DOCTORAL THESIS

A Study on Separation Media for Sustainable Water Treatment Technologies

by

Mako Oiwa

Advised by:

Tohru Saitoh

KITAMI INSTITUTE OF TECHNOLOGY

GRADUATE SCHOOL OF ENGINEERING

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ABSTRACT

A novel separation medium was developed for designing simple, highly efficient, and eco-friendly remediation technologies for treating water containing highly bioactive organic pollutants such as pharmaceuticals, personal care products, and pesticides. The separation medium, didodecyldimethylammonium bromide-montmorillonite (DDAB-MT) organoclay, was readily prepared by mixing a dialkylated cationic surfactant, didodecyldimethyl-ammonium bromide (DDAB) and a layered clay mineral, montmorillonite K30 (MT), in the aqueous solution. The possibility of DDAB-MT organoclay for treating water contaminating highly bioactive organic pollutants was studied.

DDAB-MT organoclay was used for the sorption and degradation of an organophosphate pesticide, fenitrothion, in water. The degree of sorption increased by the modification of MT with DDAB, because of the formation of hydrophobic DDAB assemblies for the sorption of hydrophobic fenitrothion. Fenitrothion ([M+1] = 278) sorbed on the organoclay rapidly converted to the degraded product anion ([M] = 262) followed by the further degradation into 3-methyl-4-nitrophenol ([M−1] = 152). The activation energy for the first-order reaction of the primary degradation of fenitrothion (79.9 kJ mol^{-1}) in the organoclay was lower than the value (94.1 kJ mol^{-1}) in water. Organoclay-mediated catalytic activity expressed over a wide pH region (pH 5−9), being advantageous for the application to different wastewaters and environmental waters. Continuous sorption and degradation of fenitrothion in contaminated water was examined by using a laboratory-scale organoclay-packed column. Fenitrothion-free effluent containing its degraded product, 3-methyl-4-nitrophenol, having lower toxicity to

aquatic organisms outflowed from the bottom of the column.

The sorption of various antibiotics, pharmaceuticals and personal care products in water onto DDAB-MT organoclay was also studied. The extent of the sorption on the organoclay was largely dependent on the DDAB content; the effect of DDAB modification on the sorption was also influenced by hydrophobicity and/or net charge of pharmaceutical. The binding constants of β-lactam antibiotics were determined from their interaction with the DDAB molecules on the organoclay and were correlated with their aqueous-octanol distribution coefficients. Additionally, it was also influenced by the net charge of the antibiotic. A wide range of β-lactam antibiotics including penicillin- and cephalosporin-type antibiotics were sorbed on the organoclay and rapidly degraded under mild conditions (pH 7, 25ºC). The continuous sorption and degradation of penicillin G in a buffer solution and synthesized hospital wastewater were demonstrated by using an organoclay-packed column. The resulting effluent was free of penicillin, and containing only penicillin degraded products.

In conclusion, DDAB-MT organoclay was useful separation medium for decontaminating water containing bioactive organic pollutants such as pharmaceuticals, personal care products, and pesticides. Because of high water permeability and hydrophobic property, the organoclay sorbed a wide range of organic pollutants and efficiently decontaminated polluted water. Moreover, β-lactam antibiotics and fenitrothion sorbed on the organoclay degraded into less toxic compounds. Continuous sorption and degradation in the contaminated water was successfully demonstrated, suggesting the usefulness of DDAB-MT organoclay as a barrier material for controlling diffusion of bioactive organic

pollutants.

ABSTRACT IN JAPANESE（論文内容の要旨）

医薬品，パーソナルケア製品，農薬などの生理活性の高い有機汚染物質含有水の処理のために，簡便で高効率かつ低環境負荷水処理技術を設計するために，新しい分離媒体を開発した。この分離媒体は，二本鎖カチオン性界面活性剤である臭化ジメチルアンモニウム（DDAB）と層状粘土鉱物であるモンモリロナイトK30（MT）を水溶液中で混合することにより、容易に調製することができた。DDAB-MT オルガノクレーによる高生理活性有機汚染物質汚染水処理の可能性を検討した。

DDAB-MT オルガノクレーを用いて，有機リン酸系農薬であるフェニトロチオンの水中での吸着・分解実験を行った。 MT を DDAB で修飾することで吸着量が増加した。これは疎水性の DDAB 集合体が形成され、疎水性のフェニトロチオンがそこに吸着されたためである。オルガノクレーに吸着したフェニトロチオン([M+1] = 278)は，速やかに分解生成物のアニオン([M] = 262)に変換され，さらに 3-methyl-4-nitrophenol([M-1] = 152)に分解された。オルガノクレーにおけるフェニトロチオンの一次分解の活性化エネルギー（79.9 kJ mol^{-1}）は，水中での値（94.1 kJ mol^{-1}）よりも低かった。オルガノクレーを用いた触媒活性は，広い pH 領域（pH5～9）で発現しており，さまざまな排水や環境水への適用に有利であった。実験室規模のオルガノクレー充填カラムを用いて、フェニトロチオン汚染水の連続的な吸着・分解実験をおこなった。 カラムの底から流出する、フェニトロチオンの分解物である 3-methyl-4-nitrophenol を含み、フェニトロチオンを含まない水は、水生生物への毒性が低い。

また，水中のさまざまな抗生物質，医薬品，パーソナルケア製品の DDAB-MT オルガノクレーへの吸着についても検討した。オルガノクレーへの吸着

量は，DDAB の含有量に大きく依存しており，吸着に対する DDAB の修飾の効果は，医薬品の疎水性や正味の電荷にも影響を受けた。 β-ラクタム系抗生物質の結合定数は,オルガノクレー上の DDAB 分子との相互作用から決定され，水-オクタノール分配係数と相関していた。 さらに，抗生物質の正味の電荷にも影響を受けていた。 ペニシリン系，セファロスポリン系を含む広範な β-ラクタム系抗生物質がオルガノクレーに吸着し，温和な条件（pH7，25℃）で速やかに分解された。 オルガノクレーを充填したカラムを用いて，緩衝液および合成病院排水中のペニシリン G の連続的な吸着と分解実験をおこなった。 得られた廃液にはペニシリンは含まれず，ペニシリンの分解物のみが含まれていた。

結論として，DDAB-MT オルガノクレーは，医薬品，パーソナルケア製品，農薬などの生理活性有機汚染物質を含む水の汚染物質除去に有用な分離媒体であった。 オルガノクレーは高い透水性と疎水性を有しているため，広範囲の有機汚染物質を吸着し，汚染水を効率的に処理することができた。さらに、オルガノクレーに吸着した β-ラクタム系抗生物質やフェニトロチオンは、毒性の低い化合物に分解された。 また，汚染水を連続的に吸着・分解することが確認され，DDAB-MT オルガノクレーが生理活性有機汚染物質の拡散を抑制するバリア材料として有用であることが示唆された。

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CHAPTER 1
INTRODUCTION

Increasing population and development of industrials causing expanding environmental pollution by organic pollutants. Recently, highly bioactive organic pollutants such as pharmaceuticals, personal care products, and pesticides are paid attention in particular. Pesticides and pharmaceuticals are known to have adverse effects on ecosystems even in small amounts [1-4]. Pesticides leak from soil into environmental water through rainwater leakage or infiltration into groundwater without going through wastewater treatment plants. Leaked pesticides are known to cause a decrease in the populations of aquatic organisms [5-8]. It has also been reported that pesticides are bioaccumulated in fish [9]. Since pesticides leakage has a wide range of adverse effects on ecosystems, a method to prevent leakage of pesticides are required. Also, pharmaceuticals are conventionally treated at wastewater treatment plants using activated sludge method or activated carbon adsorption, but these methods are not enough. The removal rate of pharmaceuticals in these wastewater treatment plants is erratic, it depends on the pharmaceutical (55-81%) [10]. Then pharmaceuticals that exceed capacity of these plants induce to increasing antimicrobial resistant bacteria [11, 12]. Therefore, there is a need for highly efficient, low cost processing and low environmental impact technologies to prevent diffusing these highly bioactive substances.

Several physical and chemical processes have been developed for the removal or degradation of pharmaceuticals in environmental waters and wastewaters [13]. Photo-catalytic methods such as photo-Fenton reaction and semiconductor photocatalytic oxidation have been reported as the rapid degradation of β-lactams which is one kind of pharmaceuticals [14, 15], but continuous ultra-violet irradiation likely boosts the cost of

wastewater treatment. Requirements of high oxidant dosage and pH adjustment (typically pH 2–4) are additional expense for large scale treatment. Activated carbon adsorption has been extensively used in practical water and wastewater treatment processes [16, 17] and applied to the removal of a wide range of pharmaceuticals [18-20]. However, the extent of removal for pharmaceuticals is largely dependent on the kind of pharmaceuticals and often insufficient because of their low hydrophobicity (log K_{ow} = 0.9–2.9 [21]) and negative charge in neutral pH region (pK_a ~ 2.7 [21]) [13, 20]. Moreover, activated carbon adsorption is expensive method because activated carbon is expensive (about US$ 20–22.00/kg [22]).

An attractive alternative may be a sorption method using surfactant-modified clay minerals namely organoclay. The organoclay can be readily prepared by mixing appropriate surfactants and clay minerals in the aqueous media [23-25]. Hydrophobic organic pollutants in water are incorporated into surfactant aggregates formed between the layers of clay minerals [23-28]. Rather polar and ionizable compounds such as phenols, pesticides, and pharmaceuticals can also sorb on the organoclay [29-40]. Moreover, recent reports about the sorption of a selected antibiotic, amoxicillin [34], [39], strongly suggest the potential usefulness of the organoclay sorption method for the treatment of hospital wastewaters containing different antibiotics. And Montmorillonite which is often used to make organoclay is known to be inexpensive (about US$ 0.04–0.12/kg [22]). Therefore, it can be high efficient and low cost material for removal highly bioactive organic pollutants in water. Thus, I considered that using organoclay for new methods to prevent directly leakage of pesticides from farmland or to remove pharmaceuticals in water at wastewater treatment facility. However, common organoclay made from monoalkylated cationic surfactant have been shown to leak surfactant from it

[41]. To use organoclay for the purpose, organoclay is required more stable.

A study has shown that an organoclay, which consists of a layered clay montmorillonite K30 and a dialkylated cationic surfactant, didodecyldimethylammonium bromide (DDAB), little leak DDAB [41]. This organoclay collected a β-lactam antibiotic, penicillin G. Moreover, collected penicillin G was degraded faster than hydrolysis in water. Therefore, I considered using this organoclay the aforementioned purpose.

In this study, properties of adsorption and promoting degradation by the organoclay for using it to the application were studied. And, the possibility of application to use a diffusion control material in farmland or a hospital wastewater treatment material was studied through continuous treatment experiments.

In Chapter 2, characteristics of the organoclay were investigated. And, one of the most commonly used organophosphorus pesticide, fenitrothion, was focused. Its adsorption and degradation properties by the organoclay were studied. Subsequently the organoclay's applicability to use in farmland as a barrier material preventing direct leakage to environmental water was studied by continuous treatment of fenitrothion contaminated water using organoclay packed column.

In Chapter 3, properties of adsorption pharmaceuticals, and personal care products and promoting β-lactam antibiotics degradation by the organoclay were studied. And the applicability to use continuous hospital wastewater treatment was studied by continuous treatment of penicillin G contaminated water using organoclay packed column.

Chapter 4 summarized the conclusions of the present study.

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CHAPTER 2 Organoclay sorption and degradation of a pesticide, fenitrothion

2.1 Introduction

Fenitrothion is one of most commonly used organophosphorus pesticides to exterminate pest insects on wide range of agricultural products [1] and also utilized as public health measures to control harmful insects such as mosquitoes and flies [2]. In the last decades, production of fenitrothion in the world is estimated around 15,000-20,000 ton/year [3]. Resulting of its widespread use, fenitrothion can extensively be detected in environmental waters [4–6] and wastewaters [7,8]. Since fenitrothion inhibits acetylcholinesterase activity in a broad range of Arthropoda, it can act to not only target insects but also non-target invertebrates such as honeybees, butterflies, and crustaceans in aquatic environment [9,10]. Although fenitrothion in aquatic environment can gradually degraded by bacterial action and solar irradiation, the degradation rate is largely dependent on the environmental conditions [1,11]. Moreover, acute toxicity as well as mutagenic or endocrine disrupting properties of fenitrothion and highly toxic intermediate degradation product, fenitrooxon, formed by light irradiation can be serious environmental concern [11–13]. Several physical, chemical and biological processes have been studied to eliminate fenitrothion and other organophosphate pesticides from wastewaters or agricultural effluents. Microbial treatment has extensively been used for degrading wide range of organic pollutants including organophosphate pesticides [14–16]. Occurrence of large amount of hydrous sludge often containing toxic or harmful pollutants is a serious problem in the microbial treatment. Advanced oxidation processes have extensively been studied to degrade wide range of organic pollutants including organophosphate pesticides [17–21]. However, the requirement of successive

consumption of oxidant, catalysis, or power for ultra-violet irradiation increases economic and environmental burdens of water treatment. Coexistence of highly concentrated dissolved organic matter can reduce the performance of oxidation processes. Moreover, occurrences of unknown by-products and highly toxic bromate ions are troublesome problem in the oxidation processes [22,23]. Activated carbon adsorption has been accepted as a powerful method to remove organophosphate pesticides [24–26]. However, degree of removal is largely dependent on the operating conditions such as contact time, solution pH, and co-existing substances. Use of expensive activated carbon can increase the cost of wastewater treatment.

Hydrolysis reaction of organophosphate pesticides promoted by the catalytic function of surfactant assemblies in the aqueous solutions (so called micellar catalysis) has extensively been studied for their degradation or detoxification [27–31]. The pesticides in the aqueous micellar solution orientate at the surfaces of cationic micelles to stabilize the intermediate compounds to degrade into less toxic products even at room temperature. However, alkaline conditions, coexistence of α-nucleophilic reagents, and/or use of functionalized surfactant were necessary for the efficient degradation of organophosphate pesticides. Moreover, the presence of cationic surfactant above critical micelle concentration in the treated water can give significant impact to aquatic organisms and ecosystems [32,33]. Recently, adsorption method using surfactant-modified clay minerals (namely organoclay sorption method) have prosperously been studied to eliminate different organic pollutants in water [34–40].

Surfactant molecules sorb on clay surfaces to form hydrophobic assemblies for effective incorporation of a wide range of hydrophobic organic pollutants. Previously, we found that an organoclay prepared by the modification of montmorillonite (MT) with a

dialkylated cationic surfactant, didodecyldimethylammonium bromide (DDAB), was a promising sorbent not only for rapid removal of β-lactam antibiotics in water but for their degradation into the inactivated forms under mild conditions [41]. Such catalytic activity was hardly observed in normal micellar or vesicular solutions and in unmodified MT but prominently appeared in DDAB-modified MT. The degradation occurred at neutral pH and the rate increased in rather weakly acidic region, being advantageous for the application to environmental water. In the present study, applicability of organoclay sorption method for a sustainable treatment of fenitrothion-contaminated water was studied. Experimental conditions or factors influencing the sorpion of fenitrothion on DDAB-MT organoclay and its degradation in the organoclay were investigated in detail. Difference and advantage were studied by comparing the degradation profile in the organoclay media from that in normal aqueous micellar system. Compatibility to continuous treatment of fenitrothion-contaminated water was tested by using an organoclay-packed column.

2.2 Material and methods

2.2.1 Chemicals

Standard material of fenitrothion (*O*,*O*-dimethyl-*O*-(3-methyl-4-nitrophenyl) phosphorothioate) and 3-methyl-4-nitrophenol were obtained from FUJIFILM Wako Pure Chemical (Osaka, Japan) and stoked as 1.00 g L^{-1} ethanol solution in a freezer (-30 °C). Other intermediate compounds were prepared by thermal- or light-induced degradation followed by the separation on TLC [42]. They were identified by measuring their mass spectra. Montmorillonite K-30 (MT, surface area: 330 m^2 g^{-1} [43], Merk, Darmstadt, Germany) was rinsed in aqueous buffer solution before use. Aqueous solution of DDAB (Tokyo Chemical Industry, Tokyo, Japan) was sonicated in a Bronson 1800 mechanical bath (St. Louis, MO, USA) for 15 min. A molecular probe, *N*-phenyl-1-naphthylamine (PN, standard material, FUJIFILM Wako Pure Chemical), for monitoring microscopic environment was stored as 1.0mM ethanol solution in a refrigerator. Buffer components used were Bis-Tris for adjusting to pH 5-7 and Tris for pH 9. Milli-Q water was used.

2.2.2 Preparation and characterization of organoclay

DDAB-MT organoclay was prepared by previous reported manner [41]. MT rinsed in buffer solution and prescribed amount of DDAB was mixed in a polypropylene conical tube for 6 h. The amount of DDAB sorption was calculated from the determination of DDAB in residual solution by a spectrophotometric method based on the ion-pair

extraction with an anionic dyestuff, methyl orange [44]. Unmodified MT and DDAB-MT organoclay were washed with water and freeze-dried to conduct their microscopic observation and the following spectrometric characterizations. Microscopic images were obtained with a scanning electron microscope (SEM) (JEOL JSM-6610LA, accelerating voltage: 20 kV, Akishima, Japan) having a secondary electron detector. The samples were coated with osmium (coating thickness: 5 nm) by using a Neoc-Pro osmium coater (Meiwafosis, Tokyo, Japan) to acquire highcontrast SEM images. Surface areas of unmodified MT and DDAB-MT organoclay were measured by using a BELSORP-max (Microtrac MRB, Osaka, Japan). Before surface area measurement, the samples were dried at 383 K for 6 h. Nitrogen adsorption was conducted at 77 K. FT-IR spectra were measured by using a Jasco FT/IR 4700 infrared spectrometer (Hachioji, Japan). The samples were prepared by mixing with KBr (1:100) and pressing into the tablets. A ZSX Primus II wavelength-dispersive X-ray fluorescence (WDX) spectrometer (Rigaku, Akishima, Japan) having a Rh tube X-ray source was used for measuring WDX spectra. For this purpose, MT and DDAB-MT organoclay were pressed (10 t) to prepare their pellets (thickness: 2 mm). X-ray irradiation diameter was 5 mm. A RINT-2000 XRD system (Rigaku, Tokyo, Japan) was used for the measurement of X-ray diffraction (XRD) spectra. The radiation wavelength used was 0.154056nm (CuKα radiation at 40 kV and 20 mA). Molecular probe study based on the fluorescence intensity of PN on the organoclay were performed in wet conditions. A 10 μL portion of PN solution was added to 10mL of aqueous suspension containing prescribed amount of DDAB and 1.0 g of MT. The emission spectra of PN on the organoclay were measured with a PerkinElmer LS-50B Luminescence Spectrometer (Waltham, MA, USA) having a solid sample attachment. The excitation wavelength was 340 nm, while slit widths were 2 nm.

2.2.3 Sorption and degradation of fenitrothion

In batch experiment, organoclay consisting of 40mg of MT and prescribed amount of DDAB was poured into 100mL of aqueous solution containing typically 0.1mg L^{-1} of fenitrothion. The resulting suspension was placed in a 100mL polypropylene conical tube to gently (10 rpm) mix for 15 min by using a rotator. Then, the supernatant solution was sampled with the use of a Hamilton gas-tight microsyringe (Hamilton, Bonaduz, Switzerland) attaching a hydrophilic PTFE disposal syringe filter (DISMIC 13- HP, diameter: 13 mm, pore size: 0.45 μm, Advantech, Tokyo, Japan). On the other hand, precipitated organoclay was placed into a polypropylene void mini-column (Muromachi Chemical, Omuta, Japan) to separate from the supernatant solution and stored in a temperature-controlled chamber (25 °C, 40 °C, 60 °C, or 80 °C) for different times (10 min ~ 14 d). The organoclay was washed with 5mL of acetonitrile and then 5mL of water to completely elute fenitrothion and degraded products. A Waters LC/MS system including an Alliance e2695 separation module, a 2489 UV/Vis detector, and a 3100 mass spectrometric detector (Milford, MA, USA) connecting with an Inertsil® ODS-3 column (inner diameter: 3.0 mm, length: 150 mm, GL Sciences, Tokyo, Japan) was used for the separation and determination of fenitrothion and degraded products. The mobile phase was initially 30% (v/v) acetonitrile containing 10mM ammonium acetate (pH 4) for 7 min followed by elevating the acetonitrile content to 60% (v/v). The flow rate of mobile phase and detection wavelength were 0.5mL min-1 and 271 nm, respectively. Ionization potential and souse temperature of mass spectrometric detector were 28 V and 350 °C, respectively. Positive ion mode was used for the detection of fenitrothion, while negative ion mode was for degraded products.

2.2.4 Continuous treatment

A glass jacket column (inner diameter: 15 mm, length: 300 mm) filling with 1.3 g of DDAB-MT organoclay consisting of 1.0 g of MT and 300 mg of DDAB was used. Temperature was kept at 40±1 °C with an EYELA CTP-1000 temperature control water circulator (Tokyo, Japan). Contaminated water was prepared by adding 10.0 mg L^{-1} fenitrothion to a ground water (hardness: 30.0 mg L^{-1}, pH 6.5) and was supplied to the top of the column by using a Yamato Masterflex® L/S mini-tube pump (Tokyo, Japan). An EYELA DC1000 fraction collector was used to collect the eluting solution from the bottom of the column. Fenitrothion and degraded products in the respective fractions were separated and determined by above-described method.

2.3 Results and discussion

2.3.1 Formation and properties of DDAB-MT organoclay

Fig. 2-1 shows SEM images of unmodified MT (A) and DDAB-MT organoclay (B). These images clearly indicate layered structures of MT clay mineral and that the layered structure maintained by the modification with DDAB. Surface area of MT (255 m^2 g^{-1}) was significantly reduced to 19.6 m^2 g^{-1} in DDAB-MT organoclay, indicating the modification with large amount of surfactant molecules that can form their assemblies for the incorporation of hydrophobic compounds in the aqueous media. Modification of MT with DDAB can be confirmed from the sharp absorption peaks ($\nu_{C\text{-}H}$: 2960, 2830 cm^{-1}) in the FT-IR spectrum of the organoclay (Fig. 2-2) and the increasing intensities of the peaks assignable to carbon and bromine in the WDX spectra (Fig. 2-3). As shown in Fig. 2-4(A), up to 300mg of DDAB added in the solution (pH 7.0) was nearly completely (>99.9%) sorbed on 1.0 g of MT, indicating very stable sorption of DDAB. Indeed, very low (< 1 mgL^{-1}) leakage of DDAB was observed by repeated washing of the organoclay with water [41]. In the present study, therefore, organoclays containing up to 300mg DDAB $(g\text{-}MT)^{-1}$ were used. Fig. 2-4(B) illustrates XRD spectra of organoclays containing different amounts of DDAB. The interlayer distance of unmodified MT estimated from 2θ (= 5.62°) was 1.57 nm, being almost same as the reported value (1.54~1.56 nm) for hydrated MT [45]. Peak shift to lower angle clearly indicates the expansion between the layers of clay minerals by the increasing sorption of DDAB. When 300mg $(g\text{-}MT)^{-1}$ of DDAB was sorbed, interlayer distance expanded to approximately 3.15 nm, being almost same as the values reported in literatures [36,46] and corresponding to hydrodynamic diameter (1.5~1.7 nm) of DDAB vesicles [47,48].

Generation of the hydrophobic region was monitored by using a molecular probe, PN,

whose emission spectrum is responsive to the polarity or hydrophobicity of surfactant assemblies [49–51] and organoclay [41]. Fig. 2-4(C) shows the emission intensity of PN incorporating in the organoclay modified with different amount of DDAB. The emission intensity enhanced by increasing sorption of DDAB. These results strongly suggest the generation of hydrophobic region that are suitable for the incorporation of hydrophobic organic pollutants.

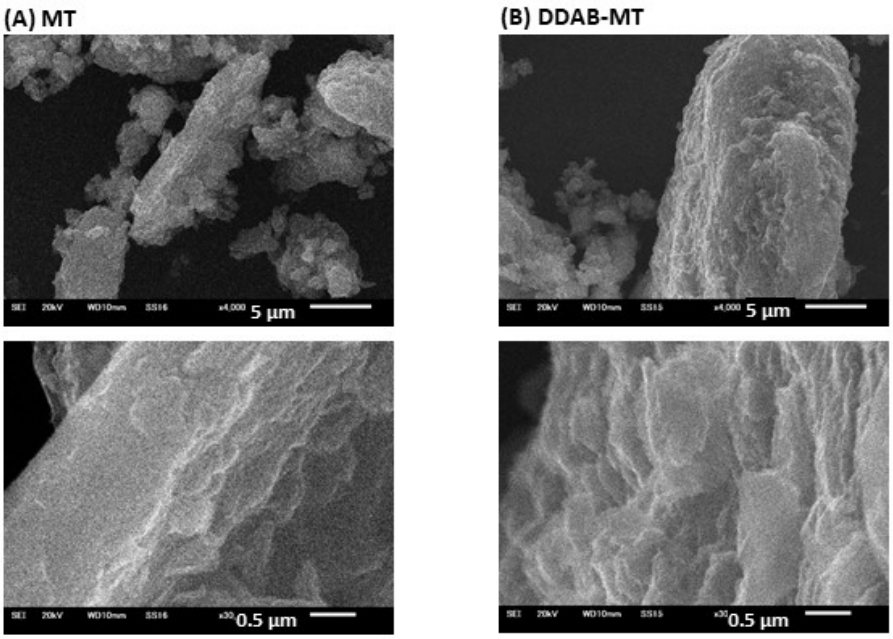

Fig. 2-1. SEM images of (A) unmodified MT and (B) DDAB-MT organoclay. Osmium coating thickness: 5 nm, accelerating voltage: 20 kV.

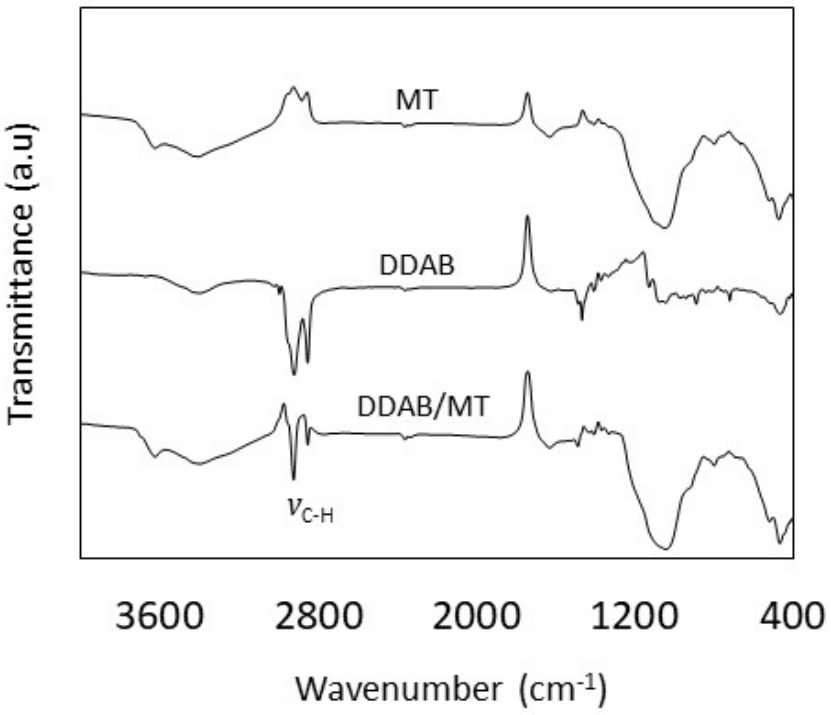

Fig. 2-2. FT-IR spectra of unmodified MT, DDAB, and DDAB-MT organoclay. Samples were prepared by mixing with KBr (1:100) and pressed to form tablets.

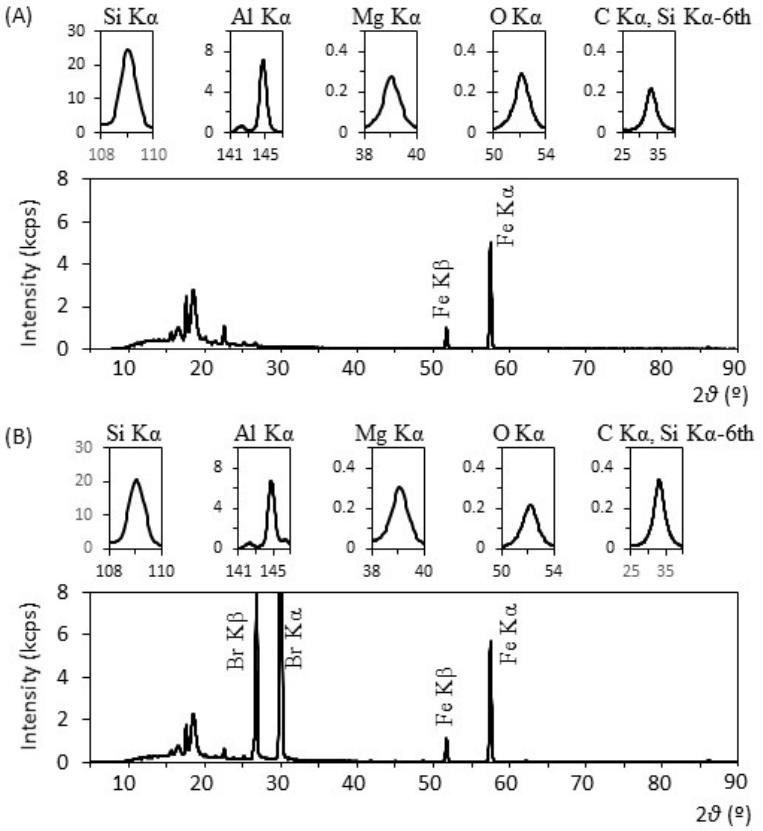

Fig. 2-3. WDX spectra of (A) unmodified MT and (B) DDAB-MT organoclay. Samples were pressed (10 t) to prepare their tablets. X-ray source: Rh tube.

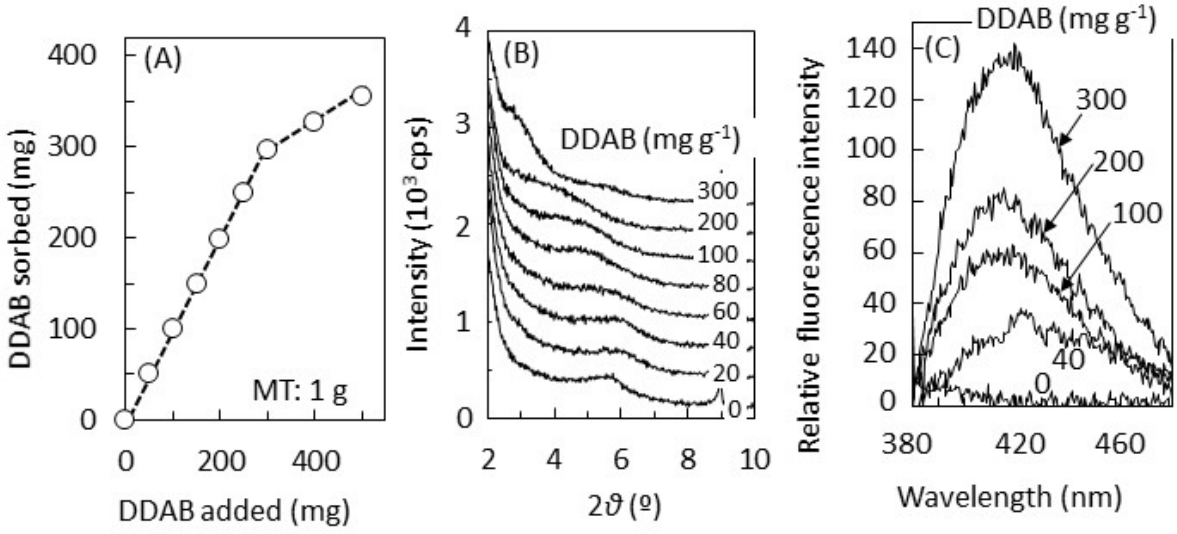

Fig. 2-4. (A) Amount of DDAB modification, (B) XRD spectra {CuKα radiation at 40 kV and 20 mA}, and (C) emission spectra of PN {excitation wavelength: 340 nm} on DDAB-MT organoclays modified with different amounts of DDAB.

2.3.2 Organoclay sorption of fenitrothion

Firstly, kinetics and equilibria of organoclay sorption of fenitrothion were studied. Fig. 2-5 (A) shows time-dependent sorption of fenitrothion onto unmodified MT and DDAB-MT organoclay. The sorption of fenitrothion on DDAB-MT leached nearly equilibrium within 5 min, while ca. 15 min was required for the equilibrium sorption onto unmodified MT. Degree of the sorption of fenitrothion increased by the modification of MT with DDAB (Fig. 2-5 (B)). These facts can be explained by generation of hydrophobic aggregates on MT surfaces suitable for incorporating hydrophobic fenitrothion (log K_{ow}=3.43 [52]).

Organoclay sorption of fenitrothion was successfully described by Langmuir (Eq. (1)) and Freundlich (Eq. (2)) model isotherm equations.

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}C_e} \qquad (1)$$

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (2)$$

Here, q_e (mg (g-organoclay)$^{-1}$) denotes the amount of equilibrium sorption, C_e (mg L^{-1}) is equilibrium concentration in the bulk aqueous solution, q_{max} is sorption capacity, b is Langmuir constant, while K_F and n are Freundlich constants. Fig. 2-6 (A) and (B) show the results of the fitting of experimental data for fenitrothion sorption to Langmuir and Freundlich equations. From the slope and intercept in Fig. 2-6 (A), the adsorption capacity of fenitrothion was calculated to be 68.5±1.2 mg (g-organoclay)$^{-1}$. Adsorption isotherms of Langmuir and Freundlich equations for the degraded product, 3-methyl- 4-nitrophenol, were also shown in Fig. 2-6 (C) and (D). From the fitting curve of Langmuir model equation, the adsorption capacity of 3-methyl-4-nitrophenol estimated was 25.3±2.1 mg

(g-organoclay)$^{-1}$. High adsorption capacities are important to retain these pollutants for designing continuous treatment of contaminated water.

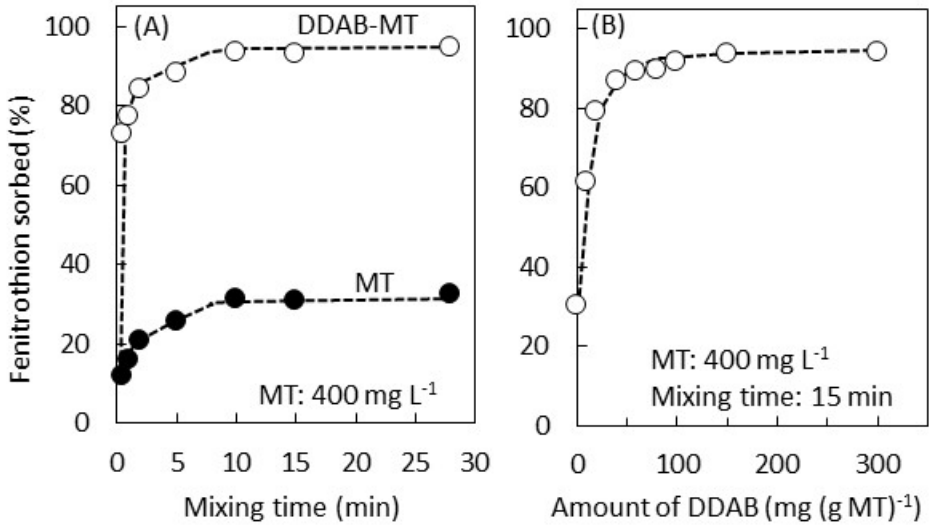

Fig. 2-5. (A) Sorption of fenitrothion on unmodified MT (●) and DDAB-MT organoclay (○) as a function of mixing time and (B) the amount of DDAB modification.

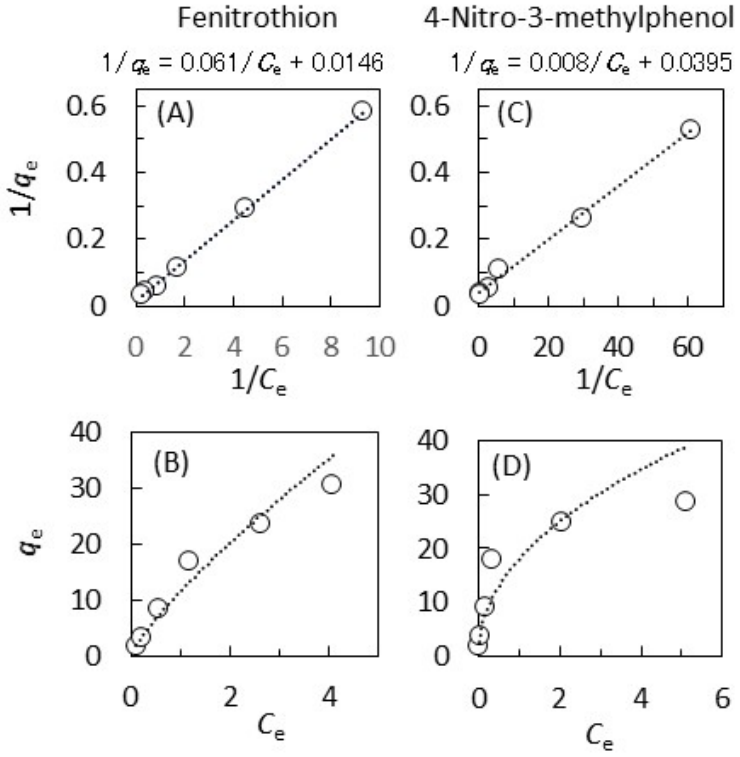

Fig. 2-6. (A, C) Fitting curves of Langmuir and (B, D) Freundlich equations for the organoclay sorption of (A, B) fenitrothion and (C, D) 4-nitro-3-methylphenol.

2.3.3 Degradation of fenitrothion

Time-dependent degradation of fenitrothion in water, unmodified MT, DDAB micellar or vesicular solution, and DDAB-MT organoclay are shown in Fig. 2-7, in which the ratio (C/C_0) of residual concentration (C) to initial concentration (C_0) of fenitrothion at the respective aging time are represented. Fenitrothion in water gradually degraded but the degradation rate was only ca. 10% for 2 weeks. Unmodified MT hardly accelerated the degradation of fenitrothion. On the other hand, the degradation rate significantly increased in DDAB-MT organoclay, probably because of the micellar catalysis-like activity of organoclay. The degradation rate in the organoclay was greater than that in normal aqueous micellar or vesicular solution of 1.20 g L^{-1} (2.6 mM) of DDAB (critical vesicle concentration: 0.9 mM [53]).

Fig. 2-8(A) shows temperature-dependent first-order reaction curves for the primary degradation of fenitrothion in the organoclay. The first order reaction can be expressed by Eq. 3.

$$\ln(C/C_0) = -kt \qquad (3)$$

Here, k [h^{-1}] denotes rate constant and t [h] is defined by aging time or period retaining in the organoclay medium. The rate constant, k, was successfully calculated from the slope of the linear curve and increased with the increase in temperature. Temperature dependence of logarithmic rate constant, ln k, can be expressed by an Arrhenius equation (Eq. 4).

$$\ln k = -E_a/RT + \ln A \qquad (4)$$

Here, E_a [J mol^{-1}] represent activation energy, R [J K^{-1} mol^{-1}] is gas constant, T [K] is

temperature, and A is frequency factor. From the slope of Arrhenius plot (Fig. 2-8(B)), activation energy, E_a, for the primary degradation of fenitrothion in the organoclay medium was successfully estimated to 79.9±2.1 kJ mol^{-1}. This value was smaller than the activation energy in water (94.1±1.8 kJ mol^{-1}) calculated based on the Arrhenius plot obtained in water (Fig. 2-8 (C)), apparently indicating catalytic ability of DDAB-MT organoclay.

Detail features of time-dependent degradation are represented in the chromatograms of fenitrothion and degradation products in DDAB-MT organoclay (Fig. 2-9 (A)) and aqueous DDAB vesicular solution (Fig. 2-9 (B)). Mass spectra of the respective peaks are also indicated in the top of this figure. In the aqueous vesicular system, fenitrothion (a, [M+1] = 278.1) converted into two intermediate anions (b and c, [M] = 262.1) followed by the degradation to 3-methyl-4-nitrophenolate ion (d, [M] = 152.1). Such degradation profile had already been reported in literatures studying micellar catalyzed degradation of organophosphate pesticides [27–31]. On the other hand, the intermediate compound b, which is a superior product occurring in micellar catalyzed degradation, was negligibly detected in the organoclay-catalyzed system. It has been reported that MT has catalytic activity for the hydrolysis of ester- or carbamate-type pesticides [54,55] and cellulose [56]. Hydroxyl moieties such as Si-OH or Al-OH groups on MT surfaces can act as brønsted acids for catalyzing hydrolysis reaction of different compounds. Therefore, catalytic ability of organoclay can be attribute to the combination of micellar catalysis-like function of DDAB assemblies and acid catalysis on MT surfaces.

Effect of DDAB modification on the first-order reaction for the primary degradation of fenitrothion can be shown in Fig. 2-10 (A). The surfactant modification was necessary for the occurrence of high catalytic activity. As above described, this is explained by

micellar catalysis-like function of DDAB assemblies on MT surfaces. As shown in Fig. 2-10 (B), organoclay-catalyzed degradation of fenitrothion occurred not only at neutral pH (pH 7) but also in weakly acidic (pH 5) and weakly alkaline conditions (pH 9). Applicability of the organoclay sorption method in a wide pH range is advantageous for the treatment of different of wastewaters and effluents. Among the solution pH tested, the fastest degradation of fenitrothion occurred at pH 5 (Fig. 2-10 (B)), supporting the mechanism that acid catalysis function on MT surfaces contributes to the organoclay catalyzed degradation of fenitrothion.

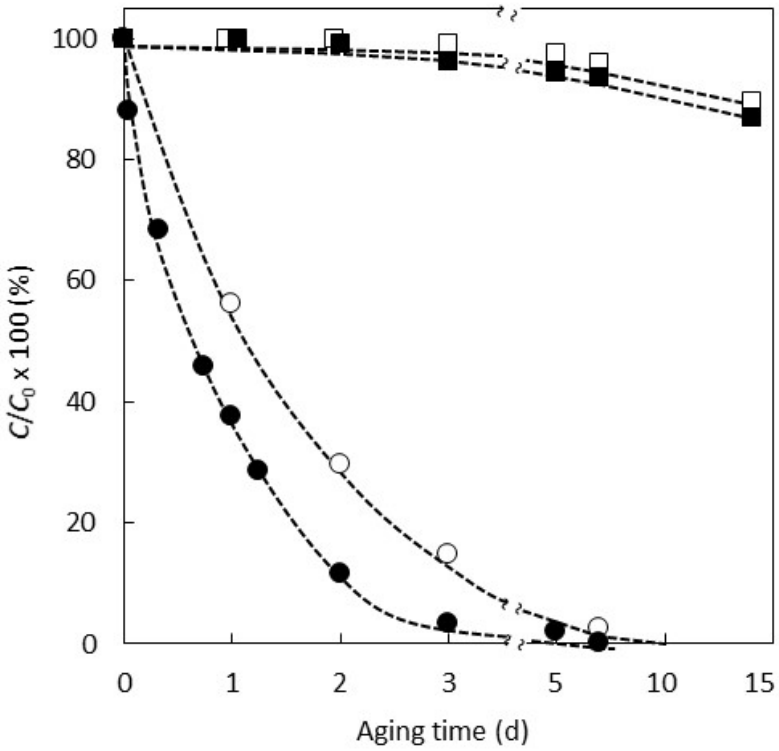

Fig. 2-7. Degradation of fenitrothion in water (□), unmodified MT (■), vesicular solution of 2.5 mM DDAB (○), and DDAB-MT organoclay (●) at 25 ± 1℃.

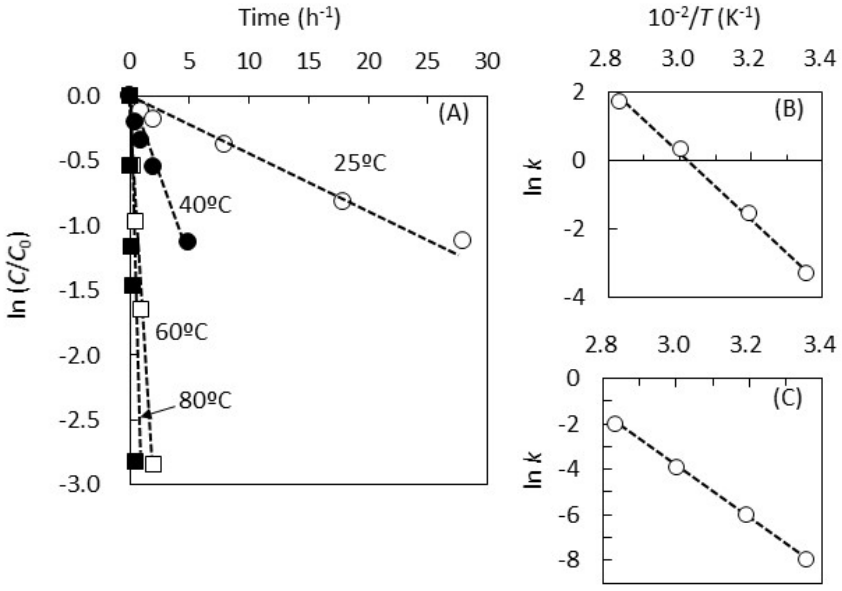

Fig. 2-8. (A) First-order reaction curve for the degradation of fenitrothion in DDAB-MT organoclay at different temperatures and (B) the Arrhenius plot as well as (C) that obtained in water.

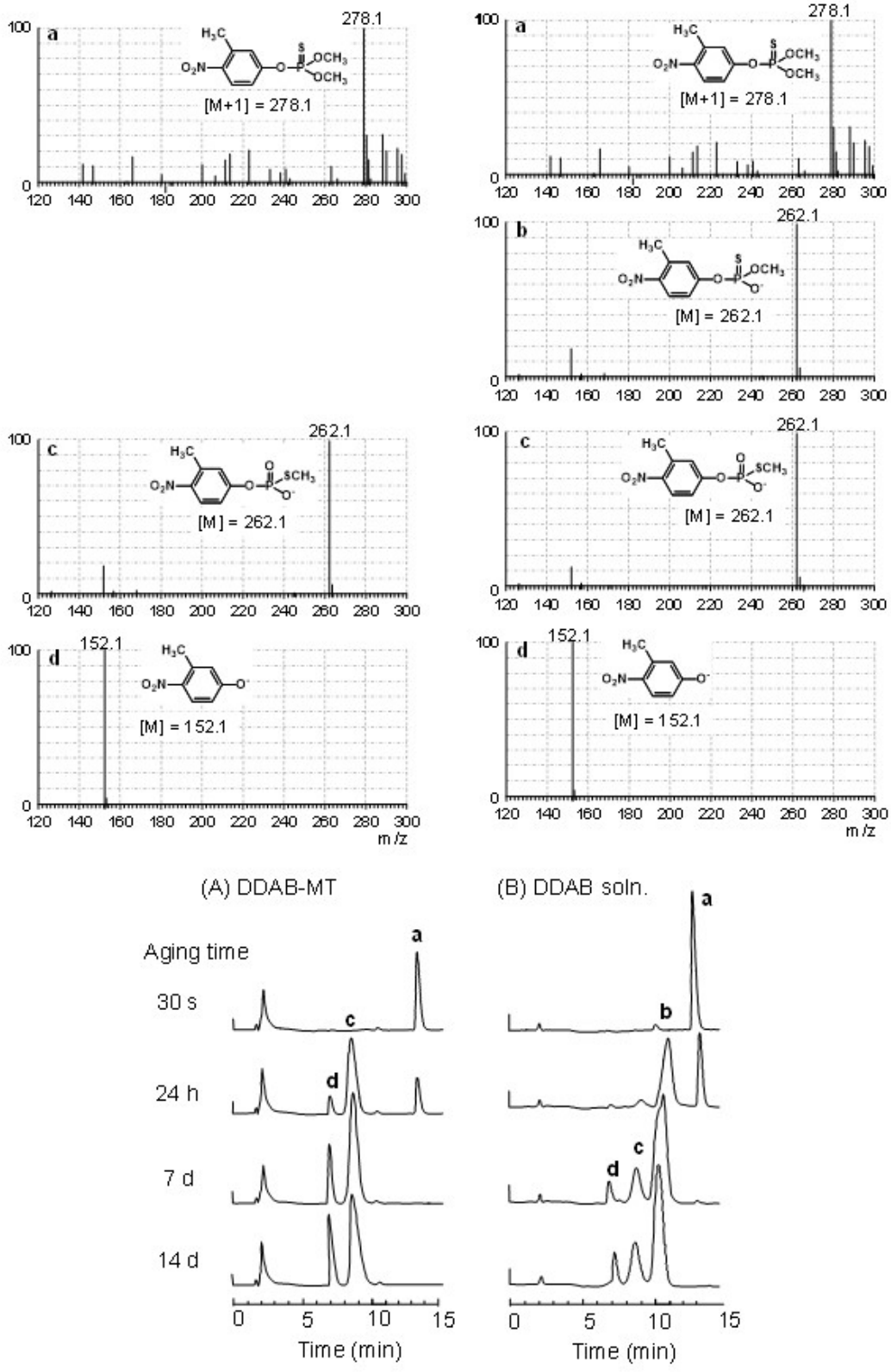

Fig. 2-9. (A) Time course of chromatograms of fenitrothion and its degraded products in DDAB-MT organoclay and (B) in 2.5 mM DDAB vesicular solution. ESI-mass spectra are shown above the chromatograms. Fenitrothion was detected in positive ionization mode, while others were in negative ionization mode. Ionization potential; 28 kV, source temperature; 350℃.

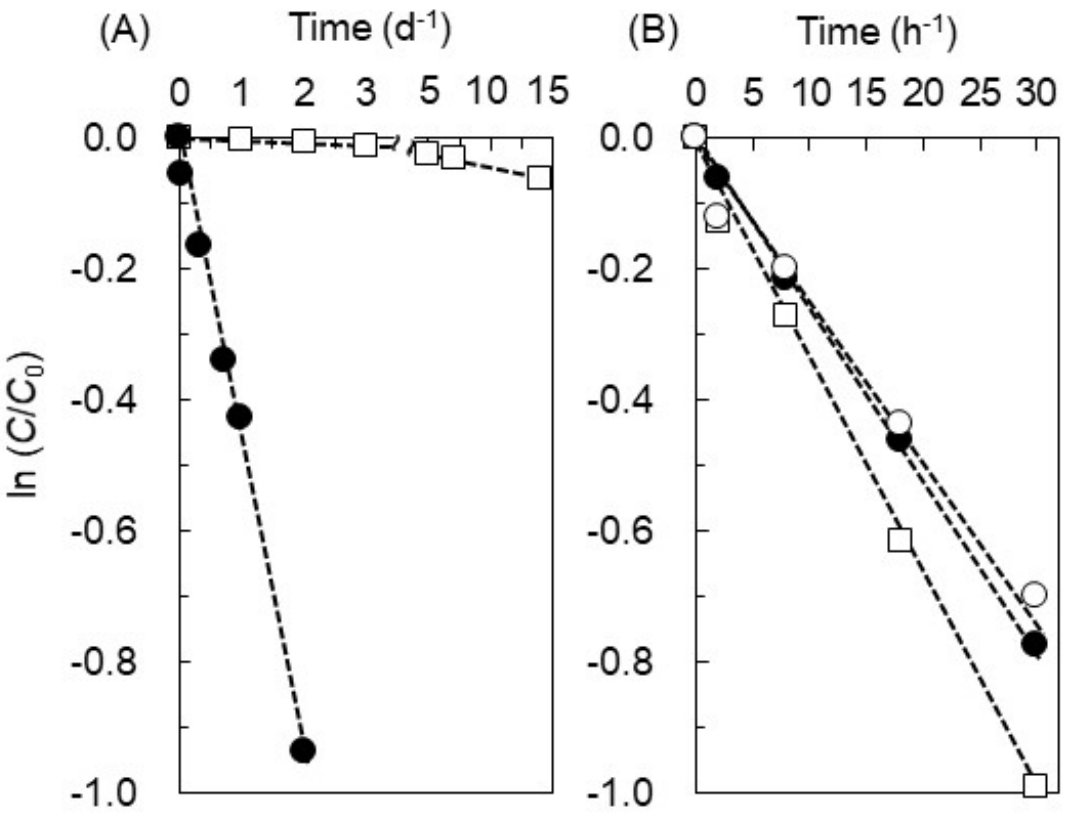

Fig. 2-10. (A) First-order reaction curves for degradation of fenitrothion in unmodified MT (□) and organoclay modified with 300 mg (g MT)$^{-1}$ of DDAB (●) at pH 7 and (B) the results in the organoclay at pH 5 (□), 7 (●), and 9 (○).

2.3.4 Continuous treatment

Recently, organoclays or organoclay-containing composites have also been studied as barrier materials for preventing the diffusion of hydrophobic organic pollutants [57,58]. Retention of hydrophobic organic pollutants is significantly improved because of their incorporation into surfactant assemblies on clay surfaces. However, the retention is limited by the sorption capacity of the organoclays. Conversion of hydrophobic pollutant into less toxic forms followed by their easy elution allows long life use of the sorbent. In the present study, usefulness of DDAB-MT organoclay as a sustainable barrier material for diffusion control of fenitrothion was studied. Fig. 2-11 depicts breakthrough curves of fenitrothion and its degraded product, 3-methyl-4-nitrophenol, obtained by passing fenitrothion-contaminated water through an organoclay-packed column. At low flow rate (4.2 mL h^{-1}) condition, fenitrothion negligibly (< 0.01 mg L^{-1}) detected in all fractions even by passing 9000 mL of contaminated solution (90 days) (Fig. 2-11 (A)). During this period, leakage of fenitrothion almost prevented, while breakthrough of a degraded product, 3-methyl-4-nitrophenol, having less toxicity to arthropoda or fishes was observed by passing 4500 mL of contaminated water. Average retention time of fenitrothion in the organoclay layer estimated from flow rate, thickness, and degree of the organoclay sorption is more than 16 h being enough time for the nearly complete degradation. At faster flow rate (48 mL h^{-1}), however, breakthrough of fenitrothion was observed after eluting 2000 mL of contaminated water (Fig. 2-11 (B)), because of the overload of fenitrothion. In this case, intermediate compound (c in Fig. 2-9, data is not shown because of low accuracy in concentration) and 3-methyl-4-nitrophenol were also detected. Regulation of flow rate was necessary for the retention of fenitrothion in the

organoclay stratum or bank to assure the nearly complete degradation.

Fig. 2-11 (C) indicates the amount of remaining DDAB in the organoclay during the continuous treatment. The value was obtained based on the difference of the integrated amount of the respective fractions from the initial quantity. Percentage of leaked DDAB from 1.3 g of organoclay containing 300 mg of DDAB was within 5% during the elution of 4000 mL of sample water and less than 2% by another 4000 mL elution. By passing these solutions through another 1.0 g of unmodified MT, DDAB in the elution solution became undetectable (<0.01 mg L^{-1}) levels. Multiple laying of organoclay and unmodified clay would be effective for sustainable treatment of organophosphate pesticide-contaminated water with minimizing loss of performance and/or environmental impact of the organoclay sorption method.

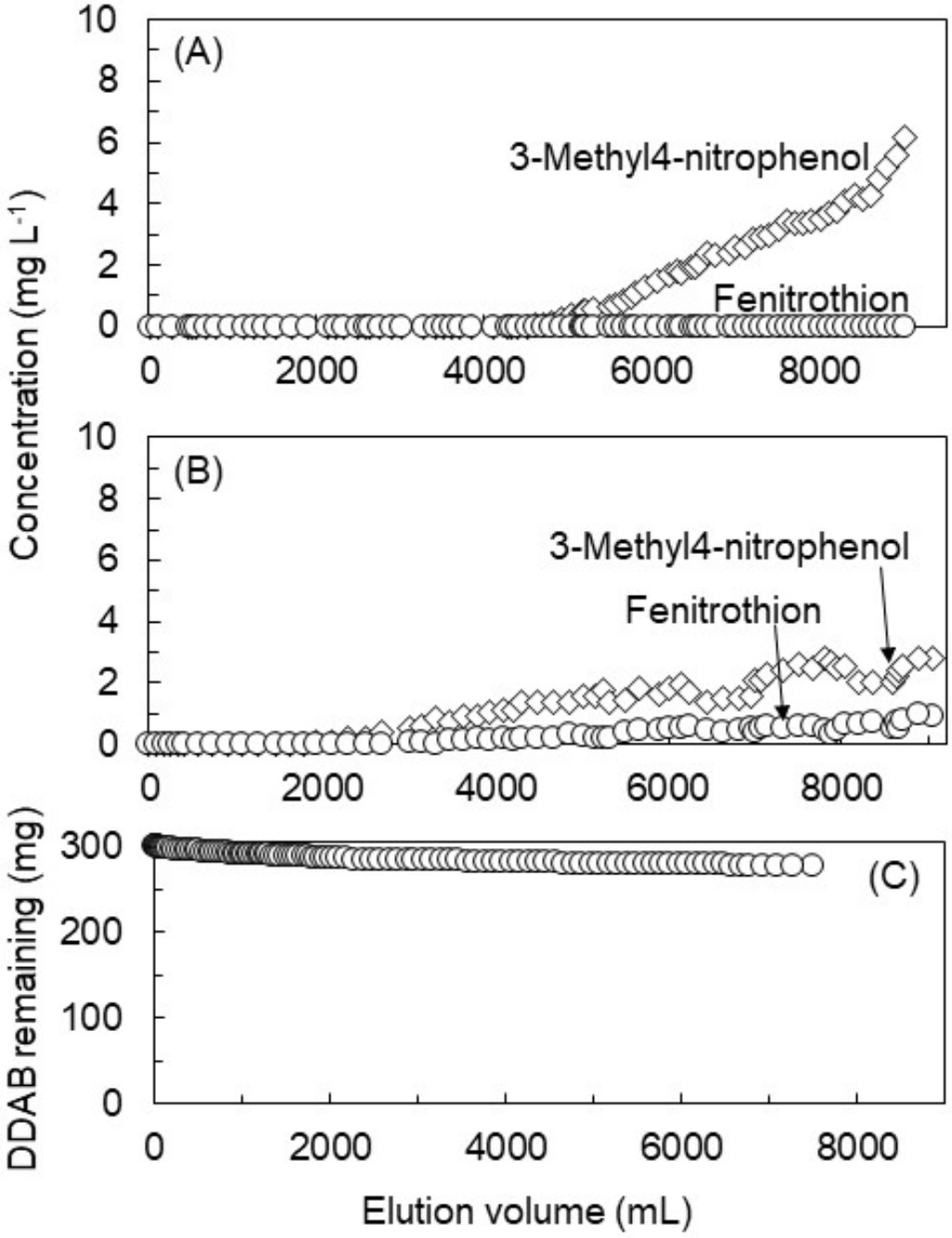

Fig. 2-11. Breakthrough curves of fenitrothion and 3-methyl-4-nitrophenol obtained by passing ground water (pH 6.8) containing 10 mM fenitrothion through a column filling the organoclay composing of 1.0 g of MT and 300 mg of DDAB {Flow rate (mL h-1): (A) 4.2 and (B) 48} and (C) the amount of DDAB remaining in the organoclay.

2.4 Conclusion

DDAB-MT organoclay was a promising sorbent for rapid sorption and degradation of fenitrothion in water. Up to 300 mg $(g\text{-}MT)^{-1}$ of DDAB stably sorbed on MT surfaces to form hydrophobic assemblies having suitable property for the efficient incorporation of hydrophobic fenitrothion. Sorption capacity of fenitrothion was calculated to be 68.5±1.2 mg $(g\text{-organoclay})^{-1}$. Fenitrothion sorbed on the organoclay rapidly degraded into an intermediate compound followed by further degradation into less toxic 3-methyl-4-nitrophenol. The first-order degradation rate increased with the increase in temperature. The activation energy for the primary degradation of fenitrothion was estimated to be 79.9±2.1 kJ mol^{-1}, being smaller than the value in water (94.1±1.8 kJ mol^{-1}). The organoclay-catalyzed degradation was faster than that of micelle- or vesicle-catalyzed degradation and occurred in wider pH region (pH 5-9). Successful demonstration of continuous sorption and degradation using a laboratory-scale organoclay-packed column strongly suggests the applicability of organoclay sorption method for diffusion control of organophosphate pesticides.

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CHAPTER 3 Organoclay sorption of antibiotics, pharmaceuticals, and personal care products in water

3.1 Introduction

The presence of antibiotics, pharmaceuticals, and personal care products in the environment has become a significant concern due to their potential to harm the microbial ecosystem. More than 60% of the commercially available antibiotics in use in the world are β-lactam compounds [1]. Despite their fairly good degradability in conventional activated sludge processes [2], the degree of degradation depends strongly on the specific antibiotic and is often insufficient [3]. Studies in the literature have reported that antibiotics may damage the microbial communities in sewage systems and aquatic environments [4, 5] and promote the genesis of antibiotic-resistant bacteria [6, 7]. The advanced oxidation method is a promising method for the near-complete degradation of antibiotics. However, the application of advanced methods increases the cost of wastewater treatment.

Recently, we designed a simple and efficient non-microbial method for eliminating β-lactam antibiotics from water [8]. Didodecyldimethylammonium bromide (DDAB)-modified montmorillonite organoclay was found to be a promising sorbent for -lactam antibiotics because of its stability in water and high capacity for the sorption of β-lactam antibiotics. Moreover, when the antibiotic penicillin G was sorbed on the organoclay, it was rapidly transformed into the degradation product penicilloic acid, which lacks the β-lactam ring necessary for antimicrobial activity. The DDAB-modified organoclay was stable against repeated washing with water, as the dialkylated surfactant molecules were

more stably sorbed on the clay surface than monoalkylated surfactants.

In the present study, the applicability of DDAB-modified organoclay to the removal of various antibiotics, pharmaceuticals, and personal care products was studied. The sorption of β-lactam antibiotics and other pharmaceuticals on organoclay modified with different amounts of DDAB was investigated to clarify the predominant factors influencing their sorption on organoclay. Moreover, the organoclay-induced degradation of various β-lactam antibiotics was also studied. The continuous treatment of penicillin-contaminated water using a laboratory-scale organoclay-packed column was examined. The applicability and limitations of the organoclay-sorption method for the treatment of hospital wastewater were discussed.

3.2 Material and methods

3.2.1 Chemicals

Didodecyldimethylammonium bromide (DDAB) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Montmorillonite K-30 (MT, surface area: 330 m2 g^{-1}) was obtained from Sigma-Aldrich (St. Louis, MO, U.S.A.). β-Lactam antibiotics, including penicillin G potassiumsalt and a buffer component, Bis–Tris, were obtained from FUJIFILM Wako Pure Chemical Industries, Ltd. (Osaka, Japan). A standard material corresponding to the breakdown product of penicillin G, penicilloic acid ((4*S*)-2-[carboxy[(phenylacetyl) amino]-methyl]-5,5-dimethylthiazolidine- 4-carboxylic acid), was obtained from LGC Standards (Teddington, U.K.). The other pharmaceuticals and personal care products used were analytical or HPLC standard grade reagents. Water was purified with a Milli-Q Integral Water Purification System (Merck Millipore, Billerica, MA, U.S.A.) with a UV irradiation unit.

3.2.2 Preparation and characterization of organoclay

The MT was rinsed with 50 mM Bis–Tris solution (pH 7) for 2 h and washed with water. The MT was then mixed with 5 mM Bis–Tris (pH 7) solution containing the prescribed amount of DDAB for 2 h to prepare the DDAB-MT organoclay. A Jasco FT/IR-4200 infrared spectrometer (Hachioji, Japan) was employed to measure the IR spectra (ν_{C-H}=2,980 cm^{-1}) of the freeze-dried organoclays. The DDAB content of the organoclay was estimated from the difference between the initial and residual DDAB concentration,

which was determined using an Orange II extraction method (Scott, 1968). The zeta potentials of organoclay samples with different DDAB contents were measured with a Zeecom ZC-M1 zeta potential analyzer (Microtec, Funabashi, Japan). The occurrence of hydrophobic regions was monitored by measuring the fluorescence intensity of a fluorescent molecular probe, *N*-phenyl-1-naphthylamine (PN), whose fluorescence spectrum and intensity are responsive to hydrophobic microenvironments, such as surfactant assemblies [9, 10]. The excitation wavelength was 350 nm, while the emission was monitored at 420 nm.

3.2.3 Procedures for organoclay sorption

The organoclay sorption experiments were performed by mixing 10.0 mL of 1 mM Bis–Tris (pH 7) containing 1.0 mg L^{-1} of an antibiotic, pharmaceutical, or personal care product and the organoclay, which was composed of 40 mg MT and the prescribed amount (0 – 16 mg) of DDAB, in a 15 mL polypropylene tube. After 1 min of gentle mixing (60 rpm), the solution was filtered by passing it through an Advantec Dismic® syringe filter (hydrophilic PTFE, diameter: 13 mm, pore size: 0.45 μm, Tokyo, Japan) to determine the residual concentration of the antibiotic or pharmaceutical. For separation and determination, 20 μL of the solution was introduced into a Waters LC/MS system composed of an Alliance e2695 separation module, a 2489 UV/Vis detector, and a 3100 mass spectrometric detector (Milford, MA, U.S.A.) with an InertSustain® C18 column (length: 150 mm, inner diameter: 3.0 mm, particle size: 5 μm, GL Sciences, Tokyo, Japan). The mobile phase composition was 20–50% (v/v) acetonitrile containing 0.27 mM formic acid and 4.73 mM ammonia (pH 5). The flow rate was 0.5 mL min^{-1}. The ionization

potential and source temperature in the mass spectrometric detector were 30 V and 350°C, respectively. To monitor the degradation of the antibiotics, the organoclay with sorbed β-lactam antibiotics was placed in a Muromak ® mini-void column (Muromachi Chemicals, Omuta, Japan) and stored in a temperature-controlled chamber for the prescribed period. The organoclay was then washed with 2.0 mL ethanol to elute the antibiotic and its degradation products. The eluate was placed in a 10 mL volumetric flask and diluted with water to adjust the solution volume. A 20 μL portion of the solution was introduced into a Waters LC/MS system as described above for the separation and determination of the β-lactam antibiotics and degradation products.

For continuous treatment using an organoclay-packed column, organoclay composed of 1.0 g MT and 400 mg DDAB was placed in a glass column (inner diameter: 15 mm, length: 300 mm). The thickness of the organoclay layer was ca. 7 mm. An aqueous buffer solution (1 mM Bis– Tris, pH 7) containing 10 mg L^{-1} penicillin G or synthesized hospital wastewater containing the same amount of penicillin G was supplied using a Tokyo Rika MP-3000 peristaltic pump (Tokyo, Japan). The properties and composition of the synthesized hospital wastewater are listed in Table 3-1. The eluted solutions were collected using a Tokyo Rika DC-1500C fraction collector. The method for monitoring oxacillin and its degradation products was the same as that described above. The temperature was adjusted to 25±1°C for all experiments.

Table 3-1. Qualities and components of synthesized hospital wastewater

pH	7.0
COD [mg/L]	570
Component	Concentration [mg/L]
NaCl	3000
KH_2PO_4	33
$NaNO_2$	220
CH_3COONH_4	110
Propionic acid	100
Butylic acid	50
Urea	1500
Creatinine	50
D-Glucose	360
Starch (soluble)	200
Albumin (bovine serum)	1

3.3 Results and discussion

3.3.1 Properties of the DDAB-MT organoclay sorbents

We have previously reported that modification of MT with DDAB in aqueous solution results in the formation of organoclay. FT-IR and XRD spectra indicated that the DDAB assemblies were apparently sorbed between layers of the MT clay minerals [8]. Fig. 3-1 shows the effects of the extent of DDAB modification on the net charge and the occurrence of hydrophobic regions on the organoclay. For quantities of DDAB up to 400 mg, the DDAB added to the aqueous buffer system (pH 7.0) was nearly quantitatively (>99%) sorbed on 1.0 g (dry) MT (Fig. 3-1 (A)). Further addition of DDAB resulted in an increase in DDAB sorption, but the sorption was not quantitative, and the DDAB content of the resulting organoclay was unstable against repeated washing with water. Therefore, a DDAB range of 0–400 mg was used for the modification of 1.0 g (dry) MT in the present study. As shown in Fig. 3-1 (B), the charge of the organoclay became less negative than that of unmodified MT as the extent of DDAB modification increased. Organoclay containing more than ca. 150 mg $(g\text{-}MT)^{-1}$ of DDAB became positively charged. The occurrence of hydrophobic regions was monitored based on the enhancement of the fluorescence intensity of the probe PN. Fig. 3-1 (C) depicts the difference (ΔF) in the fluorescence intensity of PN in the presence of organoclay and that in water. The difference increased with increasing DDAB addition, clearly indicating an increase in hydrophobic regions with the incorporation of this hydrophobic compound.

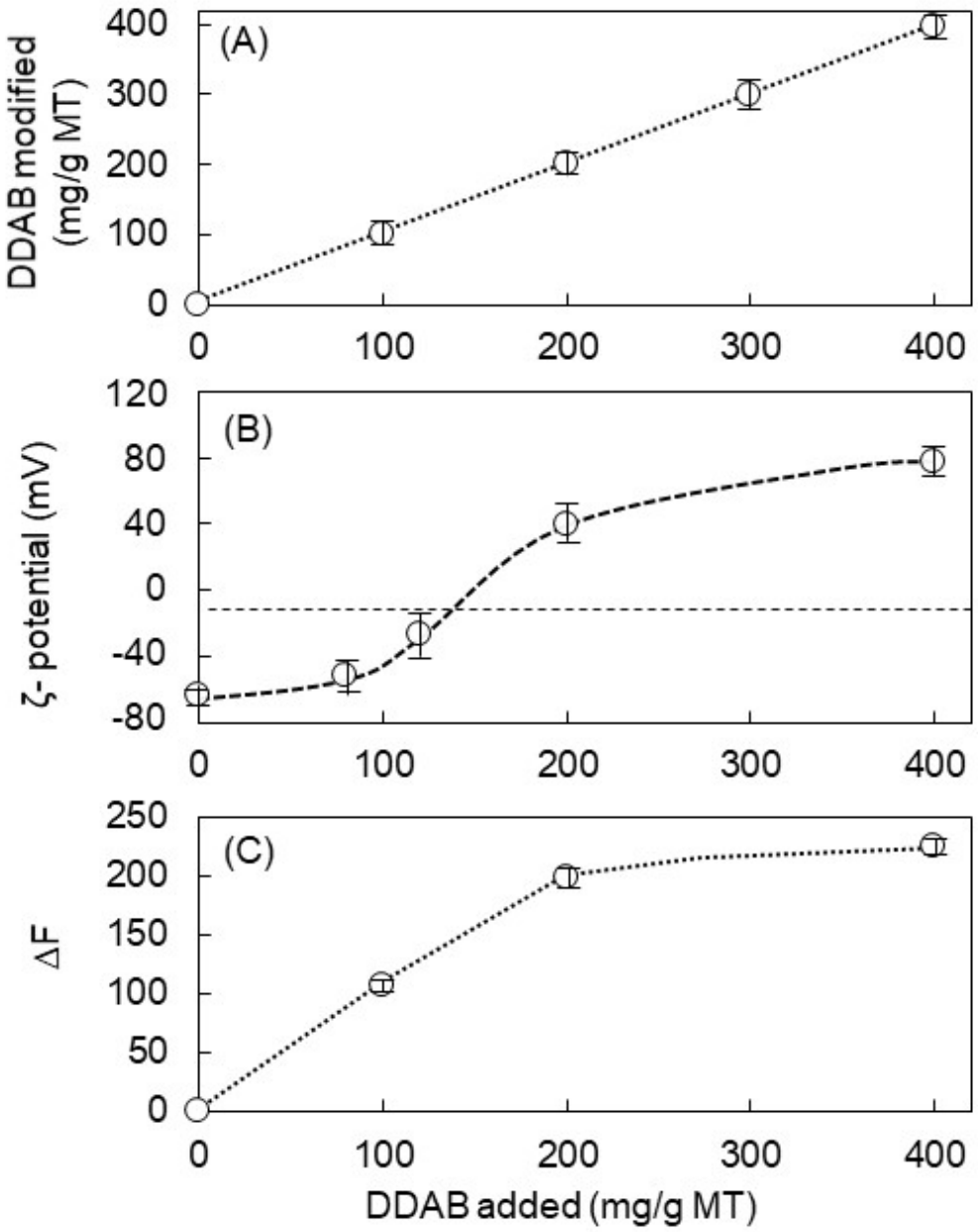


Fig. 3-1. (A) DDAB content, (B), zeta potential and (C) enhancement of fluorescent intensity (ΔF) of PN for the DDAB-MT organoclay medium as a function of amount of DDAB added [mg (g MT)$^{-1}$].

3.3.2 Sorption of antibiotics, pharmaceuticals, and personal care products on the organoclay

The chemical structures, logarithmic aqueous–octanol distribution coefficients (log $K_{ow)}$ estimated using the EPI suite (distributed by the US Environmental Protection Agency), and pK_a values of the antibiotics and other pharmaceuticals used in the present study are listed in Table 3-2. These compounds were selected because they represent popular antibiotics, pharmaceuticals, and personal care products, or are physiologically active substances with various hydrophobic and electrostatic properties with well documented potential environmental impacts [11-13]. The sorption percentage [%] of the antibiotics and other pharmaceuticals were calculated from the difference between the initial concentration (C_0 [mg L^{-1}]) and the residual one (C_{res} [mg L^{-1}]).

$$Sorption[\%] = \frac{C_0 - C_{res}}{C_0} \times 100$$

As shown in Fig. 3-2, the sorption of ibuprofen reached equilibrium within 1 min with solution mixing, indicating the usefulness of the organoclay sorption method for its rapid removal from water. The degrees of sorption of the different classes of pharmaceuticals from water onto the DDAB-MT organoclays with different DDAB contents are shown in Fig. 3-3. To simplify the presentation of the results, they are shown in separate figures. The effect of the DDAB content on the sorption depended strongly on the specific antibiotic, pharmaceutical, or personal care product. β-Lactam antibiotics (nafcillin, penicillin G, cefazolin, and cefotaxime) and anti-inflammatory drugs (ibuprofen and ketoprofen) with carboxyl groups are negatively charged at neutral pH, and thus were scarcely sorbed on the negatively charged unmodified MT. However, their sorption increased significantly with increasing DDAB content due to their strong electrostatic

interaction with the positively charged DDAB assemblies. Increased sorption was observed even at DDAB contents at which the organoclay was still negatively charged. A similar tendency has also been reported in the sorption of negatively charged chlorophenolate ions on cationic-surfactant-modified silica gels with a negative net charge [10]. The positive charge of the DDAB assemblies has a greater effect on the sorption of negatively charged species than the overall charge of the organoclay. The hydrophobic regions may also facilitate the sorption of β-lactam antibiotics and anti-inflammatory drugs. Estrogens (estriol, β-estradiol, and ethinylestradiol) and dexamethasone, which do not have acidic or basic moieties, were significantly sorbed on the unmodified MT, probably via intercalation between layers of the clay. The degree of their sorption increased with increasing DDAB content, depending on their hydrophobicity. The effect of DDAB modification on the sorption of chloramphenicol and carbamazepine was less remarkable than its effect on the sorption of estrogens and dexamethasone. Chemical structure or shape may also be an important factor for organoclay sorption. The macrolide antibiotic (erythromycin) and antidepressants (fluoxetine and imipramine) are positively charged at neutral pH; accordingly, their sorption decreased as the DDAB content of the organoclay increased due to the increase in the electro-repulsive force between the positively charged drug and DDAB assemblies. Sulfonamides (sulfamonomethoxine and sulfamethoxazole) with an amino moiety are basic drugs, and thus present as partially cationic species. However, the effect of the DDAB content on their sorption was similar to that for the negatively charged β-lactam antibiotics and anti-inflammatory drugs; the reason for this behavior is unclear. Tetracycline is a highly hydrophilic antibiotic, but was strongly sorbed on both the unmodified and DDAB-modified MT. This fact is ascribable to the existence of both

positively and negatively charged moieties in tetracycline, which would allow it to interact with the negatively charged MT surface [14] and positively charged surfactant assemblies [15]. Tetracycline has also been reported to sorb strongly on unmodified clay [16] as well as on organoclays modified with different cationic surfactants [17, 18].

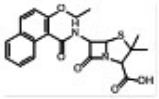
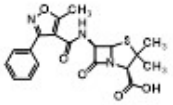
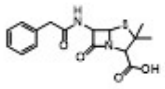
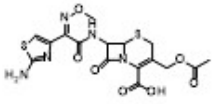
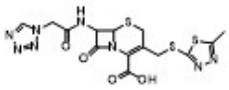
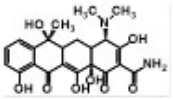
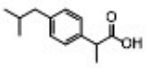
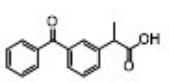
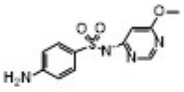
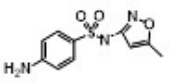
The effect of surfactant modification on the organoclay sorption of β-lactam antibiotics can be represented by the binding constant, K_b, of the antibiotic to the DDAB molecules in the organoclay [8].

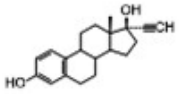
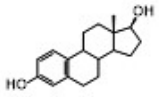
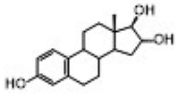
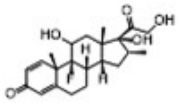
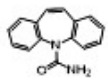
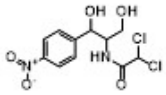
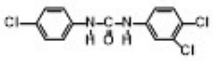
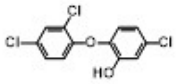
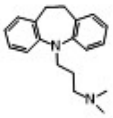
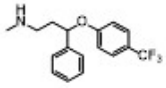
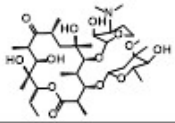
$$K_b = XV/q(100 - X)$$

Here, X denotes the difference between the sorption [%] of the antibiotic on unmodified MT and that on DDAB-modified MT, V is the solution volume [L], and q is the content [kg] of DDAB. Fig. 3-4 shows the correlation between the logarithmic binding constant (log K_b) and the logarithmic aqueous–octanol distribution coeffcient (log K_{ow}), which is a measure of the hydrophobicity of a compound. A fairly good correlation was obtained for most of the β-lactam antibiotics, indicating that hydrophobic interactions play an important role in their sorption on the organoclay. However, the K_b value for cefoperazone, which has a phenolic group, was higher than the value predicted from the correlation. This can be ascribed to the strong interaction of the phenolic moiety with the positively charged DDAB. The strong interaction of a phenolic moiety with a cationic surfactant was also reported in the sorption of phenolic compounds on cationic-surfactant-modified silica gels [10].

On the other hand, the value for ampicillin, which has an amino group, was lower than the predicted value. This can be explained by the decrease in its negative charge due to its protonated amino group. These results suggest that electrostatic interactions or electro-repulsive forces also play an important role in organoclay sorption.

Table 3-2. Structures, logarithmic aqueous–octanol distribution coefficients (log K_{ow}), and acid dissociation constants (pK_a) of antibiotics, pharmaceuticals, and personal care products

Pharmaceutical	Structure	log K_{ow}[a]	pK_a
Nafcillin		3.79	2.61[24]
Oxacillin		2.38	2.61[24]
Penicillin G		1.85	2.62[24]
Cefotaxime		0.64	2.21(-COOH), 3.15(-NH_3^+)[25]
Cefazolin		-0.58	3.6[26]
Tetracycline		-1.33	3.32(-OH), 7.78(-OH), 9.58(-NMe_2H^+) [27]
Ibuprofen		3.79	4.52 [28], 4.4 [29]
Ketoprofen		3.00	4.4 [29]
Sulfamonomethoxine		0.20	6.01 [30]
Sulfamethoxazol		0.48	5.7 [31]

Ethinylestradiol		4.12	
β-Estradiol		3.94	
Estriol		2.81	
Dexanethasone		1.72	
Carbamazepin		2.25	
Chloramphenicol		0.92	
Triclocarban		4.90	12.7 [32]
Triclosan		4.66	7.9 [32]
Imipramine		5.01	9.49 [33]
Fluoxetin		4.65	10.05 [33]
Etythromycin		2.48	8.90 [26]

a: Calculated by using EPI Suite^{TM}, United State Environmental Protection Agency

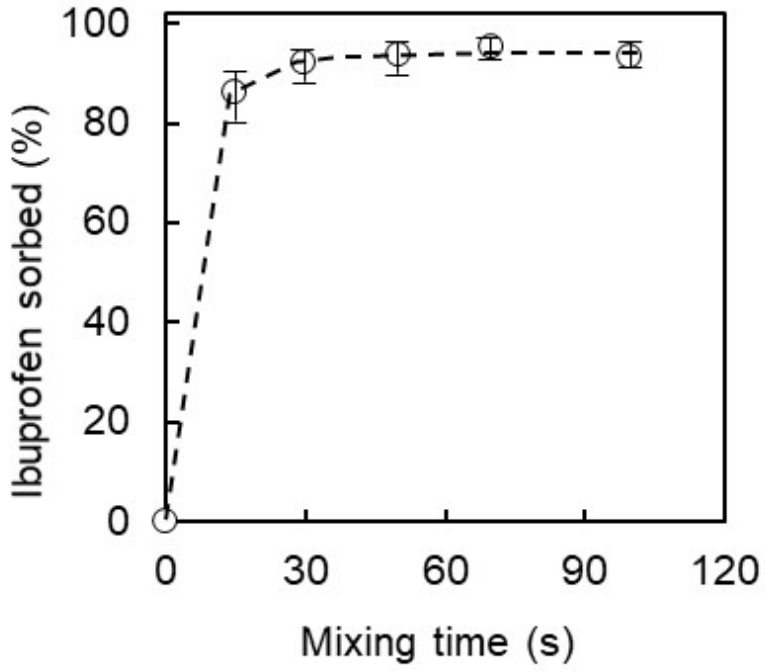


Fig. 3-2. Effect of the mixing time on the sorption of ibuprofen on the DDAB-MT organoclay.

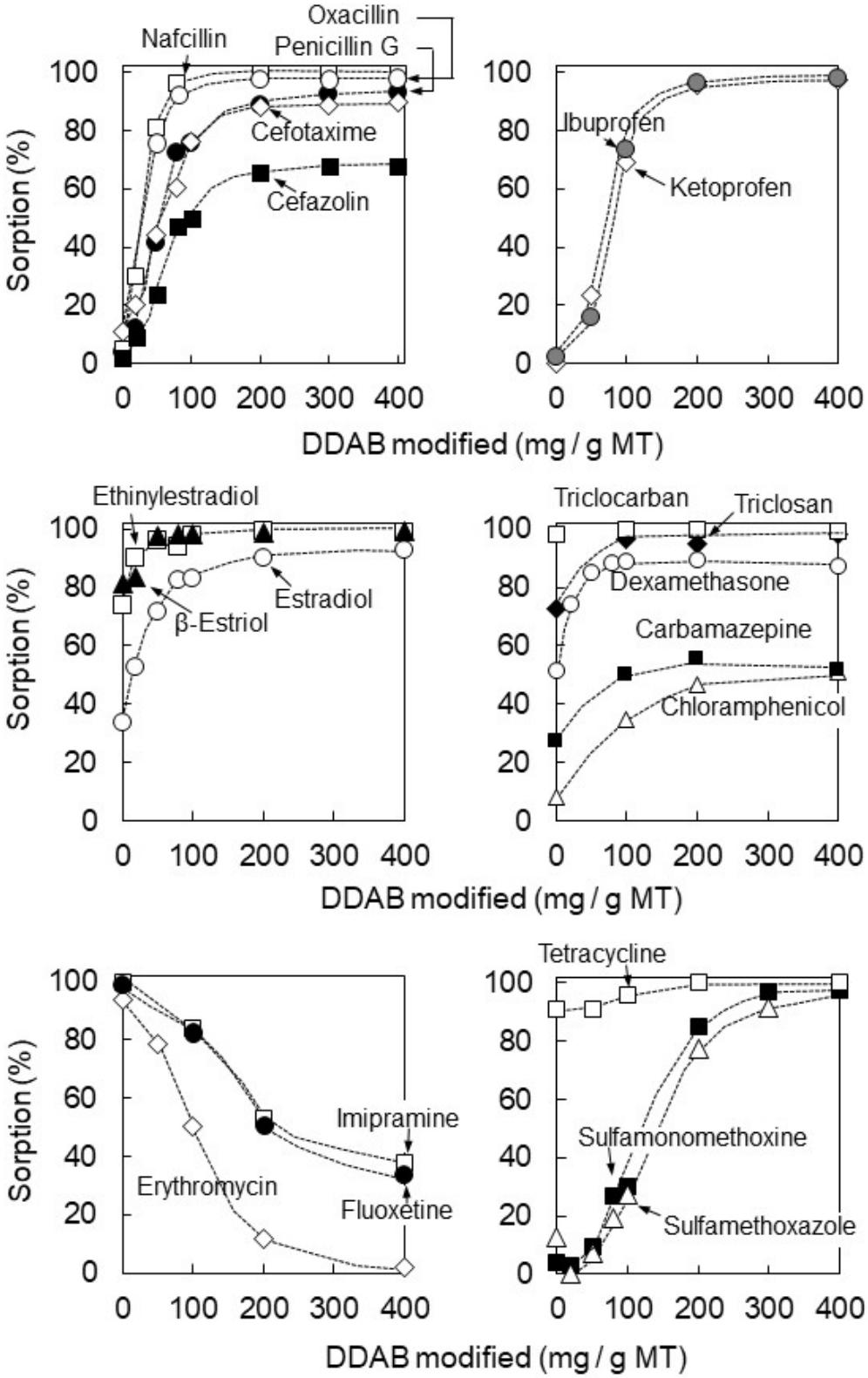


Fig. 3-3. Degrees of sorption of the antibiotics, pharmaceuticals, and personal care products on 4.0 g L^{-1}. MT modified with different amounts (0-400 mg (g MT)$^{-1}$) of DDAB (pH 7, 25℃).

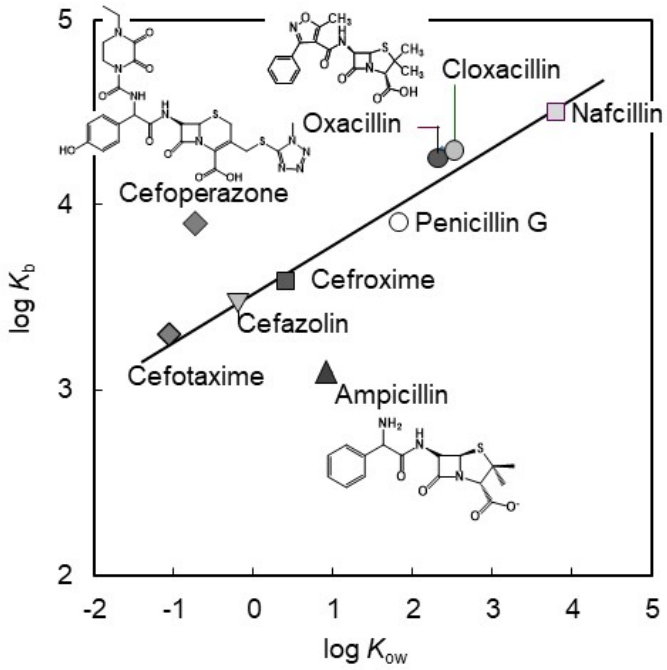


Fig. 3-4. Correlation between logarithmic binding constants (log K_b) of the different β-lactam antibiotics to the DDAB on organoclay and their aqueous-octanol distribution coefficients (log K_{ow}).

3.3.3 Organoclay-induced degradation

The time-dependent degradation of penicillin-type (A) and cephalosporin-type (B) antibiotics are summarized in Fig. 3-5, in which the remaining antibiotic is represented by the percentage ratio of the remaining concentration (C) to the initial one (C_0). All the β-lactam antibiotics were rapidly degraded following sorption on the organoclay, although their degradation ratios in the bulk aqueous solution (pH 7) after 2 h were less than 2%. The chemical and biological stabilities of β-lactams are largely dependent on their structures [19, 20]. Cephalosporin- type antibiotics with a 6-membered heterocyclic ring tend to be more stable against acid-catalyzed hydrolysis than penicillin-type ones with a 5-membered heterocyclic ring. However, cephalosporin-type antibiotics including cefuroxime, cefotaxime, and cefazolin were also rapidly degraded when sorbed on the organoclay. These results strongly suggest the usefulness of DDAB-MT organoclay for not only the sorption, but also the degradation of a wide range of β-lactam antibiotics.

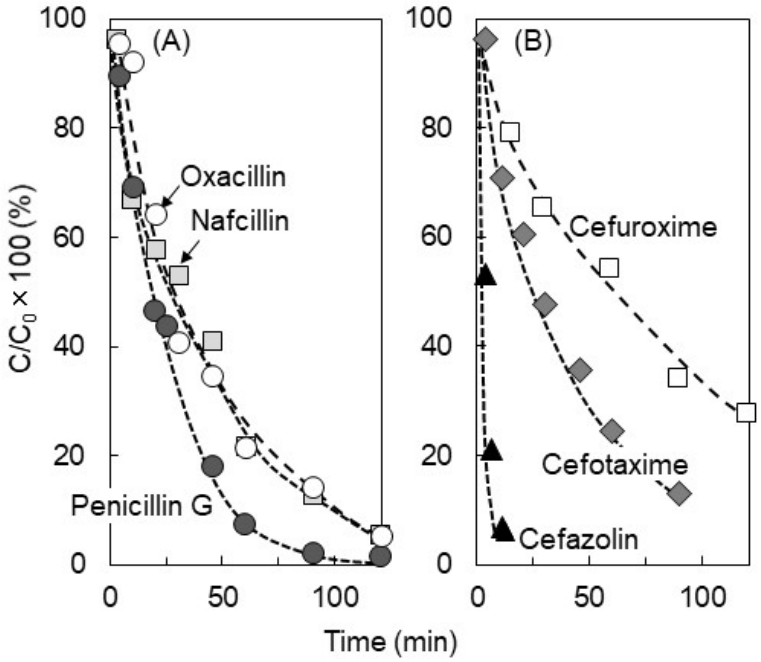


Fig. 3-5. (A) Time-dependent degradation of penicillin-type and (B) cephalosporin-type antibiotics during sorption on DDAB-MT organoclay consisting of 1.0 g of MT and 400 mg of DDAB (pH 7.0, 25℃).

3.3.4 Continuous treatment

The feasibility of continuous treatment using a small scale DDAB-MT organoclay-packed column was studied. Although the concentrations of most antibiotics in hospital effluents are normally far below the μg L^{-1} level [1, 4, 21], an aqueous solution containing 10 mg L^{-1} of penicillin G was used to clarify the applicability of this method to highly contaminated effluents. Fig. 3-6 (A) shows the breakthrough curve obtained by passing 10 mg L^{-1} penicillin G (pH 7) through the organoclay-packed column. The amount of Penicillin G detected in the effluent was negligible at elution volumes up to at least 290 mL. Only penicilloic acid (m/z=353) was detected after 200 mL of the penicillin G solution had been passed through the column. While retained in the organoclay layer, the penicillin G was converted into this degradation product, which lacks the β-lactam ring that is necessary for antibacterial activity. The results obtained using synthesized wastewater containing 10 mg L^{-1} of penicillin G are shown in Fig. 3-6 (B). The properties and composition of the synthesized wastewater are listed in Table 1 (at the end of the experimental section); the components were chosen based on a synthesized hospital wastewater formulation from the literature [12]. The elution of penicillin G was observed due to the decrease in the performance of the column resulting from the irreversible adsorption of dissolved organic components. Recently, organoclays have been studied as barrier materials for polluted percolated waters [22, 23]. The modification of clay minerals with surfactants or polyelectrolytes improves the retention of various organic pollutants and therefore reduces their leakage. The results obtained in the present study demonstrate the potential usefulness of modified clay minerals for not only the sorption of these pollutants, but also their degradation or detoxification.

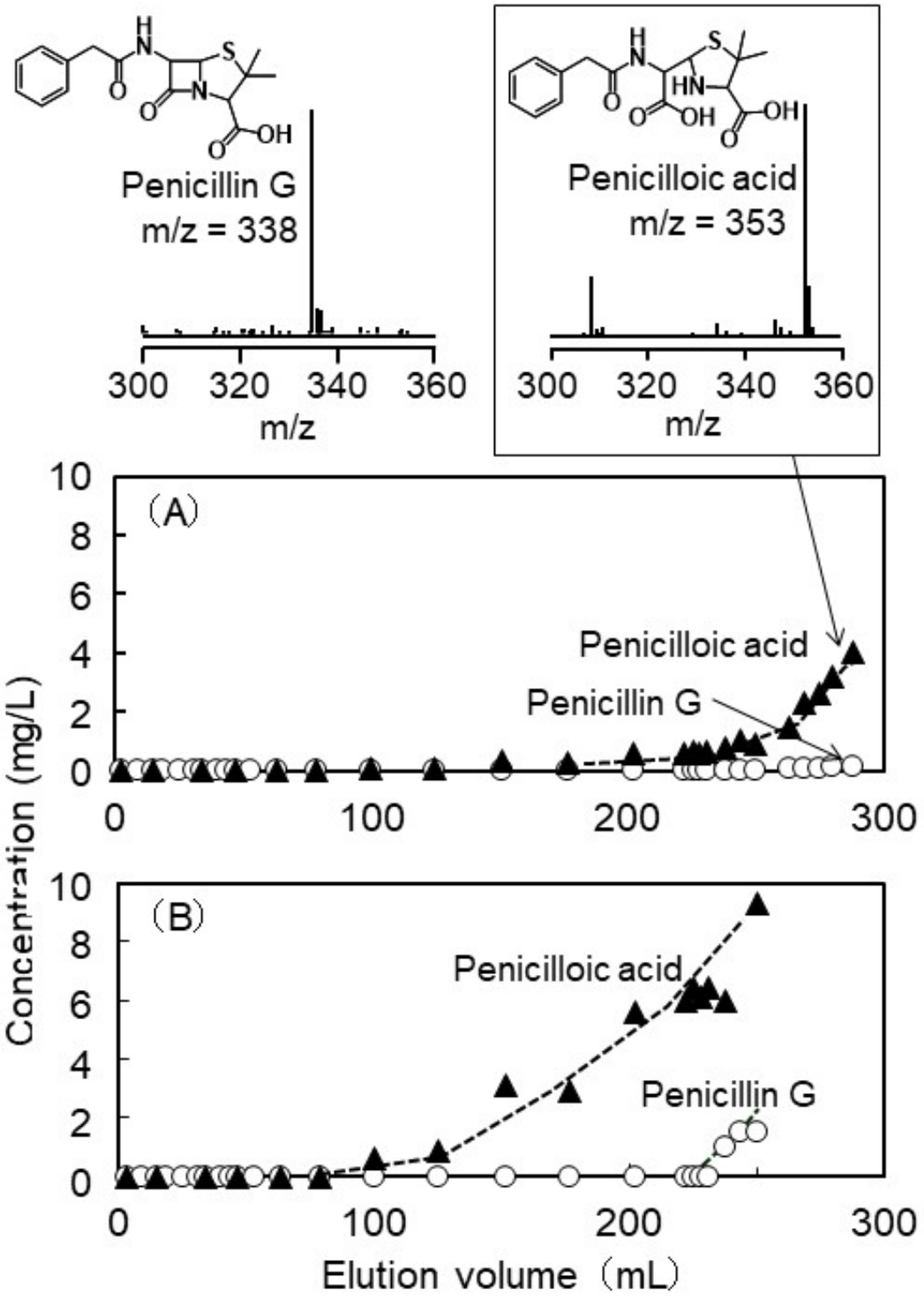


Fig. 3-6. (A) Breakthrough curves of penicillin G and its degradation product, penicilloic acid, obtained by passing aqueous buffer solution containing 10 mg L^{-1} of penicillin G and (B) synthesized hospital wastewater containing the same amount of penicillin G through a DDAB-MT organoclay-packed column (inner diameter: 15 mm, filling height: 7mm).

3.4 Conclusion

The organoclay sorption method was found to be useful for the rapid removal of various antibiotics, pharmaceuticals, and personal care products from water. The extent of their removal was largely dependent on the DDAB content, along with the hydrophobicity and net charge of the compounds. The binding constants of β-lactam antibiotics, which were determined by their interactions with the DDAB molecules on the organoclay, were correlated to the logarithmic aqueous–octanol distribution coefficient. However, electrostatic interactions also influenced their sorption on the organoclay. A wide range of β-lactam antibiotics, including penicillin-type and cephalosporin-type antibiotics, were degraded under mild conditions (pH 7, 25°C). During its retention in the organoclay layer, penicillin G (m/z=338) was converted into penicilloic acid (m/z=353), which lacks the β-lactam ring responsible for antibacterial activity, suggesting the potential applicability of the organoclay sorption method to the diffusion control of antibiotics.

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CHAPTER 4

CONCLUSION

Organoclay was studied to develop a new removal technology of high bioactive organic pollutants such as pesticides, antibiotics, pharmaceuticals and personal care products. Because conventional technologies such as activated sludge method and/or activated carbon adsorption are not enough to removal these pollutants in water and these methods are expensive to use.

In Chapter 2, the organoclay collects fenitrothion and degrade it rapidly. The factor of the collection was considered as hydrophobic interaction between fenitrothion and hydrophobic region formed by didodecyldimethylammonium bromide (DDAB). Collected fenitrothion was hydrolyzed in mild condition (pH 7, 25°C) faster than in water due to the organoclay catalytic activity. Its factors were considered by mainly DDAB micellar and clay surface acid points. Continuous treatment of fenitrothion contaminated water using the organoclay for experimenting the applicability showed that the organoclay stored more toxic fenitrothion and release less toxic degradation product (3-methyl-4-nitrophenol).

In Chapter 3, the organoclay collects antibiotics, pharmaceuticals, and personal care products rapidly and high adsorption rates. The collection depends on DDAB content, so it was considered that hydrophobicity and net charge were factors. A wide range of β-lactam antibiotics, including penicillin-type and cephalosporin-type antibiotics, were degraded under mild conditions (pH 7, 25°C). Continuous treatment of penicillin G contaminated water using the organoclay for experimenting the applicability showed the organoclay stored highly bioactive penicillin G and release inactive degradation product

(penicilloic acid).

The organoclay collected highly bioactive compounds, fenitrothion, antibiotics, pharmaceuticals, and personal care products rapidly. Because of hydrophobic interaction and electrostatic interaction. And it promoted degradation of fenitrothion and β-lactam antibiotics under mild condition. Because of catalytic activity of the organoclay. Then the organoclay showed the applicability to use as a diffusion control material. A treatment method using this organoclay is different from conventional treatment methods like activated carbon method or activated sludge method. This organoclay is prepared easily and low cost, just mixing clay and DDAB solution. And it not only adsorbs these high bioactive organic pollutants rapidly but also promotes their degradation without any helps of microorganisms. In addition, DDAB leakage from the organoclay during continuous treatment less than 10%. These results suggest that the organoclay adsorption method is useful for diffusion control material of these highly bioactive organic pollutants.