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ASSESSMENT OF AQUATIC EFFECTS OF PALM-BASED ALPHA-SULPHONATED METHYL ESTERS (SME)

RAZMAH GHAZALI*; ZULINA ABDUL MAURAD*; PARTHIBAN SIWAYANAN*; MOHTAR YUSOF* and SALMIAH AHMAD*

ABSTRACT

The toxicities of palm-based alpha-sulphonated methyl esters (SME) produced in MPOB's SME pilot plant were consistent throughout the production period, i.e. around 1.00-1.41 mg litre^{-1}. Its toxicity was comparable to two palm-based commercial SMEs whether tested in temperate or tropical environment. The surfactants were found to be less toxic when tested under tropical conditions. The toxicity is related to the carbon chain length of methyl esters used to produce SME. Higher carbon chain length will cause an increase in the toxicity of anionic surfactant as seen in palm-based SME ($C_{16/18}$) and commercial SME 1 ($C_{16/18}$). Commercial SME 2 ($C_{14/16}$) was slightly less toxic due to the lower carbon chain length. Their toxicities, however, were still within the same toxicity range, i.e. moderately toxic. Palm-based SME is not expected to cause environmental concern due to only 10% - 30% of it is used in detergent products, its biodegradability was more than 80% in only eight days and the dilution in aquatic environment will cause the local predicted environmental concentration to be very low. The use of palm-based SME will help to stimulate Malaysia's agricultural economies and lessen our dependence on imported petroleum-based surfactants.

Keywords: sulphonated methyl esters (SME), detergents, ecotoxicity, biodegradability, aquatic organisms.

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INTRODUCTION

Surfactants are used for a variety of purposes but primarily in commercial detergents, personal care and household cleaning products. They represent a particularly interesting product group because they were originally made from renewable resources, whereas today the major part is of petrochemical origin. Still, renewables have not entirely lost their importance, and are in fact regaining popularity due to their sustainability, good cost-performance ratio and environmentally friendliness.

The Malaysian Palm Oil Board (MPOB) has a technology to produce an anionic surfactant from palm oil - alpha-sulphonated methyl ester (SME) - by converting the oil to methyl ester followed by hydrogenation to reduce the unsaturation and then sulphonating the ester to SME. The 20 kg hr^{-1} SME pilot plant in MPOB is capable of producing SME with high active for cleaning products, such as liquid and powder detergents.

Due to their widespread use, surfactants have become common constituents in municipal effluent and river water. Surfactants in surface water have become an environmental concern and, as a consequence, toxicity data on their effects on freshwater and marine life gathered since the early 1950s (Lewis, 1992).

SME has good surface-active properties, excellent detergency performance, good biodegradability and is less sensitive to water hardness (Salmiah *et al.*, 1998). It is important that the ecotoxicity and biodegradability of SME be evaluated since, nowadays, in addition to excellent performance, good economic prospects and sustainability, a product must also fulfill the ecological requirements in order to be accepted worldwide.

This paper will discuss the ecotoxicity of palm-based SME produced by MPOB in tropical and

* Malaysian Palm Oil Board,
P. O. Box 10620,
50720 Kuala Lumpur, Malaysia.
E-mail: razmah@mpob.gov.my

temperate environments, its effect on tropical and temperate test species and its biodegradability. Two commercial SMEs are used for comparison.

MATERIALS AND METHOD

Test Samples

Palm-based SME ($C_{16/18:60/40}$) was produced from palm stearin methyl esters in MPOB's SME pilot plant. Two commercial palm-based SMEs, commercial SME 1 ($C_{16/18:60/40}$) and commercial SME 2 ($C_{14/16:20/80}$) were obtained from Chemithon Corporation, USA and Lion Corporation, Japan, respectively, and used for comparison. The active in each sample was more than 80%.

Test Method

Ecotoxicity test. The OECD 203 Fish Acute Toxicity Test is the most commonly used test to determine the toxic effects of materials to aquatic organisms in short-term exposure. The fish are exposed to the test substance for 96 hr. Mortalities are recorded daily and the concentrations that kill 50% of the fish (LC_{50}) determined.

Test organism. A local fish, *Tilapia nilotica*, was chosen as the test species for tropical environment for several reasons, including its ready availability throughout the year, ease of upkeep, convenience for testing, common presence throughout the country and previous experience (Razmah, 2002) confirming its suitability for ecotoxicity testing as per the OECD Guidelines for Testing of Chemicals (1992). The fish were purchased from a supplier in Rawang, Selangor, Malaysia.

The fish (2-5 cm long) were acclimatized for at least 12 days in dechlorinated tap water of 50 to 250 mg $CaCO_3$ litre^{-1} hardness. They were fed twice daily with commercial dry fish food until one day before the test. They were not fed during the test.

Samples of the palm-based and commercial SMEs were also sent to Stantec Consulting Ltd, Canada to determine their toxicities in a temperate environment. Three tests were run:

- non-GLP OECD 203 Fish Acute Toxicity Test towards rainbow trout (*Oncorhynchus mykiss*);
- non-GLP OECD 202 *Daphnia* sp., Acute Immobilization Test towards *Daphnia magna*; and
- non-GLP OECD 201 Algal Growth Inhibition Test towards *Selenastrum capricornutum*.

Conditions of exposure. Although not always possible, it is best to provide for the test conditions to be as close as possible to the natural environment (APHA, 1980). OECD 203 was adapted to tropical conditions which, inter alia, included a maximum loading of 1.0 g fish litre^{-1} water (static test), 12 to 16 hr photoperiod daily and temperature of 25°C ± 3°C.

For the temperate environment, all the conditions were the same except that the temperature was 20°C ± 1°C as stated in the standard test methods OECD 201, 202 and 203.

Test concentrations. The range-finding test was first performed to estimate the concentration range to be used in the second stage (definitive test). It was a short-term test (24 hr) with 5 fish / concentration and the concentration of SME increasing logarithmically, *e.g.* 0.1, 1.0, 10.0 and 100.0 mg litres^{-1}. The concentration of SME that killed all the fish and the concentration that killed very few or none of the fish were used as the upper and lower limits in definitive test. The definitive test used at least five concentrations in geometric series, *e.g.* 2.0, 4.0, 8.0 and 16.0 mg litres^{-1}. The test period was 96 hr and 10 fish were used per concentration.

In both tests, each concentration was tested in duplicate in the test chambers. Control test chambers with no test substance were tested simultaneously.

Observations. The conditions of the fish were observed after 24, 48, 72 and 96 hr. Fish were considered dead if there was no discernible movement and if touching of the caudal peduncle produced no reaction. The mortalities and pH, dissolved oxygen and temperature of the water were recorded daily.

Treatment of results. The acute toxicity of a chemical to aquatic organisms is expressed in terms of its LC_{50}, that is, the concentration lethal to half of the population exposed during the test. The geometric mean of the highest concentration causing no mortality and the lowest concentration causing 100% mortality were calculated for the LC_{50}.

Biodegradability test. The test was performed according to the standard method OECD 301D Closed Bottle Test (1992). A solution of 2 mg test substance in 1 litre mineral medium was inoculated with microorganisms from the secondary effluent of sewage treatment plant (7 ml litre^{-1}) and kept in completely full, closed bottles in the dark at constant temperature. The biodegradation was calculated based on the dissolved oxygen of the test solution over a 28-day period. The amount of oxygen taken up by the microbial population during biodegradation of the test substance, corrected for uptake by the blank inoculum run in parallel, was expressed as the percentage THOD (theoretical oxygen demand). The dissolved oxygen of the samples was measured every four days (in duplicate) for construction of the biodegradation curve.

RESULTS AND DISCUSSION

Ecotoxicity of Various Batches of SME Produced from the Pilot Plant

Various batches of SME produced from the pilot plant had consistent toxicity values towards *Tilapia nilotica* (*Table 1*), *i.e.* 1.00-1.41 mg litre^{-1}, and were considered as moderately toxic (according to the rating scheme in *Table 2*).

Toxicity of Palm-Based SME and Commercial SMEs towards Tropical and Temperate Test Species

The OECD 203 Test was carried out in MPOB and Canada on the three samples using *Tilapia nilotica* as test species in tropical conditions and rainbow trout in temperate conditions. The tests on *Daphnia magna* and *Selenastrum capricornutum* were done only in Canada.

The toxicities of palm-based and commercial SMEs were within the same toxicity range in both the temperate and tropical environments (*Table 3*), although somewhat less toxic under the tropical conditions.

The toxicities of SME (MPOB) and commercial SME 1 were similar while commercial SME 2 had slightly higher LC_{50} and EC_{50} values. The palm-based SME and commercial SME 1 were produced from palm stearin methyl esters (PSME) with C16-C18 carbon chain lengths while commercial SME 2 consisted of C14-C16 chain lengths. For most anionic surfactants, the toxicity increases with the chain length (Schoberl *et al.*, 1988). The longer carbon chains of PSME caused the slightly higher toxicities of SME (MPOB) and commercial SME 1 over commercial SME 2 as shown in *Table 3*.

TABLE 1. ECOTOXICITY OF VARIOUS BATCHES AND DRUMS OF SME PRODUCED FROM THE PILOT PLANT

Batch	Drum	LC_{50} (mg litre^{-1})*
December 2001	2	1.41
	4	1.41
	6	1.41
	8	1.41
17 October 2002	1	1.41
	2	1.00
28 October 2002	1	1.41
	2	1.00
	3	1.41
July 2003	1	1.13

Note: * Mean value of two tests.

TABLE 2. RATING SCHEME USED BY THE UNITED STATES FISH AND WILDLIFE SERVICES FOR AQUATIC TOXICITY

Rating	LC (mg litre^{-1})
Super toxic	< 0.01
Extremely toxic	1.01 – 0.1
Highly toxic	0.10 – 1.0
Moderately toxic	1.0 – 10.0
Slightly toxic	10.0 – 100.0
Practically non-toxic	100.0 – 1 000.0
Relatively harmless	> 1 000.0

Source: Drozd (1991).

TABLE 3. ECOTOXICITY OF PALM-BASED AND COMMERCIAL SMEs IN TEMPERATE AND TROPICAL CONDITIONS

Test/conditions	Temperate	Tropical
Acute aquatic toxicity (96 hr) on fish	Rainbow trout	*Tilapia nilotica*
a. SME (MPOB)	LC_{50} = 0.35 mg litre^{-1}	LC_{50} = 1.41 mg litre^{-1}
b. Commercial SME 1	LC_{50} = 0.35 mg litre^{-1}	LC_{50} = 1.41 mg litre^{-1}
c. Commercial SME 2	LC_{50} = 0.71 mg litre^{-1}	LC_{50} = 5.66 mg litre^{-1}
Acute aquatic toxicity (48 hr) on *Daphnia*	*Daphnia magna*	
a. SME (MPOB)	EC_{50} = 0.98 mg litre^{-1}	
b. Commercial SME 1	EC_{50} = 0.79 mg litre^{-1}	No data
c. Commercial SME 2	EC_{50} = 1.91 mg litre^{-1}	
Acute aquatic toxicity (72 hr) on algae	*Selenastrum capricornutum*	
a. SME (MPOB)	EC_{50} = 7.57 mg litre^{-1}	
b. Commercial SME 1	EC_{50} = 5.23 mg litre^{-1}	No data
c. Commercial SME 2	EC_{50} = 8.83 mg litre^{-1}	

Biodegradability of Palm-Based SME

Palm-based SME was found to be readily biodegradable with more than 80% degraded in only eight days in the OECD 301D Closed Bottle Test (*Figure 1*) (Razmah and Salmiah, 2004). The SME is not expected to cause environmental concern because its high biodegradability will leave very little residual and therefore is not toxic to water organisms. The SME exists primarily in the ionized form at environmental pHs. Due to its ionized properties, it can be assumed that bioaccumulation is insignificant. Also, as the surfactant is mainly released into the aquatic environment, very little would enter the air and soil environments.

Predicted Local (Malaysian) Environmental Concentrations of SME

The maximum concentration of SME in detergents is 10%-30%. The concentration of detergent recommended by the manufacturers is 15 g in 30 litres water (OECD-SIDS, 2003). Therefore, the concentration of SME in washing machine water is 50 mg $litre^{-1}$ assuming that the detergent contains 10% SME. Its concentration in domestic effluent from one family is 1.5 mg $litre^{-1}$ $family^{-1}$ day^{-1} as the average volume of effluent is assumed to be 1000 litres for one family (four persons) per day. The amount of effluent discharged may be higher. The removal *via* biodegradation is 80% after eight days. Assuming that the maximum concentration of SME (30%) is used in detergents and that the dilution factor is 100 when the wash is released into a river, the predicted environmental concentration calculated is 0.009 mg $litre^{-1}$.

Local predicted environmental concentration of SME

$$= \frac{\text{content in detergent (\%)/ 100 x amount of detergent (mg) used in washing machine x [100-removal rate (\%)]/ 100}}{\text{Release value (l) of domestic effluent per family per day x dilution factor}}$$

$$= \frac{30\ (\%)/100 \times 15000\ (\text{mg}) \times [100 - 80\ (\%)]/100}{1000\ (\text{l}) \times 100}$$

$= 0.009$ mg $litre^{-1}$

The predicted environmental concentration at day 0, where the wash is released directly into the aquatic environment with no biodegradation, would be 0.045 mg $litre^{-1}$.

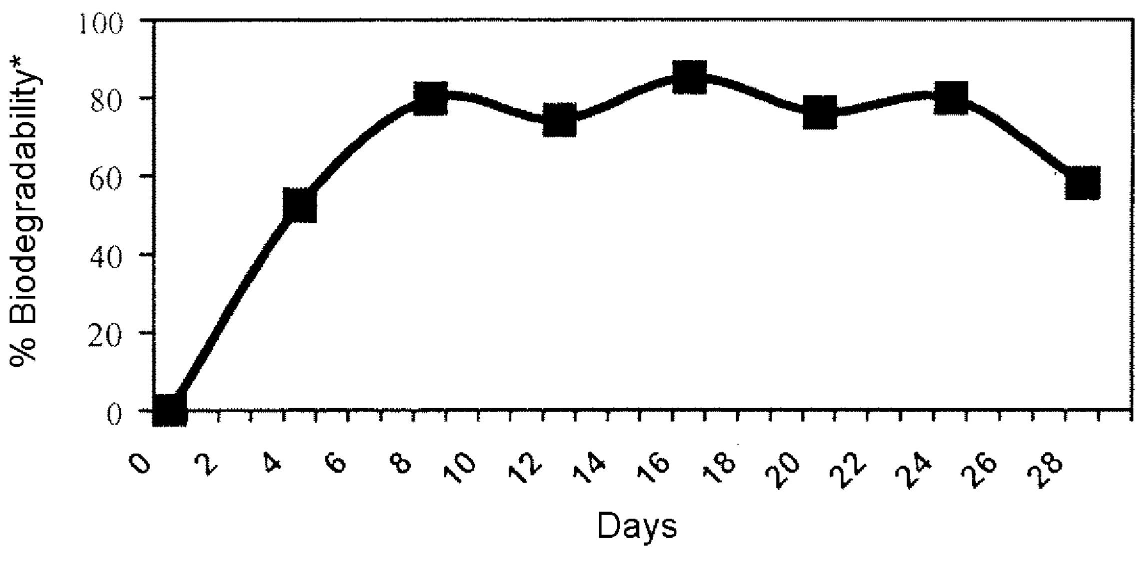
Local predicted environmental concentration

$$= \frac{\text{content in detergent (\%)/ 100 x amount of detergent (mg) used in washing machine x [100-removal rate (\%)]/ 100}}{\text{Release value (l) of domestic effluent per family per day x dilution factor}}$$

$$= \frac{30\ (\%)/100 \times 15000\ (\text{mg}) \times [100 - 0\ (\%)]/100}{1000\ (\text{l}) \times 100}$$

$= 0.045$ mg $litre^{-1}$

Compared to the LC_{50} of SME towards *Tilapia nilotica* and Rainbow trout (*Table 3*), this would be sufficiently low not to cause any impact on the aquatic organisms. Palm-based SME also showed comparable no-observed-effect-concentration (NOEC) and lowest-observed-effect-concentration



Note: * Mean value of two measurements.

Figure 1. Biodegradability of palm-based SME.

(LOEC) to the commercial SMEs (*Table 4*). LOEC is the lowest tested concentration at which the test substance has a significant effect on the test species, while NOEC is the highest tested concentration below LOEC where the stated effect was not observed. Palm-based SME has LOEC value, or will have significant effect on the algae's growth, of 2.43 mg $litre^{-1}$, which is 53 times higher than the predicted environmental concentration at day 0, *i.e.* 0.045 mg $litre^{-1}$. Again, this shows that SME is not expected to cause an impact on algae and other aquatic organisms.

TABLE 4. NOEC AND LOEC VALUES OF PALM-BASED SME AND THE COMMERCIAL SMEs

SME	NOEC* (mg $litre^{-1}$)	LOEC** (mg $litre^{-1}$)
SME (MPOB)	< 2.43	2.43
Commercial SME 1	2.43	8.1
Commercial SME 2	2.43	8.1

Notes: *No-observed-effect-concentration.
**Lowest-observed-effect-concentration.

CONCLUSION

The public concerns over the safety of detergents to the user and environment is at an all-time high. Palm-based SME is a good and sustainable active ingredient to be used in detergent formulations to replace the active ingredients derived from petrochemicals, which are not biodegradable.

The palm-based SMEs produced in MPOB's pilot plant have consistent toxicities, *i.e.* around 1.00-1.41 mg $litre^{-1}$. Their toxicities are comparable to those of commercial SMEs whether tested in temperate or tropical environment, and whether using a temperate or tropical test species. The SMEs were found to be less toxic under tropical conditions. The toxicity increased with the carbon chain length, *e.g.* $C_{16/18}$ SME being slightly more toxic than $C_{14/16}$ SME. The toxicities of all the SMEs (MPOB and commercial) were within the same toxicity range, *i.e.* moderately toxic.

SMEs are not expected to cause any environmental damage as the local predicted concentrations are likely to be very low, between 0.009 mg $litre^{-1}$ and 0.045 mg $litre^{-1}$, due to their high biodegradability (more than 80% in eight days). These concentrations are very low and will not impose any effect on the aquatic organisms.

Malaysia will benefit from using palm-based surfactants through:

a) less dependence and saving in foreign exchange from less imports of petroleum-based surfactants; and
b) promoting the use of renewable resources so that more oil palm can be planted to boost its agricultural economy.

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