



## Review

# The biodegradation of monomeric and dimeric alkylammonium surfactants



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## HIGHLIGHTS

- The biodegradation of alkylammonium surfactants is described and discussed.
- The degradation process is very complex and depends on many factors.
- Monomeric and dimeric alkylammonium surfactants are hard to be degraded.
- Amide, peptide or carbohydrate substituents facilitate the biodegradation.

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## ABSTRACT

Quaternary ammonium compounds (QACs) are salts known for having antiseptic and disinfectant properties. These compounds are toxic to aquatic organisms and should thus be removed from wastewater before its discharge into surface waters. The biodegradation of QACs takes place in the presence of microorganisms under aerobic conditions. The susceptibility of these compounds to degradation depends on numerous parameters. A number of them, such as the structure-adsorption on solids, and concentration of the QACs, as well as the presence of additional substances, have been reviewed in this article. Moreover, the biodegradability of new dimeric alkylammonium salts, i.e., cationic gemini surfactants, has been discussed and compared with that of anionic and nonionic geminis. The biodegradation study of monomeric and dimeric alkylammonium surfactants show that they are not easily degraded. The degradation process is very complex and strongly depends on the structure of the compound, adsorption-desorption processes on sludge, type of microorganism consortia and the presence of anions. Alkylammonium surfactants with biological motifs, like amide, peptides or carbohydrates, are much better degraded.

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**Abbreviations:** ACh-Cl, acetylcholine chloride; AnBUSDiC, test anaerobic biodegradation under sludge digester conditions test; ATMAC, alkyltrimethylammonium compounds; BAC, benzalkonium chloride; BNR, biologic nitrogen removal; BOD, biochemical oxygen demand; C<sub>10</sub>DMAC, didecyldimethylammonium chloride; C<sub>10</sub>TMAC, decyltrimethylammonium chloride; C<sub>12</sub>BAC, dodecylbenzyltrimethylammonium chloride; C<sub>12</sub>TMAC, dodecyltrimethylammonium chloride; C<sub>14</sub>BAC, tetradecylbenzyltrimethylammonium chloride; C<sub>14</sub>TMAC, tetradecyltrimethylammonium chloride; C<sub>16</sub>BAC, hexadecylbenzyltrimethylammonium chloride; C<sub>16</sub>TMAB, hexadecyltrimethylammonium bromide; C<sub>16</sub>TMAC, hexadecyltrimethylammonium chloride; C<sub>18</sub>DMAC, dioctadecyldimethylammonium chloride; C<sub>18</sub>TMAC, octadecyltrimethylammonium chloride; C<sub>22</sub>TMAC, docosyltrimethylammonium chloride; CMC, critical micelle concentration; DADMAC, dialkyldimethylammonium compounds; DEEDMAC, diethylesterdimethylammonium chloride; DOC, dissolved organic carbon; DTDMAC, ditallowdimethylammonium chloride; ECETOC, European Centre for the Ecotoxicology and Toxicology of Chemicals; FEC, first effect concentration; HEQ, Hamburg ester quat; ISO, International Organization for Standardization; K<sub>i</sub>, half-saturation inhibition constant; LAS, linear alkylbenzene sulphonate; LCh-Cl, lauroylcholine chloride; Me, methyl group; MIC, minimal inhibitory concentration; MITI, Ministry of International Trade and Industry-Japan; OECD, Organization for Economic Co-operation and Development; QAC, quaternary ammonium compound; SCAS, semicontinuous activated sludge; SDS, sodium dodecyl sulphate; SRT, solid retention time; VSS, volatile suspended solids; WWTP, wastewater treatment plant.

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## 1. Introduction

Quaternary ammonium compounds (QACs, quats) are molecules with at least one long hydrophobic hydrocarbon chain linked to a positively charged nitrogen atom (Fig. 1). The other alkyl groups are mostly short-chain substituents such as methyl or benzyl groups. The counter ions can be either inorganic or organic. QACs have over 10% share in a large group of surfactants, where anionic and non-ionic surfactants combined account for roughly 85% of global demand for surfactants. [1]. Despite the global trend to non-ionic surfactants, QACs will remain the widely used surfactants in pharmaceutical and fabric softener formulations, cosmetics, commercial disinfectants, industrial saniters, food preservatives, and phase transfer catalysts [2]. Global demand for non-ionic, anionic, amphoteric and cationic surfactants was over 12 million tonnes in 2010 and is projected to rise by 4.5% per year until 2018 to generate revenues of more than US\$41 billion in 2018. Asia-Pacific is the largest surfactant outlet, with a roughly 37% share of global consumption, followed by North America and Western Europe [1].

Residual surfactants are discharged to wastewater treatment plants (WWTPs) or directly to surface waters and then dispersed into the environment. However, surfactants have some negative effects on surface waters, such as reducing air/water oxygen transfer, damaging the water quality via the introduction of foam and sorption on solid particles, and exerting a toxic effect on aquatic microorganisms in trophic levels [3]. Hence, it is necessary to investigate the susceptibility of these compounds to biodegradation as well as the mechanisms of this process in the presence of mixed cultures, i.e. microbial consortia with well established mutual interactions isolated from activated sludge, wastewater, sediments, and rivers. However, it is hard to predict degradation efficiency or contamination level in the environment due to several factors.

Two types of biodegradation can be distinguished. The first type is primary biodegradation, during which a biological action causes an alteration in the chemical structure of a substance, resulting in the loss of a specific property of that substance. The second type is ultimate biodegradation (mineralisation), in which the test compound is completely utilised by microorganisms, resulting in the production of carbon dioxide, water, mineral salts, and new microbial cellular constituents (biomass) [4,5].

The ultimate biodegradability (mineralisation) of QACs in aerobic environments can be measured according to one of the

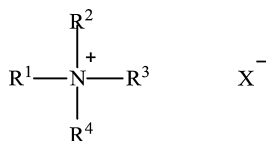


Fig. 1. Structures of quaternary ammonium salts, where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> = -CH<sub>3</sub>, -C<sub>n</sub>H<sub>2n+1</sub> (n = 8–18), -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; X = inorganic or organic ions.

five following methods: the CO<sub>2</sub> headspace test, carbon dioxide evolution (modified Sturm test), closed-bottle test, manometric respirometry test, and MITI test. According to those tests, surfactants are readily biodegradable if at least 60% biodegradation is achieved within 28 days. Ultimate biodegradability can be evaluated using the following tests: dissolved organic carbon (DOC) die-away and modified OECD screening-DOC die-away. The pass criterion of at least 70% of these two methods is considered equivalent to the pass criterion of at least 60% referred to in the methods listed earlier. In all methods testing ultimate biodegradability, pre-adaptation is not required and the 10-day window principle is not applied [5,6]. Environmental mineralisation is usually determined with either radio- or stable isotopes. The most frequently mineralisation rates are determined by using <sup>14</sup>C-labelled start material and trapping the formed <sup>14</sup>CO<sub>2</sub> [7].

The primary biodegradability of QACs can be evaluated according to one of methods mentioned in Regulation EC No 648/2004, based on the disulphine blue active substance analysis or using appropriate specific instrumental analyses, such as high-performance liquid chromatography [8].

Based on concern for the natural environment, the European Parliament and the Council of the European Union have developed regulations regarding synthetic surfactants. The Regulation EC No 648/2004, along with further amendments, harmonises the biodegradability of surfactants in detergents and restrictions on or bans of surfactants on grounds of biodegradability. In accordance with these regulations, detergents containing surfactants that meet the criteria for ultimate aerobic biodegradation (readily biodegradable surfactants) may be placed on the market without further limitations relating to biodegradability. For all surfactants in detergents failing ultimate aerobic biodegradation tests, the level of primary biodegradability shall be measured, and if it exceeds 80%, the manufacturers of industrial or institutional detergents containing surfactants may ask for derogation [8].

Although anaerobic biodegradation is not required for surfactants in the regulations discussed above, there was an intention to undertake further research to explore improved methods for measuring anaerobic biodegradability [9]. Knowledge about QAC anaerobic biodegradation is important because the strong adsorption of quaternary ammonium compounds on solid particles can occur in anaerobic environments, such as river sediments, sub-surface soil layers, or sludge digesters of wastewater treatment plants. Methods for testing anaerobic biodegradability can be divided into screening tests for the determination of basic biodegradability under stringent conditions (e.g., ISO 11734, OECD 311) and tests at the simulation level, such as the OECD 314 or AnBUSDiC tests, for the assessment of data under more realistic conditions [9–14]. However, simulation tests are complex, lengthy and expensive; therefore, most surfactants have been aerobically tested in screening tests [11].

The strategy of OECD tests consists of three levels, i.e., ready biodegradability tests or screening tests, inherent biodegradability tests and simulation tests. Biodegradability tests generally neglect

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