



Organomontmorillonites Having Different Charges for Wastewater Treatment: Adsorption of Phenol Molecules

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Abstract: The intercalation of the hexadecyl trimethyl ammonium cations into two montmorillonites with different charge values is reported. The effect of selected counter ions (Br^- , Cl^- and OH^-) on the adsorption of C16TMA was investigated. The aim of this study is to gain further insight into the influence of the type of surfactant solutions and the physicochemical properties of raw clays on their intercalation behaviours. The intercalated amounts depended on the CEC values of the starting clays and the type of C16TMA solutions. The content of surfactants was higher in the raw clay with higher charge, and followed the trend $\text{C16TMABr} > \text{C16TMACl} > \text{C16TMAOH}$. These organoclays were tested in the phenol sorption. The amount of phenol was improved with the increase of the initial concentration and decreased with the low content of surfactant intercalated within the interlayer spacing of the starting montmorillonites.

Keywords: *montmorillonites, organoclays, x-ray diffraction, adsorption, phenol.*

Introduction

Smectites are widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high surface area, and resulting strong adsorption/absorption capacities (Sheng *et al.*, 2001). In expanding clays, the most common dioctahedral smectite is montmorillonite, which has two silica-oxygen tetrahedral sheets sandwiching an aluminium or magnesium octahedral sheet, where an aluminium or magnesium ion is octahedrally coordinated to six oxygens or hydroxyls. Because of replacement of silicon by aluminium in the tetrahedral layers or similar replacement of aluminium ions by magnesium ions montmorillonite layers are negatively charged (Briendly & Brown, 1980). Thus, cations such Na, K, and Ca are attracted to the mineral surface to neutralize the negative layer charges. The total number of monovalent cations per gram clay required to compensate for the mineral's negative charge is defined as the cation exchange capacity (CEC) of the mineral. Because of the hydration of inorganic cations on the exchange sites, the clay mineral surface is hydrophilic in nature which makes natural clays ineffective sorbents for organic compounds and nonionic organic compounds (NOC) although it has a high surface area (Dultz & Bors, 2000; Prost & Yaron, 2001).

In attempt to design new adsorbents to remove non-ionic organic contaminants from waste water, several researchers have replaced the inorganic exchange cations with quaternary amine cations $[(\text{CH}_3)_2\text{NHR}]^+$, where R is a large alkyl hydrocarbon chain, yields organoclays with organophilic clay surfaces, by simple ion-exchange reaction (Mortland *et al.*, 1986; Koh & Dixon, 2001). It is generally accepted that adsorption of hydrophobic long-chain quaternary ammonium cations onto clays occurs according to the ion-exchange mechanism (Polabusova *et al.*, 1997). The adsorption extend of such cations can approach double the cation-exchange capacity (CEC).

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Earlier workers reported that the lyophilic tails from cations of long-chain quaternary ammonium salts, previously retained on the clay, lead to the adsorption of organics such as benzene, toluene, phenol, and its chlorinated compounds and herbicides (Koh & Dixon, 2001; Shen, 2002).

The Quaternary Ammonium Compounds (QAC) are a class of organic cations sharing a common structure: a positively charged ammonium moiety and one or more hydrophobic alkyl chains of varying length (Merianos, 1991). The intercalation of the hexadecyl trimethylammonium (C16TMA) cationic surfactant into swelling montmorillonites has been studied in the interest of their potential applications of the intercalated clays as sorbents for hydrophobic contaminants from aqueous solutions (Boyd *et al.*, 1988; Jaynes & Boyd, 1999). The C16TMA-clays were used as a template for the preparation of porous materials (Galarneau *et al.*, 1997; Kooli *et al.*, 2006), as well in the preparation of polymer layered silicate nanocomposites (Vaia & Giannelis, 1997; Alexandre & Dubois, 2000).

The commonly used surfactants have been limited to bromide or chloride forms. The thermal stability of quaternary alkylammonium salts depends on the basicity of the anions (Cope & Trumbull, 1960). During the exchange reaction, the anions (Br or Cl) are co-adsorbed for concentrations above the CEC values (Patzkó & Dékány, 1993; Li & Bowman, 1997). To the best of our knowledge, systematic studies between the different surfactant solutions were not reported for smectite clay minerals. Recently we have reported the effect of counter anion existing in the surfactant (C16TMA) solution on the intercalation properties of raw and acid-activated montmorillonites (Kooli & Magusin, 2005). In this study, we report the adsorption behaviour of the C16TMA onto two montmorillonites with different CEC values. Three different forms of surfactant solutions (Br, Cl, and OH) were used, and to elucidate how charge characteristics of clay affect the mechanistic function of the organoclay in NOC sorption. Sorption isotherms for phenol on various organosmectites were measured. Results from this work will provide valuable information on using organoclay as a sorbent for purifying NOC contaminated water.

Materials and Method

Materials

Two clays were purchased from different sources, and they are used as received. Na-cloisite (CN) with CEC of 0.84 meq/g was obtained from Southern Clay products, Inc. (USA). A polymer grade montmorillonite (PG) with CEC of 1.40 meq/g was received from Nanocor, (USA).

The organoclays were prepared as described previously (Kooli *et al.*, 2006). Different amounts of hexadecyltrimethylammonium (C16TMA) hydroxide or chloride $((\text{CH}_3)_3\text{N}(\text{C}_{16}\text{H}_{33})^+\text{OH}^-$ or $(\text{CH}_3)_3\text{N}(\text{C}_{16}\text{H}_{33})^+\text{Cl}^-$, from TCI company were added to 25 mL of deionised water, then one gram of each clay was suspended in this solution, and stirred overnight at room temperature. The materials were collected by filtration, washed with deionised water to remove excess of surfactants, and then dried at room temperature. For comparison, we have used the same molar amounts of C16TMA cations in the bromide form as in hydroxide and chloride one.

The corresponding amount of C16TMABr (Across organics) was dissolved in 25 mL of deionized water. Whenever necessary to completely dissolve the surfactants, the solution was heated at 50 °C. The organoclays were prepared using the procedure described above.

Phenol Sorption

Phenol adsorption isotherms were carried out by the batch equilibrium technique. 0.1 g of organoclay together with a pre-calculated amount of phenol volume of phenol stock (in methanol) and sufficient deionized water to bring the total volume to 25 ml. The pH of each sample was controlled at about 7 by HCL and NaOH solutions. Phenol has a pKa value of 10.1,

therefore, it largely exist in neutral form at pH 7. The samples were equilibrated for 4 hrs by rotating the glass tubes at room temperature. The aqueous phase was separated by centrifugation. The difference in the amount before and after sorption reveals the amount of phenol sorbed.

Characterization

The powder x-ray diffraction (XRD) patterns were recorded using a Bruker D8 advance diffractometer with $\text{CuK}\alpha$ radiation. The content of carbon, nitrogen, and hydrogen in the products were determined with EURO EA elemental analyzer. The amount adsorbed on the organoclays is calculated from the analytical carbon content. The differential thermal and thermogravimetric analyses of the surfactant montmorillonites were obtained using TA Instruments calorimeter, SDT2960. The measurements were carried out in air flow 100 ml min^{-1} heated from room temperature to 800°C , at a heating rate of 5°C min^{-1} . The pH values of the pure surfactant solutions and mixed with montmorillonites were measured by Cyber scan pH 510 from Eutech instruments (Singapore), at room temperature.

The concentration of phenol was performed by high-performance liquid chromatography (HPLC) equipped with a reverse-phase column and an ultraviolet (UV) detector with isocratic operation (1 ml min^{-1}) of mobile phase (40/60 vol. % acetonitrile/aqueous solution).

Results and Discussion

Powder XRD

Figure 1 illustrates the powder XRD of PG clay and C16TMA-PG using different forms of surfactant solutions. The PG clay exhibited a basal spacing of 1.25 nm and it expanded with the intercalation of the surfactants. At fixed starting concentration of 2.47 mmole, a value of 3.61 nm was obtained starting from C16TMABr or C16TMACl solutions. However, the basal spacing was reduced to 2.41 nm when C16TMAOH solution was used. The crystallinity of the organoclays improved after the reaction.

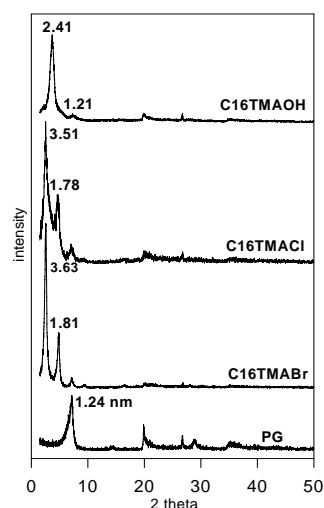


Figure 1. Powder XRD of PG clay exchanged with different surfactant solutions of 2.47 mmole.

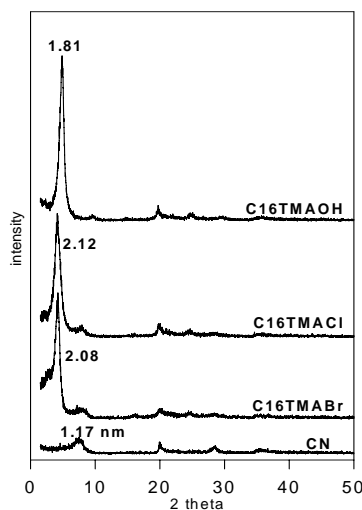


Figure 2. Powder XRD of CN clay exchanged with different surfactant solutions of 2.47 mmole.

The cloisite clay (CN) exhibited a basal spacing of 1.1 nm, indicating a less content of water between the layers. The exchange with surfactant solution (2.47 mmole) led to an expansion of 2.12 nm, independent of the used C16TMA (Br or Cl) solutions, although the up taken surfactants were beyond the CEC values (115%), no further expansion of the basal distance was observed, as reported for PG clay. This fact indicated that the excess of C16TMA

was adsorbed on external surfaces or on crystal edges (Kooli et al., 2005). However, a lower value of 1.81 nm was obtained using the C16TMAOH solution. The crystallinity of the organoclays was improved compared to starting CN clay as we reported above, due to the rearrangement of clay particles.

The initial starting concentration affected the basal spacing of the C16TMA-PG obtained from C16TMABr and C16TMACl solutions. Gradual increase of the basal spacing was observed from 1.25 nm to 2.40 nm at starting concentration of 0.83 mmole, in agreement with reported literature (Lee & Kim, 2002). The maximum of 3.62 nm was achieved at starting concentration of 2.47 mmole, and no further change in the basal spacing was observed for higher C16TMA concentrations (Figure 3).

Different behavior was noted for the CN clay (Figure 4); the starting concentrations of the surfactants did not affect the basal spacing values, independently of the loading concentrations and the forms of the surfactant solutions. It was expanded only from 1.17 nm to 2.12 nm for C16TMABr and Cl solutions, and to 1.81 nm using C16TMAOH solution.

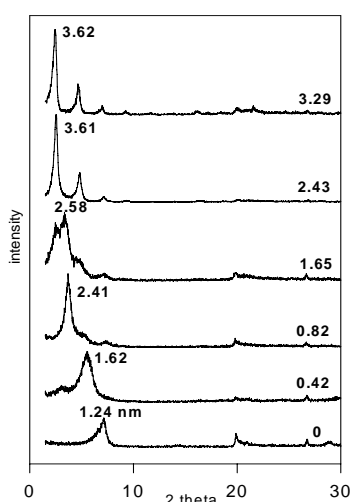


Figure 3. Powder XRD patterns of PG clay exchanged with different loading concentrations (mmole) of C16TMABr.

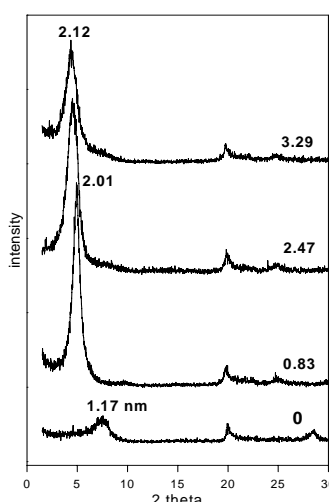


Figure 4. Powder XRD patterns of CN clay exchanged with different loading concentrations (mmole) of C16TMACl.

The intensity of the reflection at 3.61 nm increased as the basal spacing of 2.4 nm decreased upon adsorption of surfactant molecules in excess of CEC from Br and Cl solutions. Xi et al. reported that excess of adsorbed amounts above the CEC did not result in a further expansion of Wyoming montmorillonite clay (with a CEC of 0.72 mmole/g) using an octadecyltrimethylammonium bromide solution (Xi et al., 2004). In our case, the swelling was difficult to be achieved in C16TMAOH solution for PG and CN clays.

From structural point of view, the basal distance of 1.8 nm reflected a lateral-bilayer arrangement of C16TMA surfactants, while a transition to pseudotrimolecular layer arrangement occurred values of 2.1~2.4 nm, for adsorbed values below the CEC (Lagaly, 1986). The interlayer gallery of 2.8 nm (deduced from the basal spacing of 3.7 nm, at 115 % CEC) exceeded the length of the fully extended of C₁₆TMA cations ~ 2.2 nm (Venkataraman & Vasudevan, 2002), indicating that the surfactants adopted a tilted bilayer parafilm-structure with an angle of 39° with respect to the clay sheets. The tilted angle value was close to that reported in the case C16TMA adsorbed on acid-activated montmorillonites (Kooli & Magussin, 2005).

Elemental analysis

Elemental analysis of the obtained C16TMA-clays is presented in Table 1, at a fixed starting concentration of 2.47 mmole; the PG clay (with higher CEC) adsorbed more C16TMA cations than CN clay (with low CEC).

Table 1. C, H, N analysis of C16TMA-clays form different surfactant solutions

| Samples | C% | H% | N% | Ads.* |
|-------------|-------|------|------|-------|
| C16TMABr-PG | 39.23 | 5.88 | 1.34 | 1.61 |
| C16TMACl-PG | 30.77 | 4.88 | 0.96 | 1.26 |
| C16TMAOH-PG | 18.91 | 3.60 | 0.69 | 0.93 |
| C16TMABr-CN | 31.86 | 4.63 | 1.37 | 1.31 |
| C16TMACl-CN | 20.47 | 4.36 | 1.19 | 0.84 |
| C16TMAOH-CN | 18.91 | 3.60 | 0.96 | 0.78 |

* corresponds to adsorbed amounts mmole/g

The amounts up taken by both clays were much higher from the C16TMABr compared to C16TMACl solution, then dropped below the CECs (66 to 84 %) when the C16TMAOH was used. We have attempted to improve the up taken amounts, by increasing the starting concentrations of C16TMAOH up to 20 mmole. However, the adsorbed values were independent of the initial concentrations for PG and CN clays. Meanwhile, we were able to control the adsorbed amounts on PG clay using different starting concentrations below 2.47 mmole, using either C16TMABr or C16TMACl solutions.

The additional C16TMA adsorption from bromide and chloride solutions occurred beyond the CEC (115 to 140 %). The up take of alkylammonium surfactants exceeding the exchange capacity of the mineral is well known for smectite and vermiculites (Narine & Guy, 1981; Xu & Boyd, 1994; Xie et al. 2001). Adsorption is caused by the hydrophobic interactions (van der Waals forces) between the alkyl chains of surfactant ions bound to the exchange positions of the silicate and the same ions present in the solution. The formation of organo-cation aggregates on the clay surface was also found when large organic cations were adsorbed on clays in excess of the CEC (Narine & Guy, 1981).

Thermogravimetric analysis

Obviously the surfactants were intercalated into the clay minerals. The TGA-DTG analysis indicated that the hydrophilic character of the starting clay PG and CN was modified, and the weight loss related to the release of intercalated water was reduced in the range of 70 to 130 °C, due to the exchange of the Ca or Na cations by the surfactants. The intensity of the weight loss in this range is reduced in accord with the decrease in water content for the organoclay. This observation may be explained in terms of the hydrophobic nature of C16TMA montmorillonites. Since the residual water molecules in the organoclay are contained in the spaces ('pores') between the interlayer C16TMA ions, rather than being directly associated with the surfactant, they are relatively weakly held (Smith *et al.*, 1990). An additional weight loss related to C16TMA was recorded /d between 190 to 450 °C (Kooli *at al.*, 2005). The thermal behavior of the organoclays in 0.

Phenol adsorption

No adsorption was observed on pure montmorillonites under the experimental conditions prevailing here. Figure 5 shows the sorption isotherms of phenols on different organoclays exchanged with different C16TMA cations. As expected, sorption isotherms are linear over a wide range of solution concentrations consistent with the concept of phenol partitioning into the C16TMA-derived organic phase (Smith *et al.*, 1990; Smith & Galan, 1995).

The high-charge C16TMABr-PG retained more phenol than the low-charge C16TMABr-CN. Evidently the higher charge density on PG caused the formation of a more effective partition phase for phenol uptake. Close spaced C16TMA ions on CN or PG with a spacing of 1.8 nm, formed compactly packed C16TMA aggregates through enhanced nonpolar interaction of the alkyl groups of C16TMA ions. The C16TMA exchanged CN clays exhibited less sorption affinity to the phenol compared to the PG montmorillonites, independently of the carbon contents.

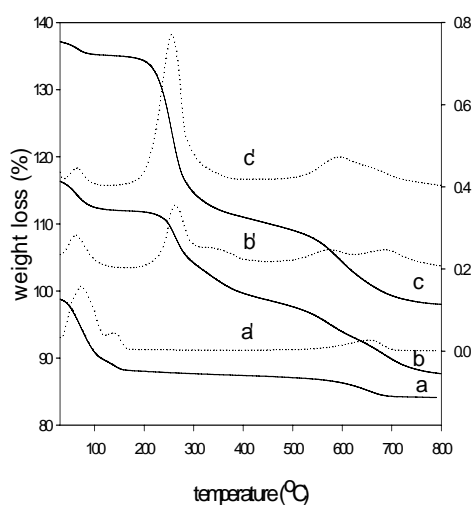


Figure 5. TGA-DTG curves of (a) PG montmorillonite, (b) C16TMABr-PG and (c) C16TMACl-CN. The dotted curves correspond to the derivative of the TGA curves respectively.

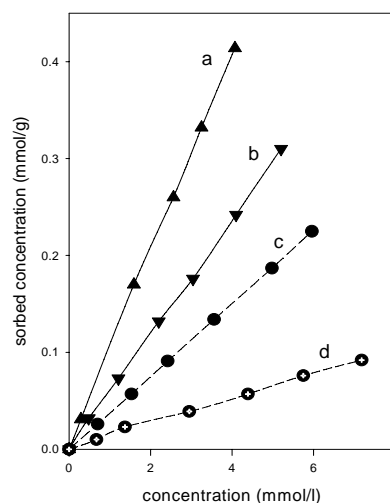


Figure 6. Sorption isotherms of phenol on different C16TMA-montmorillonites. (a) C16TMABr-PG, (b) C16TMAOH-PG, (c) C16TMABr-CN and (d) C16TMAOH-CN.

The fact that an adsorption of phenol is now observed on the montmorillonite/C16TMA complexes in all cases (in contrast to the C16TMA-free montmorillonite) is to be attributed to hydrophobization of the surface by the C16TMA. The previously hydrophilic montmorillonite surface becomes more hydrophobic especially due to the alkyl chains of the C16TMA so that the equilibrium between the dissolved and the adsorbed state of the non polar phenol is now shifted to the adsorbed state.

In the case of short surfactant, it was reported that a closer packing of the surfactant in the high-charge smectite resulted in a decrease in free area between the surfactant ions which seems to be the major factor responsible for the reduced phenol uptake (Shen, 2004). The capacity of organoclays for taking up no-ionic organic pollutants from water is closely related to the organic matter content. The C16TMA-PG was more effective than that on CN for phenol uptake due to enhanced nonpolar interaction of the alkyl groups of C16TMA on high charge density surface (Churchman *et al.*, 2006).

Conclusion

The C16TMA adsorption is influenced by charge density on smectite, and by the counter ions in the C16TMA solutions. In some cases amounts beyond the CEC values from C16TMABr and C16TMACl solutions were up taken by the montmorillonite with higher CEC values, leading to further expansion of the interlayer space up to 3.7 nm, and which not the case for a montmorillonite with a lower CEC. However, when the C16TMAOH solution was used, the adsorbed amounts were about 65 to 80 % of CEC, with less expansion of the interlayer spacing, independently of the starting raw materials.

From the perspective of pollution control (e.g. waste water treatment), an organoclay with higher carbon content is desirable. Therefore, high charge smectite should be used for preparing organoclay intercalated with organic cations with long alkyl chain.

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