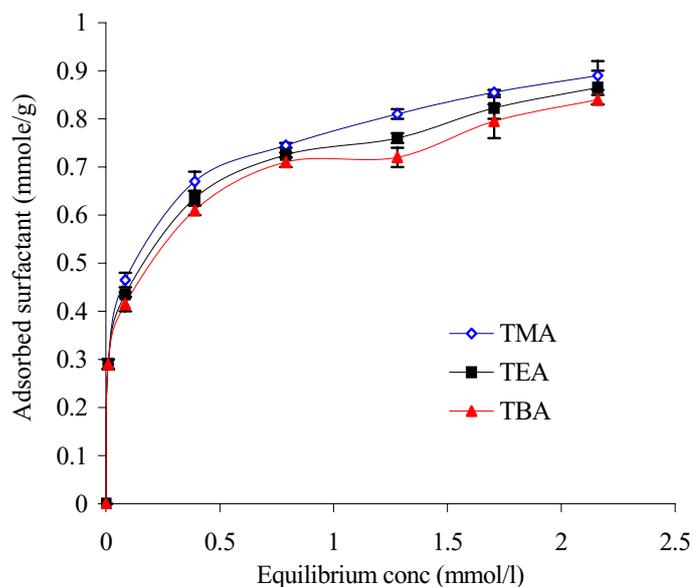
The adsorption isotherms were well described by the Langmuir model with correlation coefficients ( $R^2$ ) exceeding 0.99 (Table 2) from the linear Langmuir representation. The Langmuir adsorption capacity ranged from 0.846 to 0.896 mmol/g. Above CEC the adsorbed amount increased only slightly (Fig. 2). The amounts of TMA adsorbed were slightly higher than TEA or TBA.

Some properties of the organo-montmorillonite are presented in Table 3. It is obvious that there are some changes in the density of the produced complexes. The density of montmorillonite saturated up to 60% of CEC was greater than at a full saturation. At a full saturation more surfactant molecules were attached to the single montmorillonite particles. This interaction increased the volume of montmorillonite particle. At a partial saturation (60%) of CEC, less surfactant molecules were attached to a montmorillonite particle, thus a certain volume accommodated more montmorillonite particles, consequently the density was increased. In addition, a bulkier surfactant (e.g. HDTMA) (Fig. 1) largely reduced the density of montmorillonite and the complex may be floating on the surface of water, and sorption may not be efficient due to lack of contact with adsorbate.

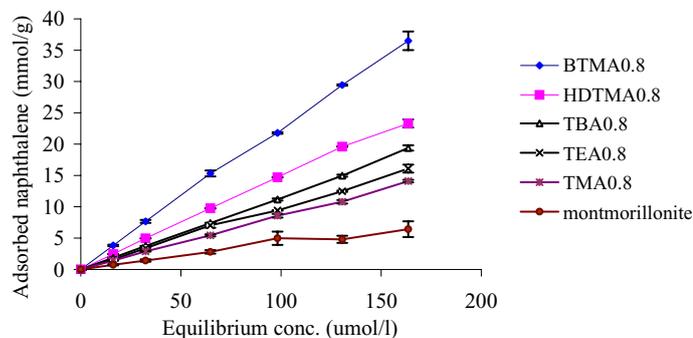
### Adsorption of benzene and naphthalene to modified montmorillonite:

Adsorption of benzene on the original hydrophilic montmorillonite particles was very low compared to hydrophobic montmorillonite particles (Fig. 3). Almost 3% of the added benzene was adsorbed on hydrophilic montmorillonite particles. Modifying the montmorillonite surfaces with TMA considerably increased amount of benzene adsorbed due to hydrophobic environment. Larger surfactants such as TEA, TBA, HDTMA or BTMA further increased the amount of benzene adsorbed. The adsorption followed the sequence of BTMA > HDTMA > TBA > TEA > TMA > montmorillonite. Our results agree with Bartelt-Hunt et al.<sup>1</sup>, Smith et al.<sup>29</sup> and Redding et al.<sup>21</sup> who reported that adsorption of benzene on HDTMA-bentonite was a function of the total carbon contents.

The adsorption isotherm fits very well to Eq (2) and indicates that saturation, probably in mono-layers is reached at high



**Figure 2.** Adsorption isotherms of cationic surfactants on montmorillonite. Surfactants adsorbed are: TMA, TEA or TBA. Organic loads at montmorillonite surfaces were determined by CHNSO analyzer. Bars indicate standard error.



**Figure 4.** Adsorption isotherms of naphthalene on montmorillonite modified with cationic surfactant such as TMA, TEA, TBA, HDTMA, or BTMA. The number indicates the loading of the surfaces (0.8 mmol surfactant/g montmorillonite). Bars indicate standard error.

**Table 1.** Physical properties of used chemicals.

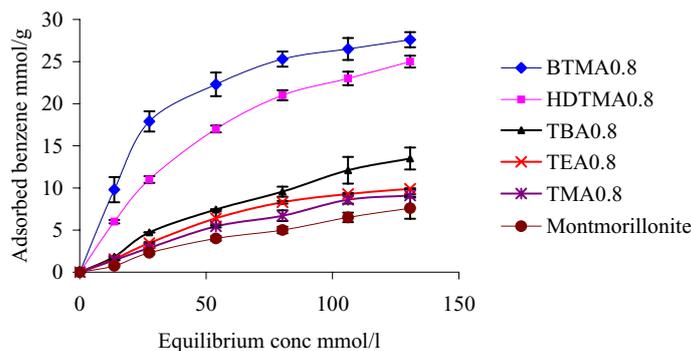
Name of surfactant	Molecular weight	Solubility in water	Toxicity LD <sub>50</sub>
TMA	109.61	Water soluble	125 mg/kg oral mouse
TEA	183.73	1419 g/l	2530 mg/kg oral rat
TBA	322.37	6000 g/l	Not available
HDTMA	320	Soluble	410 mg/kg oral rat
BTMA	185.7	800 g/l	250 mg/kg oral rat
Benzene	78	0.7 g/l	930 mg/kg oral rat
Naphthalene	128	32 mg/l	490 mg/kg oral rat

LD<sub>50</sub> is the concentration required to kill 50% of the test organism. Adopted from Ref<sup>19</sup>.

concentrations. Binding coefficients,  $K_d$ , of benzene on modified montmorillonite are presented in Table 4. The binding coefficient increased when the pre-adsorbed surfactant included an aromatic ring. This is probably due to  $\pi$ - $\pi$  interaction of benzene with the pre-adsorbed surfactant<sup>27,30</sup>.

A comparison between  $K_{oc}$  values and  $K_{ow}$  of benzene (Table 4) indicates significant differences. These data provide additional evidence of adsorption rather than partitioning between two phases. The presented results showed a shape dependence of benzene uptake from water using montmorillonite modified with different cationic surfactants. Similar results were reported previously for other cases<sup>6,15</sup>.

Adsorption isotherms of naphthalene on hydrophobic montmorillonite (Fig. 4) were linear in all cases. The binding



**Figure 3.** Adsorption isotherms of benzene on montmorillonite modified with cationic surfactant such as TMA, TEA, TBA, HDTMA, or BTMA. The number indicates the loading of the surfaces (0.8 mmol surfactant/g montmorillonite). Bars indicate standard error.

**Table 2.** Adsorption coefficients of surfactants on montmorillonite.

Surfactant	$S_m$ (mmol/g)	$K_1$ (L/mmol)	$R^2$
TMA	0.896	12.85	0.995
TEA	0.872	10.15	0.993
TBA	0.846	9.17	0.992

**Table 3.** Bulk density and color of montmorillonite-surfactant complexes.

Surfactant complex	Color	Density (g/ml)
Montmorillonite-TMA0.5	Wg	0.95±0.016
Montmorillonite-TMA0.8	Wb	0.74±0.008
Montmorillonite-TEA0.8	Wb	0.68±0.097
Montmorillonite-TBA0.5	W	0.74±0.017
Montmorillonite-TBA0.8	Wb	0.62±0.004
Montmorillonite-BTMA0.5	Wg	0.72±0.006
Montmorillonite-BTMA0.9	Wg	0.35±0.011

Wb= white brown; w= white; wg= white greenish

coefficient (Table 4) increased as the water solubility of the pre-adsorbed surfactant increased (Table 1). These results suggest a possible partitioning of naphthalene between the organic phase that is generated on the surfaces of montmorillonite. These results agree with Bartelt-Hunt et al.<sup>1</sup>, who reported an increase in  $\log K_{oc}$  values of benzene with the increase of carbon content in organobentonites.

However,  $K_{oc}$  values are significantly different from  $K_{ow}$  (Table 4). These data indicate that the interaction between naphthalene and montmorillonite surfactant complexes is due to physical adsorption. These data agree with the results of free energy calculations (Table 5). Linear mode of naphthalene adsorption was also observed in previous reports<sup>3,14,16</sup>.

**Free energy of adsorption:** The molar free energy for benzene and naphthalene adsorption on modified montmorillonite vary between  $-85.34 \pm (-6.46)$  and  $-985.82 \pm (-47.64)$  for benzene and  $-88.77 \pm (-10.24)$  and  $-513.21 \pm (-14.94)$  for naphthalene. These data are within the expected range for physical adsorption. The values calculated from  $K_{ow}$  were  $-12059.7$  and  $-19168.2$  J/mole for benzene and naphthalene respectively. Obviously  $\Delta G^0$  values calculated for adsorption were significantly different from the values of partitioning ( $K_{ow}$ ). These data indicate that the process is adsorption not partitioning, although adsorption of naphthalene tended to be linear at all cases. The values of  $\Delta G^0$  are always negative, they become even more negative when the pre-adsorbed surfactant include a phenyl ring in its structure. These data are in accord with adsorption results (Fig. 3 and 4).

**Table 4.** Adsorption coefficients of benzene and naphthalene on montmorillonite surfactant complexes.

Name of complex	Benzene			Naphthalene		
	K <sub>l</sub>	K <sub>oc</sub>	R <sup>2</sup>	K <sub>f</sub>	K <sub>oc</sub>	R <sup>2</sup>
Montmorillonite	0.006		0.95	0.057	-	0.999
Montmorillonite-TMA	0.009	8.95	0.955	0.079	81.25	0.999
Montmorillonite TEA	0.012	5.72	0.995	0.090	46.98	0.999
Montmorillonite-TBA	0.013	3.31	0.97	0.097	25.44	0.999
Montmorillonite-HDTMA	0.01	4.17	0.99	0.148	61.92	0.999
Montmorillonite-BTMA	0.034	6.58	0.99	0.263	57.67	0.999

K<sub>ow</sub> of benzene 135<sup>15</sup> and naphthalene 2290.<sup>9</sup>

**Table 5.** Changes of free energy of benzene and naphthalene adsorption on modified montmorillonite.

Name of complex	Benzene	Naphthalene
Montmorillonite	-85.34 ± (-6.46)	-88.77 ± (-10.24)
Montmorillonite-TMA	-167.49 ± (-10.52)	-179.8 ± (-4.9)
Montmorillonite TEA	-180 ± (-37.54)	-209.86 ± (-11.27)
Montmorillonite-TBA	-226.92 ± (-18.32)	-243.66 ± (-4.63)
Montmorillonite-HDTMA	-816.1 ± (-114.32)	-321.42 ± (-7.37)
Montmorillonite-BTMA	-985.82 ± (-47.64)	-513.21 ± (-14.94)
K <sub>ow</sub>	-12059.7	-19168.2

### Acknowledgement

This work is supported by Deutsche Forschungsgemeinschaft (DFG), grant no Ru 458/18. Dr Y. El-Nahhal acknowledges Alexander von Humboldt Stiftung/Foundation. Fellowship Grant no IV-PAL/1104842 STP, Germany.

### References

- Bartelt-Hunt, S.L., Burns, S.E. and Smith, J.A. 2003. Nonionic organic solute sorption onto two organobentonites as a function of organic-carbon content. *J. Coll. Inter. Sci.* **266**:251-258.
- Boyd, S.A., Lee, J.F. and Mortland, M.M. 1988. Attenuating organic contaminant mobility by soil modification. *Nature* **333**: 345-347.
- Boyd, S.A., Mortland, M.M. and Chiou, C.T. 1988. Sorptive characteristics of organic compounds on hexadecyl ammonium-smectite. *Soil Sci. Soc. Amer. J.* **52**: 652-657.
- Burris, D.R. and Antworth, C.P. 1992. In situ modification of an aquifer material by a cationic surfactant to enhance retardation of organic contaminants. *J. Contam. Hydrol.* **10**:325-337.
- El-Nahhal, Y., Nir, S., Polubesova, T., Margulies, L. and Rubin, B. 1998. Leaching, phytotoxicity and weed control of new formulations of alachlor. *J. Agric. Food Chem.* **46**:3305-3313.
- El-Nahhal, Y., Nir, S., Serban, C., Rabinowitz, O. and Rubin, B. 2000. Montmorillonite-phenyltrimethylammonium yields environmentally improved formulations of hydrophobic herbicides. *J. Agric. Food Chem.* **48**:4791-4801.
- Jaynes, W.F. and Boyd, S.A. 1991. Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays Clay Miner.* **39**:428-436.
- Jaynes, W.F. and Vance, G.E. 1999. Sorption of benzene, toluene, ethylbenzene, and xylene (BTEX) compounds to hectorite clays exchanged with aromatic organic cations. *Clays Clay Miner.* **47**:358-365.
- Karcher, W.W. 1988. Spectral atlas of polycyclic aromatic compounds including data on physico-chemical properties, Occurrence and biological activity. Kluwer Academic Publishing, Boston, Vol. 1.
- Kile, E.D., Chiou, C.T., Zhou, H., Li, H. and Xu, O. 1995. Partition of nonpolar organic pollutants from water to soil and sediment organic matters. *Environ. Sci. Technol.* **29**:1401-1406.
- Kishk, M.F., Abu-Sharar, M.T., Bakry, M.N. and Abu-Donia, B.M. 1979. Sorption-desorption characteristics of methyl-parathion by clays. *Arch. Environ. Contam. Toxicol.* **8**: 637-645.

<sup>12</sup>Koh, S.M. and Dixon, J.B. 2001. Preparation and application of organo-minerals as sorbents of phenol, benzene, and toluene. *Appl. Clay Sci.* **18**:111-122.

<sup>13</sup>Lagaly, G. 1994. Surface and interlayer reactions: Bentonites as adsorbents. *Colloid Polymer Sci.* **97**:137-144.

<sup>14</sup>Lee, J.F., Mortland, M.M., Boyd, S. A. and Chiou, C. T. 1989. Shape-selective adsorption of aromatic molecules from water by tetramethylammonium-smectite. *J. Chem. Soc., Faraday Trans. I* **85**:2953-2963.

<sup>15</sup>Lee, J.F., Mortland, M.M., Chiou, T.C., Kile, E.D. and Boyd, S. A. 1990. Adsorption of benzene, toluene and xylene by two tetramethylammonium-smectite having different charge densities. *Clays Clay Miner.* **38**:113-120.

<sup>16</sup>Lee, Y.S. and Kim, J.S. 2002. Adsorption of naphthalene by HDTMA modified kaolinite and hallaysite. *Appl. Clay Sci.* **22**: 55-63.

<sup>17</sup>Margulies, L., Rozen, H. and Nir, S. 1988. Model for comparative adsorption of organic cations on clays. *Clays Clay Miner.* **36**: 270-276.

<sup>18</sup>McAtee, J.L. Jr. and Harri, B.R. 1977. Gas chromatographic pathway for certain chloro alkylammonium montmorillonite. *Clays Clay Miner.* **25**:90-93.

<sup>19</sup>Merck, E. 1993. Reagents Diagnostics Chemicals. Federal Republic of Germany.

<sup>20</sup>Mortland, M.M., Sun, S. and Boyd, S.A. 1986. Clay-organic complexes as adsorbents for phenol and chlorophenols. *Clays Clay Miner.* **34**:581-586.

<sup>21</sup>Redding, A.Z., Burns, S.E., Upson, R.T. and Anderson, E.F. 2002. Organoclay sorption of benzene as a function of organic carbon content. *J. Coll. Inter. Sci.* **250**:261-264.

<sup>22</sup>Rosen, M.J. 1989. Surfactant and interfacial phenomena. Wiley, New York, p.431.

<sup>23</sup>Rytwo, G., Serban, C., Nir, S. and Margulies, L. 1991. Use of methylene blue and crystal violet for determination of exchangeable cations in montmorillonite. *Clays Clay Miner.* **39**:551-555.

<sup>24</sup>Rytwo, G., Nir, S. and Margulies, L. 1995. Interactions of monovalent organic cations with montmorillonite: adsorption studies and model calculations. *Soil Sci. Soc. Am. J.* **59**:554-564.

<sup>25</sup>Schwarzenbach, P.R., Gschwend, M.P. and Imboden, M.D. 1993. Environmental Organic Chemistry. John Wiley & Sons, Inc New York. USA. pp. 143-149.

<sup>26</sup>Shen, Y.H. 2002. Sorption of benzene and naphthol to organobentonites intercalated with short chain cationic surfactants. *J. Environ. Sci. Health A* **37**:43-54.

<sup>27</sup>Shen, Y.H. 2002. Removal of phenol from water by adsorption flocculation using organobentonite. *Wat. Res.* **36**:1107-1114.

<sup>28</sup>Smith, J.A., Jaffé, P.R. and Chiou, C.T. 1990. Effect of ten quaternary ammonium cations on tetrachlormethane sorption to clay from water. *Environ. Sci. Technol.* **24**:1167-1172.

<sup>29</sup>Smith, J.A., Bartelt-Hunt, S.L. and Burns, S.E. 2003. Sorption and permeability of gasoline hydrocarbons in organobentonite porous media. *J. Hazard. Mat.* **96**:91-97.

<sup>30</sup>Stevens, J.J. and Anderson, S.J. 1996. Orientation of trimethylphenylammonium (TMPA) on Wyoming montmorillonite: Implications for arene sorption. *Clays Clay Miner.* **44**:132-141.

<sup>31</sup>Yang, Y.J., Spencer, R.D., Mersmann, M.A. and Gates, T.M. 1995. Ground water contamination plume differentiation and source determination using BTEX concentration ratios. *Ground Wat.* **33**: 927-935.

<sup>32</sup>Xu, S., Sheng, G. and Boyd, S. A. 1997. Use of organoclays in pollution abatement. *Adv. Agron.* **59**:25-62.