Available online at www.sciencedirect.com
ScienceDirect
Chemosphere 69 (2007) 1574–1578
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Biodegradability and ecotoxicity of amine oxide based surfactants

M.T. García *, E. Campos, I. Ribosa

Surfactant Technology Department, IIQAB/CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain

Received 24 October 2006; received in revised form 23 May 2007; accepted 23 May 2007
Available online 12 July 2007

Abstract

The aerobic and anaerobic biodegradability as well as the aquatic toxicity of two fatty amine oxides and one fatty amido amine oxide were investigated. Aerobic biodegradation was evaluated using the CO_2 headspace test (ISO 14593) and biodegradation under anaerobic conditions was assessed employing a standardised batch test. The three amine oxide based surfactants tested were readily biodegradable under aerobic conditions but only the alkyl amido amine oxide was found to be easily biodegradable under anaerobic conditions. Toxicity to *Photobacterium phosphoreum* and *Daphnia magna* was evaluated. Bacteria (EC_{50} from 0.11 to 11 mg l^{-1}) proved to be more sensitive to the toxic effects of the amine oxide based surfactants than crustacea (IC_{50} from 6.8 to 45 mg l^{-1}). The fatty amido amine oxide showed the lowest aquatic toxicity.

Keywords: Surfactant; Aerobic biodegradation; Anaerobic biodegradation; Aquatic toxicity; Daphnia; Microtox

1. Introduction

Amine oxide based surfactants constitute a particular class of non-ionic surfactants that exhibit cationic behaviour in acid solution. They show good foaming properties and are skin compatible. These compounds, the consumption of which only in Western Europe is estimated at 14 ktons year^{-1} (Fraunhofer report, 2003), are widely used in detergent, toiletry and antistatic preparations, usually together with other surfactants. They are compatible with anionic surfactants and can be used to give synergistic advantage to formulations (Cross, 1994; Domingo, 1995). After application these compounds are usually discharged into the environment through a sewage treatment plant where they are subjected to physical and biological treatments (van Ginkel, 1995). Therefore, knowledge about their biodegradability is necessary to assess the exposure to these surfactants in the aquatic environment. However, little information is available on the ecological properties of amine oxide based surfactants. Cupkova et al. (1993) discussed the primary biodegradation of fatty amine oxides, and Ruiz-Cruz and Dabogardes (1978) reported high percentages of surfactant removal (>94%) for tetradecyl and dodecyl dimethyl amine oxides in simulation tests of activated sludge plants.

In the present work, the ultimate biodegradation of three amine oxide based surfactants under both aerobic and anaerobic conditions as well as their toxic effects on two aquatic organisms were studied. The surfactants tested have the same polar head group, the amine oxide moiety but differ in the fatty alkyl chain (number of carbon atoms and/or the presence of an amide group). The results can be useful for the selection of technically efficient surfactants with a lower impact on the aquatic environment.

2. Experimental

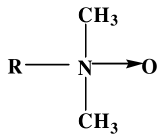
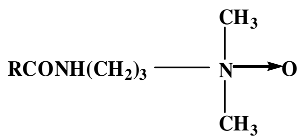
2.1. Surfactants

The commercial amine oxide based surfactants tested were: lauryl dimethyl amine oxide (C_{12}-AO), myristyl dimethyl amine oxide (C_{14}-AO) and cocoamidopropyl dimethyl amine oxide (cocoamido-AO). Surfactants were

* Corresponding author. Tel.: +34 93 400 61 00; fax: +34 93 204 59 04.
E-mail address: mtgbet@iiqab.csic.es (M.T. García).

0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.05.089

Table 1
Chemical structures and abbreviations of the amine oxide based surfactants tested

Surfactant	Structure	Abbreviation
Lauryl dimethyl amine oxide		C_{12}-AO
Myristyl dimethyl amine oxide		C_{14}-AO
Cocoamidopropyl dimethyl amine oxide		Cocoamido-AO

supplied by Goldschmidt España S.A. The surfactant structures and abbreviations used are given in Table 1.

2.2. Aerobic biodegradation test

The CO_2 headspace test (ISO 14593, 1999) was employed to evaluate the biodegradability of the amine oxide based surfactants under aerobic conditions. This method allows the evaluation of the ultimate aerobic biodegradation (mineralization to carbon dioxide) of an organic compound in aqueous medium by measuring the net increase in total inorganic carbon over time with respect to unamended blanks. The amine oxide based surfactants were tested at a concentration of 20 mgC l^{-1}. Samples were inoculated with activated sludge collected from a municipal wastewater treatment plant (Manresa, Barcelona) and then incubated in the dark at 22 ± 1 °C in sealed vessels (250 ml) with a headspace of air (headspace/liquid volume ratio, 1/2). Sodium *n*-dodecyl sulphate was used as reference substance. Three replicates of the surfactants, blank and reference substance were performed for each sampling day. The tests ran for 28 days. Every sampling day, after injecting a sodium hydroxide solution to the vessels, shaking for 1 h and allowing to settle, suitable volumes were withdrawn by syringe from the liquid phase of each vessel and kept in small beakers carefully filled to the brim and covered with a cap to prevent CO_2 exchange with the air. The concentration of inorganic carbon was determined in a carbon analyzer (Shimadzu TOC-5050). The extent of biodegradation was expressed as a percentage of the theoretical amount of inorganic carbon based on the initial amount of the test compound.

2.3. Anaerobic biodegradation test

A batch test system based on the method proposed by Birch et al. (1989) was applied. This method evaluates the extent of ultimate anaerobic biodegradation of a chemical based on the production of biogas (methane and carbon dioxide) with respect to a blank without the addition of the test substance. Sludge samples from the anaerobic digester of a municipal wastewater treatment plant (Manresa, Barcelona) were used as inoculum. Total and volatile solids of the anaerobic sludge samples were determined according to Standard Methods (APHA, 1998a,b) and the values obtained ranged from 43 to 50 g l^{-1} and from 45% to 55%, respectively. After collection, sludge was washed with a mineral salt solution, as described in the ECETOC-test (ECETOC, 1988), to reduce the amount of inorganic carbon to a value $\leqslant$10 mg l^{-1}. A final re-suspension step enabled adjustment of the dried solids concentration to 4.2–4.8 g dry solids l^{-1}. C_{12}-AO and C_{14}-AO were tested from 15 to 150 mgC l^{-1} and cocoamido-AO from 35 to 275 mgC l^{-1}. Each surfactant concentration was tested in triplicate. Five replicates with anaerobic sludge but without any added surfactant were performed to determine the endogenous biogas production (control digesters). All samples were incubated in 250 ml pressure-resistant glass bottles at 36 ± 1 °C and the gas/liquid volume ratio was 3:7. The bottles were fitted with gas tight septa and aluminium crimp seals. After sealing the vessels and incubating them for about 1 h excess gas was released to the atmosphere. Incubation proceeded in the dark. The evolved pressure was measured with a digital manometer connected to a syringe needle and the increase in headspace pressure in the closed bottles was used to follow the mineralization process. The incubation time was 90 days. At the end of the test, after allowing the sludge to settle, suitable volumes were withdrawn by syringe from the clear supernatant of each vessel and kept in small beakers carefully filled to the brim and covered with a cap to prevent CO_2 exchange with the air. The dissolved portion of the evolved carbon dioxide was determined as the concentration of inorganic carbon in the clear supernatant using a carbon analyzer (Shimadzu TOC-5050).

2.4. Daphnia magna immobilization test

D. magna, laboratory bred, not more than 24 h old, were used in this test (OECD, 1984), where the swimming incapabilility is the end point. The pH of the medium was 8.0 and the total hardness was 250 mg l^{-1} (as $CaCO_3$), with a Ca/Mg ratio of 4/1. Tests were performed in the dark at 20 °C. Twenty daphnia, divided into four batches of five animals each, were used at each test concentration. For each surfactant, 10 concentrations in a geometric series were tested in the concentration range first established in a preliminary test. The percentage immobility at 48 h was plotted against concentration on logarithmic-probability paper and a linear relationship was obtained. The Probit Method was employed as statistical procedure to determine the IC_{50} (the estimated concentration to immobilise 50% of the daphnia after 48 h exposure) and the corresponding 95% confidence interval (CI).

2.5. Photobacterium phosphoreum luminiscence reduction test (Microtox^R Test)

P. phosphoreum is a marine luminiscent bacterium that is naturally adapted to a saline environment. These