

# A Study on the Sorption Characteristics of Polycyclic Aromatic Hydrocarbon (PAH) and Cadmium by Bentonite

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## 1. Introduction

From the point of view of adsorption, bentonite is the most important inorganic components in a barrier system of radioactive disposal site. Its importance comes 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. Clays in bentonite show several promising applications in contamination prevention and environmental protection as clay slurry walls and barriers in disposal sites. To evaluate sorptive properties for common organic matter and radioactive cation on the bentonite, we used quaternary ammonium cations of the general form  $[(\text{CH}_3)_3\text{NR}]^+$ , polycyclic aromatic hydrocarbon (PAH), and  $\text{Cd}^{2+}$ .

## 2. Materials and Methods

### 2.1. Sorption of organic matters

The bentonite used in this study was Bentonil-GTC4 (cation exchange capacity (CEC) = 104 cmol/kg) obtained from the Süd-Chemie Korea Co.. The Na-saturated bentonite was prepared by washing the bentonite with 0.1 M NaCl repeatedly and then with water until free of chloride was identified. The  $<2\text{-}\mu\text{m}$  particle fractions were obtained by wet sedimentation.

Various types of organic compounds (Table 1) such as TMA (trimethylammonium), DTMA (dodecyltrimethylammonium) and HDTMA (hexadecyltrimethylammonium) bromide (Aldrich Chemical Co., Milwaukee, WI) were dissolved in deionized water and used for the experiment.

Sorption of PAH on bentonite was evaluated using a batch equilibration technique. A weight of 20 mg of bentonite and 25 mL of deionized water were placed in 25-mL glass centrifuge tubes. A stock solution was prepared by dissolving an appropriate amount of solute in methanol (HPLC grade).

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

Compound	Formula	MW	Solubility	Log $K_{ow}$
HDTMA	$(\text{CH}_3)_3(\text{CH}_2)_{15}\text{CH}_3$	364.46	complete	
DTMA	$(\text{CH}_3)_3(\text{CH}_2)_{11}\text{CH}_3$	308.35	complete	
TMA	$(\text{CH}_3)_3\text{CH}_3$	154.06	complete	
Naphthalene	$\text{C}_{10}\text{H}_8$	128.17	240 $\mu\text{M}$	3.36

A desired amount of stock solution containing PAH 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 mg/L. 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 PAH concentrations were quantified by ultraviolet (UV) absorbance measurements (UV/vis spectrophotometer, HP 8453).

### 2.2. Adsorption of cadmium

Adsorption of  $\text{Cd}^{2+}$  by bentonite was evaluated using batch equilibration assay. Bentonite (20 mg) was weighed into 20 mL centrifuge tubes, along with 20 mL of deionized water. Cadmium (0.4 ml of 1000 mg  $\text{L}^{-1}$   $\text{Cd}^{2+}$  as  $\text{Cd}(\text{NO}_3)_2$ ) was then added using a microsyringe to produce an initial concentration of 20 mg  $\text{L}^{-1}$ . The pH of the bentonite 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 bentonite [1]. The  $\text{Cd}^{2+}$  concentration was measured using an Inductively Coupled Plasma Atomic Emission Spectrophotometer (Shimadzu, ICPQ 1000, Tokyo, Japan).

## 3. Results and Discussion

### 3.1. PAH sorption

PAH was interacted with bentonite containing different alkyl chain sizes (Fig. 1). The sorption amount of naphthalene by HDTMA-bentonite almost linearly increased in proportion to the amount of HDTMA added to the clay (Fig. 1). In DTMA- and TMA-bentonite, there was also an increase of naphthalene sorption along with the organic amount to some extent, but no greater than the case in HDTMA-bentonite. This result suggests that the PAH sorption is significantly influenced by the properties of organic compounds (*e.g.*, alkyl chain length sizes) added on the bentonite. Additionally, there was a partially-decreased naphthalene sorption at about 60% saturation of the CEC (0.6 CEC) in DTMA-bentonite (Fig. 1). 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. 1).

In HDTMA-bentonite with a large alkyl chain, the sorption of PAH increased in proportion to the loading

of organic compound on the bentonite, while there was a weak sorption in bentonite with a shorter alkyl chain, especially TMA-smectite, showing very slight sorption at a specific loading (e.g., 0.6 CEC). According to Sheng *et al.* [2], when R is a relatively small group (e.g., R = -CH<sub>3</sub>) the organic cations in the interlamellar region of bentonite are isolated from each other. Such bentonite has relatively high surface areas and display characteristics of surface adsorbents. Alternatively, when R is a large alkyl group (e.g., hexadecyltrimethyl-ammonium (HDTMA), R = -C<sub>16</sub>H<sub>33</sub>), the resultant bentonite has low surface areas and act as partitioning media in the sorption of organic matter 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.

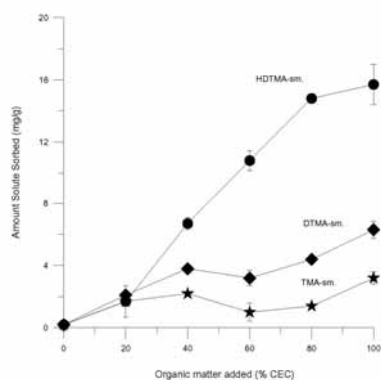


Figure 1. Sorption of naphthalene (PAH) on the bentonite with various organic matters

### 3.2. Adsorption of Cd<sup>2+</sup>

The adsorption of Cd<sup>2+</sup> by bentonite linearly decreased as the loading of organic matter increased (Fig. 2). This means that exchange of Na<sup>+</sup> with organic cations decreased the ability of the bentonite to adsorb Cd<sup>2+</sup>. In other words, the presence of quaternary ammonium cations on the exchange complex may greatly influence the adsorption ability of bentonite for Cd<sup>2+</sup>. In addition, in the bentonite highly filled with quaternary alkylammonium (e.g., at 1.0 CEC of HDTMA-bentonite), the Cd<sup>2+</sup> adsorption was very slight (Fig. 2a). However, the Cd<sup>2+</sup> adsorption by the bentonite with a short alkyl chain (*i.e.*, TMA-bentonite) was not much diminished by the loading of organic matter on the bentonite, showing a remarkable adsorption of Cd<sup>2+</sup> even at 1.0 CEC in TMA-bentonite (Fig. 2b).

The result indicates that Cd cations can be partially exchanged with 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 Cd<sup>2+</sup> and the organic cations in the bentonite 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 [3]. 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 [4,5]. However, TMA, because of its only small C-1 chain, is expected to be slightly adsorbed on the hydrophobic surfaces of bentonite, rendering several TMA on exchange sites displaced by Cd<sup>2+</sup>. Furthermore, monovalent cations are known to be effectively displaced by bivalent cations from exchange sites, according to the concentration-charge rule [6]. Consequently, it seems that the bentonite saturated fully with small and large organic matter can adsorb and retain radioactive cations to some degree.

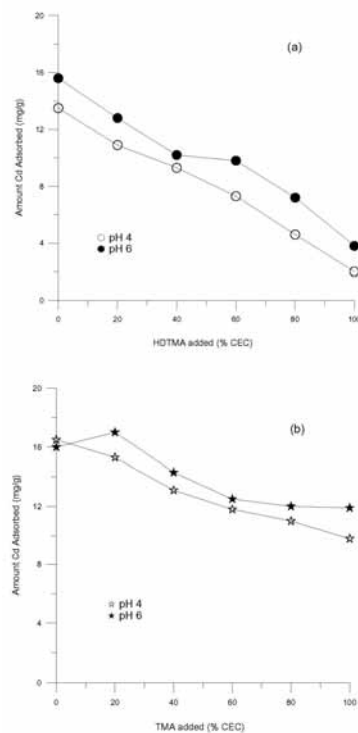


Figure 2. Adsorption of cadmium on the bentonite loaded with different organic matter

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