

# ORGANO-CLAYS AS SORBENTS OF HYDROPHOBIC ORGANIC CONTAMINANTS: SORPTIVE CHARACTERISTICS AND APPROACHES TO ENHANCING SORPTION CAPACITY

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**Abstract**—When clay minerals, notably smectites, intercalate organic cations, their interlayer surfaces change from hydrophilic to hydrophobic. The resultant intercalates, known as organo-clays (OCs), have a large affinity for hydrophobic organic contaminants (HOCs). Organo-clays are used as sorbents of HOCs in wastewater treatment and as sorptive barriers in landfill liners. The structural and sorptive characteristics of OCs with respect to HOCs have been studied extensively, and a large volume of literature has accumulated over the past few decades. The interactions of OCs with HOCs and the various approaches to improving the sorption capacity of OCs are reviewed here, with particular reference to the application of novel analytical techniques, such as molecular modeling, to characterizing the OC–HOC interaction.

**Key Words**—Hydrophobic Organic Contaminants, Organo-clays, Sorption, Environmental Remediation, Interlayer Space.

## INTRODUCTION

Clay minerals are phyllosilicates in which the individual layers are composed of a tetrahedral (T) and an octahedral (O) sheet in either a 1:1 or 2:1 proportion. In the smectite group of phyllosilicates, among which montmorillonite (Mnt) is the prime example, the O sheet is sandwiched between two inward-pointing T sheets. Due to isomorphous substitution (*e.g.* Al<sup>3+</sup> for Si<sup>4+</sup> in the T sheet and/or Al<sup>3+</sup> for Mg<sup>2+</sup> in the O sheet), the layers carry a permanent negative charge which is balanced by inorganic cations ('counterions') occupying interlayer space (Brigatti *et al.*, 2013; He *et al.*, 2014).

Clay minerals are ubiquitous in soils and sediments. Because of their small particle size, large surface area, and unique charge characteristics, clay minerals can sorb a wide range and variety of contaminants (Mortland, 1970; Theng, 1974; Yariv and Cross, 2002; Li *et al.*, 2004; Chappell *et al.*, 2005; Yuan *et al.*, 2013). Being abundant, inexpensive, and environmentally benign, clay minerals (unmodified or after surface modification) have found applications in different environmental remediation processes (Bailey *et al.*, 1999; Churchman *et al.*, 2006; Gates *et al.*, 2009; Gupta and Suhas, 2009; Ruiz-Hitzky *et al.*, 2010; Gupta and Bhattacharyya, 2012).

The interlayer surface of smectites (*e.g.* Mnt), however, is essentially hydrophilic because of the presence of hydrated counterions, and hence has a low

affinity for HOCs (Chiou, 2002; Yuan *et al.*, 2013). This incompatibility between mineral surface and contaminant species can be overcome by replacing the interlayer inorganic counterions with organic cations. The resultant organically modified smectites, referred to as 'organo-clays' (OCs), are efficient sorbents of dissolved HOCs. Organo-clays can also serve as sorptive barriers in landfill liners, preventing the down-gradient movement of contaminants to groundwater and aquifers (McBride *et al.*, 1975; Mortland *et al.*, 1986; Boyd *et al.*, 1988a, 1988b; Jaynes and Boyd, 1990; Lee *et al.*, 1990; Zhu, L. *et al.*, 1997; Lo, 2001; Lo and Yang, 2001; Probst and Yaron, 2001; Beall, 2003; Smith *et al.*, 2003; Bartelt-Hunt *et al.*, 2005; Theng *et al.*, 2008; Zhu, R. *et al.*, 2009a; Sarkar *et al.*, 2012; Yuan *et al.*, 2013).

The synthesis, characterization, and sorptive characteristics of OCs have been described in several reviews (Beall, 2003; Čapková *et al.*, 2003; de Paiva *et al.*, 2008; Theng *et al.*, 2008; Sarkar *et al.*, 2012; He *et al.*, 2013, 2014). Nevertheless, some aspects of the interlayer structure (particularly in an aqueous phase where most sorption processes take place) and sorptive characteristics of OCs still need to be clarified. In this respect, molecular modeling has provided valuable information (Heinz *et al.*, 2007; Zhu, R. *et al.*, 2011a, 2011b; Liu *et al.*, 2009; Fu and Heinz, 2010a, 2010b; Praus *et al.*, 2011).

Enhancing the sorption capacity of OCs, a critical aim in the environmental application of OCs, has been addressed by several investigators in terms of the structural and sorptive characteristics of OCs (Smith *et al.*, 1990; Borisover *et al.*, 2010a, 2010b, 2012; Park *et al.*, 2011; Zhu, R. *et al.*, 2010, 2014a; Zhu, J. *et al.*,

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2011b; Lee and Tiwari, 2012; Yuan *et al.*, 2013; Nafees and Waseem, 2014). The OCs can generally be categorized into two types. Type I OCs are obtained by intercalation of small, compact organic cations, such as tetramethylammonium (TMA), while type II OCs are formed by modifying smectites with cationic surfactants such as hexadecyltrimethylammonium (HDTMA) (Theng *et al.*, 2008; Yuan *et al.*, 2013). Accordingly, the approaches used to enhance sorption capacity are often type-specific.

The present comprehensive review of the literature summarizes the information on structural and sorptive characteristics of OCs before describing systematically the various approaches to enhancing their sorption capacity. The environmental applications of OCs are also outlined, and the issues that need to be resolved by future studies are indicated.

### STRUCTURAL CHARACTERISTICS OF OCs

Because OCs have many industrial applications, notably as components in the formulation of polymer nanocomposites, paints, cosmetics, and oil-well drilling fluids, their structural characteristics have been the subject of many investigations (Chen *et al.*, 2008; de Paiva *et al.*, 2008; Akkal *et al.*, 2013; Bergaya *et al.*, 2013; Galimberti *et al.*, 2013). This review focuses on the structural characteristics of OCs which relate to their sorption behavior and efficiency, with special reference to interlayer complexes of Mnt with quaternary ammonium cations (QACs) (Smith *et al.*, 1990; Theng *et al.*, 2008; Sarkar *et al.*, 2012; Yuan *et al.*, 2013).

X-ray diffraction (XRD) has been the most widely used technique for assessing the intercalation of QACs

into smectite and their arrangement in the interlayer space (Lagaly, 1976; Zhu, J. *et al.*, 2003; Kwolek *et al.*, 2003; Xi *et al.*, 2005, 2007, 2010; He *et al.*, 2006a, 2006b, 2010; Slade and Gates, 2007; Lagaly *et al.*, 2013). In type I OCs, the organic cations form discrete “pillars” in the interlayer space (Barrer, 1978; Janeba *et al.*, 1998; Kwolek *et al.*, 2003; Zhu, R. *et al.*, 2012a; Zhao and Burns, 2012a, 2012b, 2013). On the other hand, cationic surfactants in type II OCs can adopt various interlayer arrangements, such as lateral monolayer, lateral bilayer, pseudo-trilayer, paraffin-type monolayer, and paraffin-type bilayer, with their alkyl chains assuming an all-*trans* conformation (Figure 1a) (Lagaly, 1976; Zhu, J. *et al.*, 2003; He *et al.*, 2005a, 2005b; Zhao and Burns, 2012a, 2012b; Lagaly *et al.*, 2013). Studies using spectroscopic techniques (Fourier transform infrared – FTIR, Raman), nuclear magnetic resonance (NMR), and thermal analysis, however, have indicated that cationic surfactants are intercalated with different all-*trans/gauche* conformation ratios the magnitude of which tends to increase with surfactant loading and molecular size (Figure 1b) (Vaia *et al.*, 1994; Xie *et al.*, 2001; He *et al.*, 2004a, 2004b; Osman *et al.*, 2004; Zhu, J. *et al.*, 2005).

Note that the majority of investigations to date have described the use of dry OCs. The environmental applications (*e.g.* wastewater treatment) of OCs, however, are commonly carried out in the presence of water which can enter and expand the interlayer space of the samples (Xu and Boyd, 1995; Zhu, J. *et al.*, 2008, 2011a). Thus, information on the structural characteristics of dry OCs cannot simply be extrapolated to aqueous conditions. The effect of water on the structural properties of OCs has not been investigated fully.

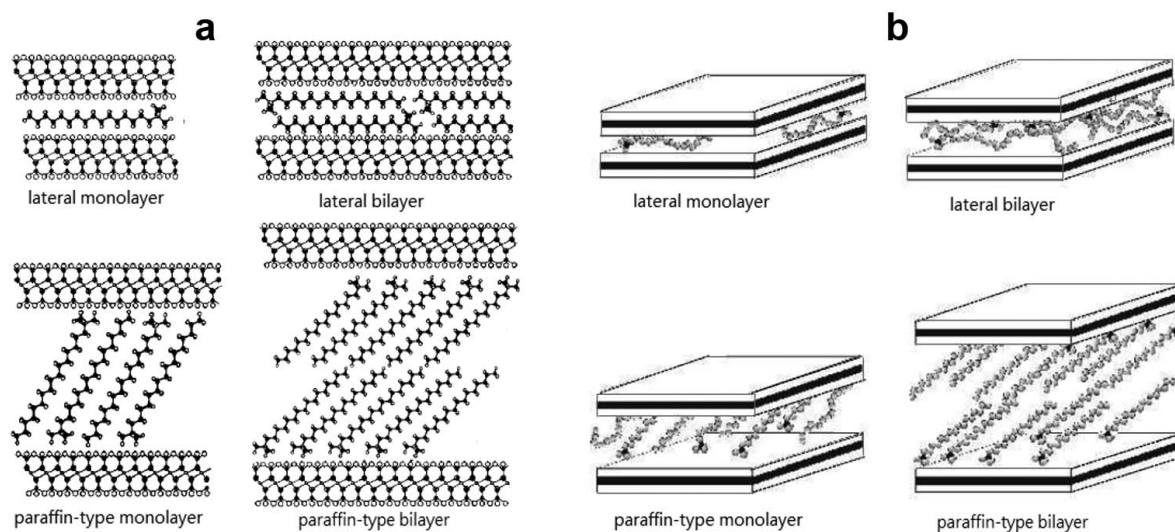


Figure 1. Diagram showing the arrangements of HDTMA in the interlayer space of montmorillonite with increasing loading level: (a) arrangements derived from XRD measurements (image reproduced from Zhu, J. *et al.*, 2003); (b) arrangements derived from NMR spectroscopic analysis (image reproduced from He *et al.*, 2004c, with the permission of The Clay Minerals Society).

Recently, molecular modeling has proven to be a powerful tool in investigating the interlayer structure of clay minerals and OCs, as it can give an atomic-level (or even electronic-level) insight into the interlayer structure of the samples. In addition, molecular modeling can conveniently show the effect of various factors (*e.g.* smectite layer-charge density, water addition/saturation) on structural characteristics (Cygan *et al.*, 2004; Heinz *et al.*, 2005, 2007; Liu *et al.*, 2007, 2009; Zhu, R. *et al.*, 2011a, 2011b; Zhao and Burns, 2012a, 2012b, 2013; Greathouse and Cygan, 2013; Zhou *et al.*, 2014).

Here we summarize the results of experimental and molecular modeling studies of the interlayer structure of OCs, using TMA-Mnt and HDTMA-Mnt as representatives of types I and II OCs, respectively. The interlayer TMA cations in (dry) Mnt act as pillars, propping the silicate layers apart permanently (Figure 2a). The resultant TMA-Mnt is therefore highly porous, giving a specific surface area (SSA) of 100–300 m<sup>2</sup>/g (Lee *et al.*, 1989; Kukkadapu and Boyd, 1995; Ruan *et al.*, 2008; Zhu, R. *et al.*, 2014a). As low-charge Mnt requires less TMA to balance the negative layer charge, the interpillar separation here is greater than that in high-charge samples. Accordingly, the SSA of TMA complexes with low-charge Mnt is greater than the value given by its high-charge counterpart (Ruan *et al.*, 2008; Zhu, R. *et al.*, 2014a).

*et al.*, 2014a). The basal spacing of TMA-Mnt, deduced from molecular modeling studies, is comparable to the value measured by XRD (Čapková *et al.*, 2000, 2003; Zhu, R. *et al.*, 2012a; Zhao and Burns, 2012a; Scholtzova *et al.*, 2013). Those workers further showed that the hydrogen atoms at the opposite ends of the TMA cation were recessed ('keyed') into the ditrigonal cavities in the siloxane plane of opposing silicate layers.

Using XRD, Ruan *et al.* (2008) showed that water saturation of TMA-Mnt does not cause significant interlayer expansion, suggesting that the water molecules essentially occupy the pore space between the TMA pillars (Figure 2b). Molecular modeling results indicate that the interlayer water molecules are associated with both TMA cations and siloxane surfaces (Martos-Villa *et al.*, 2013), while FTIR spectroscopy would suggest a preference for TMA over siloxane (Stevens *et al.*, 1996). Indeed, molecular modeling (Zhu, R. *et al.*, 2011a; Marry *et al.*, 2008, 2011) and neutron scattering (Sandi *et al.*, 1999) studies indicate that the interlayer water molecules in Mnt are H-bonded to oxygen atoms of the siloxane surface.

In any case, the intercalation of small QACs into Mnt increases the hydrophobicity of the interlayer space (Lee *et al.*, 1990), enhancing the affinity of the resultant OC for HOCs. When the QAC loading level is <1.0 times the

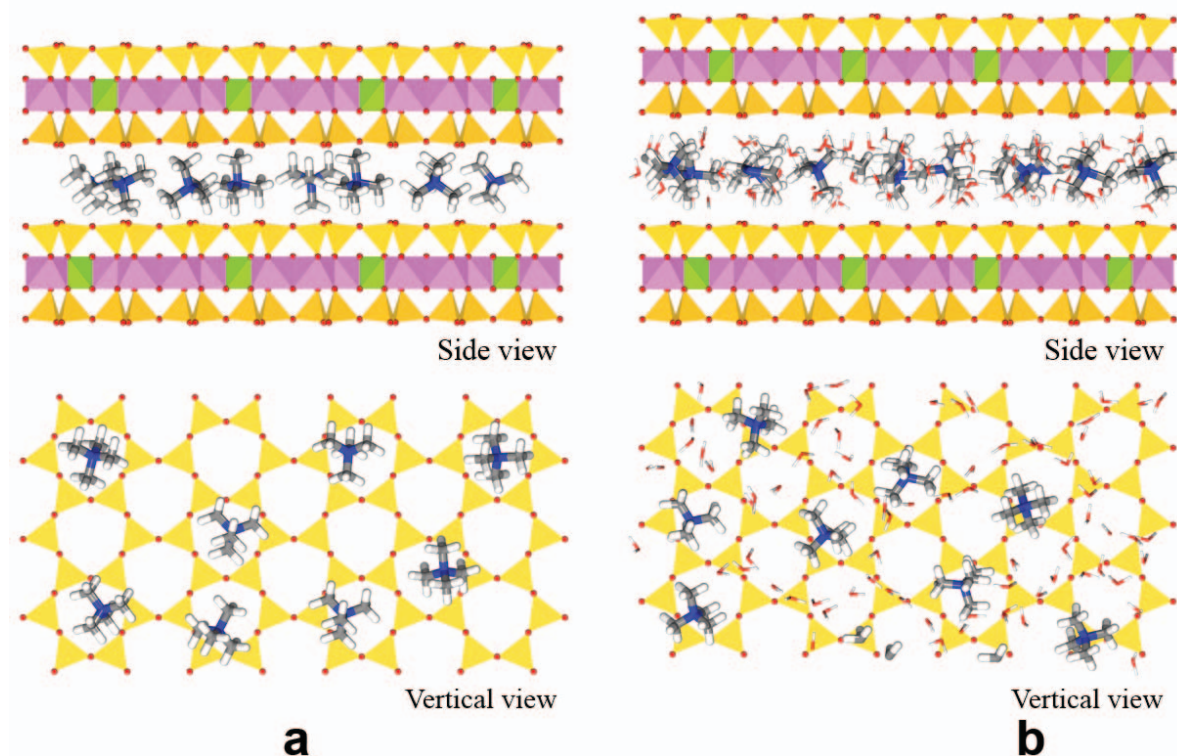


Figure 2. Interlayer structure of dry TMA-Mnt (a) and water-saturated TMA-Mnt (b). The structural models are drawn according to Čapková *et al.* (2003), Zhao and Burns (2012a, 2013), Zhu, R. *et al.* (2012a), and Martos-Villa *et al.* (2013). Both the side view (top) and the vertical view (bottom) are shown. Polyhedra: Mnt layer; thick line: TMA; thin line: water.

cation exchange capacity (CEC) of the Mnt sample, the interlayer space is partly occupied by hydrated inorganic counterions. The (partial) intercalation of trimethylphenylammonium (TMPA) ions was reported by [Sheng and Boyd \(1998\)](#) to disrupt the formation of a stable network of water molecules around the remaining inorganic cations (*e.g.*  $\text{Ca}^{2+}$ ).

In the case of (dry) HDTMA-Mnt, the interlayer space is commonly close to being fully occupied by surfactant cations (Figure 3a). Thus, type II OCs have low porosity and a small SSA (several tens of  $\text{m}^2/\text{g}$ ), the value of which decreases as the loading level of HDTMA increases ([Rutherford \*et al.\*, 1997](#); [Wang \*et al.\*, 2004](#); [Yildiz \*et al.\*, 2005](#); [He \*et al.\*, 2006b](#)). Both experimental (*e.g.* FTIR and NMR measurements) and molecular modeling studies indicate that the alkyl chains of HDTMA tend to adopt a *gauche* conformation, and that this tendency increases with surfactant loading and Mnt layer charge ([Vaia \*et al.\*, 1994](#); [He \*et al.\*, 2004a, 2004b, 2004c](#); [Liu \*et al.\*, 2007, 2009](#); [Zhu, J. \*et al.\*, 2005](#); [Zhao and Burns, 2012a, 2012b](#); [Lagaly \*et al.\*, 2013](#)).

X-ray diffraction indicates that water saturation of HDTMA-Mnt causes interlayer expansion, the extent of which is inversely related to the surfactant loading level, as well as a change in the interlayer arrangement of surfactant cations ([Zhu, J. \*et al.\*, 2008](#); [Zhu, R. and Zhu, L., 2008](#)) (Figure 3b). These findings have been substantiated by molecular modeling studies ([Liu \*et al.\*, 2007](#); [Zhu, R. \*et al.\*, 2011a, 2011b](#); [Zhou \*et al.\*, 2014](#)). Hydration may also lead to partial detachment of the alkyl chains of HDTMA from the interlayer surface. The detached chains may then form nano-sized aggregates, although a substantial portion of the intercalated surfactant remains attached to the siloxane surface. As would be expected, the exposed siloxane area in HDTMA-Mnt is much smaller than in TMA-Mnt under both dry and wet conditions. Additionally, the structural characteristics of type I and type II OCs, involving different small organic cations and cationic surfactants, are quite similar to those described above for TMA-Mnt and HDTMA-Mnt, respectively.

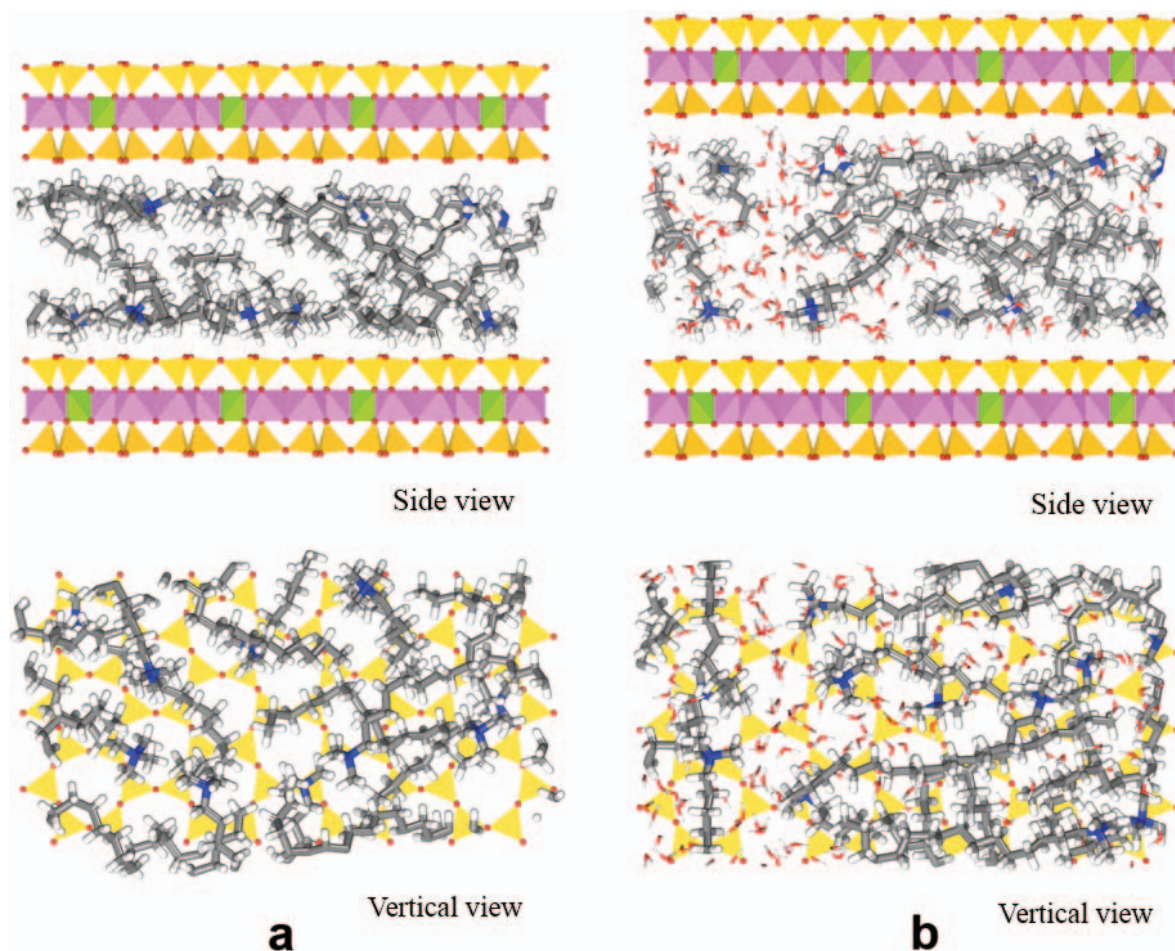


Figure 3. Interlayer structure of dry HDTMA-Mnt (a) and water-saturated HDTMA-Mnt (b). The structural models are drawn according to [Zhao and Burns \(2012a, 2013\)](#), [Zhu, R. \*et al.\* \(2011a, 2011b\)](#), and [Zhou \*et al.\* \(2014\)](#). Both the side view (top) and the vertical view (bottom) are shown. Polyhedra: Mnt layer; thick line: HDTMA; thin line: water.

## SORPTIVE CHARACTERISTICS OF OC

Before discussing the sorptive characteristics of OCs, it seems appropriate to clarify the meaning of terms such as ‘sorption’, ‘adsorption’, and ‘partition’. In the *Handbook of Clay Science* (Bergaya and Lagaly, 2013), ‘adsorption’ generally refers to the uptake of solutes by clay surfaces (and OCs), and ‘partition’ to the uptake of HOCs by type II OCs, while ‘sorption’ is not often used in the handbook. In many other publications (Smith *et al.*, 1990; Smith and Galán, 1995; Chiou, 2002), ‘sorption’ describes the process of solute entry and incorporation into a solid, including attachment of the solute to the solid surface; while ‘adsorption’ only applies to the uptake of a solute by a solid surface, and ‘partition’ refers to the distribution of contaminants between two phases. In early research on the subject, Chiou *et al.* (1979, 1981) proposed that the uptake of HOCs by soil organic matter (SOM) from an aqueous medium was primarily a partition process between bulk water and SOM. Since then, the term ‘partition’ has been used extensively to describe the uptake of dissolved solutes by solid organic phases (Boyd *et al.*, 1988a, 1988b; Chiou, 2002; Theng *et al.*, 2008).

For the sake of convenience, the structures of the various organic cations used in the formation of type I and type II OCs are shown in Table 1. Note that different names have been used for the same compound in different publications (*e.g.* cetyltrimethylammonium and hexadecyltrimethylammonium), and these are unified in the present review to avoid any confusion.

*Sorptive characteristics of type I OCs*

Having free interlayer space (Figure 2), the sorptive characteristics of type I OCs are similar to other porous

sorbents, such as zeolites and activated carbon. The isotherms for the sorption of HOCs by TMA-Mnt reported by Boyd *et al.* (1988b) and Ruan *et al.* (2008) were highly non-linear, and the sorption capacity of the OCs was heavily dependent on the SSA of the samples. Being hydrophobic, the exposed siloxane surface (*i.e.* the part not occupied or blocked by either organic cations or hydrated inorganic counterions) is considered to be the main sorption site for HOCs (Jaynes and Boyd, 1991a). Type I OCs have therefore been referred to as the adsorptive type (Jaynes and Vance, 1999; Theng *et al.*, 2008).

The hydrophobicity of the siloxane surface is also affected by the location of the negative layer charge. The siloxane surface of smectites in which the layer charge arises primarily from isomorphous substitution in octahedral sites is more hydrophobic than that in tetrahedrally substituted minerals (Sposito and Prost, 1982; Sposito *et al.*, 1999). The OCs derived from the former samples would therefore be efficient at sorbing HOCs. The same can be said of OCs that derive from low-charge smectites because such samples have a large interlayer free space (Figure 4) (Jaynes and Boyd, 1990; Lee *et al.*, 1990; Jaynes *et al.*, 1992; Meier *et al.*, 2001; Shen, 2004; Ruan *et al.*, 2008).

As noted above, intercalated organic cations play a key role in converting the interlayer space of smectite from hydrophilic to hydrophobic, and in making the interlayers accessible to HOCs (Jaynes and Boyd, 1990, 1991a; Sheng *et al.*, 1997). The nature of the organic cations can also exert a positive influence on sorption efficiency. Trimethylphenylammonium (TMPA)-Mnt was found by Nzengung *et al.* (1996) to take up more naphthalene than TMA-Mnt, though TMPA is larger than TMA. This finding may be explained in terms of

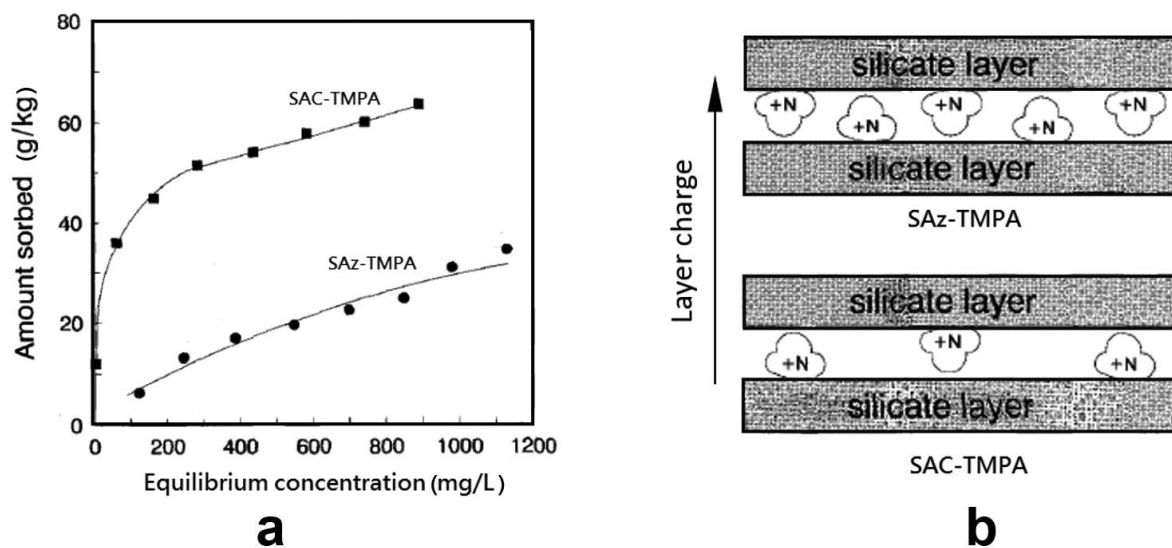
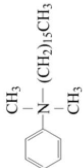
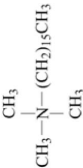
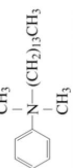

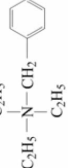
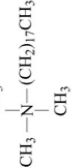
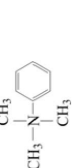
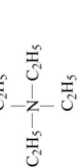
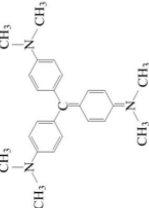
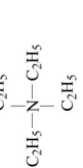
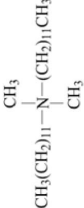
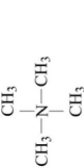
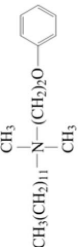

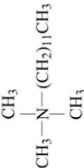
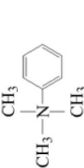
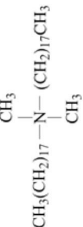
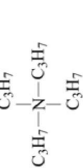


Figure 4. The effect of layer charge on the sorption of benzene by two TMPA-modified montmorillonites: (a) sorption isotherms; (b) schematic drawing of the interlayer structure of the two OCs. SAC: low-charge Mnt; SAz: high-charge Mnt (image reproduced from a paper by Jaynes and Boyd, 1991a, with the permission of The Clay Minerals Society).

Table 1. Molecular structure of the organic cations and surfactants.

Organic cations	Abbreviation	Molecular structure	Organic cations	Abbreviation	Molecular structure
Benzylhexadecyldimethylammonium	BHDA		Hexadecyltrimethylammonium	HDTMA	
Benzyltetradecyldimethylammonium	BTDDA		Hexadecylpyridinium	HDPY	
Benzyltriethylammonium	BTEA		Octadecyltrimethylammonium	ODTMA	
Benzyltrimethylammonium	BTMA		Tetraethylammonium	TEA	
Crystal violet	CV		Tetraethylammonium	TEA	
Didodecyldimethylammonium	DDDMA		Tetramethylammonium	TMA	
Dodecyl(dimethyl(2-phenoxyethyl)ammonium	DDPA		Trimethylphosphonium	TMP	
Dodecyltrimethylammonium	DDTMA		Trimethylphenylammonium	TMPPA	
Diocetadecyldimethylammonium	DODMA		Tetrapropylammonium	TPA	

$\pi$ - $\pi$  interactions between TMPA and HOC (Smith *et al.*, 1990). As TMPA is also less hydrated than TMA, its complex with Mnt is less shape-selective with respect to HOCs than TMA-Mnt (Jaynes and Boyd, 1990). Similarly, trimethylphosphonium(TMP)-Mnt is a better sorbent of HOCs than TMA-Mnt (Kukkadapu and Boyd, 1995; Lawrence *et al.*, 1998), presumably because TMP is less hydrated than TMA so that a smaller proportion of the siloxane surface is covered by TMP than by TMA.

The interlayer hydrated organic cations can also have a negative effect on HOC sorption by covering up or blocking siloxane surfaces, making these inaccessible to HOCs (Sheng *et al.*, 1997; Chun *et al.*, 2003). Increasing the size of the organic cations would therefore reduce the capacity of the OCs for sorbing HOCs. This effect can account for the observation by Smith *et al.* (1990) and Shen (2002) that TMA-Mnt and benzyltriethylammonium (BTEA)-Mnt are better at taking up HOCs than either tetraethylammonium (TEA)- or benzyltrimethylammonium-Mnt.

The sorption of benzene by smectite complexes with tetraalkylammonium ions for which the number of carbon atoms in the alkyl group ranged from 1 to 6 was assessed by Chun *et al.* (2003). Interestingly, the sorption capacity of the OCs did not vary in a systematic manner with the size of the organic cations. On the one hand, benzene sorption decreased with increase in alkyl chain length due to the 'cover-up' effect while, on the other hand, uptake increased with the size of the organic cation because of solute partitioning. Using molecular modeling, Zhu, R. *et al.* (2012a) also observed that tetrapropylammonium(TPA)-Mnt could take up more tetrachlorodibenzo-*p*-dioxin (by a partition mechanism) than TMA-Mnt although the latter complex had a larger area of exposed siloxane (for sorption) compared with the TPA-Mnt (Figure 5).

The behavior of type I OCs toward HOCs is further influenced by the loading level of the organic cations. High loading levels would increase interlayer hydrophobicity and, at the same time, reduce interlayer accessibility (Sheng *et al.*, 1997). The sorption capacity of TMPA-Mnt was found by Sheng and Boyd (1998) to increase initially as the loading level of TMPA increased

from 0.17 to 0.65 times the CEC of the clay-mineral sample, and then declined as the loading level was further increased. At low loadings (of TMPA), the presence of  $\text{Ca}^{2+}$  ions in the interlayer space appeared to inhibit the formation of a stable network of water molecules around the counterions. Nevertheless, the OC sample could still act as an efficient sorbent of HOCs although its sorption capacity diminished at high TMPA loadings due to the resultant decrease in available sorption sites.

Bartelt-Hunt *et al.* (2003) and Upson and Burns (2006) reported similarly for the sorption of HOCs by benzyltriethylammonium (BTEA)-Mnt, observing an optimal loading level of  $\sim 0.5$  times the CEC. Redding *et al.* (2002) and Smith *et al.* (2003) also noticed a decrease in benzene sorption by BTEA-Mnt as the organic cation loading exceeded 0.5 and 0.4 times the CEC of Mnt, respectively. The capacity of BTEA-Mnt for sorbing toluene and xylenes was found (Yildiz *et al.*, 2004) to increase with organic cation loading, as Shen (2002) found in the case of naphthol. The optimal loading level of organic cations is clearly influenced by various factors, notably the molecular structure of the cations, and the density and location of the negative layer charge in the clay-mineral structure.

The molecular structure of HOCs may also affect significantly their sorption by type I OCs. Having a relatively rigid structure, type I OCs can take up HOCs without undergoing appreciable interlayer expansion (Ruan *et al.*, 2008). Molecular modeling further suggests that the intercalated organic cations can 'key' into the ditrigonal cavities of opposing siloxane surfaces (Zhu, R. *et al.*, 2012a), giving rise to a stable molecular sieve-like structure showing size- and/or shape-selectivity in sorbing HOCs. The sorption of three aromatic molecules by TMA-Mnt was found (Lee *et al.*, 1989, 1990) to decrease in the order benzene > toluene > xylene which was inversely related to molecular size. Likewise, Lawrence *et al.* (1998) observed that more phenol and 4-chlorophenol were taken up by TMP-Mnt compared with 2-chlorophenol and 3-chlorophenol. Those authors suggested that the latter two solutes failed to intercalate into TMP-Mnt because of their large molecular size.

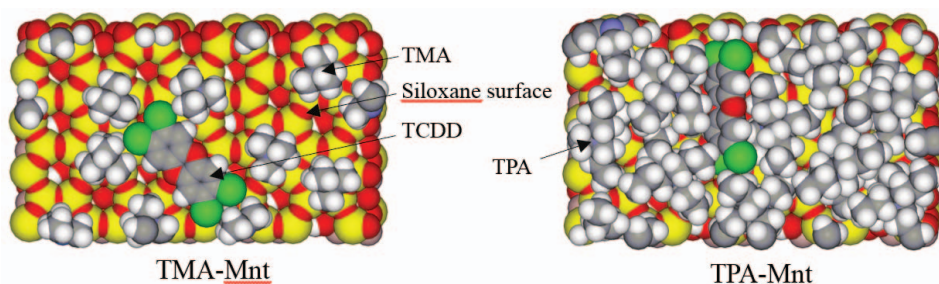


Figure 5. Snapshots of tetrachlorodibenzo-*p*-dioxin (TCDD) sorption to TMA-Mnt and TPA-Mnt. The upper layer of Mnt is removed in order to obtain a view of the OC interlayer structure (image reproduced from Zhu, R. *et al.*, 2012a, with the permission of Elsevier).

Chun *et al.* (2003) reported that HOCs with a planar aromatic structure and delocalized  $\pi$ -electrons (*e.g.* benzene) were more easily sorbed by OCs than non-aromatic compounds (*e.g.* trichloroethylene), presumably because aromatics could associate with the charged head groups of the organic cations through cation– $\pi$  interactions (Qu *et al.*, 2008).

The interactions of type I OCs with HOCs clearly occur through sorption to both the exposed siloxane surfaces and the interlayer organic cations. Thus the sorption capacity of type I OCs can be affected by the layer-charge density of the clay mineral, the molecular structure and loading level of the organic cations, and the structure and size of the HOCs. Sorption of HOCs may be promoted by increasing the accessible surface areas of the OCs and the affinity between the organic cation pillars and HOCs.

#### Sorptive characteristics of type II OCs

Because of their small SSA and pore volume, type II OCs would be expected to have sorptive characteristics that are quite different from those of type I OCs. In addition, the interlayers of type II OCs can expand in the presence of water, making for a rather complicated sorptive behavior.

Earlier studies suggested that the long alkyl chains of intercalated cationic surfactants would make the interlayer surface of montmorillonite hydrophobic, promoting the sorption of HOCs (Mortland *et al.*, 1986; Boyd *et al.*, 1988a, 1988b; Groisman *et al.*, 2004a). For example, the sorption of phenols by HDTMA-Mnt and hexadecylpyridinium (HDPY)-Mnt increased with the hydrophobicity of the solutes (Mortland *et al.*, 1986). By forming an organic phase, interlayer cationic surfactants can also take up HOCs by a partitioning process (Boyd *et al.*, 1988a, 1988b). For example, the organic phase formed by dioctadecyldimethylammonium (DODMA) cations was nearly 10 times more efficient than soil organic matter in taking up pentachlorophenol (PCP) from solution (Boyd *et al.*, 1988b; Lee *et al.*, 1990).

Since then, partition has been regarded as being the dominant – if not the sole – mechanism for the uptake of HOCs by type II OCs, based on the following observations: (1) linear sorption isotherms over a limited range of solute concentrations (Figure 6a); (2) non-competitive sorption of two or more solutes from water (Figure 6a); (3) parallel correlation between the organic carbon-normalized sorption coefficient ( $K_{oc}$ ) and the octanol-water partition coefficient ( $K_{ow}$ ) of the solutes (Figure 6b); and (4) weak solute uptake and low heats of sorption. Accordingly, type II OCs are considered as organophilic-type OCs (Smith *et al.*, 1990; Jaynes and Boyd, 1991b; Jaynes and Vance, 1999; Chen and Zhu, 2001; Redding *et al.*, 2002; Groisman *et al.*, 2004b; Lee *et al.*, 2004; Zhu, R. and Zhu, L., 2008; Zhu, R. *et al.*, 2008; Yuan *et al.*, 2013).

The evidence indicates, however, that the sorptive characteristics of surfactant-derived organic phases in

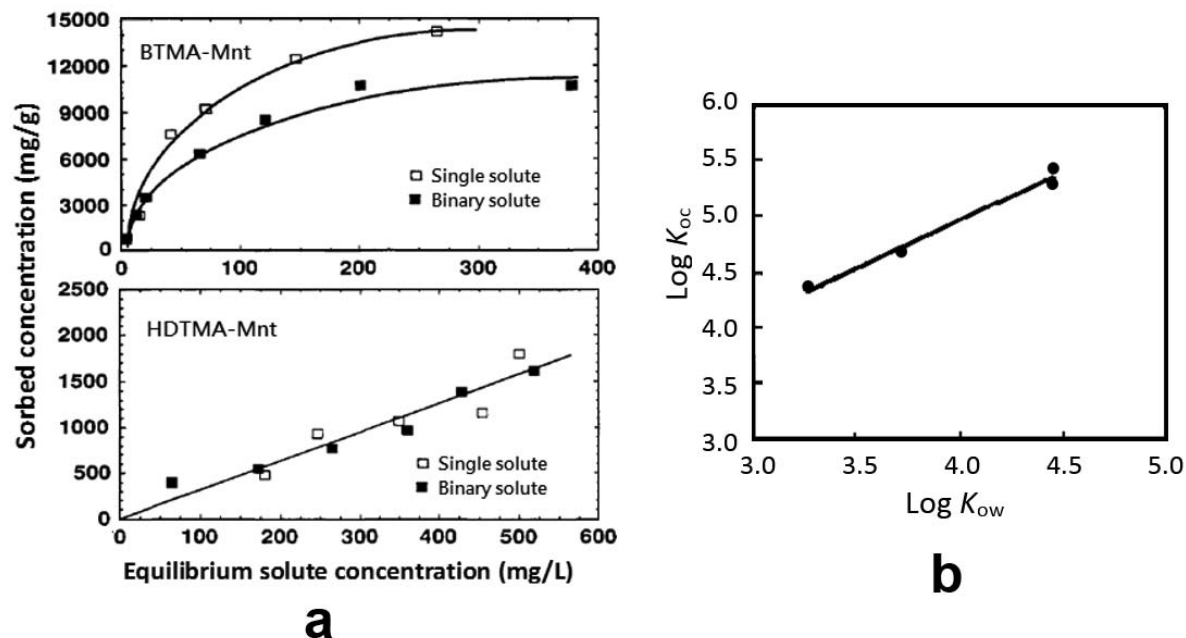


Figure 6. Sorptive characteristics of type II OCs: (a) sorption of tetrachloromethane to BTMA-Mnt and HDTMA-Mnt from single and binary solute systems. The sorption isotherms for HDTMA-Mnt are linear and non-competitive (image reproduced from Smith *et al.*, 1990, with the permission of American Chemical Society); (b) relationship between  $\log K_{ow}$  and  $\log K_{oc}$  for the sorption of several HOCs by ODTMA-Mnt (image reproduced from Chen and Zhu, 2001, with the permission of *Journal of Environmental Sciences*).



type II OCs are different from those of SOM and other bulk organic phases. In particular, the isotherms for the sorption of HOCs may deviate from linearity over a wide range of solute concentrations, showing an upward or downward curvature, or a double-sigmoid shape (Mortland *et al.*, 1986; Sheng *et al.*, 1996a, 1996b; Zhu, L. *et al.*, 1998; Slade and Gates, 2004a; Alkaram *et al.*, 2009). For example, Sheng *et al.* (1996a) found that the isotherms for the sorption of benzene, nitrobenzene, and chlorobenzene by HDTMA-Mnt had a double-sigmoid shape, while those of trichloroethylene (TCE) and carbon tetrachloride showed an upward curvature (Figure 7a). On the other hand, the isotherms for the sorption of some phenols generally curved downward (Figure 7b) (Mortland *et al.*, 1986; Boyd *et al.*, 1988b; Zhu, L. *et al.*, 1997, 1998; Zhu, L. and Chen, 2000).

Similarly, the  $K_{oc}$  for the sorption of a given HOC by type II OCs can vary widely (Dentel *et al.*, 1998; Chen *et al.*, 2005; Zhu, R. *et al.*, 2007), rather than being constant as is generally presumed (Chiou, 2002). This observation may be ascribed to the influence on  $K_{oc}$  values of such factors as surfactant structure and loading level (Smith *et al.*, 1990; Dentel *et al.*, 1998; Yilmaz and Yaper, 2004; Upson and Burns, 2006; Zhu, R. *et al.*, 2007; Xu and Zhu, 2009), clay-mineral type and layer charge (Jaynes and Boyd, 1991b; Zhu, R. *et al.*, 2007, 2008), and coexisting solutes (Sheng *et al.*, 1996a, 1996b; Juang *et al.*, 2002) (Figure 8). Thus, type II OCs formed by intercalation of cationic surfactants with long alkyl chains or with more than one alkyl chain, or by using high-charge smectites, generally have a larger than expected  $K_{oc}$  (Smith *et al.*, 1990; Dentel *et al.*, 1998; Shen, 2002; Slade and Gates, 2004a; Zhu, R. *et al.*, 2007; Xu and Zhu, 2009). Over a wide range of

surfactant loading (0.2 to 2.0 times the CEC), the  $K_{oc}$  value of a given HOC would first increase (up to ~1.0 times the CEC) and then decrease (Bonczek *et al.*, 2002; Chen *et al.*, 2005). Nevertheless, the use of  $K_{oc}$  is preferable to that of  $K_d$  (sorption coefficient) in evaluating sorption efficiency as cationic surfactants are much more expensive than clay minerals (Jaynes and Vance, 1996; Bartelt-Hunt *et al.*, 2003).

Various explanations have been proposed to account for the above-mentioned phenomena. One explanation is that the sorption of HOC by type II OCs is controlled by multiple mechanisms. Boyd *et al.* (1988a), for example, have proposed that HDTMA-Mnt plays a dual role in the sorption of benzene and TCE, with the clay-mineral component acting as a solid adsorbent and the organic phase of HDTMA as a partition medium. The combination of adsorption with partition is reflected by an isotherm with a downward curvature (Dentel *et al.*, 1998; Zhu, L. *et al.*, 1998, 2003; Juang *et al.*, 2002; Rawajfih and Nsour, 2006). At relatively low loading levels (<1.0 times the CEC), the cationic surfactant would form an adsorptive film (monolayer) over the siloxane surface of Mnt having a high affinity for HOCs, while at high loading levels (>1.0 times the CEC), the surfactant would form an organic phase showing a weak affinity toward HOCs (Zhu, L. *et al.*, 2003; Chen *et al.*, 2005).

Several other studies, however, suggest that the alkyl chains (attached to the siloxane surface) cannot form an efficient partition medium for HOCs; rather, they compete with HOCs for sorption sites on the siloxane surface, decreasing the sorption of HOCs (Smith *et al.*, 1990; Borisover *et al.*, 2010a, 2010b). Further, the partitioning of HOCs on type II OCs may be supple-

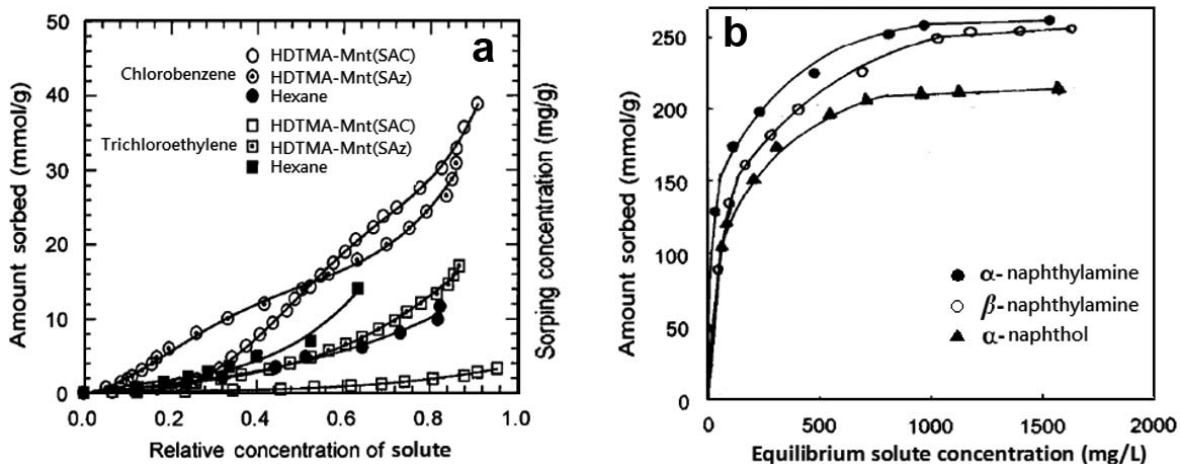


Figure 7. Sorption isotherms of HOCs on type II OCs over a wide solute concentration: (a) sorption of chlorobenzene and trichloroethylene to two HDTMA-Mnt samples (with different charge density; cf. Figure 4) and to hexane. The isotherms have a double-sigmoid (type III) shape (image reproduced from Sheng *et al.*, 1996a, with the permission of the American Chemical Society); (b) isotherms for the sorption of three HOCs to HDTMA-Mnt (image reproduced from Zhu, L. *et al.*, 1997, with the permission of the American Chemical Society).

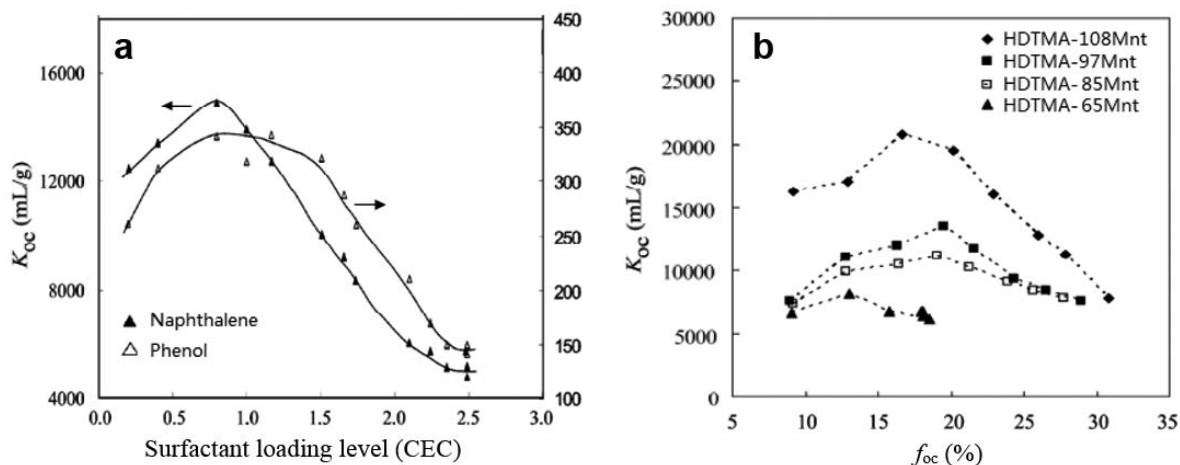


Figure 8. Variation of  $K_{oc}$  for some HOC with surfactant loading level and clay-mineral layer charge. (a)  $K_{oc}$  values for the sorption of naphthalene and phenol by myristylpyridinium-Mnt as a function of surfactant loading level (image reproduced from Chen *et al.*, 2005, with the permission of the American Chemical Society). (b)  $K_{oc}$  value for the sorption of naphthalene by four HDTMA-Mnt with different layer charge and surfactant loading levels.  $f_{oc}$ : organic carbon contents of OCs; HDTMA-xxMnt: OCs with different layer charges, the number denotes the layer charge of Mnt (meq), image reproduced from Zhu, R. *et al.*, 2007, with the permission of Elsevier).

mented by ‘solvation’, by the solute, of the ammonium groups on the alkyl chains of HDTMA. When this occurs, the isotherm deviates from linearity, showing a steadily increasing upward curvature with an increase in solute concentration (Figure 7a) (Jaynes and Vance, 1996; Sheng *et al.*, 1996a, 1996b; Sheng and Boyd, 2000).

An alternative explanation for the variation of  $K_{oc}$  is that the interlayer arrangement of organic cations affects their affinity toward HOCs as well as their accessibility to HOCs (Sheng *et al.*, 1996a, 1996b). Jaynes and Boyd (1991b), for example, suggested that the interlayer HDTMA in a high-charge smectite was more accessible to HOCs than that in a low-charge sample with a smaller interlayer spacing. As a result, the interlayer spacing and  $K_{oc}$  for the low-charge OC was smaller than the value measured for the high-charge counterpart. Similarly, intercalation of HDTMA in a flat-lying pseudotrilayer arrangement gave rise to a larger interlayer spacing than that in a paraffin-like arrangement, and hence was more accessible to HOCs (Sheng *et al.*, 1996a).

In investigating the effect of molecular weight of cationic surfactant on the sorption behavior of OCs, Jaynes and Vance (1996) found that with increasing molecular weight, *i.e.* dodecyltrimethylammonium (DDTMA) < HDTMA < didodecyltrimethylammonium (DDDMA) < DODMA, the  $K_{oc}$  of the BETXs (benzene, ethylbenzene, toluene, and xylenes) studied first increased (from DDTMA-Mnt to DDDMA-Mnt) and then decreased (for DODMA-Mnt). Those authors suggested that OCs in which the surfactants adopted a paraffin-like arrangement, giving a basal spacing of 2.54–2.76 nm, had a high capacity for sorbing BETXs; further increasing basal spacing might allow the desorption process to compete with that of sorption.

To explain the variation of  $K_{oc}$  with the loading level of cationic surfactant on OCs, Bonczek *et al.* (2002) suggested that at low loading level (*i.e.* <0.8 times the CEC), the monolayer arrangement of cationic surfactant (HDTMA), and the presence of hydrated inorganic cations in close proximity to organic domains, should be responsible for the relatively small  $K_{oc}$ . As the loading level exceeded 1.5 times the CEC, the ion-pair on the charged head of HDTMA might diminish the hydrophobicity of the interlayer space, which then would lead to the decrease in  $K_{oc}$  also. In this case, the medium loading level of surfactants (~1.0 times the CEC) with a bilayer arrangement can give the maximum  $K_{oc}$ .

Similarly, R. Zhu and his coworkers (Zhu, R. *et al.*, 2007, 2008, 2010; Zhu, J. *et al.*, 2008) proposed that the arrangement of cationic surfactants, notably their packing density, plays a significant role in HOC sorption. As packing density increases, the  $K_{oc}$  first increases to a maximum and then decreases (Figure 9). The thermodynamics calculation further shows that the  $\Delta H$  value for naphthalene sorption by several OCs gradually changes from negative to positive as HDTMA packing density increases (Zhu, R. and Zhu, L., 2008). Polyparameter linear free-energy relationship (pp-LFER) analysis further suggests that, at low packing density, cationic surfactants fail to form a cohesive organic phase into which HOCs can be sorbed, while at high packing density, the overcrowding of cationic surfactants would sterically hinder interlayer access of HOCs (Zhu, R. *et al.*, 2012b). Those authors thus suggested that the sorption capacity of type II OCs may be ‘‘tuned’’ by adjusting the packing density of interlayer surfactants.

A similar suggestion was put forward by Changchaivong and Khaothiar (2009) and Xu and Zhu (2009). The latter authors suggested that when

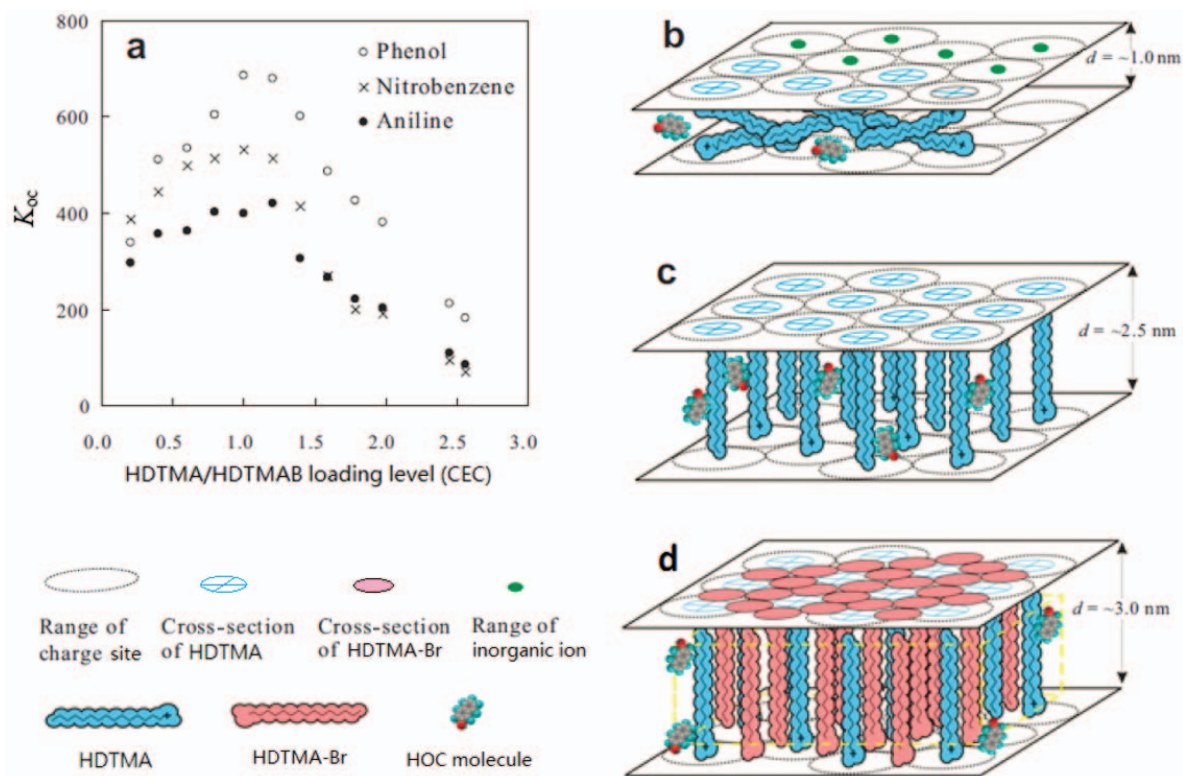


Figure 9. Effect of surfactant loading level on the sorption capacity and interlayer structure of HDTMA- or HDTMAB-Mnt: (a)  $K_{oc}$  values for the sorption of three organic contaminants by HDTMA-Mnt; (b) interlayer structure of HDTMA-Mnt for a surfactant loading level below the CEC of Mnt; (c) interlayer structure of HDTMA-Mnt for a surfactant loading level equal to the CEC; and (d) interlayer structure of HDTMA-Mnt for a surfactant loading level above the CEC (image reproduced from Zhu, J. *et al.*, 2008, with the permission of The Clay Minerals Society).

octadecyltrimethylammonium (ODTMA) together with its counter anion ( $Cl^-$ ) was present within the interlayers of Mnt, in addition to the steric hindrance effect, the strong hydration of the cation–anion pair could also contribute to the decrease in  $K_{oc}$  for nitrobenzene and naphthalene. For DODMA-Mnt, however, a decrease in  $K_{oc}$  was observed even when the loading level was  $<0.7$  times the CEC, consistent with the findings by Jaynes and Vance (1996). This observation was ascribed to the high packing density of DODMA, as it has a much larger molecule size than ODTMA.

The interactions of type II OCs with HOCs are clearly rather complicated and the proposed explanations are not always self-consistent. Note that much of the structural information obtained using dry OCs cannot be extrapolated to water-saturated samples, because the intercalated water molecules and HOCs may significantly alter the interlayer structure and composition (Sheng *et al.*, 1996a, 1996b; Slade and Gates, 2004a, 2004b; Ko *et al.*, 2007; Zampori *et al.*, 2008; Zhou *et al.*, 2010). For example, layer expansion by water molecules and HOCs can increase the interlayer accessibility to HOCs (Sheng *et al.* 1996a). In addition, the composition of the mixture of sorbed HOCs and surfactants (*i.e.* the interlayer organic phases) changes as the sorbed HOCs increase,

which can affect further sorbing of HOCs from bulk water (Sheng *et al.* 1996a, 1996b).

Recently, molecular modeling has been shown to be a powerful tool in studying the sorptive characteristics of type II OCs, as the results can show directly atomic-level insights into the interlayer structure of water-saturated OCs. Molecular-dynamics simulation studies by Zhu, R. *et al.* (2011a) and Zhao and Burns (2012b) showed that HOC molecules are primarily sorbed into the HDTMA aggregates of HDTMA-Mnt, in line with a partition mechanism as proposed in previous experimental studies (Figure 10a). The siloxane surfaces (which are partly covered by HDTMA) are less efficient at sorbing HOCs, although the oxygen atoms on the siloxane surface can form H bonds with the hydroxyl groups of HOCs (*e.g.* phenol) (Zhu, R. *et al.* 2011a). Sharpley *et al.* (2013) calculated the free energy of sorption of polychlorinated dibenzo-p-dioxins (PCDD) into the interlayers of HDTMA-Mnt (Figure 10b). The results of the latter study showed that the organic cations created a hydrophobic region (alkyl chain aggregates) for the sorption of PCDD, leading to a negative sorption free energy. These modeling results were in good agreement with the pp-LFERs results, which indicated that the sorbed HOC molecules should face a less polar

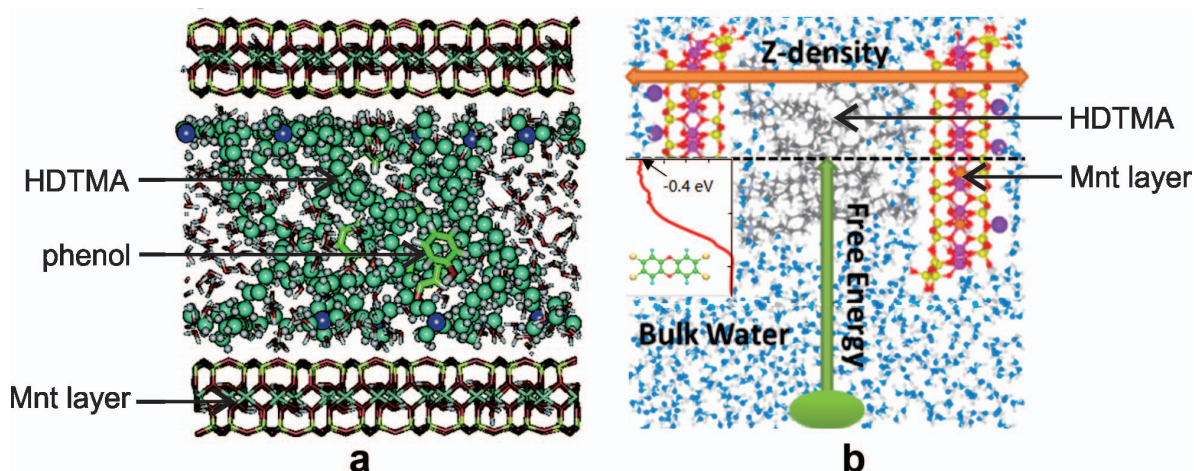


Figure 10. Atomic-level insight into the interlayer structure of HDTMA-Mnt, provided by molecular dynamics simulation: (a) snapshot of phenol molecules seen to be primarily associated with HDTMA aggregates (image reproduced from Zhu, R. *et al.*, 2011a, with the permission of the American Chemical Society); (b) calculated free-energy change for the intercalation of tetrachlorodibenzo-*p*-dioxin from bulk water into HDTMA-Mnt interlayer (image reproduced from Shapley *et al.*, 2013, with the permission of the American Chemical Society).

environment (within surfactant aggregates) compared with bulk water, and HDTMA-Mnt had stronger H-bond acceptor capability (arising from the oxygen atoms on the siloxane surface) than bulk water (Zhu, R. *et al.* 2011a, 2012b).

In summary, the sorption of HOCs by type II OCs is more than just a partition process. First, the nano-sized and confined organic phases behave differently from bulk organic phases in sorbing HOCs. The affinity of interlayer surfactants for, and their accessibility by, HOCs are affected by the arrangement of cationic surfactants and the presence of residual inorganic counterions. Second, the sorption of HOCs is affected strongly by the surface properties of the clay-mineral component, including layer-charge density and distribution, interlayer expansion during HOC sorption, and participation of siloxane surfaces. Third, the structure and composition of the interlayer organic phase (*i.e.* the solute-surfactant mixture) may change when the amount of HOC sorbed reaches a certain level.

Owing to a partition-dominated sorption mechanism and interlayer expandability, type II OCs are well suited to treating wastewater containing high concentrations of multiple HOCs, and cleaning up oil spills (Sheng *et al.*, 1996a, 1996b; Adebajo *et al.*, 2003; Carmody *et al.*, 2007; Carvalho *et al.*, 2012; Yuan *et al.*, 2013). Type II OCs are also efficient at taking up organic contaminants of large molecule size and/or high hydrophobicity compared with microporous type I OCs or activated carbon (Alther, 1995, 2002; Groisman *et al.*, 2004a; Upson and Burns, 2006; Polubesova *et al.*, 2006). The presence in the system of humic substances (ubiquitous in sediments and soils) can reduce the sorption of HOCs by type II OCs (Zhao and Vance, 1998). Interlayer expandability is very useful when type II OCs are used as landfill liners because expansion would increase liner

density, and hence retard the migration of HOCs to soil and groundwater (Lo, 2001; Lo and Yang, 2001).

#### APPROACHES TO ENHANCING THE SORPTION CAPACITY OF TYPE I OCs

The sorption capacity of type I OCs may be enhanced by using one or more of the following approaches: (1) increasing the surface areas of OCs; (2) strengthening specific interactions between OCs and HOCs; and (3) increasing the accessibility of sorption sites (Table 2).

##### *Approaches based on increasing the specific surface area of OCs*

Smectites can potentially expose a very large (~750 m<sup>2</sup>/g) interlayer surface area (Brigatti *et al.*, 2013). The approach of the present authors to enhance the sorption capacity of type I OCs, therefore, was to expose as much of this (siloxane) surface as possible, an objective which may be achieved by intercalating small and weakly hydrated organic cations into low-charge smectites (Barrer, 1978; Smith *et al.*, 1990; Lawrence *et al.*, 1998; Meier *et al.*, 2001; Shen, 2004; Ruan *et al.*, 2008).

High-charge smectites can also be used to prepare type I OCs if their layer charge is first reduced through the Hofmann-Klemen (1950) effect (Slade and Gates, 2004a; Komadel *et al.*, 2005; Ruan *et al.*, 2008; Zhu, L. *et al.*, 2008). To this end, the counterions of the smectites are replaced with small inorganic cations (*e.g.* Li<sup>+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>). When the products are heated at relatively high temperature (*e.g.* 150–300°C), these cations migrate to the ditrigonal cavities in the tetrahedral sheet and/or the vacant octahedral sites in the structure, reducing the layer charge of the samples

Table 2. Approaches to enhancing the sorption capacity of type I OCs.

Approach	Corresponding theory	Representative OC	References
Using smaller organic cations	Increasing the SSA of the OC	TMA-Mnt	Smith <i>et al.</i> (1990); Chun <i>et al.</i> (2003)
Using organic cations with weak hydration capacity	Increasing accessibility of sorption sites	TMP-Mnt	Kukkadapu and Boyd (1995); Lawrence <i>et al.</i> (1998)
Choosing an appropriate loading level of organic cations	Increasing the SSA of the OC	BTEA-Mnt; TMPA-Mnt	Sheng and Boyd (1998); Bartelt-Hunt <i>et al.</i> (2003); Redding <i>et al.</i> (2002)
Reducing the layer charge of the clay minerals	Increasing the SSA of the OC	TMA-Mnt; BTMA-Mnt	Ruan <i>et al.</i> (2008); Zhu, L. <i>et al.</i> (2008)
Restricting layer collapse of the clay minerals	Increasing the SSA of the OC	TMA-Mnt	Zhu, R. <i>et al.</i> (2014a)
Mild heating of OC (e.g. 150°C)	Increasing the accessibility of sorption sites	TMA-Mnt	Borisover <i>et al.</i> (2010a, 2012)
'One-step' sorption method	Increasing the accessibility of sorption sites	TMA-Mnt; CV-Mnt	Shen (2002); Upson and Burns (2006); Wei <i>et al.</i> (2009)
Choosing organic cations with special groups (e.g. aromatic rings)	Enhancing specific interactions between OC and HOC	BTMA-Mnt; TMPA-Mnt	Jaynes and Boyd (1990); Stevens <i>et al.</i> (1996); Kameda <i>et al.</i> (2012)

(Quirk and Theng, 1960; Jaynes *et al.*, 1992; Theng *et al.*, 1997; Hrobarikova *et al.*, 2001; He *et al.*, 2001; Komadel, 2003; Komadel *et al.*, 2005). By this method, the layer charge of clay minerals can be reduced conveniently, and the synthesized type I OCs then have larger SSA values and better sorption capacities (Ruan *et al.*, 2008; Zhu, L. *et al.*, 2008).

This thermally induced migration of cations, however, is often uneven, giving rise to cation-poor layers that are prone to collapse as charge reduction proceeds (Hrobarikova *et al.*, 2001; Komadel 2003; Komadel *et al.*, 2005). As the collapsed interlayers are inaccessible to extraneous organic cations and surfactants, the SSAs of the corresponding OCs, and their sorption capacity, will decrease.

A new route to synthesis of reduced-charge TMA-Mnt was described by Zhu, R. *et al.* (2014a) in which layer collapse is restricted (Figure 11a). It involves the replacement of a small proportion (20–40%) of the Li<sup>+</sup> ions (of the Li<sup>+</sup>-exchanged Mnt) with TMA ions, heating the Li<sup>+</sup>/TMA-Mnt at 200°C for 12 h (to induce migration of most of the Li<sup>+</sup> ions into the Mnt layers), and replacing the remaining Li<sup>+</sup> with TMA. The OCs prepared in this manner have a larger SSA and better sorption capacity than traditional reduced-charge TMA-Mnt (Figure 11b).

The sorption capacity of type I OCs may also be enhanced by adjusting the loading level of organic cations, as this parameter can evidently affect the microstructure of the resultant OCs also. In many cases, a loading level of <0.5 times the CEC gives rise to OCs with a large sorption capacity (Redding *et al.* 2002; Smith *et al.* 2003; Bartelt-Hunt *et al.*, 2003; Upson and Burns, 2006). Optimizing loading levels is also important in controlling operating expenses. The optimal loading level is dependent on factors such as molecular structure of the organic cations, and layer-charge density and heterogeneity of the clay mineral samples (Shen, 2002). A low loading level can be recommended when using large organic cations and high-charge smectites (Smith *et al.*, 1990; Ruan *et al.*, 2008).

#### *Approaches based on increasing accessibility to sorption sites*

Several approaches to increasing interlayer accessibility have been developed (Shen, 2002; Wei *et al.*, 2009; Borisover *et al.*, 2010a, 2012; Zhu, R. *et al.*, 2014b). In the so-called 'one-step' sorption process, the synthesis of OCs and the sorption of HOCs are combined (Shen, 2002; Zhu, L. and Zhu, R., 2011) (Figure 12a). In this instance, the organic cations and HOC molecules are simultaneously intercalated into the clay minerals so as to reduce the size- and shape-selective effects that come into play during the sorption of HOCs by traditional OCs. By adding a small amount of BTMA (0.5 times the CEC of the smectite) to an aqueous solution of phenol, Shen (2002) was able to remove ~90% of the HOC.

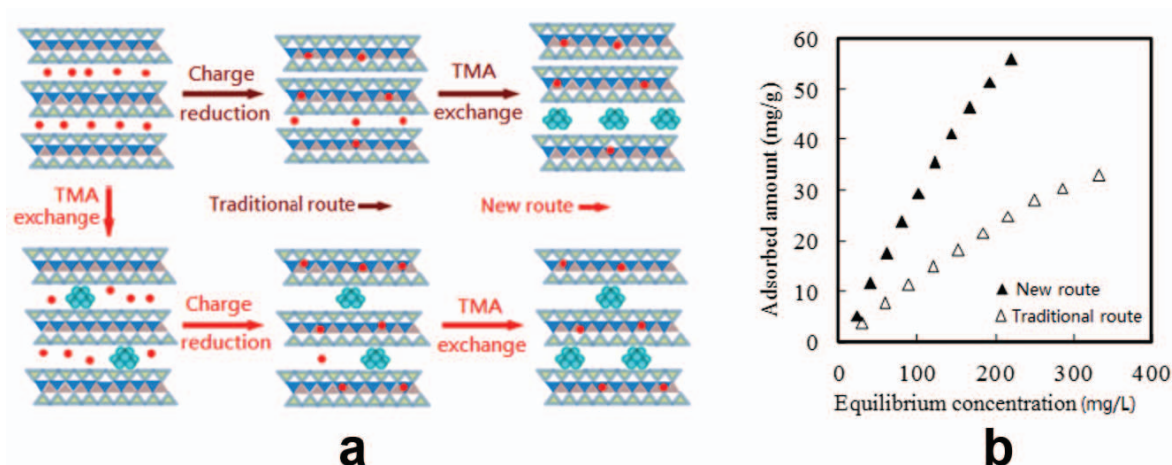


Figure 11. New route for synthesizing interlayer TMA complexes with reduced-charge Mnt so as to restrict layer collapse and increase specific surface area: (a) diagram showing the synthesis route; (b) comparing the sorption of nitrobenzene by traditional and new reduced-charge TMA-Mt (image reproduced from Zhu, R. *et al.*, 2014a, with the permission of Elsevier).

Removal efficiency was not affected by either solution pH (4–9) or ionic strength ( $>0.1$  mol/L NaCl), and the sorbents could be recovered readily by sedimentation. In addition, the strong attraction between organic cations and the clay surface ensures almost complete removal of organic cations from aqueous solutions (Shen, 2002; Upson and Burns, 2006; Wei *et al.*, 2009).

The ‘one-step’ sorption process is particularly suitable for the treatment of dye wastewater, as it may contain cationic dyes and HOCs simultaneously. In this case, the cationic dyes function as modifiers for synthesizing OCs which then act as sorbents of HOCs (Wei *et al.*, 2009; Zhu, J. *et al.*, 2010). Cationic dyes and HOCs with an aromatic structure, present in the wastewater, can also combine through specific  $\pi$ – $\pi$  interactions (Rytwo and Gonen, 2006; Rytwo *et al.*, 2007). For example, Mnt can remove both crystal violet (CV) and

2-naphthol more efficiently using the ‘one-step’ sorption process than with the traditional (two-step) process, using pre-synthesized CV-Mnt (Wei *et al.*, 2009) (Figure 12b). Furthermore, the isosteric sorption enthalpy for 2-naphthol sorption in the ‘one-step’ process is more negative than in the traditional process, probably because 2-naphthol can bind to CV via  $\pi$ – $\pi$  interaction, and be intercalated in combination with CV (Zhu, J. *et al.*, 2010).

The accessibility of interlayer sorption sites can also be increased by heating the OCs at a mild temperature. Heating BTMA-Mnt and TEA-Mnt at 150°C was observed by Borisover *et al.* (2010a, 2012) to increase their sorption capacity for HOCs, with little effect on the interlayer structure of the OCs. Those authors suggested that mild heating caused dehydration of OCs, enabling HOCs to compete effectively with water molecules for sorption

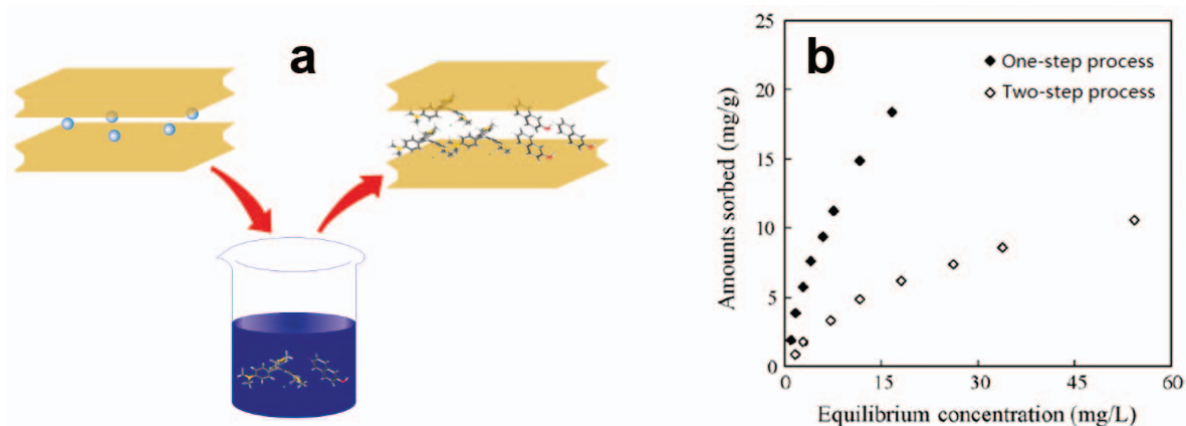


Figure 12. One-step sorption of organic cations and HOCs to clay minerals: (a) schematic drawing of the one-step sorption process; (b) sorption of both crystal violet and 2-naphthol to Mnt through the one-step process (top curve); sorption of 2-naphthol through the two-step process (*i.e.* crystal violet is sorbed before 2-naphthol) (bottom curve) (image reproduced from Wei *et al.*, 2009, with the permission of Elsevier).

sites. The overall consequence of mild heating is therefore one of enhancing solute access to interlayer sites.

#### Approaches based on increasing OC affinity for HOCs

As mentioned above, organic cations and HOCs having phenyl groups in their structure, can combine through  $\pi$ - $\pi$  interactions, increasing the capacity of the OCs for sorbing HOCs (Meier *et al.*, 2001; Kameda *et al.*, 2012). The most frequently used organic cations containing an aromatic structure, are trimethylphenylammonium (TMPA) (Jaynes and Boyd, 1990; Sheng *et al.*, 1997; Sheng and Boyd, 1998; Jaynes and Vance, 1999), benzyltrimethylammonium (BTMA) (Smith *et al.*, 1990; Shen, 2002, 2004; Zhu, L. *et al.*, 2008), and benzyltriethylammonium (BTEA) (Smith *et al.*, 1990; Jaynes and Vance, 1999; Redding *et al.*, 2002; Bartelt-Hunt *et al.*, 2003; Smith *et al.*, 2003) (Table 1). TMPA is also less hydrated than TMA (Jaynes and Boyd, 1990) and TMPA-Mnt has a larger basal spacing than TMA-Mnt (Stevens *et al.*, 1996). For these reasons, TMPA-Mnt is superior to TMA-Mnt in sorbing HOCs. Although less often used, smectite complexes with methylphenylpyridinium (MPyr) (Jaynes and Vance, 1999), and tetraphenylphosphonium (TPP) (Kameda *et al.*, 2012) are similarly better at sorbing HOCs than their counterparts with non-aromatic organic cations.

Other non-quaternary ammonium species have also been used to prepare high-sorbing type I OCs, including L-carnitine, L-cystinedimethylester, and thiamine (Cruz-Guzman *et al.*, 2004). When intercalated into a low-charge Mnt, the functional groups of these compounds can interact specifically with simazine. Thus, carnitine-Mnt and cystinedimethylester-Mnt are better at sorbing simazine than TMPA-Mnt and HDTMA-Mnt.

#### APPROACHES FOR ENHANCING THE SORPTION CAPACITY OF TYPE II OC

Because of the complicated structural and sorptive characteristics of type II OCs, the strategies for improving their sorption capacity have not been as well established as those of type I OCs. Nevertheless, several practical approaches to enhancing their sorption capacity are available (Table 3). For example, the loading level of cationic surfactant generally should be  $\sim 1.0$  times that of the clay mineral CEC (Zhu, L. *et al.*, 2003; Chen *et al.*, 2005; Zhu, R. *et al.*, 2007). Using smectites with greater layer charge and cationic surfactant with longer alkyl chain can generally achieve better sorption capacity for the resulting OCs (Smith *et al.*, 1990; Sheng *et al.*, 1996a; Shen 2004; Zhu, R. *et al.*, 2007; Yuan *et al.*, 2013).

#### Co-intercalation of cationic surfactants with other organic compounds

As noted above, hydration of the residual inorganic counterions in type II OCs tends to decrease HOC

Table 3. Approaches to enhancing the sorption capacity of type II OCs.

Approach	Corresponding theory	Representative OC	Reference
Using cationic surfactants of large size (e.g. long alkyl chain, more than one alkyl chain)	Probably increasing both the affinity and accessibility of the interlayer space	DODMA-Mnt; DODMA-Mnt	Smith <i>et al.</i> (1990); Xu and Zhu (2009)
Choosing an appropriate loading level of cationic surfactants ( $\sim 1.0 \times$ CEC)	Probably increasing the affinity of the interlayer space	HDTMA-Mnt	Zhu, R. <i>et al.</i> (2007); Zhu, J. <i>et al.</i> (2008)
Choosing clay minerals of high layer charge density	Probably increasing both the affinity and accessibility of the interlayer space	HDTMA-Mnt	Shen (2004); Zhu, R. <i>et al.</i> (2007)
Co-intercalation with other organic cations	Probably increasing both the affinity and accessibility of the interlayer space	BTEA-HDTMA-Mnt; Polyacrylamide-HDTMA-Mnt	Smith <i>et al.</i> (1995); Wang <i>et al.</i> (2010)
Mild heating of OC (e.g. 150°C)	Increasing the accessibility of sorption sites	HDTMA-Mnt	Borisover <i>et al.</i> (2010a, 2010b, 2012)
'One-step' sorption method	Increasing the accessibility of sorption sites	HDTMA-Mnt; CV-HDMTA-Mnt	Khenifi <i>et al.</i> (2009); Li <i>et al.</i> (2013); Zhu, R. <i>et al.</i> (2014b)
Choosing organic cations with special groups (e.g. aromatic rings)	Enhancing specific interactions between OC and HOC	BDHA-Mnt	Nguyen <i>et al.</i> (2013); Xu <i>et al.</i> (2014)

sorption (Bonzek *et al.*, 2002). One should therefore attempt to achieve complete replacement of the interlayer inorganic counterions. In view of the high cost of organic surfactants, their co-intercalation with other organic compounds is an attractive option. The co-intercalated organics may also increase the hydrophobicity of the interlayers, and alter the arrangement of the intercalated cationic surfactants giving rise to increased sorption of HOCs (Smith and Galán, 1995; Zhu, L. and Chen, 2000; Zhu, J. *et al.*, 2011b).

Smith and Galán (1995) have investigated the co-intercalation of HDTMA with small organic cations (BTEA) into smectite. The resultant ‘dual organic cation’ OCs, have sorptive characteristics of both type I and type II OCs but their capacity for sorbing HOCs is superior to that of the corresponding type II OCs. For example, the 40BTEA/40HDTMA-Mnt (40% of the CEC’s loading level for both BTEA and HDTMA) is better than 40HDTMA-Mnt, but not as good as 40BTEA-Mnt, in taking up benzene.

The intercalation of cationic polymers with a large charge/volume ratio, even in small amounts, can lead to the neutralization of a large proportion of the negative charge of clay minerals as well as a change in the arrangement of cationic surfactants in the interlayers of OCs. Intercalation of 4 wt.% of cationic polyacrylamide/polydiallyldimethylammonium into HDTMA-Mnt was found by Zhu, R. *et al.* (2010) and Wang *et al.* (2010) to increase the packing density of HDTMA, and to enhance significantly phenol sorption (Figure 13). When the amount of intercalated polymer was raised (to 8 wt.%), however, and the HDTMA chains became tightly packed, HOC sorption decreased. These findings once again show that the packing density of interlayer cationic surfactants plays a critical role in the sorption of HOCs by type II OCs.

#### Increasing specific interactions between OCs and HOCs

Specific interactions between certain organic cations and HOCs can also enhance the sorption capacity of type II OCs, as Smith *et al.* (1990) have shown for interlayer

complexes of Mnt with benzylhexadecyldimethylammonium (BHDA) and dodecyldimethyl(2-phenoxyethyl)ammonium (DDPA), both of which have a phenyl group attached to the charged head. The sorption capacity of both OCs is much larger than that of complexes formed using cationic surfactants with comparable alkyl chain lengths. For example, the log  $K_{oc}$  values (in parentheses) for the sorption of tetrachloromethane decrease in the order: DDPA-Mnt (2.07) > BHDA-Mnt (1.96) > HDTMA-Mnt (1.70) > DDTMA-Mnt (1.26). Similarly, BHDA-Mnt is much better at sorbing phenolic compounds than DODMA-Mnt (Nguyen *et al.*, 2013), presumably because the aromatic rings of BHDA can interact specifically with the HOCs (phenolic compounds). For the same reason, benzyltetradecyldimethylammonium (BTDDA)-Mnt can take up more naphthalene and diuron than HDTMA-Mnt, although the alkyl chains of HDTMA are longer (Nzengung *et al.*, 1996).

The role of  $\pi$ - $\pi$  interactions in the sorption of naphthalene by BDHA-Mnt has been investigated by Xu *et al.* (2014). The  $K_{oc}$  value of naphthalene with BDHA-Mnt was found to be ~1.6 times greater than the value obtained with HDTMA-Mnt, and the intercalated naphthalene in BDHA-Mnt was held strongly. In support of these observations,  $^1\text{H-NMR}$  spectroscopy indicated strong electron donor-acceptor ( $\pi$ - $\pi$ ) interactions between the aromatic rings of BHDA and naphthalene.

#### Thermal treatment of OCs

By removing some of the interlayer water molecules, thermal treatment has the effect of increasing the accessibility by HOCs of both types I and II OCs. For example, Borisover *et al.* (2010a, 2010b, 2012) reported that when HDTMA-Mnt was heated at 150°, its capacity for sorbing nitrobenzene, atrazine, phenol, and *m*-nitrophenol was greatly enhanced. Those authors suggested that the removal of residual water from the interlayers of HDTMA-Mnt by heating, and the failure of the dried HDTMA-Mnt to rehydrate fully on contact with water, work together to enhance sorbate-sorbent interactions and sorption capacity. When the heating

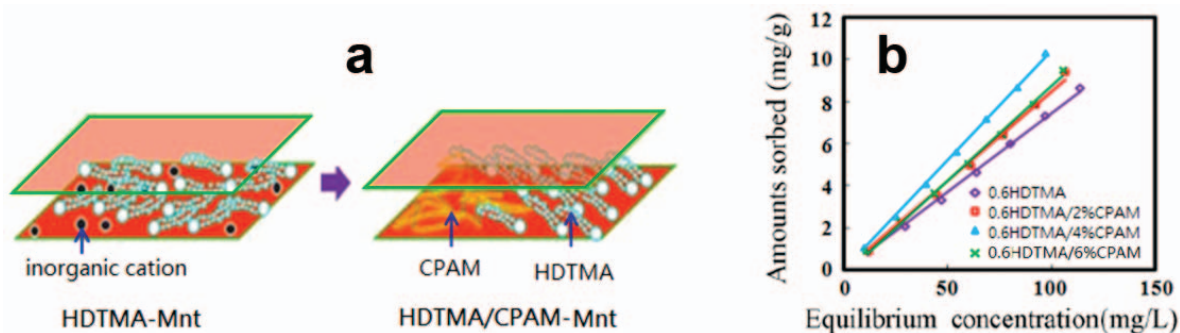


Figure 13. (a) Schematic drawing of the microstructure of HDTMA-Mnt and HDTMA/CPAM-Mnt; (b) HDTMA/CPAM-Mnt showed better sorption capacity toward nitrobenzene than the corresponding HDTMA-Mnt. The loading level of organic cations: 0.6 times of the CEC for HDTMA and 2–6 wt.% for CPAM (image reproduced from Wang *et al.*, 2010, with the permission of Elsevier).



temperature was increased to 250°C, carbon was lost and the basal spacing of the OC decreased, leading to a decline in sorption capacity. The strong attraction between the long alkyl chains of HDTMA and the Mnt surface had an inhibitory effect on sorbate–sorbent interactions. Thus, the enhancement of sorption capacity was less apparent with type II than with type I OCs (Borisover *et al.*, 2008, 2010a, 2010b, 2012; Yariv *et al.*, 2011).

#### 'One-step' sorption of organic cations and HOCs

The simultaneous (one-step) sorption of organic cations and HOCs can similarly increase the accessibility of the interlayers of type II OCs (Khenifi *et al.*, 2009; Zhu, R. *et al.*, 2014b). Using the one-step sorption process, Khenifi *et al.* (2009) observed that HDTMA-Mnt could take up more 2,4-dichlorophenol and PCP, and at a faster rate, than was the case using the traditional pre-synthesized OC. Similar results were reported by Li *et al.* (2013) for PCP which, they suggested, was taken up primarily by partition as was the case with traditional type II OCs. Again, overloading of cationic surfactant (>1.2 times the CEC) could decrease HOC sorption as shown by traditional type II OCs (Ma and Zhu, 2007; Khenifi *et al.*, 2009).

The one-step sorption process for the simultaneous removal of multi-contaminants (crystal violet, HDTMA, 2-naphthol) from water was used by Zhu, R. *et al.* (2014b). Being organic cations, crystal violet (CV) and HDTMA were almost completely intercalated into Mnt, changing the interlayer space from hydrophilic to hydrophobic. The resultant as-synthesized OCs could then remove 2-naphthol from water efficiently. Interestingly, this dual-organic cation OC (CV-HDTMA-Mnt) was better at sorbing 2-naphthol than the combination of CV-Mnt plus HDTMA-Mnt. In addition, the isotherms for the sorption of 2-naphthol by both CV-HDTMA-Mnt and HDTMA-Mnt were linear. On the other hand, CV-Mnt gave a non-linear isotherm, and showed a much lower sorption capacity, suggesting that the interlayer HDTMA in CV-HDTMA-Mnt played an important role in taking up 2-naphthol.

The one-step sorption process has other advantages besides enhancing sorption capacity. One of these is the saving on application costs because there is no need to synthesize traditional OCs. Another advantage is that the sorbent can be dispersed readily in water, and recovered by sedimentation. Furthermore, the risk of environmental contamination by residual cationic surfactants is low because these compounds are strongly bound to the clay-mineral surface (Zhang *et al.*, 1993; Upson and Burns, 2006; Ma and Zhu, 2007; Zhu, R. *et al.*, 2014b).

#### FUTURE STUDIES

As efficient sorbents of HOCs, OCs are potentially suited to remediating contaminated waters and soils. In

order to realize this potential, ways to enhance sorption capacity, and to reduce application costs are needed. Future research should therefore focus on clarifying the structural and sorptive characteristics of OCs, particularly those of type II. For example, the arrangement of cationic surfactants in the interlayer space of water-saturated OCs, and how it affects their affinity for HOCs, is still not fully understood. Molecular modeling is proving to be a powerful tool in elucidating both the microstructure of OCs and the intercalation of solutes into the interlayer micropores of OCs (Zhu, R. *et al.*, 2011a; Zhao and Burns, 2012a, 2012b). The application of sophisticated instrumental techniques, such as X-ray absorption fine structure spectroscopy, can also provide atomic-level insight into the orientation and arrangement of organic compounds at solid surfaces (Hähner *et al.*, 1996a, 1996b; Fisher *et al.*, 1998). The search for more efficient methods of enhancing sorption capacity, however, should not stand in the way of using OCs for environmental remediation.

With respect to type I OCs, improving solute access to the interlayer space may be the simplest way of enhancing sorption capacity. This would involve maximizing the exposure of interlayer siloxane surfaces by reducing the layer charge of the clay-mineral samples without causing interlayer collapse. In type II OCs, the arrangement of the interlayer cationic surfactants, especially the packing density, appears to be a determining factor influencing their affinity for HOCs. One can therefore optimize the sorption capacity of type II OCs by adjusting the arrangement of the intercalated cationic surfactants. Using organic cations with special groups that can strongly interact with HOCs can also enhance the sorption capacity of both type I and type II OCs.

The structure of clay minerals lends itself to multi-functional modifications. Other contaminants besides HOCs can be taken up by smectites intercalated with organic cations containing special functional groups (Sheng *et al.*, 1999; Groisman *et al.*, 2004b; Stathi *et al.*, 2007), or by OCs containing other functional reagents (Zhu, L. and Zhu, R., 2007; Zhu, R. *et al.*, 2009b; Huang *et al.*, 2012; Okada *et al.*, 2014). An example of this is the simultaneous intercalation of polyhydroxymetal cations and cationic surfactants to yield novel organo-inorgano clays capable of co-sorbing HOCs and oxyanions (Ma and Zhu, 2006; Zhu, L. and Zhu, R., 2007; Zhu, R. *et al.*, 2009b). Another example is the incorporation of Al/Pd phthalocyanine into OCs to yield materials that can catalyze the *in situ* degradation of sorbed phenols (Xiong *et al.*, 2005a, 2005b). The synthesis, surface properties, and catalytic activity of OCs merit further investigation.

#### CONCLUSIONS

The present review was primarily concerned with the interlayer structure of organo-clays (OCs) in an aqueous

environment as this factor can profoundly affect its sorptive characteristics. Hydration of the intercalated organic cations and siloxane surfaces of OCs can evidently change their interlayer structure. In the case of type I OCs, the process causes shrinkage of the interlayer pores whereas in type II OCs a rearrangement of the cationic surfactants occurs. As a result, the interactions between OCs and HOCs are affected markedly. Having a porous structure, type I OCs behave similarly to traditional porous adsorbents (*e.g.* activated carbon) in terms of sorbing HOCs. The exposed (hydrophobic) siloxane surface and the organic cation ‘pillars’ in type I OCs are the primary adsorption sites for HOCs. By comparison, the interlayer structure and sorptive characteristics of type II OCs are more complicated. Here the nano-size aggregates of cationic surfactants (‘organic phases’), formed in the interlayer space, are the principal sorption sites for HOCs which are taken up through a partition mechanism. The microstructure of these aggregates, and their affinity for HOCs, can be affected significantly by the charge density of the clay-mineral component as well as by the molecular structure and loading level of the cationic surfactants. The interlayer siloxane surfaces, being more or less covered by the cationic surfactants, play a minor role in the sorption of HOCs.

The various approaches to enhancing the capacity of OCs for sorbing HOCs have been described here as this topic has not been reviewed previously. The first approach was to select suitable clay minerals and organic cations. Type I OCs should be synthesized using clay minerals of low charge density, and organic cations of small size and low hydration energy. Type II OCs, on the other hand, should be formed using high-charge clay minerals and long-chain cationic surfactants. Sorption capacity may also be enhanced using organic cations that contain special groups (*e.g.* aromatic rings) capable of interacting specifically with HOCs. For type I OCs, the loading level of organic cations should also be kept below 1.0 times the CEC of the clay mineral sample, and ~1.0 times the CEC for type II OCs. Co-intercalation of organic compounds (*e.g.* cationic polymers, nonionic surfactants) may enhance the sorption capacity of type II OCs by altering the arrangement of the interlayer organic cations. Mild heating of OCs may increase the hydrophobicity of their interlayers, enhancing sorption capacity. Finally, the simultaneous sorption of organic cations and HOCs in the so-called one-step process can enhance sorption capacity by increasing the interlayer accessibility of the OCs.

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