

## Influence of clay mineral structure and surfactant nature on the adsorption capacity of surfactants by clays

M.J. Sánchez-Martín<sup>a,\*</sup>, M.C. Dorado<sup>a</sup>,  
C. del Hoyo<sup>b</sup>, M.S. Rodríguez-Cruz<sup>a</sup>

<sup>a</sup> Instituto de Recursos Naturales y Agrobiología, CSIC, Apdo, 257, 37071 Salamanca, Spain

<sup>b</sup> Departamento de Química Inorgánica, Facultad de Ciencias Químicas,  
P. de la Merced s/n, 37008 Salamanca, Spain

Received 15 January 2007; received in revised form 16 April 2007; accepted 17 April 2007

Available online 24 April 2007

### Abstract

Adsorption of three surfactants of different nature, Triton X-100 (TX100) (non-ionic), sodium dodecylsulphate (SDS) (anionic) and octadecyltrimethylammonium bromide (ODTMA) (cationic) by four layered (montmorillonite, illite, muscovite and kaolinite) and two non-layered (sepiolite and palygorskite) clay minerals was studied. The objective was to improve the understanding of surfactant behaviour in soils for the possible use of these compounds in remediation technologies of contaminated soils by toxic organic compounds. Adsorption isotherms were obtained using surfactant concentrations higher and lower than the critical micelle concentration (cmc). These isotherms showed different adsorption stages of the surfactants by the clay minerals, and were classified in different subgroups of the L-, S- or H-types. An increase in the adsorption of SDS and ODTMA by all clay minerals is observed up to the cmc of the surfactant in the equilibrium solution is reached. However, there was further TX100 adsorption when the equilibrium concentration was well above the cmc. Adsorption constants from Langmuir and Freundlich equations (TX100 and ODTMA) or Freundlich equation (SDS) were used to compare adsorption of different surfactants by clay minerals studied. These constants indicated the surfactant adsorption by clay minerals followed this order ODTMA > TX100  $\gg$  SDS. The adsorption of TX100 and ODTMA was higher by montmorillonite and illite, and the adsorption of SDS was found to be higher by kaolinite and sepiolite. Results obtained show the influence of clay mineral structure and surfactant nature on the adsorption capacity of surfactants by clays, and they indicate the interest to consider the soil mineralogical composition when one surfactant have to be selected in order to establish more efficient strategies for the remediation of soils and water contaminated by toxic organic pollutants.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Adsorption; Surfactant; Clay minerals; Triton X-100; SDS; ODTMA; Surfactant nature; Clay structure

### 1. Introduction

The presence of toxic hydrophobic organic compounds (HOCs) from industrial or agricultural activities, accidental spills or uncontrolled dumping in soils and aquifers is increasingly frequent and generates important environmental problems. In recent years, this has given rise many investigations aimed at developing biological and physicochemical techniques related to the remediation of such systems (soils and water) contaminated by these organic compounds [1,2].

HOCs are adsorbed by soil and sediment components (clay minerals and organic matter), which limits the rate of their extraction from aquifers by conventional technologies such as the successive pumping of water (pump-and-treat). A novel technology in this field is based on HOC extraction by means of a mobile phase that increases their mobility, controlled by the increase in the apparent solubility of the compound in water. An increase in the efficiency of this process has been achieved with *in situ* surfactant-enhanced soil flushing technology [3,4]. Surfactants are good solvents of sparingly soluble organic compounds. Their addition to the hydrophobic pollutant–water system can increase the apparent solubility of the pollutant by its adsorption in the hydrophobic interior of the micelles or aggregates of surfactant molecules formed from

\* Corresponding author. Tel.: +34 923 219606; fax: +34 923 219609.  
E-mail address: [mjesusm@usal.es](mailto:mjesusm@usal.es) (M.J. Sánchez-Martín).

a given concentration, known as critical micelle concentration (cmc). In fact, in recent years many investigations have indicated surfactant-enhanced desorption for organic pollutants on soils [5–8]. However, although surfactants may facilitate the transport of solubilized pollutants, they themselves may be adsorbed by the soil matrix [9–11].

The adsorption of surfactants by soils can result in much surfactant being unavailable for the micellar solubilization of HOCs, thereby decreasing its efficiency for desorption. The presence of adsorbed or immobilized surfactant in soils gives rise to the partition or adsorption of HOCs in the soil–water system, which may contribute to a decrease in the desorption of organic compounds [12]. Therefore, the efficacy of a surfactant-based remediation technology will depend on the distribution of the pollutant in the soil–water system between the surfactant adsorbed and the surfactant in solution (micelles). On the other hand, this property of surfactants (especially of cationic type) to be adsorbed by soil components enables the creation of adsorbent zones for the immobilization of HOCs in soils and can be used in technologies aimed at preventing the pollution of waters by these compounds [13–15].

Surfactant adsorption by soils depends on the type of surfactant and the soil properties. In this sense, the results of different studies addressing the adsorption of anionic and non-ionic surfactants by soils with different composition have revealed discrepancy when attempting to establish the mechanisms by which these compounds are adsorbed by the soil. Whereas some authors have reported a relationship between adsorption and the soil organic matter content [16,17], others have found a relationship between adsorption and the soil clay content [18–20]. Despite these differences, however, only some works [21,22] have attempted to study the influence of the mineralogical composition of the clay fraction in the adsorption of surfactants to explain the behaviour of such compounds in the soil.

Considering the great variability of the soil mineralogical composition, the objective of the present work was to determine the adsorption capacity of surfactants by different clay minerals, and the influence in this process of the ionic or non-ionic nature of the surfactant and its concentration in the clay mineral–water system. Results from this investigation will provide additional insight to evaluate the possibility of using surfactants both in water-decontaminating techniques and for preventing pollution by HOCs and to establish more efficient soil remediation strategies.

To achieve our objective, we studied the adsorption of three surfactants of different type: Triton X-100 (TX100) (non-ionic); sodium dodecylsulphate (SDS) (anionic) and octadecyltrimethylammonium bromide (ODTMA) (cationic) by six clay minerals, four layered (montmorillonite (M), illite (I), muscovite (Mu) and kaolinite (K)), and two non-layered (sepiolite (S) and palygorskite (P)), frequently present in soils. Bearing in mind the surfactant property of existing in aqueous solution as monomers or micelles, depending on their concentration, concentrations lower and higher than the cmc of the surfactant were used. The surfactants TX100 and SDS were selected because they have been reported to be effective for the removal of various hydrophobic pollutants from different supports and ODTMA

was selected as model of a cationic surfactant. We used a series of clay minerals in this study because work published in the literature on the adsorption of surfactants only covers some isolated minerals.

## 2. Materials and methods

### 2.1. Clay minerals

A series of clay minerals (<1 mm) with different structures, representative of the different types of clays in soils, were used in the study: Tidinit montmorillonite (M) (Morocco), Cuenca kaolinite (K) (Spain), Peñausende muscovite (Mu) (Spain), Vallecas sepiolite (S) (Spain), Bercimuel palygorskite (P) (Spain) and Fithian illite (I) (Illinois) from the American Petroleum Institute. The characteristics of these samples are included in Table 1. The cation exchange capacity (CEC) was determined by the ammonium acetate method [23]. Carbon content was determined using an automatic Wösthoff Carmograph 12H Omega (Bochum, Germany) carbon analyzer. Specific surface area was determined by the N<sub>2</sub> adsorption–desorption method at –196 °C on an Micromeritics Gemini analyzer (Norcross, USA). Also, the internal surface area was determined for montmorillonite and muscovite, using the method of Dyal and Hendricks [24]. Natural clay minerals and these samples treated with the surfactants were studied qualitatively by the X-ray diffraction technique [25] using Cu K $\alpha$  radiation on a PW1710 Philips Analytical diffractometer controlled by a X'Pert Quantify software (EA Almelo, The Netherlands).

### 2.2. Surfactants

Polyethylene glycol *tert*-octylphenyl ether-Triton X-100 (TX100) was supplied by Sigma–Aldrich (St. Louis, MO). It is a non-ionic surfactant (C<sub>8</sub>H<sub>17</sub>C<sub>6</sub>H<sub>4</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>x</sub>OH) with a cmc of 0.15 g/L (0.24 mM) [26] and it has an average of 9.5 ethylene oxide units per molecule with an average molecular weight of 625 g/mol. Sodium dodecylsulphate-SDS (C<sub>12</sub>H<sub>24</sub>NaSO<sub>4</sub>) is an anionic surfactant with a cmc of 2.38 g/L (8.25 mM) [5] and its molecular weight is 288.4 g/mol. Unlabelled SDS (95% purity) and <sup>14</sup>C-labelled SDS with a specific activity of 2.00 MBq/mg ( $\geq$ 95% purity) were supplied by Aldrich Chemical Co (Milwaukee, WI). Octadecyltrimethylammonium bromide-ODTMA (CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>N(Br)(CH<sub>3</sub>)<sub>3</sub>) was supplied by Sigma–Aldrich. It

Table 1  
Characteristics of the clay minerals studied

Clay mineral	CEC (cmol/kg)	OC (%)	Specific surface (m <sup>2</sup> /g)	<i>d</i> (001) (Å)
Montmorillonite	82	0.06	750 <sup>a</sup>	13.4
Illite	15	1.74	57	10.0
Kaolinite	6.1	0.10	12	7.16
Muscovite	21	0.10	105 <sup>a</sup>	10.0 (12.6) <sup>b</sup>
Sepiolite	5.0	0.08	189	12.3
Palygorskite	27	0.46	254	10.6

<sup>a</sup> Total superficial area.

<sup>b</sup> Impurities of montmorillonite.

is a cationic surfactant with a cmc of 0.12 g/L (0.30 mM) [27], and a molecular weight of 392.5 g/mol. The three surfactants were used as received.

### 2.3. Adsorption isotherms

Adsorption isotherms of surfactants by clay minerals were obtained using the batch equilibrium technique. A sorbent/solution ratio of 1:200 was used to study adsorption of TX100 or SDS, and a lower sorbent/solution ratio of 1:500 was used to study adsorption of ODTMA to avoid removal of too much solute and to allow accurate determination of residual values of surfactant. A series of surfactant solutions with concentrations in the range 25–10,000  $\mu\text{g/mL}$  were used, the purpose was to include lower and higher concentrations than the cmc of each surfactant. The suspensions were shaken intermittently at adequate temperature to maintain surfactant in solution ( $30 \pm 2^\circ\text{C}$ ) for 24 h in a thermostatted chamber (1 h every 2 h). Preliminary experiments revealed contact for 24 h to be long enough for equilibrium to be reached. Subsequently, the suspensions were centrifuged at 4000–10,000 rpm for 5–30 min, and the surfactant equilibrium concentration was determined. The amount of surfactant adsorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the clay mineral. All experiments were carried out by duplicate or triplicate when necessary.

### 2.4. Analytical determination of surfactants

TX100 concentrations were determined in the equilibrium solutions by UV spectroscopy at 223 nm using a Varian Cary 100 spectrophotometer (Palo Alto, CA). The linear range of TX100 concentrations used to determine the equilibrium concentrations was 1–100  $\mu\text{g/mL}$  ( $r \geq 0.99$ ;  $p < 0.001$ ). Higher concentrations than this range were previously diluted. To determine the  $^{14}\text{C}$ -SDS concentration at equilibrium, a 1-mL aliquot of supernatant solution was withdrawn from each tube, 4 mL of scintillation liquid was added, and its activity was measured in disintegrations per minute (dpm) on a LS 6500 liquid scintillation counter (Beckman Coulter, Fullerton, CA). In all solutions, determinations were carried out in duplicate, and the coefficient of variation was always  $< 2\%$ . The dpm value recorded for the supernatant aliquot was related to the dpm obtained for the aliquots of the respective standards of surfactant solutions and the equilibrium concentration was determined. ODTMA concentrations were carried out from the total organic carbon determination in solution using a carbon analyzer Shimadzu 5050 (Shimadzu, Columbia, MD). Potassium hydrogen phthalate ( $> 99.95\%$  of purity) (Sigma–Aldrich) was used to prepare standards in the range of 10–1000  $\mu\text{g/mL}$  concentrations. Determinations of all surfactants were always performed against a clay mineral blank to correct for possible interferences in the measurement of the surfactant, and clay-free controls were also treated in the same way as the samples to quantify the loss of compounds through mechanisms other than sorption by clay minerals.

### 2.5. Data analysis

Adsorption data were fitted to the Freundlich and Langmuir models. The linearized form of the Freundlich adsorption equation is:  $\log C_s = \log K_f + n_f \log C_e$ , where  $C_s$  (mg/g) is the amount of adsorbed surfactant;  $C_e$  ( $\mu\text{g/mL}$ ) is the equilibrium concentration of surfactant in solution,  $K_f$  ( $\text{mg}^{1-n_f} \text{L}^{n_f} / \text{g}$ ) is a constant that indicate the adsorption capacity of surfactants by clay minerals and  $n_f$  is a coefficient which indicate the variation in adsorption as a function of concentration. The linearized form of Langmuir adsorption equation is  $C_e/C_s = C_e/K_1 + 1/K_1 K_2$  where  $K_1$  (mg/g) is a constant that indicate the maximum capacity of surfactants by clays and  $K_2$  (L/mg) is an index of adsorption energy and determines the magnitude of the initial slope of the isotherm. Standard deviation (S.D.) was used to indicate variability in the adsorption constants among duplicates.

## 3. Results and discussion

### 3.1. Adsorption of Triton X-100

Adsorption isotherms of TX100 by all the clay minerals studied are shown in Fig. 1. Fig. 1A shows the isotherms in the complete range of concentrations used (25–10,000  $\mu\text{g/mL}$ ) and Fig. 1B shows the isotherms in enlarged scale up to when the first degree of saturation of the clay mineral surface was obtained. According to the initial slope of the isotherms they correspond to the L- and S-types [28]. L-type isotherms indicate an initial rapid adsorption and an adsorption that becomes increasingly more difficult for the adsorbate molecules as the sites are filled. These isotherms point to a strong interaction between the surfactant and the clay surface and were obtained for montmorillonite and illite. The S-type isotherms indicate an increased affinity for the adsorbate: the more solute there is already adsorbed, the easier it is for additional amounts to become fixed. This implies a side-by-side association between adsorbed molecules, helping to hold them to the surface and these isotherms were obtained for muscovite, kaolinite, sepiolite and palygorskite.

Additionally, based on the shapes of the upper part of the curves, all isotherms can be classified in subgroup 4 of the L- and S-types of Giles' classification [28], with a first *plateau* (or inflection), a linear portion and a second *plateau*. The adsorption of TX100 by the different clay minerals should occur in the form of monomers until the first *plateau*, or first degree of saturation of the adsorbent surface, forming a monolayer or hemimicelle of surfactant. The adsorption limit is reached when the surfactant is present in the clay-surfactant system equilibrium solution at concentrations close to or slightly above the cmc (150  $\mu\text{g/mL}$ ); i.e., when the molecules of surfactant in solution begin to form micelles and equilibrium is set up between the monomers of surfactant that tend to form micelles in solution and those that tend to be retained by the clay surface [29,30]. This situation is given for TX100 initial concentrations in solution of  $< 1000 \mu\text{g/mL}$  in M;  $< 750 \mu\text{g/mL}$  in I and S and  $< 250 \mu\text{g/mL}$  in K, Mu and P indicating differences in the adsorption capacity of the surfactant by the clay minerals studied.

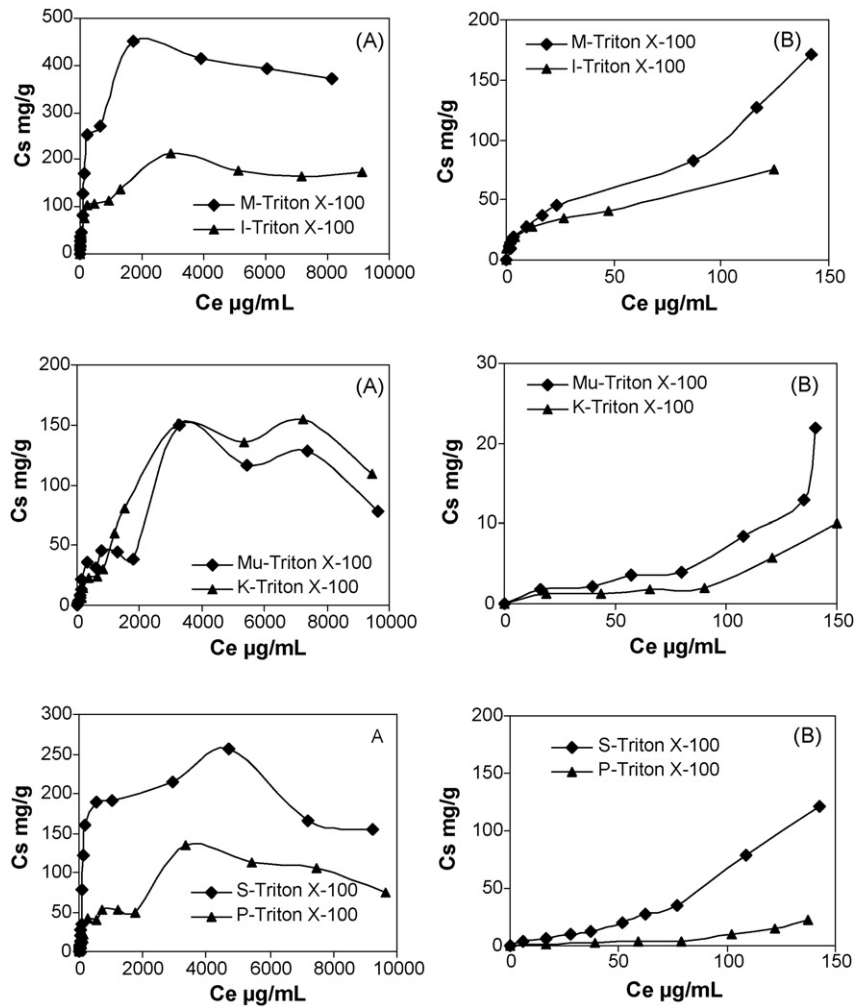


Fig. 1. Adsorption isotherms of Triton X-100 by all the clay minerals studied in the complete range of concentrations used (A) and up to when the first degree of saturation of the clay mineral surface was obtained (B).

The adsorption of surfactant monomers should occur through an ion-dipole-type interaction or hydrogen bond between the hydrophilic or polar part of the surfactant molecule and the water molecules around the exchange cations of the clay minerals, as occurs with other polar organic compounds [31,32].

After the first *plateau*, the isotherms of all clay minerals show a rapid increase in TX100 adsorption with the concentration of surfactant before to reach a more or less irregular stabilization of adsorption. This increase in adsorption should give rise to the formation of a bilayer or admicelle by adsorption of surfactant monomers on the hemicelles present on the surface of the adsorbent, through van der Waals forces. The additional adsorption of TX100 increased rapidly for the clay minerals M, I and S with isotherms showing a short first *plateau*, indicating that the molecules of adsorbed TX100 expose a surface that has nearly the same affinity for more solute as the original surface had. The longer *plateau* shown by the isotherms of Mu, K and P would indicate that a high-energy barrier must be overcome before additional adsorption can occur on new sites. Addressing the adsorption of other non-ionic surfactants by montmorillonite, some authors have also indicated dispersion of clays in the presence of elevated surfactant concentrations as

possible cause of this rapid increase in adsorption [33], or the retention of surfactant micelles in the remaining voids of the clay surface or between the structures forming the admicelles after a sufficiently large critical mass of surfactant has been adsorbed [34]. Yuan and Jafvert [35] explained this situation on the basis of the presence of mixtures of surfactant oligomers with different chain lengths and with different adsorption characteristics.

The isotherms obtained were fitted to the Freundlich adsorption equation ( $r \geq 0.88$ ,  $p < 0.001$ ) and to the Langmuir adsorption equation ( $r \geq 0.91$ ,  $p < 0.001$ ) and the values of the  $K_f$  and  $n_f$  (Freundlich) and  $K_1$  and  $K_2$  (Langmuir) constants are included in Table 2. The  $K_1$  values ranging between 99 and 385 mg/g. The highest values correspond to the layered minerals M and I and the non-layered mineral S in agreement with the information obtained from the shape of the isotherms. The  $K_2$  values, related to the energy of the adsorbent–adsorbate interaction, range between 0.0004 (K) and 0.0086 (M), the highest values also corresponding to the minerals with the highest adsorption capacity.  $K_f$  constant values range between 0.30 and 15.5, varying in the same sense as the  $K_1$  values. The values of  $n_f$  are very low (0.29–0.71), indicating considerable variation in

Table 2

Freundlich constants ( $K_f$ ,  $n_f$ ), Langmuir constants ( $K_1$ ,  $K_2$ ) and correlation coefficients ( $r$ ) for the adsorption of Triton X-100 by clay minerals

Clay mineral	$K_f \pm \text{S.D.}^a$	$n_f \pm \text{S.D.}^a$	$r$	$K_1 \pm \text{S.D.}^a$	$K_2$	$r$
Montmorillonite	$11.5 \pm 2.56$	$0.45 \pm 0.02$	0.97	$385 \pm 1.13$	0.0086	0.99
Illite	$15.5 \pm 0.57$	$0.29 \pm 0.01$	0.98	$175 \pm 1.73$	0.0079	0.99
Muscovite	$0.32 \pm 0.00$	$0.69 \pm 0.02$	0.94	$111 \pm 3.27$	0.0008	0.91
Kaolinite	$0.30 \pm 0.04$	$0.71 \pm 0.05$	0.96	$166 \pm 11.5$	0.0004	0.91
Sepiolite	$2.80 \pm 0.37$	$0.54 \pm 0.03$	0.88	$172 \pm 2.35$	0.0081	0.98
Palygorskite	$0.37 \pm 0.06$	$0.68 \pm 0.04$	0.93	$99 \pm 1.54$	0.0011	0.94

<sup>a</sup> Data are given by mean  $\pm$  standard deviation.

adsorption with the concentration of surfactant in solution, as expected from the shape of the isotherms.

The value of  $K_1$  found for the adsorption of TX100 by montmorillonite lies within the range of values found for the adsorption of other non-ionic surfactants, such as Brij 56 and Igepal CO 720 by smectite [33] and Brij 35 by different montmorillonites [34]. The greatest adsorption of TX100 by M with respect to the other minerals studied can be explained by its high specific surface, the surfactant is adsorbed into the inter-layer space of the mineral, in agreement with the increase in the  $d(001)$  basal spacing observed only in this silicate by X-ray diffraction (Fig. 2). This spacing increases from 13.4 Å in the natural sample to 17.8 Å when the concentration of TX100 increase, indicating the intercalation of the surfactant into the interlayer space of the montmorillonite. The increase of 8.2 Å over the value of 9.6 Å of dehydrated M probably corresponds an arrangement of the molecules adsorbed in two layers parallel to the basal surface [33]. The  $d(001)$  spacing was not further increased for initial concentrations above 6000  $\mu\text{g/mL}$  indicating that the access of the surfactant to the interlayer space is limited. In the rest of the clay minerals no modifications of the  $d(001)$  basal spacing was observed after the adsorption of TX100 with respect to the natural samples.

The adsorption capacity of TX100 by the non-layered clay mineral sepiolite is also high, although its specific surface is lesser than that of palygorskite. It can be explained by considering the possible adsorption of the surfactant on the structural channels of the mineral, greater than in the case of palygorskite [36].

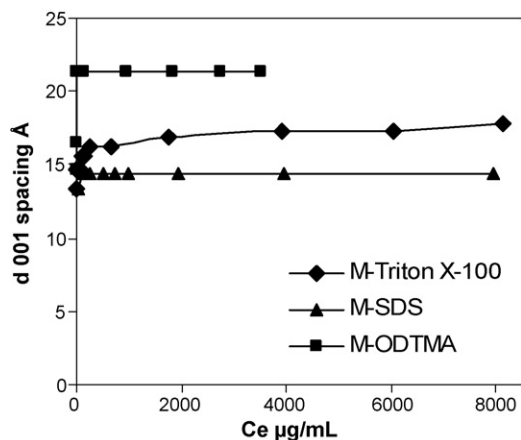


Fig. 2. Modification of the  $d(001)$  basal spacing of montmorillonite after adsorption of Triton X-100, SDS and ODTMA at different concentrations.

### 3.2. Adsorption of SDS

On the basis of their initial slope (Fig. 3), the isotherms of SDS adsorption by the clay minerals studied, obtained in a concentration range between 25 and 10,000  $\mu\text{g/mL}$ , correspond to the S-type of the classification of Giles et al. [28]. However,

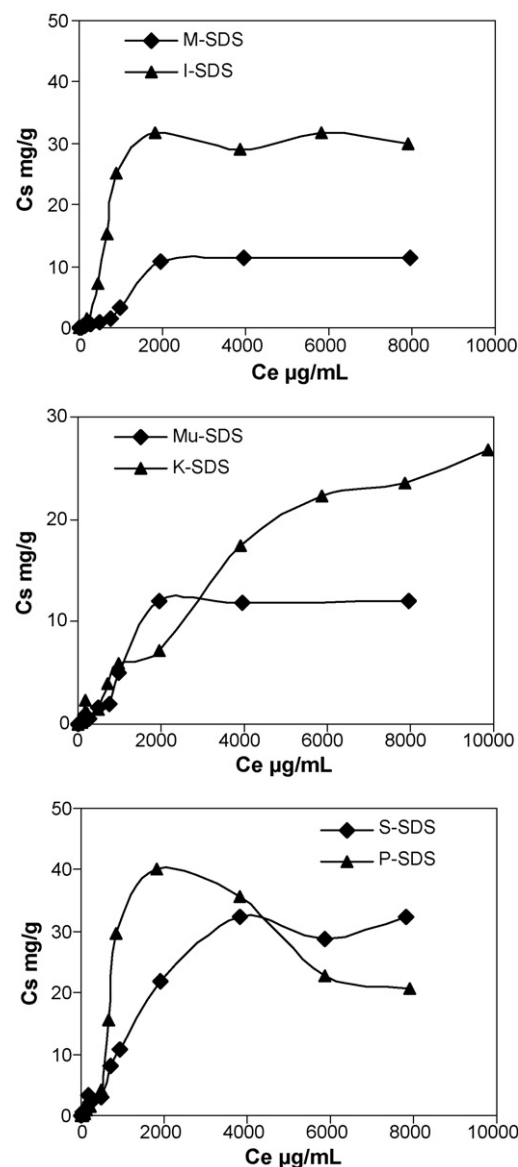


Fig. 3. Adsorption isotherms of SDS by all the clay minerals studied in the complete range of concentrations used.

Table 3  
Freundlich constants ( $K_f$ ,  $n_f$ ), Langmuir constants ( $K_1$ ,  $K_2$ ) and correlation coefficients ( $r$ ) for the adsorption of SDS by clay minerals

Clay mineral	$K_f \pm \text{S.D.}^a$	$n_f \pm \text{S.D.}^a$	$r$	$K_1 \pm \text{S.D.}^a$	$K_2$	$r$
Montmorillonite	0.002 ± 0.001	1.04 ± 0.23	0.98	48.3 ± 7.39	0.0001	0.34
Illite	0.008 ± 0.003	1.04 ± 0.04	0.94	90.1 ± 9.69	0.0002	0.26
Muscovite	0.007 ± 0.001	0.88 ± 0.04	0.96	24.8 ± 1.91	0.0002	0.63
Kaolinite	0.010 ± 0.002	0.88 ± 0.05	0.96	87.0 ± 1.09	0.0001	0.30
Sepiolite	0.016 ± 0.006	0.89 ± 0.04	0.97	66.2 ± 4.08	0.0001	0.69
Palygorskite	0.006 ± 0.001	1.05 ± 0.09	0.92	44.2 ± 1.21	0.0002	0.56

<sup>a</sup> Data are given by mean ± standard deviation.

according to the shape of the upper part of the curve, they correspond to different subgroups of this classification. The isotherms obtained for M, I and Mu correspond to subgroup 2, showing a *plateau* indicating saturation of the adsorbent surface. An isotherm with almost no *plateau*, corresponding to subgroup 3, was obtained for K, indicating the possible adsorption of several layers of the adsorbate by this mineral, and isotherms with a maximum corresponding to the subgroup mx were obtained for the non-layered silicates (S and P).

The shape of the isotherms responds to different adsorption states of the surfactant by the different clay minerals studied as in the case of the TX100 adsorption. An increase of surfactant monomer adsorption occurs for all the minerals when the SDS concentration in solution increases until a point when the surfactant concentration in the equilibrium solution reaches a value close to or slightly higher than the cmc (2.38 µg/mL). In this state, the adsorption of SDS by M, I and Mu becomes stabilized, forming a hemimicelle at the adsorbent surface. Liu et al. [37] also indicated the stabilization of the SDS adsorption by soils when the cmc is reached, indicating the surfactant adsorption by electrostatic forces with positive charges existing on the edge surface of the minerals. This type of isotherm has also been described for the adsorption of the anionic surfactants dodecylbenzene sulphonate by kaolinite [38] and by soils [18], Aerosol-OT and SDS by soils [39].

The adsorption of SDS by kaolinite increased, but without becoming stabilized in the concentration range studied. Ko et al. [40] reported a *plateau* of SDS sorption by kaolinite at above 10 times the cmc of surfactant. For this mineral, the increase in SDS adsorption when the equilibrium concentration is greater than the cmc would indicate a different mechanism of adsorption of SDS monomers than for the rest of the layered clay minerals. SDS may be adsorbed by K as an anion owing to the ability of this mineral to develop a variable charge and to adsorb completely dissociated anions by ligand exchange [38,41]. The adsorption of SDS by the layered minerals, M, I and Mu, should not be possible through the same mechanism of adsorption indicated for K owing to their low anion exchange capacity and the almost negligible variable charge that these minerals may generate [42].

The adsorption isotherms of SDS by the non-layered minerals show a maximum before the stabilization of adsorption. A greater interaction between the molecules of adsorbate in solution than between the molecules of adsorbate and the adsorbent must occur when the SDS concentration in solution increases due to an increase in the electrostatic repulsion between anionic

head groups when total coverage of the non-layered mineral adsorbent surface is attained [37].

The isotherms obtained for the complete range of concentrations used were fitted to the Freundlich adsorption equation ( $r \geq 0.92$ ,  $p < 0.001$ ) and to the Langmuir adsorption equation ( $r \geq 0.26$ ). All adsorption constants obtained are included in Table 3 although correlation coefficients of fitted Langmuir equation are not always significant. The  $K_f$  values ranged between 0.002 and 0.016. The highest values correspond to K and S and the lowest to M. The  $n_f$  values ranged between 0.88 and 1.05, showing that there was no strong variation in adsorption with the concentration of surfactant in solution. The  $K_f$  values obtained were not related with the specific surface of clay minerals and they were always lower than those obtained for the adsorption of TX100 (more than one order of magnitude), even though the cmc of SDS is very high (2.38 g/L) and the surfactant is in the form of monomers over a broad concentration range. This indicates the influence of the structure of the surfactant in the adsorption process.

It should be noted that the adsorption of SDS by the different clay minerals did not modify the  $d(001)$  basal spacing corresponding to each of them, as seen from the X-ray diagrams obtained with samples treated with SDS at different concentrations.

### 3.3. Adsorption of ODTMA

Fig. 4 shows the adsorption isotherms of ODTMA by the clay minerals in the complete range of concentrations studied (25–6000 µg/mL). These isotherms correspond to subgroup 2 of the H-type of Giles' classification [28] for all the minerals indicating high affinity between the adsorbent and adsorbate. Adsorption was almost complete at low initial concentrations of the adsorbate, the equilibrium concentration of the solution being very close to zero. When the surfactant concentration was increased adsorption stabilizes and a *plateau* was reached. The equilibrium concentration at which this *plateau* was reached differed from one mineral to another, although for all the clay minerals it was completely attained for an initial concentration below the cmc of the surfactant (120 µg/mL) [43,44]. This type of isotherm has also been reported by other authors in the adsorption of other cationic surfactants by different clay minerals [45–47].

The isotherms obtained were fitted to the Freundlich adsorption equation, with values of ( $r \geq 0.84$  ( $p < 0.001$ )) and to the Langmuir adsorption equation, with higher correlation

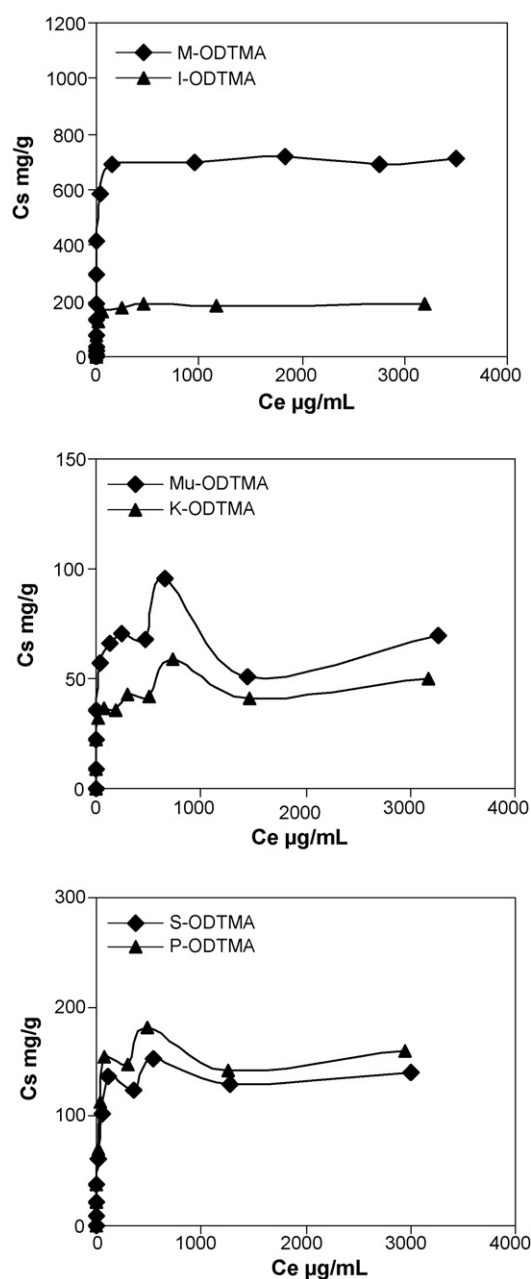


Fig. 4. Adsorption isotherms of ODTMA by all the clay minerals studied in the complete range of concentrations used.

coefficients ( $r \geq 0.99$ ,  $p < 0.001$ ). Table 4 shows the values of the adsorption constants obtained from these equations for the different minerals together with the linear correlation coefficients.  $K_f$  constants ranged between 29.6 and 175, and the  $n_f$  coefficients ranged between 0.06 and 0.25, indicating strong dependence of the adsorption with the concentration of surfactant in solution. The  $K_1$  values indicating the maximum ODTMA adsorption capacity by the clay minerals ranged between 714 and 49.0. The highest adsorption value corresponded to montmorillonite with the highest value of CEC and the order of adsorption for the different minerals was  $M > I > S > P > Mu > K$ . The adsorption of ODTMA should occur through cation exchange of the inorganic cations of the clay minerals by the organic cations [43,48]. Moreover, it was higher than that of TX100 for all the minerals, with the exception of K and S, which have a very low CEC (Table 1).

ODTMA adsorption values as a function of the surfactant initial concentration were normalized with respect to the CEC of each of the clay minerals. It was seen that the maximum adsorption values lie in a broad range, representing 2.8; 4.1; 1.1; 2.0; 8.6 and 1.8 times the CEC of M, I, Mu, K, S and P, respectively. These results show that there was not linear relationship between adsorption and CEC of different clay minerals, the maximum adsorption of ODTMA was always greater than the CEC of each of them, and this was depending on the packing of organic cations on the mineral external surfaces. An increase in the adsorption of organic cations by clay minerals greater than the CEC has also been found for the adsorption of hexadecyltrimethylammonium and benzyldimethyl tetradecylammonium by M [49] and thioflavin-T for S [47]. Adsorption greater than the CEC of the minerals is attained owing to the presence of initial concentrations several-fold higher than the CEC, but always lower than the cmc of the surfactant, which means that the surfactant is always in the form of monomers. The excess ODTMA adsorbed can be explained in terms of the additional adsorption of molecules of ODTMA bromide by a hydrophobic interaction [45,48] or through a mechanism of molecular aggregation [47].

The process of ODTMA adsorption by the clay minerals was also monitored by X-ray diffraction. Modification of the  $d(001)$  basal spacing was only found in the case of montmorillonite. This spacing increased from 13.6 Å in the natural sample to 21.1 Å in the samples treated with a solution of ODTMA at a concentration of 2000 µg/mL (Fig. 2). The increase in the basal spacing observed upon increasing the concentration of ODTMA in solution ranged between 5 and 11.5 Å and must cor-

Table 4  
Freundlich constants ( $K_f$ ,  $n_f$ ), Langmuir constants ( $K_1$ ,  $K_2$ ) and correlation coefficients ( $r$ ) for the adsorption of ODTMA by clay minerals

Clay mineral	$K_f \pm S.D.^a$	$n_f \pm S.D.^a$	$r$	$K_1 \pm S.D.^a$	$K_2$	$r$
Montmorillonite	175 ± 1.81	0.21 ± 0.00	0.84	714 ± 3.34	0.290	0.99
Illite	71.8 ± 0.82	0.15 ± 0.00	0.90	188 ± 0.55	0.129	0.99
Muscovite	34.0 ± 0.26	0.11 ± 0.01	0.88	66.7 ± 0.15	0.089	0.99
Kaolinite	29.6 ± 1.53	0.06 ± 0.01	0.89	49.0 ± 2.72	0.029	0.99
Sepiolite	40.9 ± 1.08	0.18 ± 0.02	0.96	139 ± 1.37	0.069	0.99
Palygorskite	32.6 ± 4.56	0.25 ± 0.19	0.88	158 ± 1.89	0.083	0.99

<sup>a</sup> Data are given by mean ± standard deviation.

respond to a monolayer, bilayer or pseudotrilyer arrangement of ODTMA molecules, with the hydrocarbon chain parallel to the surface of the silicate [45,50]. The  $d$  (001) spacing was not further increased even when the surfactant concentration was increased three times more and the surfactant was present in solution as micelles. Nevertheless, Mishael et al. [27] using techniques of fragmentation and fluorescence electron microscopy have shown that under certain experimental conditions there is evidence to suggest direct adsorption of ODTMA micelles by montmorillonite.

In the other clay minerals, no modifications in the  $d$  (001) basal spacing with respect to the natural samples were observed after the adsorption of ODMTA. In the case of the non-layered minerals S and P, the adsorption of ODTMA could occur in the structural channels owing to the similar size of the channels and head group of cationic surfactant [51].

#### 4. Conclusions

The surfactants TX100, SDS and ODTMA are adsorbed by the clay minerals montmorillonite, illite, kaolinite, muscovite sepiolite and palygorskite to a greater or lesser extent. The adsorption isotherms obtained indicate different adsorption states for each of the clay minerals and for each of the surfactants. When the cmc of the surfactant in the equilibrium solution is reached, adsorption tends to stabilize, especially in the case of surfactants having charge (SDS and ODMTA). These compounds are adsorbed as monomers and form hemimicelles on the adsorbent surface. In the case of TX100, adsorption by all the minerals increases considerably when the equilibrium concentration is much higher than the cmc of the surfactant. This compound could be adsorbed forming admicelles on the adsorbent surface or as micelles on voids remaining on the surface of the clays or in the voids between the structures that form the admicelles adsorbed. This situation does not occur with charged surfactants, possibly because adsorption is depending on the specific sites of the clay minerals in accordance with their positive or negative charge. The results obtained show that the highest adsorption was obtained for the cationic surfactant ODMTA, except for the minerals kaolinite and sepiolite, with a lower CEC. The greatest adsorption of TX100 is seen for montmorillonite and illite, and that of SDS for kaolinite and sepiolite. It may be seen that the adsorption of the surfactants by the clay minerals depends on both the nature of the surfactants and the structure of the clay minerals. The results obtained indicate that the selection of a surfactant, to be used in technologies aimed at soil and water remediation or to prevent soil contamination by toxic organic compounds, requires a previous knowledge of the fraction clay mineralogy of the soil where it is going to be applied. The type of clay minerals will determine the efficiency of this technology and will permit to decide on the selection of a cationic, anionic or non-ionic surfactant to be applied.

#### Acknowledgements

This work was funded in Spain by the “Ministerio de Ciencia y Tecnología” and the “Junta de Castilla y León” as part of

Projects REN2000-0884/TECNO and CSI15-03, respectively. The authors thank L.F. Lorenzo, J.M. Ordax and A. González Núñez for technical assistance.

#### References

- [1] J.A. Smith, S.E. Burns, *Physicochemical Groundwater Remediation*, Kluwer Academic, New York, 2001.
- [2] K.L. Roehl, T. Meggyes, F.G. Simon, D.I. Stewart, *Long-term Performance of Permeable Reactive Barriers*, Elsevier, Amsterdam, 2005.
- [3] D. Di Cesare, J.A. Smith, Surfactant effects on desorption of nonionic compounds, *Rev. Environ. Contam. Toxicol.* 134 (1994) 1–29.
- [4] D.A. Sabatini, R.C. Knox, J.H. Harwell, *Surfactant-Enhanced Subsurface Remediation*, American Chemical Society, Washington, 1995.
- [5] R. Doong, W. Lei, T. Chen, C. Lee, J. Chen, W. Chang, Effect of anionic and non-ionic surfactants on sorption and micellar solubilization of monocyclic aromatic compounds, *Water Sci. Technol.* 34 (1996) 327–334.
- [6] S. Deshpande, L. Wesson, D. Wade, D.A. Sabatini, J.H. Harwell, Doufax surfactant components for enhancing contaminant solubilization, *Water Res.* 34 (2000) 1030–1036.
- [7] M. Sánchez-Camazano, S. Rodríguez-Cruz, M.J. Sánchez Martín, Evaluation of component characteristics of soil-surfactant-herbicide system that affect enhanced desorption of linuron and atrazine preadsorbed by soils, *Environ. Sci. Technol.* 37 (2003) 2758–2766.
- [8] M.J. Sánchez Martín, M.S. Rodríguez-Cruz, M. Sánchez-Camazano, Study of the desorption of linuron from soils to water enhanced by the addition of an anionic surfactant to soil-water system, *Water Res.* 37 (2003) 3110–3117.
- [9] D.H. Lee, R.D. Cody, D.J. Kim, S. Choi, Effect of soil texture on surfactant-based remediation of hydrophobic organic-contaminated soil, *Environ. Int.* 27 (2002) 681–688.
- [10] Z. Zheng, J.P. Obbard, Evaluation of an elevated non-ionic surfactant critical micelle concentration in a soil/aqueous system, *Water Res.* 36 (2002) 2667–2672.
- [11] G.G. Ying, Fate, behavior and effects of surfactants and their degradation products in the environment, *Environ. Int.* 32 (2006) 417–431.
- [12] M.S. Rodríguez-Cruz, M.J. Sánchez-Martín, M. Sánchez-Camazano, Enhanced desorption of herbicides sorbed on soils by addition of Triton X-100, *J. Environ. Qual.* 33 (2004) 920–929.
- [13] S.A. Boyd, W.F. Jaynes, B.S. Ross, Immobilization of organic contaminants by organo clays: application to soil restoration and hazardous waste containment, in: R.A. Baker (Ed.), *Organic Substances and Sediments in Water*, Lewis Publishers, New York, 1991, pp. 181–201.
- [14] G.Y. Sheng, X.R. Wang, S.N. Wu, S.A. Boyd, Enhanced sorption of organic contaminants by smectitic soils modified with a cationic surfactant, *J. Environ. Qual.* 27 (1998) 806–814.
- [15] M.S. Rodríguez-Cruz, M.J. Sánchez-Martín, M.S. Andrades, M. Sánchez-Camazano, Comparison of pesticide sorption by physicochemically modified soils with natural soils as a function of soil properties and pesticide hydrophobicity, *Soil Sediment Contam.* 15 (2006) 401–415.
- [16] K. Fytianos, E. Voudrias, A. Papamichaeli, Behaviour and fate of linear alkylbenzene sulfonate in different soils, *Chemosphere* 36 (1998) 2741–2746.
- [17] I.F. Paterson, B.Z. Chowdhry, P.J. Carey, S.A. Leharne, Examination of the adsorption of ethylene oxidepropylene oxide triblock copolymers to soil, *J. Contam. Hydrol.* 40 (1999) 37–51.
- [18] Z. Ou, A. Yediler, Y. He, A. Kettrup, T. Sun, Adsorption of alkylbenzene sulfonate (LAS) on soils, *Chemosphere* 32 (1996) 827–839.
- [19] B.J. Bronawell, H. Chen, W. Zhang, J.C. Westall, Sorption of non-ionic surfactants on sediment materials, *Environ. Sci. Technol.* 31 (1997) 1735–1741.
- [20] Y.H. Shen, Sorption of non-ionic surfactants to soil: the role of soil mineral composition, *Chemosphere* 41 (2000) 711–716.
- [21] L. Zhu, K. Yang, B. Lou, B. Yuan, A multi-component statistic analysis for the influence of sediment/soil composition on the sorption of a non-ionic surfactant (Triton X-100) onto natural sediments/soils, *Water Res.* 37 (2003) 4792–4800.



- [22] M.S. Rodríguez-Cruz, M.J. Sanchez-Martín, M. Sanchez-Camazano, A comparative study of adsorption of an anionic and non-ionic surfactant by soils based on physicochemical and mineralogical properties of soils, *Chemosphere* 61 (2005) 56–64.
- [23] M.L. Jackson, *Soil Chemistry Analysis*, Prentice Hall, Englewood Cliffs, NJ, 1958.
- [24] R.S. Dyal, S.D. Hendricks, Total surface of clays in polar liquids as a characteristic index, *Soil Sci.* 69 (1950) 421–428.
- [25] M. Robert, Principes de détermination qualitative des minéraux argileux a l'aide des rayons X, *An. Agron.* 26 (1975) 363–399.
- [26] S. Sun, W.P. Inskeep, S.A. Boyd, Sorption of nonionic organic compounds in soil-water systems containing a micelle-forming surfactant, *Environ. Sci. Technol.* 29 (1995) 903–913.
- [27] Y. Mishael, T. Undabeytia, G. Rytwo, B. Papahadjopoulos-Sternberg, B. Rubin, S. Nir, Sulfometuron incorporation in cationic micelles adsorbed on montmorillonite, *J. Agric. Food Chem.* 50 (2002) 2856–2863.
- [28] C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, *J. Chem. Soc.* 111 (1960) 3973–3993.
- [29] Z. Liu, D.A. Edwards, R.G. Luthy, Sorption of non-ionic surfactants onto soil, *Water Res.* 26 (1992) 1337–1345.
- [30] M. Scherer, S. Richter, R.L. Valentine, P.J.J. Alvarez, Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean up, *Crit. Rev. Environ. Sci. Technol.* 30 (2000) 363–411.
- [31] M. Sánchez-Camazano, M.J. Sánchez-Martín, Factors influencing interactions of organophosphorus pesticides with montmorillonite, *Geoderma* 29 (1983) 107–118.
- [32] J.A. Rausell-Colon, J.M. Serratos, Reactions of clays with organic substances, in: A.C.D. Newman (Ed.), *Chemistry of Clays and Clay Minerals*, The Mineralogical Society, London, 1987, pp. 371–422.
- [33] Y. Deng, J.B. Dixon, G.N. White, Intercalation and surface modification of smectite by two non-ionic surfactants, *Clays Clay Miner.* 51 (2003) 150–161.
- [34] L.S. Sonon, M.L. Thompson, Sorption of a non-ionic polyoxyethylene lauryl ether surfactant by 2:1 layer silicates, *Clays Clay Miner.* 51 (2005) 45–54.
- [35] C. Yuan, C.T. Jafvert, Sorption of linear alcohol ethoxylate surfactant homologs to soils, *J. Contam. Hydrol.* 28 (1997) 311–325.
- [36] S. Yariv, Introduction to organo-clay complexes and interactions, in: S. Yariv, H. Cross (Eds.), *Organo-Clay Complexes and Interactions*, Marcel Dekker, New York, 2002, pp. 39–111.
- [37] M. Liu, D. Roy, G. Wang, Reactions and transport modelling of surfactant and anthracene in the soil flushing process, *Waste Manag.* 5 (1995) 423–432.
- [38] N.V. Sastry, J.M. Séquaris, M.J. Schwuger, Adsorption of polyacrylic acid and sodium dodecylbenzenesulfonate on kaolinite, *J. Colloid Interface Sci.* 171 (1995) 224–233.
- [39] Z.N. Atay, O. Yenigün, M. Asutay, Sorption of anionic surfactants SDS, AOT and cationic surfactant Hyamine 1622 on natural soils, *Water Air Soil Pollut.* 136 (2002) 55–67.
- [40] S.O. Ko, M.A. Schlautman, E.R. Carraway, Partitioning of hydrophobic organic compounds to sorbed surfactants. 1. Experimental studies, *Environ. Sci. Technol.* 32 (1998) 2769–2775.
- [41] J.B. Dixon, S.B. Weed, *Minerals in Soil Environments*, Soil Science Society of America, Madison, WI, 1977.
- [42] C.J.B. Mott, Anion and ligand exchange, in: D.J. Greenland, M.H.B. Hayes (Eds.), *The Chemistry of Soil Processes*, John Wiley and Sons, New York, 1981, pp. 179–219.
- [43] E. Sabah, M. Turan, M.S. Celik, Adsorption mechanism of cationic surfactants onto acid- and heat-activated sepiolites, *Water Res.* 36 (2002) 2964–2957.
- [44] L. Zhu, B. Chen, S. Tao, C.T. Chiou, Interactions of organic contaminants with mineral-adsorbed surfactants, *Environ. Sci. Technol.* 37 (2003) 4001–4006.
- [45] S. Xu, S.A. Boyd, Cationic surfactant adsorption by swelling and non-swelling layer silicates, *Langmuir* 11 (1995) 2508–2514.
- [46] J. Wang, B. Han, M. Dai, H. Yan, Z. Li, R.K. Thomas, Effects of chain length and structure of cationic surfactants on the adsorption onto Na-kaolinite, *J. Colloid Interface Sci.* 213 (1999) 596–601.
- [47] B. Casal, J. Merino, J.M. Serratos, E. Ruíz-Hitzky, Sepiolite-based materials for the photo- and thermal-stabilization of pesticides, *Appl. Clay Sci.* 18 (2001) 245–254.
- [48] Z. Li, L. Gallus, Adsorption of dodecyl trimethylammonium and hexadecyltrimethylammonium onto kaolinite—competitive adsorption and chain length effect, *Appl. Clay Sci.* 35 (2007) 250–257.
- [49] S. Koh, J. Dixon, Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene, *Appl. Clay Sci.* 18 (2001) 111–122.
- [50] Z. Klapayta, T. Fujita, N. Iyi, Adsorption of dodecyl- and octadecyltrimethylammonium ions on a smectite and synthetic micas, *Appl. Clay Sci.* 19 (2001) 5–10.
- [51] Z. Li, C. Willms, K. Kniola, Removal of anionic contaminants using surfactant-modified palygorskite and sepiolite, *Clays Clay Miner.* 51 (2003) 445–451.