

Removal of detergents and fats from waste water using allophane

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Abstract

Micelles, consisting of an anionic surfactant and a fatty acid released from a fat, were removed from an aqueous phase using the ion exchange characteristics of a natural clay mineral, allophane. The UV spectral measurements revealed that the concentrations of the anionic surfactant and the fatty acid in the aqueous phase decreased and that these species were removed from the aqueous phase. The adsorption of the surfactant and the fatty acid onto the allophane was confirmed by FT-IR spectroscopy. Furthermore, this adsorption was confirmed by the adsorption of anthracene added as a probe molecule.

Keywords: Allophane; Adsorption; Micelle; Surfactant; Fatty Acid

1. Introduction

We should keep water as clean as possible to reduce harmful influences on the natural environment of the earth. Oils or fats and water are easily separated using the difference between their density and their lyophobicity. The waste water emitted from our houses or restaurants contains oils or fats and detergents. These compounds are difficult to be separated from the aqueous phase because they form micelles and are dispersed and stabilized in water. Some hydrophobic toxic compounds are encapsulated in the micelles and are difficult to be removed from there. Simple procedures for such separation are required in order to widely expand the techniques for water purification to our houses, restaurants, and small factories all over the world. The main components of household detergents are anionic surfactants. Such materials can be removed by an ion exchange procedure due to their structure, i.e., the lipophilic groups are aligned in the direction of the exterior of the micelle.

Some clay minerals have a high activity for ion exchange, adsorption, and catalyst uses. They are also available for water purification (Xu et al., 1998; Bergaya et al., 2006; Cea et al., 2007). Allophane, a natural clay mineral distributed throughout the world, is a hydrated aluminosilicate ($1-2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 5-6\text{H}_2\text{O}$) having a 3.5–5.0 nm-sized hollow spherical structure with 0.3–0.5 nm-sized defects on its surface (Kitagawa, 1971; Henmi and Wada, 1976; Wada and Wada, 1977; Hall et al., 1985; van der Gaast et al., 1985). The walls in the hollow spheres consist of inner silica and outer alumina layers with the hydroxylated or hydrated surface. Some studies suggest that these surfaces have a high ability to adsorb ionic or polar pollutants due to an amphoteric ion-exchange activity (Theng, 1972; Clark and McBride, 1984; Hanudin et al., 1999; Gustafsson, 2001; Hashizume et al. 2002; Jara et al., 2006) and their high surface area (Kitagawa, 1971; Hall et al., 1985). Allophane is therefore available for removal of the micelles consisting of anionic surfactants and fats from aqueous phase. In previous studies, some hydrophobic pollutants were removed from water using the layered clay minerals such as montmorillonite and kaolinite hydrophobically modified with the surfactant molecules (Polubesova et al., 2004; Li and Gallus, 2005; Polubesova et al., 2005; Rodoríguez-Cruz et al., 2005; Zadaka et al., 2007; Sánchez-Martín et al., 2008). In addition, the clay minerals adsorbed the micelles formed by adding the surfactant molecules to the polluted water (Polubesova et al., 2004; Polubesova et al., 2005; Zadaka et al., 2007). The allophane has, in part, been applied to wall materials to control humidity in the air using its moderate hydrophilicity. However, the chemical properties of allophane have not been effectively utilized. Basic studies are needed on the adsorption of the organic ions and their micelles using the ion exchange characteristics.

In this study, we tried to remove the micelles consisting of an anionic surfactant, sodium linear alkylbenzene sulfonate, and a fatty acid, linoleic acid, from the aqueous phase using the ion exchange characteristics of allophane. This study is important for developing a sure method of removing the micelles consisting of surfactants and fats. A fatty acid was, however, used instead of fats in this study. Linoleic acid is a fatty acid eliminated from one of the typical fats. The quantitative analysis of the fats is difficult because they are easily hydrolyzed in an aqueous phase. Fatty acids are more difficult than fats to remove from an aqueous phase due to their higher solubility. Therefore, it is worth while investigating the removal of the fatty acids. UV spectral measurements were conducted to observe the decrease in the concentrations of the anionic surfactant and the fatty acid in the aqueous phase. Furthermore, the adsorption of the surfactant and the fatty acid onto the allophane was confirmed by the IR spectrum of the allophane. We tried to investigate the methodology of an easy observation of the micelle removal from the aqueous phase by using an aromatic probe molecule, i.e., anthracene was added to the micelle systems in order to incorporate into the lipophilic part inside of the micelle.

2. Experimental Section

2.1. Materials

Sodium linear alkylbenzene sulfonate (LAS), poly(oxyethylene)isooctylphenylether (TritonX-100), linoleic acid, and anthracene purchased from Wako Pure Chemicals, reagent grade, were used without further purification. Water, which was deionized and then distilled, was used as a dispersion medium. The allophane was extracted by elutriation of Kanuma soil from Tochigi, Japan (Wada and Wada, 1977; Hall et al., 1985; Wada, 2001). The soil grains were suspended in water and agitated on a reciprocal shaker. The clear suspension was separated from it by centrifugation (Daiki Ataka MD-3), and consequently contained the allophane aggregates having an average diameter of 15 μm . The fine particles ($<0.2 \mu\text{m}$) were obtained by drying the supernatant resulting from filter pressing of the nearly clear dispersion at 0.85 MPa. The allophane sample was finally dried at 300°C. The ratio of Al/Si in the allophane was 1.25 by XPS analysis (ULVAC PHI5600). The specific surface area and average pore diameter of the allophane were 312 m^2g^{-1} and 3.8 nm, respectively, by BET measurement (Micrometrics ASAP 2000). The allophane sample was observed to consist of the spherical aggregates having diameter of 30–90nm by scanning electron microscopy (Hitachi S-4100). The anion exchange capacity of the allophane was estimated to be $1.0 \times 10^{-4} \text{ mol g}^{-1}$ at around pH6 by NO_3^- adsorption. This value corresponds to an anion exchange capacity of the allophane at around pH6, $5\text{--}10 \times 10^{-5} \text{ mol g}^{-1}$ (Theng et al., 1982).

2.2 Measurements

An aqueous dispersion system, 30 cm^3 , containing LAS ($2.0 \times 10^{-2} \text{ mol dm}^{-3}$) and anthracene ($1.0 \times 10^{-5} \text{ mol dm}^{-3}$) was prepared and labeled System L. A system containing the same concentrations of TritonX-100 instead of LAS and anthracene as in System L was also prepared and labeled System T. An aqueous dispersion system, 30 cm^3 , labeling System LL-1/2 or LL contained the same concentrations of LAS and anthracene as in System L and an additional 2.0×10^{-3} or $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ of linoleic acid, respectively. The dispersion system containing the same concentrations of TritonX-100 instead of LAS, anthracene, and linoleic acids as in System LL was also prepared and labeled System TL. The compositions of each system are summarized in Table 1. The concentration of the surfactants in all the aqueous dispersion systems were much higher than their critical micelle concentrations (Goon et al., 1997; Rodoríguez-Cruz et al., 2005; Sánchez-Martín et al., 2008). The allophane, 1.0 g, was suspended in these aqueous dispersion systems as well as the aqueous solutions, 30 cm^3 , of LAS ($1.0 \times 10^{-2}\text{--}1.0 \times 10^{-1} \text{ mol dm}^{-3}$) and linoleic acid ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$). The suspensions were shaken for 0.1–5 hours and then centrifuged. The UV absorption spectra of the resulting clear solutions were measured as a function of time using a Shimadzu UV-2500PC spectrophotometer. The amounts of the adsorbed compounds were estimated from the concentration differences. In this study, the amounts of the species adsorbed on the allophane were simply estimated by the UV absorption measurements. The pH values in all the systems after reaching the adsorption equilibria were around 6. It was difficult to observe the adsorption of only anthracene from the aqueous phase onto the allophane due to its low solubility in water.

A thin liquid film of linoleic acid was placed between two pieces of KBr plates. The allophane sample after absorbing linoleic acid and/or LAS for 5 hours was pressed in the KBr pellets. The FT-IR spectra of these samples were measured using a Shimadzu FTIR-8300 spectrophotometer. The spectra of the species adsorbed on the allophane were obtained by subtracting those of the allophane.

3. Results and Discussion

The adsorption equilibrium constants of LAS, K_{LAS} , and linoleic acid, K_{Lin} , on allophane are written as

$$K_{LAS} = \frac{[LAS-Allo]}{[LAS][Allo]}$$

$$K_{Lin} = \frac{[Lin-Allo]}{[Lin][Allo]}$$

$$[Allo] = [Allo]_0 - [LAS-Allo] - [Lin-Allo]$$

where Allo is the adsorption site on the allophane surface, Lin is an abbreviation of linoleic acid, and LAS-Allo and Lin-Allo are LAS and linoleic acid adsorbed on the Allo by the ion exchange characteristics of the allophane, respectively.

The initial Allo concentration, $[Allo]_0$, was defined as the molar amount of the adsorption site existing on the allophane dispersed in 1 dm³ of water. The value of $[Allo]_0$ was estimated to be 3.9×10^{-3} mol dm⁻³ by the Langmuir isotherm shown in Figure 1. This value corresponds to the molar amount per gram of the allophane, 2.1×10^{-4} mol g⁻¹, twice the anion exchange capacity of the allophane. This amount indicates that the adsorption of LAS on the allophane is due to not only the ion exchange, but also the hydrophobic interaction between the LAS molecules. The amounts of some surfactant molecules adsorbed on kaolinite or some other clay minerals were larger than twice of their ion exchange capacities due to the hydrophobic interaction of the surfactant molecules (Li and Gallus, 2005; Sánchez-Martín et al, 2008).

This adsorption behavior was confirmed to follow the Langmuir isotherm. The values of K_{LAS} and K_{Lin} were experimentally obtained to be 62 and 25 mol⁻¹ dm³, respectively. The K_{Lin} were determined by the adsorption equilibrium in a 1.0×10^{-3} mol dm⁻³ of aqueous linoleic acid solution due to its solubility limitation.

Figure 2 shows the time course of the relative concentration of each species in the allophane-suspension system containing LAS and anthracene (System L). The concentration was normalized by each initial concentration. The following figures are the same as described in Fig. 2. The concentrations of both species similarly decrease and reach their adsorption equilibria in about one hour. The anionic surfactant, LAS, should be mainly adsorbed on the surface of the allophane by the ion exchange characteristics of the allophane. This is because the amount of LAS adsorbed per gram of the allophane was 1.0×10^{-4} mol g⁻¹, corresponding to the anion exchange capacity of the allophane. Anthracene is suggested to be encapsulated in the LAS micelles adsorbed on the allophane surface because it is hydrophobic and is hardly adsorbed on a hydrophilic allophane surface.

We also observed the concentration of each species in the allophane-suspension system containing TritonX-100 and anthracene (System T) although the results are not graphically shown here. TritonX-100 is a nonionic surfactant and is hardly adsorbed on the allophane surface compared to LAS. As expected, TritonX-100 or anthracene was essentially not adsorbed on the allophane.

Figure 3 shows the change in the relative concentration of each species in the allophane-suspension system containing LAS, linoleic acid, and anthracene (Systems LL). In this system, the concentrations of the three components decrease due to their adsorption on the allophane to maintain the micelle structure of these species. The concentration of LAS reaches that of its adsorption equilibrium in about one hour similarly to that in System L, whereas those of linoleic acid and anthracene reach those of their equilibria in 1–2 hours. The concentration of linoleic acid significantly decreases compared to that of LAS, indicating that the linoleic acid is not only inside the micelle, but also directly adsorbed on the allophane surface. Anthracene molecules were adsorbed together with the linoleic acid because the decrease ratio of anthracene is larger than that of LAS. On the other hand, in System TL, the concentration of

TritonX-100 essentially did not decrease similar to System T, whereas the linoleic acid and anthracene, however, clearly decreased. This result demonstrates that the linoleic acid is directly adsorbed on the allophane surface. Although the results for System TL are not graphically shown, the adsorption equilibrium constants in all the systems will be discussed below. The decrease in the concentration of linoleic acid and anthracene in System LL is significantly larger than that in System TL. This indicates that they formed the micelle to be adsorbed on the allophane.

The distribution equilibrium constants of linoleic acid, $K_{\text{Lin(M)}}$, and anthracene, $K_{\text{Ant(M)}}$, between the inside of the micelles adsorbed on allophane and the liquid phase are written as

$$K_{\text{Lin(M)}} = [\text{Lin(M)-Allo}]/[\text{Lin}]$$

$$[\text{Lin(M)-Allo}] = [\text{Lin}]_0 - [\text{Lin}] - [\text{Lin-Allo}]$$

$$K_{\text{Ant(M)}} = [\text{Ant(M)-Allo}]/[\text{Ant}]$$

where Lin(M)-Allo and Ant(M)-Allo are linoleic acid and anthracene encapsulated in the micelles of the LAS adsorbed on allophane, respectively, and Ant is an abbreviation of anthracene.

Figure 4 shows the dependence of the amount of each adsorbed species on the initial concentration of linoleic acid in the allophane-suspension system containing LAS and anthracene, in which the micelles were adsorbed on the allophane. The amount of each species adsorbed on the allophane was obtained from the concentration loss over 5 hours while the adsorption reached its equilibrium. The amount of the adsorbed LAS was nearly independent of the initial concentration of linoleic acid. On the other hand, the amount of the adsorbed linoleic acid clearly increased with an increase in its initial concentration. The equilibrium constants of LAS, linoleic acid, and anthracene in each system are summarized in Table 2. The adsorption equilibrium constants of LAS, K_{LAS} , and linoleic acid, K_{Lin} , are 61–66 and 25–29 mol⁻¹ dm³ in these systems, respectively. This adsorption of LAS and linoleic acid is due to the ion exchange characteristics of the allophane. The adsorption equilibria of these ionic species are almost independent of the adsorption of the other species. On the other hand, the distribution constants of linoleic acid, $K_{\text{Lin(M)}}$, and anthracene, $K_{\text{Ant(M)}}$, are larger in the system containing a higher concentration of linoleic acid. This distribution of linoleic acid, and anthracene is regarded as the adsorption of them to maintain the micelle structure. This type of adsorption mainly contributed to the concentration loss of linoleic acid in Systems L-1/2 and LL. The percentages of the contribution were estimated to be 95% and 97% in Systems L-1/2 and LL, respectively. The amount of the adsorbed LAS should be related to the ion exchange capacity of the allophane. However, the amounts of the adsorbed linoleic acid and anthracene are not directly related to this. These results indicate that the micelles grown to a larger size were encapsulated inside the LAS spheres.

Figure 5 shows the FT-IR spectrum of the LAS and linoleic acid adsorbed from the system containing their micelles on the allophane. The peaks originating from the C–H stretching vibration of these compounds are observed at 3000–2800 cm⁻¹. In addition to these, the peaks are observed at 1685, 1578, 1466, and 1410 cm⁻¹. The peaks at 1685 and 1578cm⁻¹ are assigned to the C=O stretching vibration of the carboxylic group and the CO₂⁻ anti-symmetric stretching vibration of the carboxylate group, respectively. These peaks were not observed in the spectrum of the allophane adsorbing only LAS but were observed in that absorbing only linoleic acid. This result confirms that linoleic acid was also adsorbed from the aqueous system containing the micelles. The present results agree with the fact that the carboxylic acid is well-known to form the carboxylate and be absorbed on the allophane (Klug and Forsling, 1999; Rosenqvist et al., 2003; Lee and Reeder, 2006; Nishikiori et al., 2009).

The SO₂ anti-symmetric vibration was also observed at 1182 cm⁻¹ in addition to some vibration peaks due to linoleic acid. The IR analysis confirmed that LAS and linoleic acid were co-adsorbed from the system containing the micelles. The C=O stretching band was expected to be more strongly observed because the neutral species of linoleic acid should exist

in the hydrophobic part in the center of the micelle. However, the adsorption structure was probably transformed by the dehydration of linoleic acid during the drying process of the sample. This process is essential for IR measurement. Linoleic acid also consists of hydrophilic and hydrophobic parts as a surfactant and can be a constituent of the surfactant sphere form. The evaporation of the water molecules adsorbed on the allophane surface causes the strong interaction between the species forming the micelles and the allophane surface. Consequently, the linoleic acid was, in part, transformed to lenolate anion-like form and adsorbed on the allophane.

The sulfonate groups of LAS in the micelles interact with the positively charged surface of the allophane particle. The micelles were mainly adsorbed on the allophane surface by the ion exchange characteristics since the amount of the adsorbed LAS was smaller than the anion exchange capacity of the allophane. The micelles are suggested to be stably adsorbed in the interspaces among the particles consisting of the aggregates of the original allophane because the size of such spaces, the pore size of 2–5 nm (Ohashi et al., 2002), is similar to the micelle diameter. The larger-sized micelles are also incorporated in the pores swelling in water.

4. Conclusions

Linoleic acid as a fatty acid and LAS as an anionic surfactant were adsorbed and removed from the aqueous phase containing their micelles using a natural clay mineral, allophane. The adsorption of linoleic acid and LAS on the allophane was also confirmed by the FT-IR analysis. Furthermore, this adsorption was confirmed by the adsorption of anthracene added as a probe molecule. In this study, a fatty acid was used instead of the fat. A similar adsorption action is expected when using some fat compounds.

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Figure Captions

Figure 1. Langmuir isotherm of LAS adsorption on allophane. The abscissa and ordinate indicate the equilibrium concentration of LAS, [LAS], and the amount of LAS adsorbed per gram of allophane, $C_{\text{LAS-Allo}}$, respectively.

Figure 2. Time course of the concentration of each species in System L containing LAS (■) and anthracene (▲) during their adsorption on allophane.

Figure 3. Time course of the concentration of each species in System LL containing LAS (■), linoleic acid (●), and anthracene (▲) during their adsorption on allophane.

Figure 4. Dependence of the concentration loss of each species on the initial concentration of linoleic acid in the systems containing LAS and anthracene (Systems L, LL-1/2, and LL) after their adsorption on allophane for 5 h.

Figure 5. IR spectrum of LAS and linoleic acid adsorbed from their emulsion on allophane.

Table 1. Initial compositions of each micelle system.

	Surfactant / mol dm ⁻³	linoleic acid / mol dm ⁻³	anthracene / mol dm ⁻³
System L	LAS, 2.0×10^{-2}	0	1.0×10^{-5}
System L-1/2	LAS, 2.0×10^{-2}	2.0×10^{-3}	1.0×10^{-5}
System LL	LAS, 2.0×10^{-2}	4.0×10^{-3}	1.0×10^{-5}
System T	TritonX-100, 2.0×10^{-2}	0	1.0×10^{-5}
System TL	TritonX-100, 2.0×10^{-2}	4.0×10^{-3}	1.0×10^{-5}

Table 2. Equilibrium constants of each system.

	$K_{LAS} / \text{mol}^{-1} \text{ dm}^3$	$K_{Lin} / \text{mol}^{-1} \text{ dm}^3$	$K_{Lin(M)}$	$K_{Ant(M)}$
LAS solution	62		-	-
Lin solution	-	25	-	-
System L	61	-	-	0.18
System L-1/2	60	25 ^a	1.7	0.72
System LL	66	25 ^a	2.8	0.92
System T ^b	-	-	-	0
System TL ^b	-	29	0	0.048

^a The value was determined by the equilibrium equation in the linoleic acid (Lin) system.

^b TritonX-100 was essentially not adsorbed on the allophane.

Figure 1

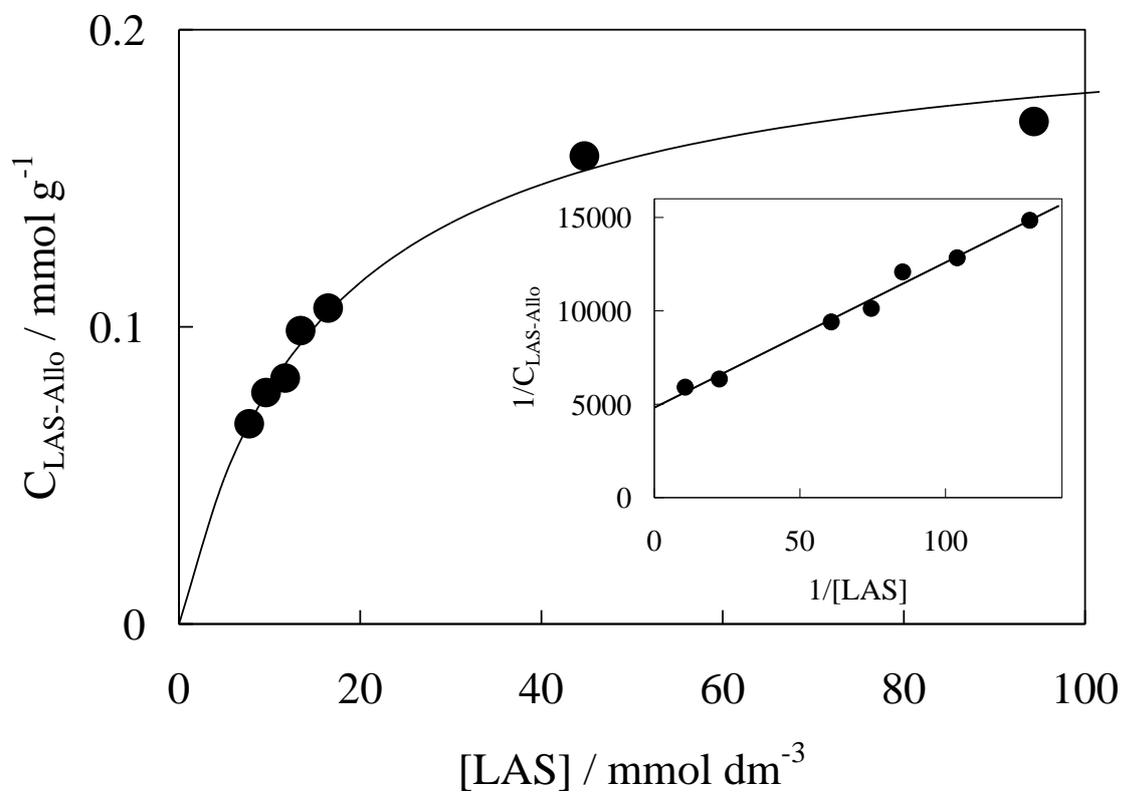


Figure 2

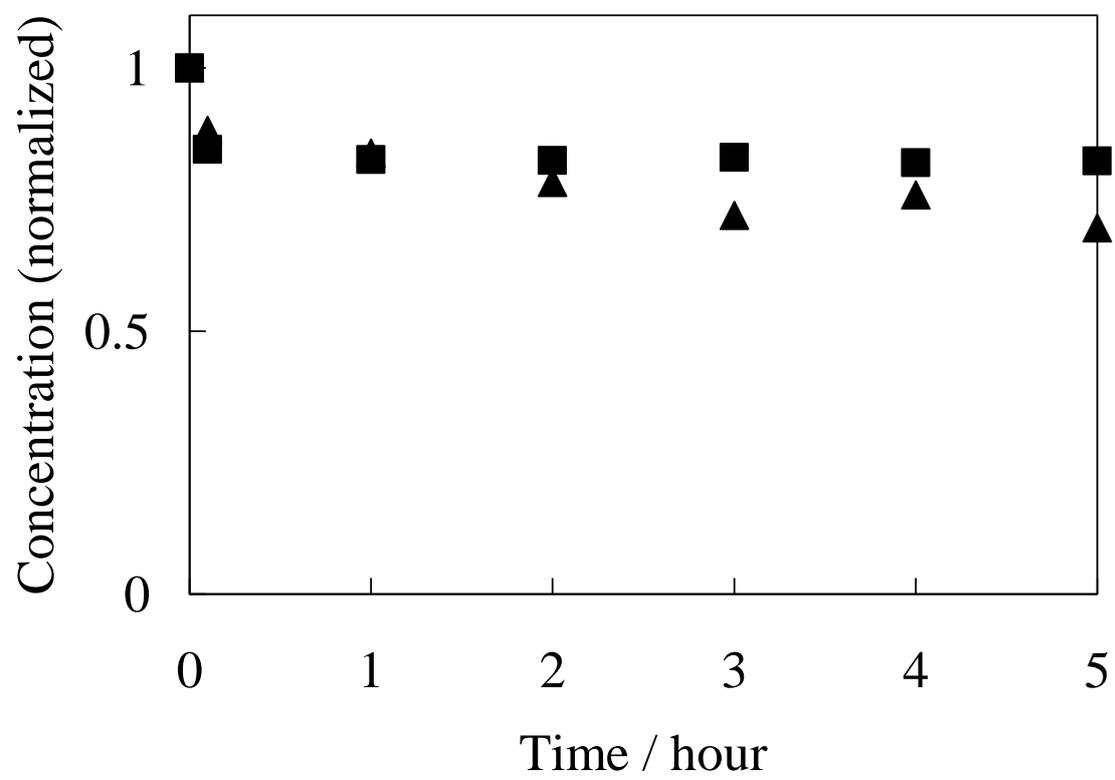


Figure 3

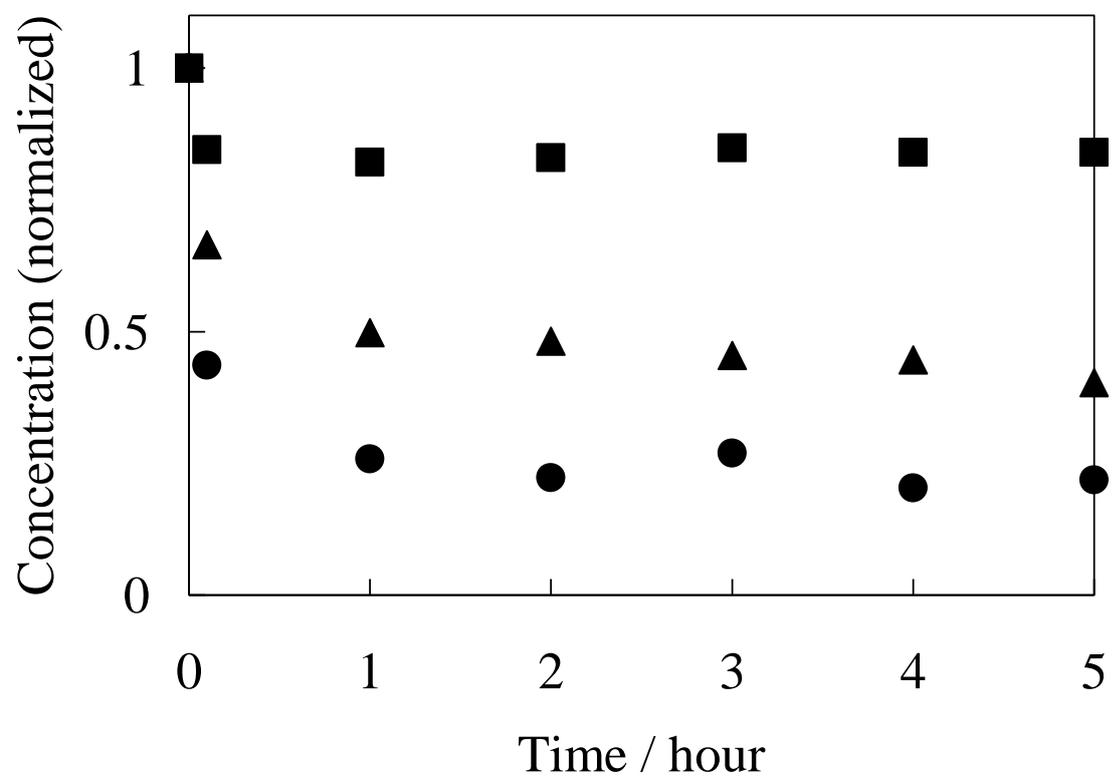


Figure 4

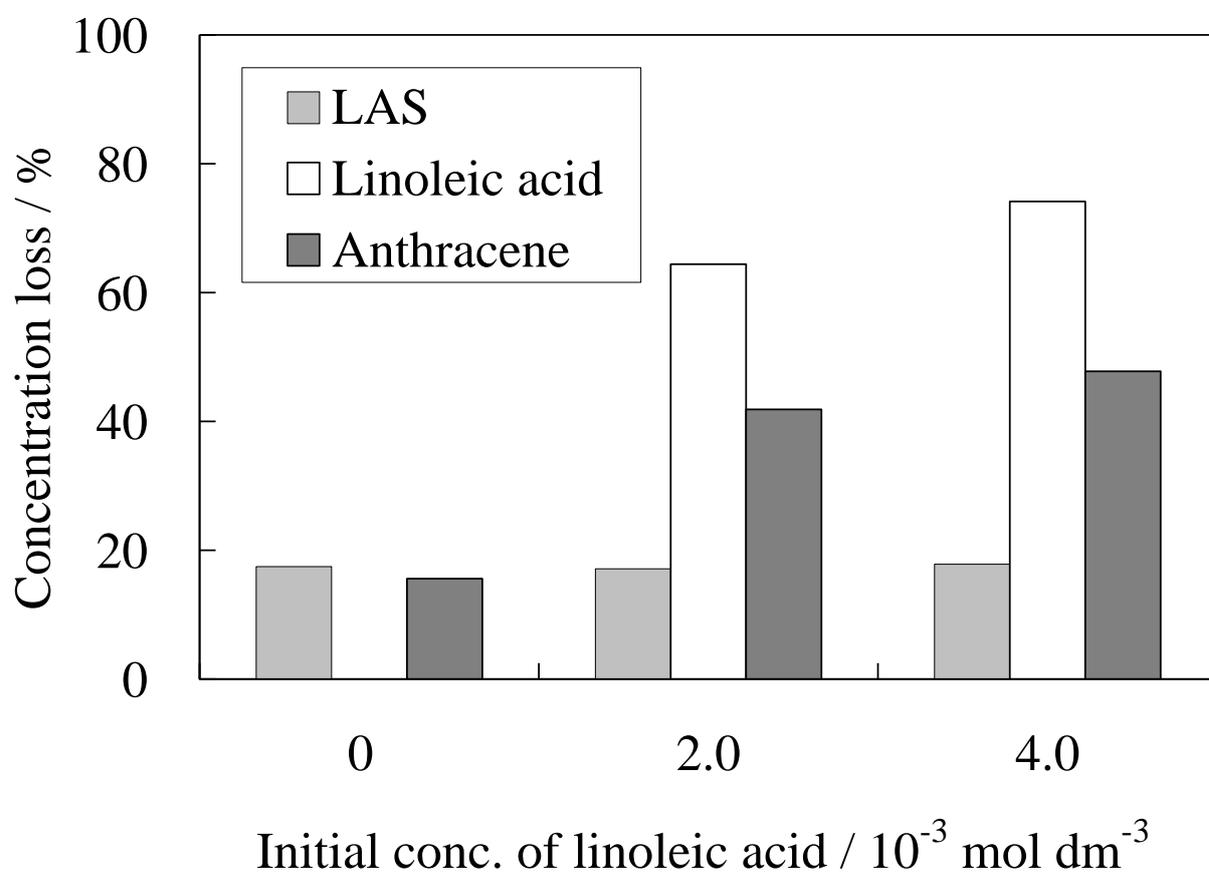


Figure 5

