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THE EFFECT OF DISALT ON THE BIODEGRADABILITY OF METHYL ESTER SULPHONATES (MES)

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ABSTRACT

The biodegradability of methyl ester sulphonates (MES) was found to be affected by the disodium salt (disalt) content. The higher the disalt content, the lower is the biodegradability of MES. Disalt has a lower surface activity and is sparingly soluble in water when compared to the monosodium salt MES. These characteristics lower the biodegradability of disalt when compared to the monosodium salt. The biodegradability of a commercial MES sample was found to be better than linear alkylbenzene sulphonates (LAS), thus offering an additional advantage for the commercialization of oleochemical-based surfactant.

Keywords: MES, disalt, biodegradability, surfactant, LAS.

INTRODUCTION

In the mid-eighties, branched alkylbenzene sulphonate (BAS) was the most widely used surfactant in Malaysia. Despite its several positive attributes, such as good cleaning ability, good solubility, good foaming power and commercially cheap, it causes serious environmental problem. This is brought about by its incomplete biodegradation, causing it to persist in the environment.

The Malaysian Government has taken steps to ban the use of BAS in Malaysia in 1995 under the Environmental Quality Order 1995 (Prohibition on the Use of Controlled Substances in Soap, Synthetic Detergent and Other Cleaning Agents) (Environmental Quality Report, 1995). With the banning of BAS, LAS became the primary surfactant used by the Malaysian detergent manufacturers. Even though LAS exhibits good primary biodegradation, the remaining benzene-derivative metabolites, after the initial microbial breakdown, could still be toxic to the environment.

Since the price of LAS is more expensive than BAS, this development offered an opportunity for oleochemical-based surfactants to compete with LAS. For MES, in particular, it is not only based on renewable resources but also has excellent environmental properties. In addition, it also offers price advantage.

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MES was developed from renewable raw materials. It has been studied several decades ago, at about the same time as alkyl sulphates or alkylbenzene sulphonates (Inagaki, 1991). Since then, many studies concerning the reaction mechanism, manufacturing process, their properties and applications have been carried out. However, they have not yet taken position as major surfactants for household detergents, such as alkyl sulphates or alkylbenzene sulphonates have, even though they exhibit good cleaning properties, good biodegradation properties and are largely unaffected by water hardness (Gode *et al.*, 1987). Only Lion Corporation in Japan and Stepan Company in USA have produced MES on a commercial basis (Salmiah *et al.*, 2000).

The evaluation of environmental compatibility of substances is generally based on two crucial criteria, namely biodegradation and ecotoxicity. Biodegradation as the principal mechanism operating in sewage treatment plants and self-cleaning processes which occur in surface waters, decides the fate of a substance in the environment and indicates whether it is likely to have a toxic effect on aquatic organisms (Mohd Naziruddin *et al.*, 1995). The current requirement considers the biodegradability of a material to be used in a consumer product is as important as its performance.

A substance may be considered to be readily biodegradable if the following levels of biodegradation are achieved in 28 days (OECD,

1992):
- O_2 uptake as a percentage of theoretical O_2 demand (ThOD*) - 60%
- CO_2 generation as a percentage of theoretical carbon dioxide ($ThCO_2$**) - 60%

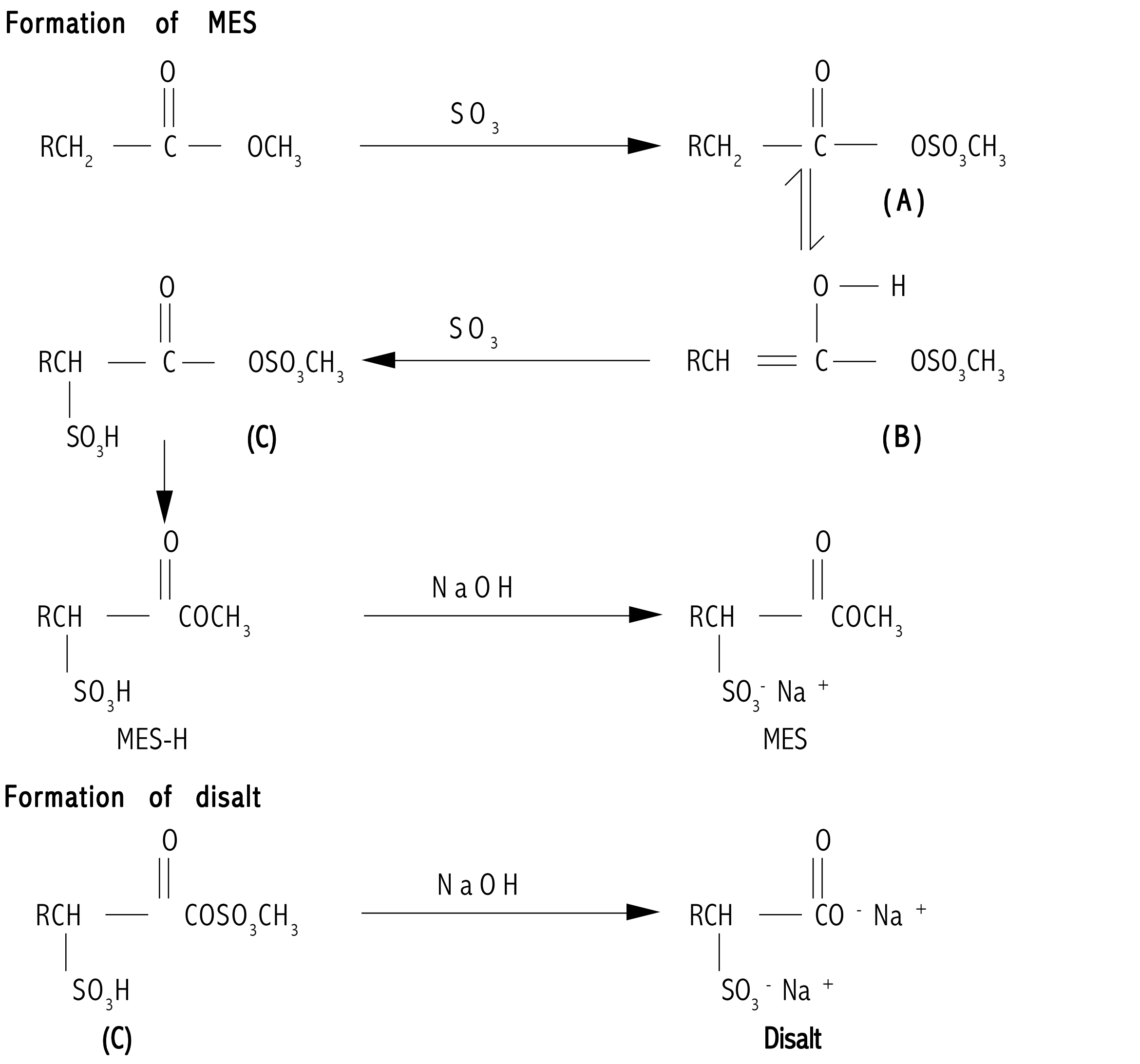
Notes: *The total amount of oxygen required to oxidize a chemical completely.
** The quantity of carbon dioxide calculated to be produced from the known or measured carbon content of the test compound when fully mineralized.

The biodegradation of MES is excellent, as one would expect for fatty derived materials (Drozd, 1991). Many studies have demonstrated that the biodegradation of MES was found to start very quickly and then proceeded rapidly to ultimate degradation in sewage treatment plants and in river water (Steber and Wierich, 1989; Masuda *et al.*, 1993). The biodegradation of MES does not leave any recalcitrant residues at all. By comparison with other surfactants, smaller amounts are needed to obtain satisfactory detergency, thus lowering the organic load in wastes discharged to the environment.

This paper looks into the effect of disalt, a by-product formed during the production of MES, on the biodegradability of the monosodium salt MES, and also the biodegradability of commercial MES when compared with LAS.

FORMATION OF DISALT

MES is prepared by reacting saturated fatty methyl ester with sulphur trioxide (SO_3) (*Figure 1*). Fatty methyl ester reacts with SO_3 forming sulphonate (A). The keto form of (A) tautomerises into an enol intermediate (B), which activates the alpha carbon for sulphonation with an additional molecule of SO_3 to form (C). Upon ageing, (C) eliminates SO_3 and rearranges to form fatty methyl ester sulphonic acid



Source: Salmiah *et al.* (2000).

Figure 1. Mechanism for the formation of methyl ester sulphonates and disalt.

(MES-H). MES-H is dark in colour. After bleaching with hydrogen peroxide, MES-H is neutralized with a base to form the white MES (Salmiah *et al.*, 2000).

Two molecules of SO_3 are required to sulphonate one molecule of ester. If too much SO_3 is present during the sulphonation, excess (C) will be present in the product mixture. Upon neutralization, (C) will be converted to sulphonated soap or more commonly known as disalt. The higher the SO_3 excess, the more disalt are generated (Biermann *et al.*, 1987).

Besides having poor solubility in water, disalt has other inferior properties when compared to monosodium salt (Inagaki, 1991). Disalt has lower surface activity and therefore lower detergency when compared to MES (Zahariah, 1994; Salmiah *et al.*, 1998).

In the mid-eighties, the possibility of reducing the disalt formation by re-esterifying with methanol was discovered. Re-esterification with methanol however, creates another disadvantage where flammability and toxicity of methanol had to be addressed. A better procedure to produce MES was discovered in the early nineties by reacting good quality fatty methyl ester with sulphur trioxide followed by ageing. The dark colour MES-H is bleached and neutralized in the presence of methanol and dried in a special drier. This procedure reduced the formation of disalt to 6%.

RESEARCH METHODOLOGY

Various MES were used in this study. These include MES with high and low disalt content, MES with various carbon chain lengths and also commercial MES. The details are explained below. Commercial LAS was also used for comparison.

Materials

(a) MES derived from palm kernel oil with carbon chain length of 12-18. It was produced in MPOB using the mini sulphonation pilot plant. No re-esterification was conducted and therefore the disalt content of the MES were in the range of 20%-30% based on active matter.
(b) Commercial MES (with 4% disalt content) and LAS.
(c) C_{16} MESs with 0.98% and 30.0% disalt contents.
(d) C_{18} MESs with 0% and 29.0% disalt contents.

The MESs with low disalt content were prepared by crystallization.

Test Methods

The OECD standard methods (1992) for ready biodegradability were used to assess the biodegradability of the MESs. The methods used were the OECD 301D Closed Bottle Test and the OECD 301B Carbon Dioxide (CO_2) Evolution Test. The solution of the test substance in mineral medium was inoculated with inoculum (derived from the secondary effluent of a treatment plant receiving predominantly domestic sewage) in the dark at constant temperature (22°C ± 2 °C).

In the Closed Bottle Test, degradation was followed by analysis of dissolved oxygen over a 28-day period while in the CO_2 Evolution Test, degradation was followed by determining the CO_2 produced over a 28-day period.

RESULTS AND DISCUSSION

Biodegradability of MES Produced in MPOB

When MES (produced in MPOB) was subjected to the Closed Bottle Test and the CO_2 Evolution Test, the percentage of biodegradability was quite low, *i.e.* below the 60% level. The results are shown in *Figure 2*.

The low biodegradability of MES could be due to two factors. One factor is the organisms in the inoculum may not biodegrade some new chemicals, such as MES, because they are not familiar with these

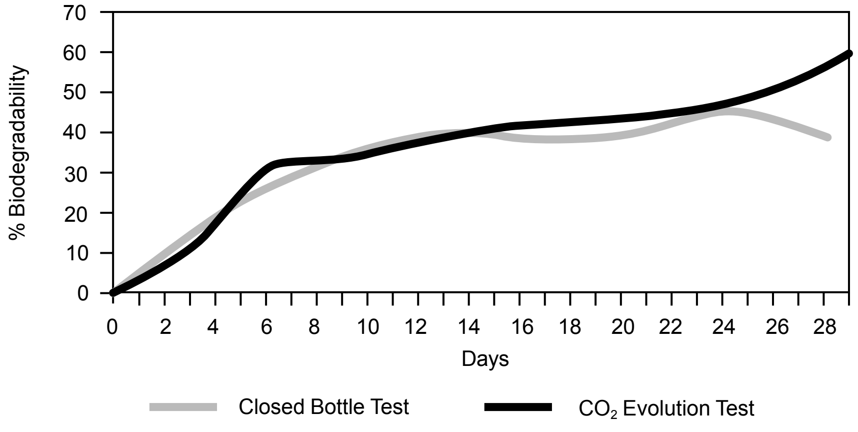


Figure 2. Biodegradation of methyl ester sulphonates in Closed Bottle Test and CO_2 Evolution Test.

chemicals (Painter, 1992). Most detergents in Malaysia use LAS as a surfactant. Therefore, the inoculum will take longer time to develop the enzyme to degrade MES. As a result, the biodegradability of MES obtained in this study is low due to the unavailability of the enzyme.

The inoculum used in this study was not pre-exposed or pre-adapted to the test substance (acclimatized) following the OECD standard methods which states that the inoculum may be pre-conditioned to the experimental conditions, but not pre-adapted to the test substance (OECD, 1992).

Another factor which may cause the low biodegradability of MES is the high disalt content. As mentioned earlier, high disalt content may have an effect on the biodegradation of MES.

Biodegradability of Methyl Ester Sulphonates (MPOB) *vs.* Commercial Methyl Ester Sulphonates

When the commercial MES was subjected to the Closed Bottle Test together with the MES produced in MPOB, the result showed that the commercial MES degraded rapidly and reached the pass level on day 6 (*Figure 3*). It was found that the commercial MES contained much lower disalt content, *i.e.* around 4% compared to 20%-30% of MES from MPOB. The results clearly demonstrate that high disalt content reduces the biodegradation of MES. In this respect, the first factor discussed in the previous subsection, that is whether the inoculum was familiar or not to MES, could be ruled out because the commercial MES degrades very well in this test.

Biodegradability of Commercial Methyl Ester Sulphonates *vs.* Linear Alkybenzene Sulphonates

The commercial MES has also been subjected to Closed Bottle Test together with LAS. The result shows that MES has higher biodegradability than LAS (*Figure 4*). This indicates that MES biodegrades faster and better than LAS.

Biodegradability of Low Disalt Methyl Ester Sulphonates *vs.* High Disalt Methyl Ester Sulphonates

The biodegradability of MESs with various disalt contents has been studied. Two sets of tests have been

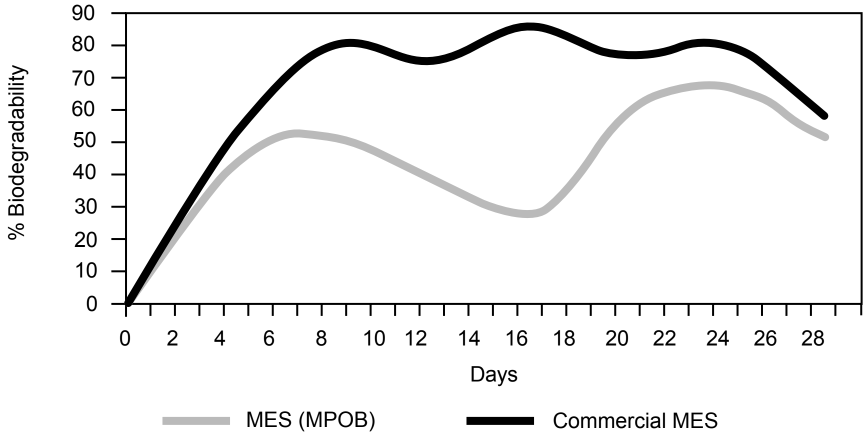


Figure 3. Biodegradation of methyl ester sulphonates (MPOB) and commercial methyl ester sulphonates in Closed Bottle Test.

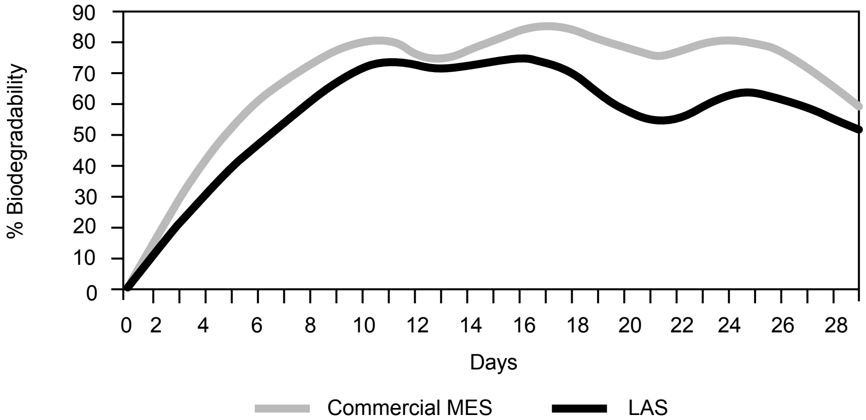


Figure 4. Biodegradation of commercial methyl ester sulphonates and linear alkylbenzene sulphonates in the Closed Bottle Test.

conducted:

(a) C_{16} MESs with different disalt contents, 0.98% and 30.0%.
(b) C_{18} MESs with different disalt contents, 0.0% and 29.0%.

General conclusion that can be derived from these tests is MES with low percentage of disalt content shows slightly higher biodegradability than MES with high disalt content (*Figures 5* and *6*).

The data obtained through the Closed Bottle Test sometimes did not give a smooth plot of percent biodegradability because this test is quite sensitive towards any variation in test performance, inoculum, *etc.* and also because of the set-up of the test where separate bottles were taken for analysis during the 28-day test period (the measurement of dissolved oxygen is not continuous).

CONCLUSION

The results obtained clearly demonstrated that the presence of disalt reduces biodegradability of MES due to its low surface activity and poor solubility in water. MES with disalt content around 20%-30% has low biodegradability compared to MES with lower disalt content. MES with low disalt content biodegrades well in the ready biodegradability test methods. The commercial MES biodegrades better than LAS, thus offering an additional advantage for the commercialization of oleochemical-based surfactant.

In MPOB, a pilot plant has been set up that can produce MES on a bigger scale and with low disalt content (below 6%). This will help to promote the use of oleochemical-based surfactant in detergent formulation in Malaysia.

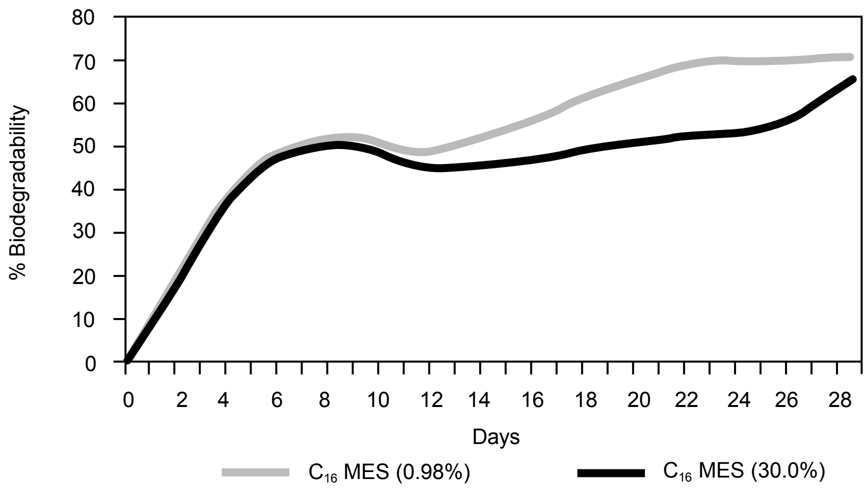


Figure 5. Biodegradation of C_{16} methyl ester sulphonates with different disalt contents (%) in Closed Bottle Test.

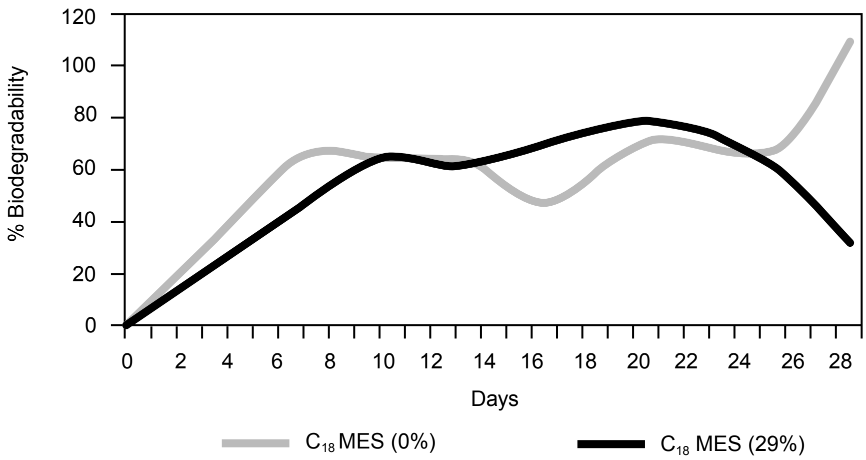


Figure 6. Biodegradation of C_{18} methyl ester sulphonates with different disalt contents (%) in Closed Bottle Test.

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