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The Removal of 2-Phenylphenol from Aqueous Solution by Adsorption onto Organoclays

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The adsorption of 2-phenylphenol onto organically pillared clays (a natural montmorillonite and a synthetic saponite) was investigated. Organoammonium salts used for the clay modification were trimethylphenylammonium bromide, 3-(trifluoromethyl)phenyltrimethylammonium bromide, and neostigmine bromide. All the organically pillared clays adsorbed 2-phenylphenol from water. The adsorbed amount of 2-phenylphenol was smaller as the cation-exchange capacity of host was larger, showing possible pore volume engineering.

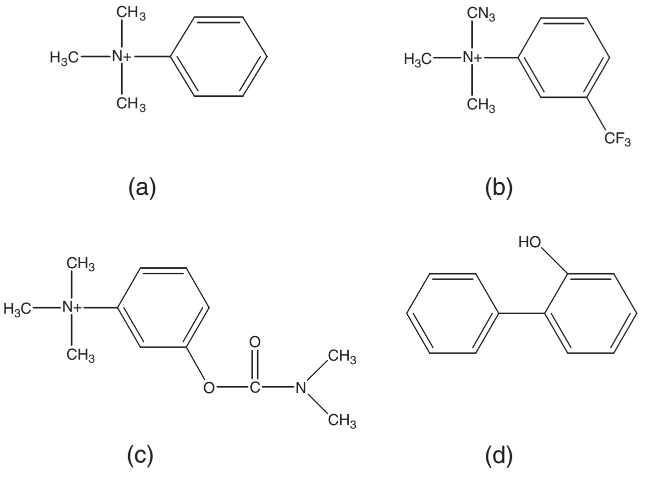
The concentration of certain molecular species in the environment is a topic of a wide range of scientific and practical viewpoints such as the removal of toxic compounds and the concentration of noble elements. Adsorption based processes are one promising approach to this goal, therefore designing adsorbents for target molecules is worth conducting. In this study, the removal of 2-phenylphenol (hereafter abbreviated as 2PP), which is a well known antifungal agent,[1,2] from water was investigated using a series of organically pillared clays as adsorbents.

Smectite, which is a layered clay mineral consisting of negatively charged silicate layer and a charge compensating interlayer cation,[3] is a known material with possible applications for adsorption, catalysis, and photofunctions.[4] Since smectites are cation exchangers, they are useful adsorbents for such cationic species as radioactive ions in nuclear wastes[5–7] and heavy metals.[8] The adsorption of nonionic species is also possible, through ion–dipole interactions as well as hydrogen bonding.[9] When the interlayer cations are replaced with organoammonium cations, the surface properties of smectites are suitable for the adsorption of various nonionic organic species.[10–12]

Organically pillared clay is a class of organically modified clays, where a relatively small organoammonium cation, such as tetramethylammonium ion, holds silicate layers like pillars and forms nanospaces surrounded with organic cations and silicate layer.[13–24] One objective of the present study is to highlight the possible design of the porous structures of organically pillared clays for a target molecule, so two smectites with different layer charge and three organoammonium ions were used as the building blocks of nanoporous structures. Among organically pillared clays, organic cation containing aromatic rings acted as pillars to adsorb aromatic compounds as a result of affinity between aromatic rings.[22,23] Accordingly, three organic cations with aromatic rings were used to create nanospaces in the interlayer space for the adsorption of 2PP.

Experimental

Materials. Natural Na–montmorillonite (Kunipia F obtained from Kunimine Ind. Co., Japan; hereafter abbreviated as KF) and a synthetic saponite (Sumecton SA from Kunimine Ind. Co., Japan; hereafter abbreviated as SA) were used. The cation exchange capacities (CEC) are 119 and 70 mequiv$\cdot$(100 g clay)$^{-1}$ for KF and SA, respectively. Trimethylphenylammonium chloride (abbreviated as TMPA), 3-(trifluoromethyl)phenyltrimethylammonium bromide (abbreviated as CF3TMPA), and neostigmine bromide $(CH_3)_3N^+$-$(C_6H_4)CO_2N(CH_3)_2\cdot Br^-$ (abbreviated as CONH) were purchased from Tokyo Kasei Ind. Co. and used as received. The molecular structures of the organoammonium ions used in the present study are shown in Scheme 1. 2-Phenyphenol, abbreviated as 2PP, was obtained from Tokyo Kasei Ind. Co. and used as received.



Scheme 1. Molecular structures of (a) TMPA, (b) CF3TMPA, (c) CONH, and (d) 2PP.

Table 1. The Characteristics of Organoammonium–Clays Prepared in the Present Study

	$d(001)$/nm	Δd/nm	Carbon content /%	Nitrogen content /%	Amount of organic cation exchanged /mequiv·(100 g clay)$^{-1}$
KF	1.26	0.30	—	—	—
SA	1.27	0.31	—	—	—
TMPA–KF	1.51	0.55	9.7	1.1	110
CF3TMPA–KF	1.51	0.55	9.3	1.1	96
CONH–KF	1.71	0.77	11.3	1.9	99
CONH–SA	1.51	0.55	8.6	1.5	73

Preparation of Pillared Clays. Organoammonium–clays were prepared from KF and SA by cation exchange with aqueous solutions where the added amount of the organoammonium ion was 1.1 times in excess of the CEC. After the aqueous phase was separated by centrifugation, the solid product was washed with deionized water until negative $AgNO_3$ test was obtained and subsequently dried under reduced pressure at room temperature.

Characterizations. XRD patterns were recorded on a Rigaku RAD IIB powder diffractometer equipped with monochromatic Cu Kα radiation, operated at 20 mA, 40 kV. CHN analysis was performed on a Perkin-Elmer 2400II instrument. TG-DTA curves were measured with a Rigaku TAS-2000 instrument with a heating rate of 10 K min^{-1}. using α-Al_2O_3 as the standard material under air. UV–visible absorption spectra were recorded on a Shimadzu UV 3100 PC spectrophotometer.

Adsorption of 2PP from Water. Adsorption of 2PP from aqueous solution was conducted as follows. Adsorbents (25 mg) were allowed to react with 30 mL of aqueous 2PP solution in a 50 mL glass vessel for 1 day at room temperature in the dark. Blank samples without adsorbents were also prepared to estimate vaporization losses and the adsorption on the glass vessel. After the adsorbents were separated by centrifugation, the concentration of the remaining 2PP in supernatant was determined by UV absorption spectroscopy (absorption λ_{max} at 282 nm). Adsorption isotherms were obtained by plotting the adsorbed amounts of 2PP (Q) versus the equilibrium concentrations (C_e).

Results and Discussion

Sample Preparation. The basal spacings and the amounts of the adsorbed organoammonium ions on the organo–clays are summarized in Table 1. The adsorbed amounts were determined from the carbon contents by CHN analysis (C content base) to be 110, 96, and 99 mequiv·(100 g clay)$^{-1}$ for TMPA–, CF3TPMA–, CONH–KF, respectively, and 73 mequiv·(100 g clay)$^{-1}$ for CONH–SA. Taking the CEC of the host materials (70 and 119 mequiv·(100 g clay)$^{-1}$ for SA and KF, respectively) into consideration, quantitative ion exchange was confirmed.

The gallery heights of the organoammonium–clays were determined by subtracting the thickness of the silicate layer (0.96 nm) from the observed basal spacing. The gallery heights of TMPA– and CF3TMPA–KF were 0.55 nm, which is indicative of a monolayer arrangement of the intercalated organoammonium ions. The gallery heights of CONH–KF and –SA were 0.77 and 0.55 nm, respectively, suggesting that the monolayer arrangements of the intercalated CONH ions and the variation of the orientation depending on the layer charge density as schematically shown in Figure 1. The above discussion on the orientation (or arrangement) of the intercalated organoammonium ion was based on their molecular structures (Scheme 1).

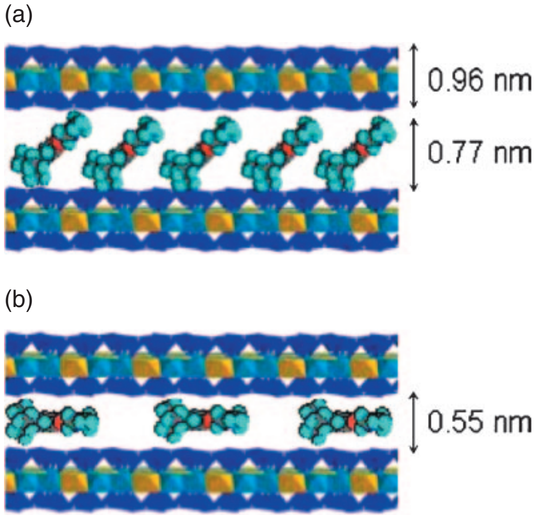


Figure 1. Schematic drawings of (a) CONH–KF and (b) CONH–SA.

Adsorption of 2PP. The adsorption isotherm of 2PP for CF3TMPA–KF is shown in Figure 2. According to the Giles classification, the isotherm of 2PP for CF3TMPA–KF was type-S, showing the weak affinity between adsorbate and adsorbents.[25,26] If compared with those for TMPA– and CONH–KF, only a small amount of 2PP was adsorbed on CF3TMPA–KF when the equilibrium concentration was low. The amount of the adsorbed 2PP increased to some extent with the increase in the equilibrium concentration, while the shape of the isotherms did not indicate the strong adsorbent–adsorbate interactions. For the adsorption of benzene onto a series of quaternary ammonium–montmorillonites, Chun et al. reported the larger amounts of benzene adsorbed when the size of quaternary ammonium cations were smaller.[17] It was explained that the size of quaternary ammonium cations were larger, the distance between the cations in the interlayer as well as the interlayer volume was smaller. It was thought, due to the larger molecular size of CF3TMPA than that of TMPA, the space for the 2PP in the interlayer space was smaller to cause the lower adsorption capacity. In addition, oleophobic effects of CF_3 groups may be concerned.

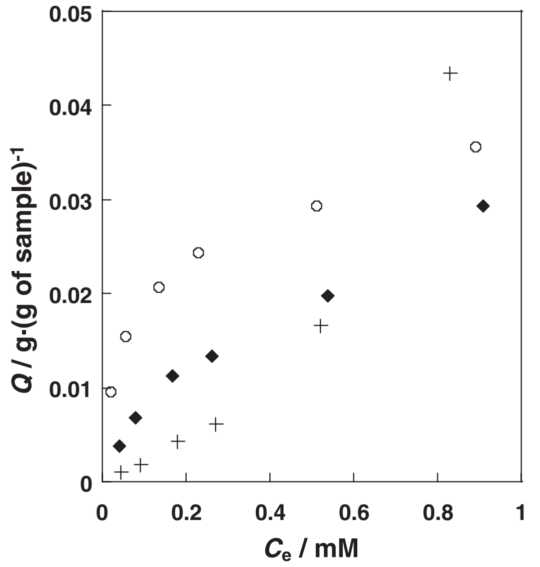


Figure 2. Adsorption isotherms of 2PP for CONH–KF (circle), TMPA–KF (square), and CF3TMPA–KF (cross).

Table 2. Adsorption Parameters of 2PP onto the Organoammonium–Clays

	R^2	a	W_s/g•(g of sample)$^{-1}$
TMPA–KF	0.9960	3.60	0.031
CONH–KF	0.9818	20.1	0.031
CONH–SA	0.9552	36.1	0.053

On the contrary to the adsorption on CF3TMPA–KF, the adsorption isotherms of 2PP on the TMPA– and CONH–KF were fitted to the Langmuir equation ($1/W = 1/W_s + (1/aW_s)(1/C)$) by plotting $1/C$ versus $1/W$ (where W is 2PP adsorbed onto organo–clay, C is equilibrium concentration). The adsorption constant (a), the adsorbed amount of 2PP as monolayer (W_s) and the R^2 value (a measure of linearity) were determined for each isotherm. It is thought that there is good affinity between the aromatic ring of TMPA or CONH in the interlayer cation and aromatic ring of 2PP. The adsorption constant (a) of CONH–KF for 2PP (20.1, Table 2) was larger than that of TMPA–KF (3.60). This means that the interactions between CONH and 2PP were larger than that between TMPA and 2PP.

In order to compare the geometry of nanospace, CONH–SA, where SA has smaller layer charge density than that of KF, was used for the adsorption of 2PP. Note that the adsorption of 2PP on pristine SA and KF showed similar isotherm and capacity. The adsorption isotherms of 2PP on the CONH–SA (Figure 3) were also fitted to the Langmuir equation. The adsorbed amount of 2PP onto CONH–SA as monolayer (W_s) was 0.053 g•(g of sample)$^{-1}$ (Table 2) and this was the largest W_s value achieved in the present systems. The amount of CONH cation in the clays were 99 and 73 mequiv•(100 g clay)$^{-1}$ for KF and SA, respectively (Table 1). It was reported that the amounts of organic compounds adsorbed in the interlayer spaces increased as the CEC of host materials was lower because of the increase of the interlayer nanospace volume.[27,28]

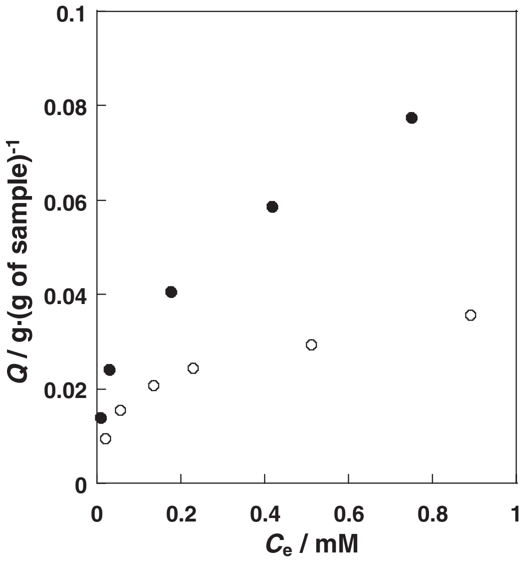


Figure 3. Adsorption isotherms of 2PP for CONH-KF (open circle) and CONH-SA (filled circle).

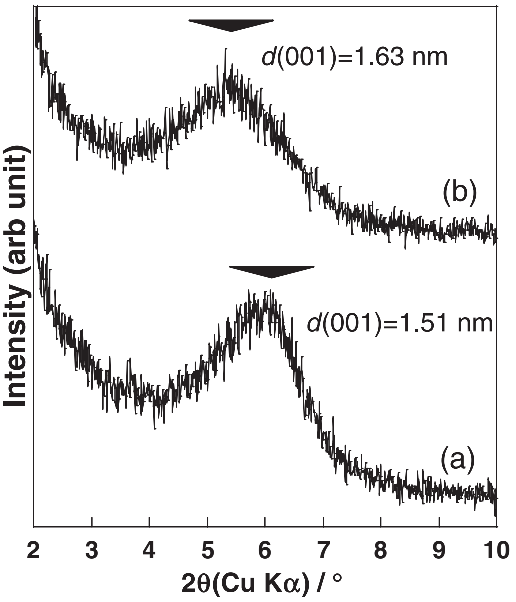


Figure 4. XRD patterns of CONH-KF (a) before and (b) after the adsorption of 2PP.

The adsorption constant (a) of CONH–SA for 2PP (36.1) was larger than that of CONH–KF (20.1) (Table 2).

The basal spacing of the CONH–KF increased from 1.51 nm (Figure 4a) to 1.63 nm (Figure 4b) after the adsorption of 2PP as a result of the rearrangement of the interlayer CONH to accommodate 2PP, while the basal spacing did not change for all other systems. This is a unique phenomenon for the adsorption using organically pillared clays, though for organophilic silicates there are several examples of interlayer expansion by the adsorption of nonionic compounds.[29–32] It is also worth noting the change in the color of CONH–SA from colorless to yellow by the adsorption of 2PP. Though the origin of the color development is not clear at present, the color change (in combination with the effective adsorption) can be used as an indicator to detect 2PP in water as proposed for the phenol detection by organoammonium smectites.[22,23]

Conclusion

The adsorption of 2-phenylphenol from aqueous solution onto organically modified clays was examined to find the effects of the surface modification with different functionality on the adsorption capacity. The layer charge density of parent clay was another parameter to determine the adsorption of 2-phenylphenol. Among tested adsorbents, the neostigmanine-modified saponite was most effective to remove 2-phenylphenol from the viewpoints of strong adsorbate–adsorbent interactions as well as the color development upon the adsorption, which is attractive to construct a colorimetric sensor to detect 2PP.

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References

1 S. Tayama, N. Kamiya, Y. Nakagawa, *Mutat. Res.* **1989**, *223*, 23.

2 S.-L. Cheng, H.-C. Wang, P.-C. Yang, *J. Formosan Med. Assoc.* **2005**, *104*, 585.

3 H. Van Olphen, *An Introduction to Clay Colloid Chemistry*, Wiley-Interscience, **1977**.

4 M. Ogawa, K. Kuroda, *Chem. Rev.* **1995**, *95*, 399.

5 R. Pusch, *Nucl. Technol.* **1979**, *45*, 153.

6 M. Takahashi, M. Muroi, A. Inoue, M. Aoki, M. Takizawa, K. Ishigure, N. Fujita, *Nucl. Technol.* **1987**, *76*, 221.

7 N. Kozai, T. Ohnuki, S. Muraoka, *J. Nucl. Sci. Technol.* **1993**, *30*, 1153.

8 L. Mercier, C. Detellier, *Environ. Sci. Technol.* **1995**, *29*, 1318.

9 B. K. G. Theng, *The Chemistry of Clay Organic Reactions*, Adam Lilger Ltd., London, U. K., **1974**.

10 J. W. Jordan, *J. Phys. Chem.* **1949**, *53*, 294.

11 R. M. Barrer, *Clays Clay Miner.* **1989**, *37*, 385.

12 M. Ogawa, K. Kuroda, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2593.

13 J.-F. Lee, M. M. Mortland, S. A. Boyd, C. T. Chiou, *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2953.

14 M. Ogawa, T. Handa, K. Kuroda, C. Kato, T. Tani, *J. Phys. Chem.* **1992**, *96*, 8116.

15 M. Ogawa, M. Takahashi, C. Kato, K. Kuroda, *J. Mater. Chem.* **1994**, *4*, 519.

16 M. Ogawa, M. Takahashi, K. Kuroda, *Chem. Mater.* **1994**, *6*, 715.

17 Y. Chun, G. Sheng, S. A. Boyd, *Clays Clay Miner.* **2003**, *51*, 415.

18 W. F. Jaynes, G. F. Vance, *Clays Clay Miner.* **1999**, *47*, 358.

19 R. M. Barrer, G. S. Perry, *J. Chem. Soc.* **1961**, 842.

20 R. M. Barrer, G. S. Perry, *J. Chem. Soc.* **1961**, 850.

21 W. F. Jaynes, S. A. Boyd, *J. Air Waste Manage. Assoc.* **1990**, *40*, 1649.

22 T. Okada, M. Ogawa, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1165.

23 T. Okada, M. Ogawa, *Chem. Commun.* **2003**, 1378.

24 R. Ishii, T. Ikeda, T. Itoh, T. Ebina, T. Yokoyama, T. Hanaoka, F. Mizukami, *J. Mater. Chem.* **2006**, *16*, 4035.

25 C. H. Giles, D. Smith, A. Huitson, *J. Colloid Interface Sci.* **1974**, *47*, 755.

26 C. H. Giles, T. H. MacEwan, S. N. Nakhwa, D. Smith, *J. Chem. Soc.* **1960**, 3973.

27 V. A. Nzengung, E. A. Voudrias, P. Nkedi-Kizza, J. M. Wampler, C. E. Weaver, *Environ. Sci. Technol.* **1996**, *30*, 89.

28 J.-F. Lee, M. M. Mortland, C. T. Chiou, D. E. Kile, S. A. Boyd, *Clays Clay Miner.* **1990**, *38*, 113.

29 T. Okada, Y. Watanabe, M. Ogawa, *Chem. Commun.* **2004**, 320.

30 I. Fujita, K. Kuroda, M. Ogawa, *Chem. Mater.* **2005**, *17*, 3717.

31 M. Ogawa, R. Goto, N. Kakegawa, *Clay Sci.* **2000**, *11*, 231.

32 M. Ogawa, T. Wada, K. Kuroda, *Langmuir* **1995**, *11*, 4598.