Biodegradation of 2-Sulfonatofatty Acid Methyl Ester (α-SFMe)

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The biodegradability of 2-sulfonatofatty acid methyl ester (α-SFMe), an anionic surfactant recently developed for heavy-duty household detergents, was studied by the shake culture method, river die-away test and biochemical oxygen demand measurement method (MITI test).

Biodegradation was followed by the methylene blue active substances (MBAS) analysis and/or dissolved organic carbon (DOC), or biochemical oxygen demand (BOD).

The biodegradation of α-SFMe was found to start quickly, and then to proceed rapidly to ultimate degradation at sewage treatment plants and in natural river water.

1 Introduction

2-sulfonatofatty acid methyl ester (α-SFMe) has been regarded as a potential surfactant for heavy duty detergents because of its excellent detergent properties, but the difficulties in the large-scale production of α-SFMe of consistent quality has prevented their commercial application in detergents until recently. New manufacturing technology developed by Lion Corp. (Tokyo, Japan) has overcome technical problems associated with their production and allowed the commercialization of a new compact detergent formulation containing α-SFMe as the main active ingredient[1,2].

Alpha-SFMe is derived from natural fats and oils through sulfonation of fatty acid methyl esters. Today the stabilized supply and reasonable price of palm oils have also enhanced α-SFMe’s potential as a detergent surfactant.

From the viewpoint of environmental acceptability, α-SFMe has an advantage of high biodegradability[3,4]. In addition, smaller amounts of surfactant are needed to obtain satisfactory detergency, thus lowering the organic load in wastes discharged to the natural environment.

In this study, primary and ultimate biodegradation of α-SFMe was assessed by methylene blue analysis and DOC removal in the shake culture method (Japanese Industrial Standards (JIS) K 3363)[5] and in a river die-away test[6], and its ultimate biodegradation based on oxygen consumption in the MITI test[7] (modified OECD method 301 C[8]).

2 Materials and Methods

2.1 Test compounds

Samples of four anionic surfactants and two heavy-duty household granular detergents were selected for this investigation as shown in Table-1.

2.2 Activated sludge

Activated sludge was obtained from a domestic sewage treatment plant, and was used for the shake culture test and the MITI test. In the river die-away test, test water was collected at Oyakibashi on Morito-river, a typical suburban river receiving domestic sewage, in Kohzu, Odawara city.
2.3 Biodegradation test

2.3.1 Shake culture method

A. Surfactant

The culture medium was prepared by adding yeast extract (50 mg/L) to the biochemical oxygen demand (BOD) dilution water (Table-2) described in Japanese Industrial Standard (JIS) K 01029), the Testing Methods for Industrial Wastewater. Then, surfactant was added to the medium to give solutions at nominal concentration of 30 mg/L. Following inoculation with activated sludge (100 mg/L), the flasks were incubated at 25°C in subdued light for 15 d, according to JIS K 33635), the Testing Method for Biodegradability of Synthetic Detergent. Microorganisms were acclimatized twice, each for 3 d, prior to the 15 d incubation.

B. Detergent

The two commercial detergents which contain α-SFMe or LAS as a main surfactant, were dissolved in the BOD dilution water (100 mg/L). The medium was cultured at 25°C after inoculation with activated sludge (100 mg/L).

2.3.2 River die-away test

River die-away tests were performed to estimate the biodegradability of the surfac-
tants in a river. River water was filtered with gauze, folded four times, to remove suspended solids. The test surfactant was dissolved into the filtrate (5 mg/L), and the solution was maintained at 22 ± 2°C.

2.3.3 MITI test

The 10 mg/L and 30 mg/L of activated sludge in the modified BOD dilution waters (Table 2) were prepared and each test surfactant, as sole carbon source, was dosed to them at 5 and 50 and 100 mg/L, respectively. BOD was measured by automatic electrolytic meter (Ohkura Electric Co., LTD. Coulometer), and biodegradability was calculated as the ratio of BOD to the measured total oxygen demand (TOD). The ratio (BOD/TOD) indicates the degree of ultimate degradation.

2.4 Analytical method

2.4.1 Methylene blue active substances (MBAS)

A concentration of anionic surfactant was measured as MBAS according to JIS K 33635). As for Soap, MBAS was measured under alkaline conditions. MBAS indicates intact parent surfactant because partially degraded surfactants are not detected. Therefore, the analytical results determine the degree of primary biodegradation.

2.4.2 Dissolved organic carbon (DOC)

The concentrations of total carbon (TC) and inorganic carbon (IC) in the supernatant were measured using a TOC-500 type of the total organic carbon analyzer (Shimadzu Corporation) after the centrifugation of test solution at 3,000 rpm. DOC was calculated as the difference between TC and IC. Ultimate biodegradation is evaluated by DOC analysis.

2.4.3 Total oxygen demand (TOD)

TOD was measured using a 225 Type TOD analyzer (IONICS Corporation).

Measured MBAS and DOC were corrected by subtraction of results in parallel unfed control runs.

3 Results and discussion

3.1 Biodegradation by shake culture method

A. Surfactant

Fig. 1 shows the biodegradation of surfactants in the shake culture test. Alpha-SFMe as well as AOS lost about 90% of its methylene blue activity in 1 d and 100% in 2 d. More than 80% of organic carbon in the surfactants disappeared in 2 d and 100% in 5 d. On the other hand, LAS lost its methylene blue activity in about 5 d, and more than 40% of organic carbon still remained after 15 d. These results show that α-SFMe is a readily biodegradable surfactant in terms of both primary and ultimate degra-
dation under shake culture conditions. This indicates that α-SFMe can be expected to degrade rapidly in municipal sewage treatment plants.

B. Detergent

Fig. 2 shows the biodegradation of detergent formulations in the shake culture test. Because of the high detergent performance of α-SFMe, the surfactant content in the α-SFMe formulation is only about a half of that in the LAS formulation. Therefore, the initial concentrations both MBAS and DOC were different between the two detergents though their culture formulations were adjusted to the same concentration (100 mg/L). The high biodegradability of α-SFMe and its smaller concentration in detergent formulation combine to make the MBAS and DOC of α-SFMe detergent rapidly decrease in a few days. Therefore, it is expected that application of α-SFMe in detergent formulations will reduce the organic load in domestic sewage.

3.2 Biodegradation in river die-away test

Alpha-SFMe and AOS showed fast and smooth biodegradation in river water and their methylene blue activities disappeared in 3 d as shown in Fig. 3. Soap took 5 d to lose its methylene blue activity instead of its faster first biodegradation, to show a degradation curve consisting of two stages. It was considered that soap produced insoluble materials by double-decomposition in river water, which precipitated, thereby delaying its biodegradation. This phenomenon would be expected to occur in river water when soap was discharged into the natural environment at higher concentrations.

The concentration of dissolved oxygen was decreased as the biodegradation of surfactants proceeded, from 7.2 to 4.5 mg/L, then gradually recovered to 6.5~7.0 mg/L on the sixth day of the test. Therefore, the aerobic condition of the test water was maintained throughout the test period though temporary reduction of the concentration of dissolved oxygen was observed. But a continuous oxygen supply is maintained and the concentration of surfactant is...
far lower (less than 0.2–0.5 mg/L as MBAS) in the actual river water. Therefore, the primary biodegradation of the surfactants tested would readily take place in the natural environment.

3.3 Biodegradation in MITI test

Fig. -4 shows the biodegradation of the surfactants measured with BOD/TOD in the MITI test. In case of LAS, the onset of biodegradation was delayed as its concentration increased. However, the biodegradation of α-SFMe started quickly and proceeded rapidly in the early stage at all surfactant concentrations tested. These results indicate that the microorganisms are readily acclimatized to α-SFMe, and degrade it. Fig. -4 also shows that both α-SFMe and LAS were biodegraded ultimately.

\[ \text{Fig. -4 Biodegradation of } \alpha-\text{SFMe and LAS detected by BOD (Biochemical Oxygen Demand).} \]

4 Conclusion

The biodegradability of α-SFMe was studied by shake culture method, river die-away test and MITI test. The results indicated that the biodegradation of α-SFMe starts quickly, and then proceeds rapidly to ultimate degradation at sewage treatment plants and in natural river water. An effluent containing the breakdown products of α-SFMe should show low toxicity to fish.

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7) Law Concerning Examination and Regulation of Manufacture, etc. of Chemical Substances (Japan).
2-スルホネート脂肪酸メチルエステル（α-SFMe）の生分解性

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家庭用合成洗剤に最近使用されるようになった2-ス

ルホネート脂肪酸メチルエステル（α-SFMe）の生分解性について、振とう培養法、リバーグライアウェイ試験及び自動酸素消費量測定装置を用いた生物化学的酸素消費量（BOD）測定法（MITI法）で検討した。

生分解はメチレンブルー活性物質（MBAS）、溶存有機炭素（DOC）あるいはBODを測定することによって追跡した。

試験の結果、α-SFMeは下水処理場や自然の河川水中で一次分解が容易に始まり、分解は順調に完膚分解に到ることが示唆された。

（連絡者：増田光輝）

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