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A Study on the Sorption Characteristics of Polycyclic Aromatic Hydrocarbons(PAHs) and Cadmium by Organoclays

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유기점토에 의한 다환방향족 탄화수소와 카드뮴의 흡착특성 연구

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다환방향족 탄화수소(PAHs)와 중금속의 거동은 주로 토양 및 퇴적물내의 다양한 성분과의 상호 반응에 의해 결정된다. 토양구성 성분중 스멕타이트는 양적으로 풍부하고 큰 표면적을 가지고 있어서 오염물의 거동에 커다란 영향을 끼친다. 본 실험에서, 헥사데실트리메틸암모니움(HDTMA)으로 표면개질된 스멕타이트로 다환방향족 탄화수소에 대한 흡착 실험을 실시하였을 때, 헥사데실트리메틸암모니움의 첨가량에 따라 선형적으로 오염물의 흡착량이 증가하였다. 그러나, 트리메틸암모니움(TMA)으로 표면개질된 스멕타이트는 헥사데실트리메틸암모니움이나 도데실트리메틸암모니움(DTMA)으로 표면개질된 스멕타이트보다 다환방향족 탄화수소의 흡착능력이 떨어졌다. 한편, 동일한 스멕타이트로 물속에 존재하는 카드뮴을 제거하는 실험에서 계면활성제의 첨가량이 많지 않을 때는 카드뮴 흡착량이 높았으나, 계면활성제의 첨가량이 증가하면서 반대로 카드뮴의 흡착량은 감소하였다. 이러한 결과는 유기점토에 의한 유기 혹은 무기오염물 흡착 경향성이 점토에 첨가되는 계면활성제의 크기와 첨가량에 의해 크게 좌우됨을 보여준다. 이것은 다시 말해, 계면활성제의 첨가량에 따라 점토광물 층간에 형성되는 양이온성 계면활성제의 안정성과 배열 구조가 환경 오염물들의 효과적인 제거를 결정하는 중요한 요소임을 의미한다.

주요어 : 스멕타이트, 헥사데실트리메틸암모니움, 트리메틸암모니움, 도데실트리메틸암모니움, 계면활성제

The fate and behavior of polycyclic aromatic hydrocarbons(PAHs) and heavy metals in the environment are mainly controlled by their interactions with various components of soils and sediments. Due to their large surface area and abundance in many soils, smectites may greatly influence the fate and transport of the contaminants. In our experiment, PAH sorption by hexadecyltrimethylammonium(HDTMA)-modified smectite linearly increased in proportion to the amount of HDTMA added on the clay. However, trimethylammonium(TMA)-modified smectite did not show superiority in its sorption of PAH compared with the HDTMA-smectite or dodecyltrimethylammonium(DTMA)-smectite. Meanwhile, the smectites modified with the same cationic surfactants adsorbed Cd^{2+}(heavy metal) significantly from water at low surfactant loading level, but the Cd^{2+} adsorption linearly decreased as the loading of surfactant increased. The result shows that the sorption tendency of organoclays for organic or inorganic contaminants was significantly influenced by the amount and size of the surfactants added on the clay. This reveals that the stabilization and configuration of cationic surfactant formed on the clay interlayer of different sizes may be an important factor in controlling the sorptive capacity of each pollutant in the environment.

Key words : Smectites, HDTMA, TMA, DTMA, surfactants

1. INTRODUCTION

From the point of view of adsorption, clay minerals are the most important inorganic components in soil. Their importance comes not only from their abundance but also from the high specific area and exchange capacity values and for some clay minerals, from their appreciable internal surface which is accessible to organic or inorganic molecules. Organoclays formed by displacing the

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*Corresponding author: esyblue@hanmir.com inorganic exchange cations with different organic cations show several promising applications in contamination prevention and environmental remediation including the treatment of waste effluents as extenders for activated carbon and in clay slurry walls, hazardous waste landfills and petroleum tank forms as components of clay barriers(Lee *et al.*, 1989; Smith and Jaffe, 1994; Sheng *et al.*, 1996; Lee and Kim, 2002a).

The mechanisms controlling sorption compounds on organoclays are dependent on the type of organic cations forming organoclays(Boyd *et al.*, 1991). In this study, we used quaternary ammonium cations of the general form $[(CH_3)_3NR]^+$ where R is an aromatic or alkyl hydrocarbon group replacing inorganic cations on smectite clays to evaluate their sorptive properties for common organic/inorganic contaminants. Polycyclic aromatic hydrocarbons (PAHs) are common pollutants in groundwater and soil systems accompanying with heavy metals. We examined the sorptive removal of both aqueous PAHs and Cd^{2+}(heavy metal) using several organoclays by conducting a batch equilibration technique, and investigated the effect of the saturation degree of cationic surfactants on the removal.

2. MATERIALS AND METHODS

2.1. Preparation of organoclays

The clay used in this study was a smectite (Bentonil-GTC4, Cation Exchange Capacity(CEC)= 104 cmol/kg) obtained from the Süd-Chemie Korea Co (Lee and Kim, 2002b-d). The Na-saturated clay was prepared by washing the clay with 0.1 M NaCl repeatedly and then with water until free of chloride was identified. The <2 μm clay fractions were obtained by wet sedimentation.

Three different types of surfactants such as TMA(trimethylammonium), DTMA(dodecyltrimethylammonium) and HDTMA(hexadecyltrimethylammonium) bromide (Aldrich Chemical Co., Milwaukee, WI) were dissolved in deionized water and used to prepare the corresponding organoclays (Table 1).

The Na-saturated smectite samples(20 mg) were placed into 25 mL glass centrifuge tubes (Corex II, Corning Co., NY) containing different volumes of surfactant solutions(4.0 cmol L^{-1}), corresponding to 0.1~1.0 times the CEC of the clay, and were followed by the addition of deionized water to bring the total volume to 20 mL. The tube was shaken on a reciprocating shaker at room temperature for 2 days. The suspension was centrifuged at 8000 rpm for 20 min at 25°C, and the supernatant was decanted. After the treated clay was washed with one portion of deionized water, it was used for adsorption experiments.

2.2. X-ray diffraction

Basal spacings(d_{001}) of surfactant-modified smectites were determined by X-ray diffraction analysis. X-ray diffraction patterns were recorded using CuKα radiation and a Rigaku Geigerflex RAD3-C automated X-ray diffractometer(Tokyo, Japan) that employs a goniometer fitted with a θ-compensating slit, a 0.15 mm receiving slit, and a diffracted-beam graphite monochromator, from 2° to 10° 2θ, in steps of 0.02° 2θ, at 1 s per step.

2.3. PAHs sorption experiments

Sorption of naphthalene and phenanthrene(Aldrich Chemical Co., Milwaukee, WI, Table 1) on surfactant-modified smectite was evaluated using a batch equilibration technique. A weight of 20 mg of surfactant-modified smectites and 25 mL of deionized water were placed in 25 mL glass centrifuge tubes. A stock solution was prepared by

Table 1. Selected properties of the surfactants and PAHs used in this study*.

Compound	Formula	MW	Solubility in distilled water	Log K_{ow}
HDTMA	$(CH_3)_3(CH_2)_{15}CH_3$	364.46	complete	
DTMA	$(CH_3)_3(CH_2)_{11}CH_3$	308.35	complete	
TMA	$(CH_3)_3CH_3$	154.06	complete	
Naphthalene	$C_{10}H_8$	128.17	240 M	3.36
Phenanthrene	$C_{14}H_{10}$	178.23	7.2 M	4.57

*PAH data from Karcher(1988)

dissolving an appropriate amount of solute in methanol(HPLC grade). Stock concentrations and volumes transferred were designed to make an initial aqueous solution for the sorption experiments by maintaining a methanol concentration of 0.2% by volume in the intial aqueous solutions, a level at which methanol has no measurable effect on sorption(Kibbey and Hayes, 1993).

A desired amount of stock solution containing naphthalene and phenanthrene was mixed with a deionized water in a glass centrifuge tube(Corex II, 25 mL) within a few minutes using a microliter syringe to produce initial concentrations of 20 and 0.6 mg/L, respectively. The tubes were capped immediately with Teflon-lined septa, and shaken for 48 h on a reciprocating shaker at room temperature. After equilibration, the tubes were centrifuged at 8000 rpm for 20 min to separate liquid and solid phases. Aqueous naphthalene and phe-nanthrene concentrations were quantified by ultraviolet(UV) absorbance measurements(UV/vis spectrophotometer, HP 8453) at wavelengths of 222 and 251 nm, respectively. Analytical determinations utilized external standard calibration curves over their linear response regions within the instrumental and method detection limits. The recovery of naphthalene and phenanthrene in the blank samples without organoclays was >90%. The amount of PAHs sorbed was calculated from the differences between the amount added and that remaining in the equilibrated solutions.

2.4. Adsorption of cadmium

Cd^{2+} was chosen as one of the heavy metals to understand its adsorption characteristics on organoclays. Adsorption of Cd^{2+} by surfactant-modified smectites was evaluated using batch equilibration assay. Clays(20 mg) were weighed into 20 mL centrifuge tubes, along with 20 mL of deionized water. Cadmium(0.4 ml of 1000 mgL^{-1} Cd^{2+} as $Cd(NO_3)_2$) was then added using a microsyringe to produce an initial concentration of 20 mgL^{-1}. The pH of the clay suspensions was adjusted to be between 4 and 6 using 0.1 M HCl and 0.1 M NaOH. pH values <3 were avoided because of dissolution of smectite(Triantafyllou *et al.*, 1999). The contents in the tubes were mixed on a rotator for 7 days at a room temperature. The liquid and solid phases were separated by centrifugation (8000 rpm, 20 min). The Cd^{2+} concentration was measured using an Inductively Coupled Plasma Atomic Emission Spectrophotometer (Shimadzu, ICPQ 1000, Tokyo, Japan). The adsorption amount of Cd^{2+} was determined by the difference between the amount added and that remaining in the supernatant at equilibrium. The Cd^{2+} adsorption by organoclays was performed in duplicate.

3. RESULTS AND DISCUSSION

3.1. Interlayer change of clays

After smectites were intercalated with quaternary ammonium cations, their basal spacings(d_{001}) were changed depending on the size of the alkyl(R) groups of the surfactants(Table 2). There was little change in the basal spacing on TMA-smectite, but much more change on HDTMA-smectite as surfactant loading increased. For example, a basal spacing(14.1Å) of TMA-smectite filled with TMA cations to about 100% saturation of the CEC(1.0 CEC) shows a monolayer configuration of quaternary alkylammonium on the interlayer of the clay, while 19.5Å of HDTMA-smectite fully saturated to the CEC shows a pseudotrimolecular layer structure of the surfactant (Lagaly, 1982), indicating the existence of a large expansion of the interlayer by the long alkyl chain of the surfactant.

3.2. PAHs sorption

Naphthalene and phenanthrene as organic contaminants were interacted with organoclays containing different alkyl chain sizes(Fig. 1). The sorption amount of naphthalene by HDTMA-smectite almost linearly increased in proportion to the amount of HDTMA added to the clay(Fig. 1a). In DTMA and TMA-smectites, there was also an

Table 2. Interlayer spacings of smectite at different amounts of added surfactants.

Added surfactant (%CEC)	Interlayer spacing (Å) of smectite		
	TMA	DTMA	HDTMA
0	13.7	13.7	13.7
20	13.8	14.2	14.3
40	14.0	14.2	15.1
60	13.9	14.2	17.2
80	14.0	14.2	17.8
100	14.1	17.2	19.5

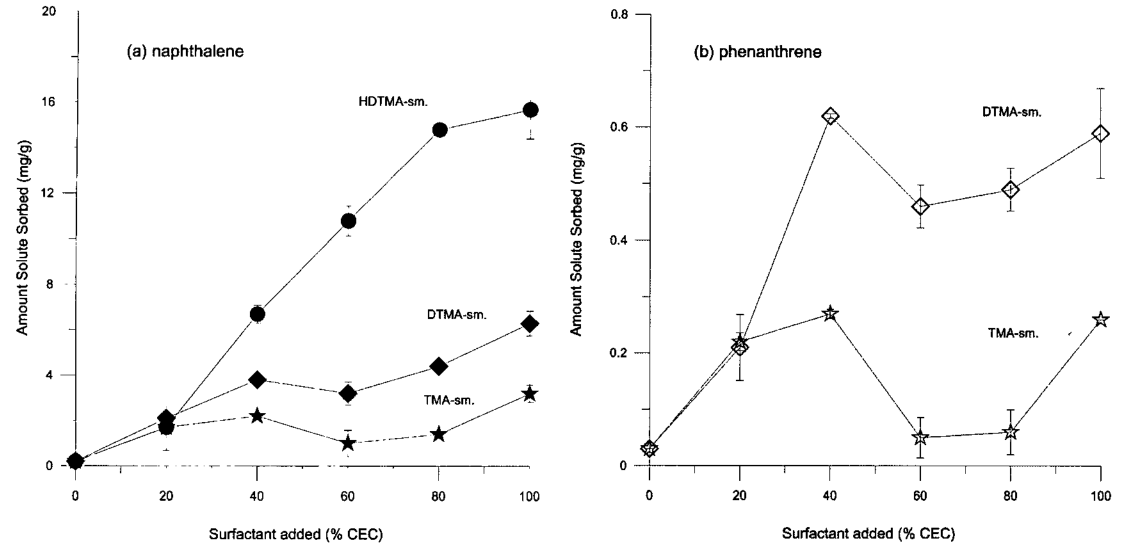

Fig. 1. Sorption of (a) naphthalene and (b) phenanthrene on organoclays at different amounts of added surfactants.

increase of naphthalene sorption along with the surfactant amount to some extent, but no greater than the case in HDTMA-smectite. This result suggests that the naphthalene sorption is significantly influenced by the properties of surfactants (*e.g.*, alkyl chain length sizes) added on the clay. Additionally, there was a partially-decreased naphthalene sorption at about 60% saturation of the CEC(0.6 CEC) in DTMA-smectite(Fig. 1a). In the case of TMA-smectite, there was obvious decrease of naphthalene sorption at about 0.6~0.8 CEC, with a very slight sorption shown at the loading levels(Fig. 1a). Similar phenomena such as solute sorption decreases around 0.6~0.8 CEC were also observed for phenanthrene sorption by the organoclays(Fig. 1b).

In HDTMA-smectite with a large alkyl chain, the sorption of naphthalene increased in proportion to the loading of surfactants on the clay, while there was a weak sorption in organoclays with a shorter alkyl chain, especially TMA-smectite, showing very slight sorption at a specific surfactant loading(*e.g.*, 0.6 CEC). According to Sheng *et al.* (1996), when R is a relatively small group(*e.g.*, R=$-CH_3$) the organic cations in the interlamellar region of smectite are isolated from each other. Such organoclays have relatively high surface areas and display characteristics of surface adsorbents. Alternatively, when R is a large alkyl group (*e.g.*, hexadecyltrimethylammonium(HDTMA), R =$-C_{16}H_{33}$), the resultant organoclays have low surface areas and act as partitioning media in the sorption of organic contaminants from water. Therefore, it is assumed that organic cations such as TMA do not form a continuous organic phase on the clay surfaces and in the interlayers due to their small size. Hence, when the quantity of TMA cations in smectite is higher than about 60% of CEC, the size of the adsorptive regions between neighboring organic cations diminishes sufficiently so that some of this surface cannot accommodate the adsorbate molecule. However, at the maximum of the CEC, the interlayer TMA cations may strongly function as pillars to keep the interlayers apart slightly, so that there may be a little increase of PAH sorption. In other words, larger areas of the clay surface at about 1.0 CEC would be available if the organic cations on opposing clay surfaces interacted, as suggested schematically by Janes and Boyd(1991). Meanwhile, in the organoclays with a long alkyl chain(*e.g.*, HDTMA-smectite), there may be a linear uptake of PAH without a specific decrease of sorption from water as shown in Fig. 1a. It seems that the long organic phase probably functions as a partition medium for PAH and may be highly effective in removing such aromatic compounds from a contaminated environment.

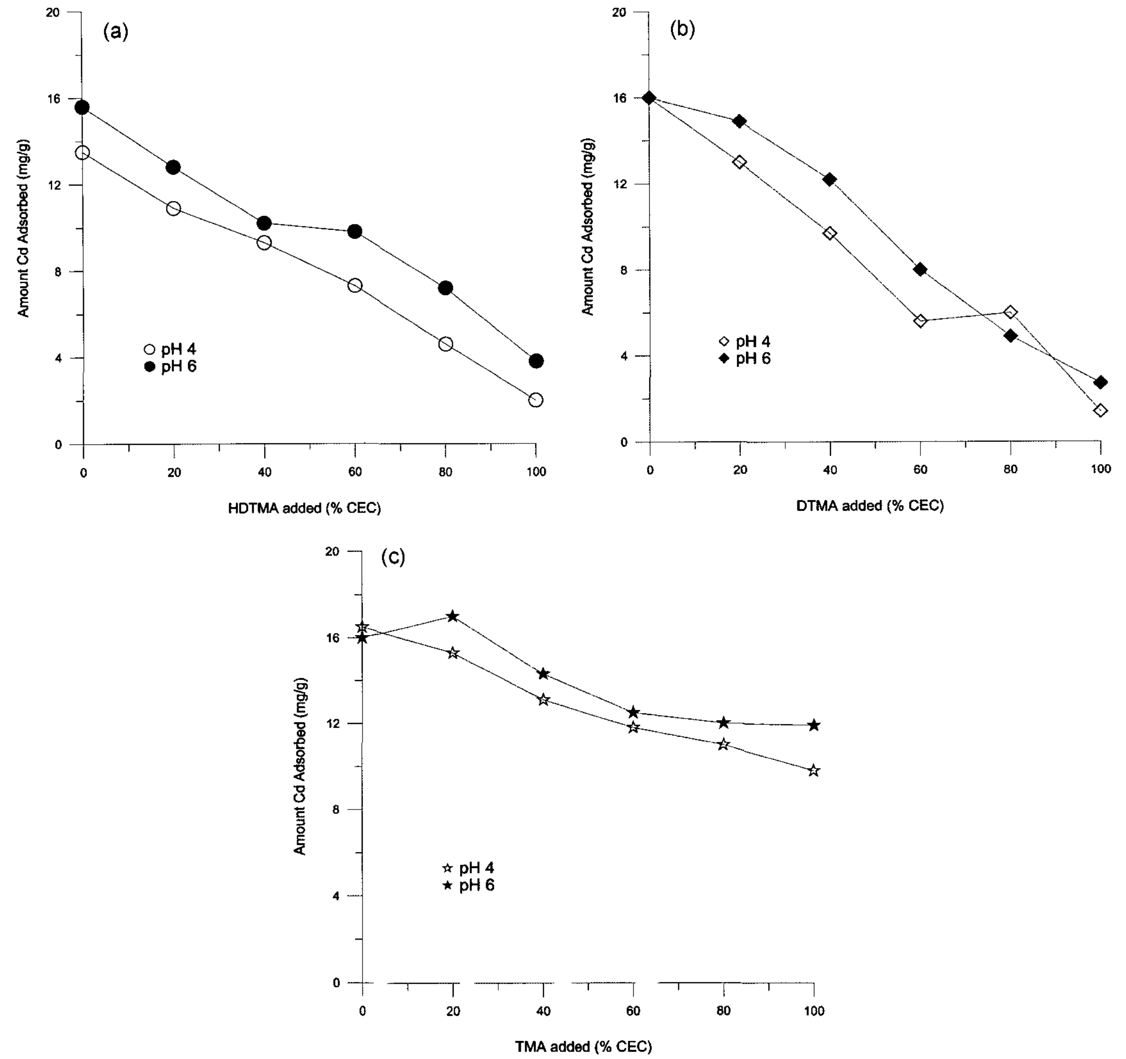

Fig. 2. Adsorption of cadmium on (a) HDTMA-smectite, (b) DTMA-smectite, and (c) TMA-smectite at different amounts of added surfactants.

3.3. Adsorption of Cd^{2+}

The adsorption of Cd^{2+} by the organoclay linearly decreased as the loading of cationic surfactant increased(Fig. 2). This means that exchange of Na^+ with organic cations decreased the ability of the clay to adsorb Cd^{2+}. In other words, the presence of quaternary ammonium cations on the exchange complex may greatly influence the adsorption ability of clays for heavy metals. In addition, in the organoclays highly filled with quaternary alkylammonium(*e.g.*, at 1.0 CEC of HDTMA and DTMA-smectite), the Cd^{2+} adsorption was very slight(Fig. 2a, b). However, the Cd^{2+} adsorption by the organoclay with a short alkyl chain(*i.e.*, TMA-smectite) was not much diminished by the loading of surfactant on the clay, showing a remarkable adsorption of Cd^{2+} even at 1.0 CEC in TMA-smectite (Fig. 2c).

The result indicates that Cd cations can partially remove small organic cations such as TMA, as compared with large quaternary alkyl ammoniums(*e.g.*, HDTMA). There would probably exist a competitive adsorption between the heavy metals and the organic cations in the organoclay with small cations. Some researchers suggested that quaternary ammonium cations are strongly adsorbed on mineral surfaces and may not be easily displaced by heavy metals(Theng *et al.*, 1967; Xu and Boyd, 1994; Sheng *et al.*, 1999). In aqueous systems, quaternary ammonium cations can be retained by both the outer and interlayer surfaces of clay via an ion-exchange process and are not easily displaced by inorganic cations (Zhang *et al.*, 1993; Xu and Boyd, 1995; Sullivan *et al.*, 1998; Gao *et al.*, 2001). However, TMA, because of its only small C-1 chain, is expected to be slightly adsorbed on the hydrophobic surfaces of clay, rendering several TMA on exchange sites displaced by heavy metals. Furthermore, monovalent cations are known to be effectively displaced by bivalent cations from exchange sites, according to the concentration-charge rule(McBride, 1994). Consequently, the organoclays saturated fully with small quaternary alkylammonium(*e.g.*, TMA-smectite) or filled partially(*e.g.*, <100% of the CEC) with large ones(*e.g.*, HDTMA- and DTMA-smectites) can adsorb and retain heavy metals to some degree and will be strategically applicable to contaminated sites for the purpose of remediation.

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