



Evaluation of the anaerobic biodegradation of linear alkylbenzene sulfonates (LAS) using OECD 308 water/sediment systems

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ABSTRACT

Linear alkylbenzene sulfonates (LAS) are the most widely used anionic surfactants in household detergents and cleaning products. We have evaluated LAS anaerobic degradation in sediments following OECD 308 guidelines. Four different classes of sediments were collected from non-polluted areas and tested to check the influence of: fine and coarse texture, low and high organic carbon content, and freshwater and marine origin. The concentrations of LAS and possible degradation metabolites in sediment and water phases were monitored by high resolution mass spectrometry over an incubation period of 160 days. LAS removal was between 0 and 63%, depending on the sediment used, and it was accompanied by formation of sulfophenyl carboxylic acids (SPCs). The best results were observed for marine sediments having low organic carbon and silt + clay contents (0.5% and 13%, respectively), whereas degradation was negligible in freshwater sediments. The large differences in degradation observed across the sediments tested were attributed to their physicochemical properties influencing LAS bioavailability and the heterogeneity of microbial communities. Further research is also needed to address some shortcomings observed during the application of the OECD 308 and to ensure that test results obtained with these guidelines model anaerobic biodegradation under realistic environmental conditions.

1. Introduction

During the last decades there has been a growing concern regarding the environmental behavior (sources, transport, distribution, and interaction with biota) of synthetic organic compounds. Among them, surfactants are one of the most commonly used class of chemicals, having a current production of over 15 billion tons per year [1]. They are used as complex mixtures of different components in a large variety of applications such as household cleaning and personal care products (e.g., shampoos and detergents), and in industry (e.g., emulsifiers, wetting agents and additives in hydraulic fracturing fluids) [2]. This research is focused on linear alkylbenzene sulfonates (LAS), anionic surfactants that were marketed for the first time in the mid-1960s as replacements for the poorly degradable tetrapropyl benzenesulfonates (TPS). LAS alkyl chains typically have between 10 and 14 carbon units, and each of these homologues consists of all possible secondary positional isomers. More than 80% of the LAS consumption takes the form of household detergents, as key components of washing powders and liquids, dishwashing products, and multipurpose cleaners. After use, LAS are ultimately discharged into aquatic ecosystems through both treated and untreated wastewater discharges, and are deposited into agricultural soils as part of sludge from wastewater treatment plants

(WWTPs). Although the removal of LAS in WWTPs is very efficient [3], typically more than 99%, LAS concentrations in the ppb-ppm range have been reported in both terrestrial and aquatic sewage-impacted environments [4,5].

Once in the environment, naturally occurring bacteria are capable of the degradation of LAS in oxic environments such as the water column [6]. This process consists of the oxidation of the alkyl chain to form sulfophenyl carboxylic acids (SPCs). There is, however, a fraction of LAS that ends up in river and coastal sediments because of the relatively high adsorption capacity of these surfactants and their affinity for the organic carbon in the sediment [7]. In the case of aquatic areas subjected to pollution, anaerobic conditions are present below a top-most layer a few millimeters thick. There is an outgoing debate whether LAS can be degraded or not in this type of anaerobic environment. On one hand, concentrations of the order of several g/kg of LAS have been found in sewage sludge after anaerobic digestion. Various laboratory assays incubating either sludge or river sediment spiked with LAS found no evidence of biotransformation [8–10]. Inhibition of the anaerobic digestion has been related to toxicity due to the high concentrations usually employed in these test [11,12] and/or to the low bioavailability of LAS due to adsorption to the particulate phase [13]. On the other hand, positive results have been reported using continuous stirred tank

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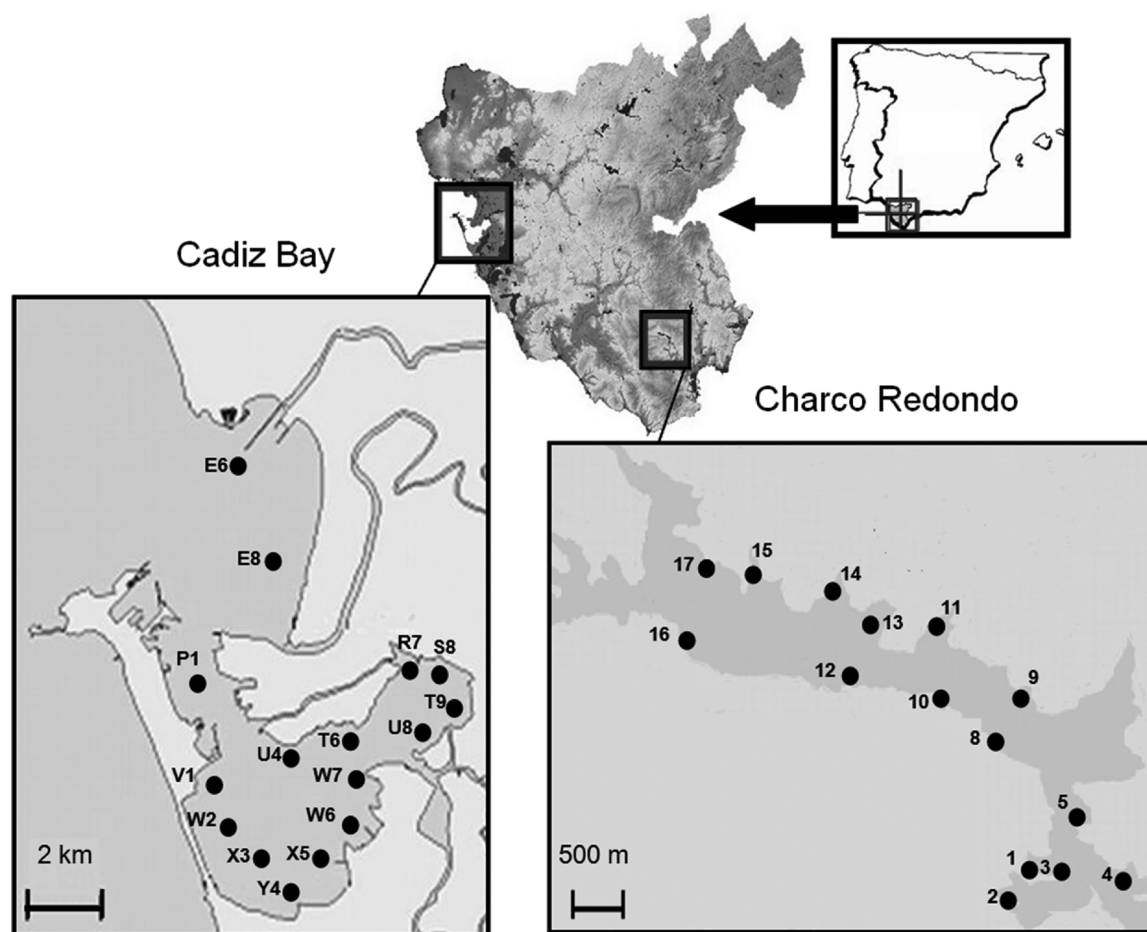


Fig. 1. Location of sampling stations at Cadiz Bay (marine environment) and Charco Redondo (freshwater environment) (Cadiz, SW Spain).

reactors (CSTR) and up-flow anaerobic sludge blanket (UASB) reactors [13–15]. Some field studies [16–18] have also suggested the possibility of the disappearance of linear alkylbenzenes, precursors in LAS synthesis, and of LAS itself, in anaerobic sediments.

More recently, our research group reported, after analysis of dissolved and particulate phases from incubation experiments, that LAS were removed up to 79% after 165 days in sulfate-reducing marine sediments [19]. This removal was attributed to primary biodegradation of the surfactant molecules as it was accompanied by increasing concentrations of SPCs. Initial ω -oxidation of the LAS molecule by the anaerobic communities was observed to take place by means of a mechanism known as “fumarate addition” [20]. Fumarate was added to the end of the LAS alkyl chain to form new metabolites named methyl-sulfophenyl-dicarboxylic acids (Me-SPdCs). These degradation products were later degraded to SPCs, which were shortened by β -oxidation [21]. Via this mechanism, LAS can be biotransformed into the same metabolites (SPCs) as those otherwise formed through the aerobic pathway. The rate of the entire anaerobic process, however, seems to be much slower than in the aerobic case (months vs days, respectively).

The main goal of the research shown in this manuscript was to characterize, for the first time, the anaerobic degradation of LAS in sediments under standardized conditions, following the OECD 308 guidelines for testing chemicals (“Aerobic and Anaerobic Transformation in Aquatic Sediment Systems”) (2002) [22]. The assays proposed by these guidelines simulate a water-sediment system for studying the transformation of an organic compound in an aquatic environment within different European and international regulatory frameworks. So far, such guidelines have mostly been applied to assess the aerobic biodegradation of contaminants of emerging concern

(CECs) such as pharmaceuticals [23,24], pesticides [25], and endocrine disruptors [26]. All these experiments were conducted in simulated freshwater sediment systems. The application of OECD 308 to evaluate anaerobic biodegradation is much more limited and was never conducted for surfactants, which due to their high production volume are predominant over other CECs in sewage-impacted sediments [27]. The main differences between the experimental set-up according to these guidelines and the series of experiments that we previously carried out [19,21] were: a) incubation must be performed using non-polluted sediments, and b) at least two different types of sediments must be tested. These two conditions require sampling in pristine areas and collecting sediments with different organic carbon contents and textures. Thus, according to the OECD guidelines, one sediment should have high organic carbon content (2.5–7.5%) and fine texture (silt + clay > 50%), and the other sediment should have a low organic carbon content (0.5–2.5%) and a coarse texture (silt + clay < 50%). Moreover, the difference between the organic carbon contents should be at least 2%, whereas the difference in silt + clay content for the two sediments should be at least 20%. In the case of LAS, which have been reported to be present not only in freshwater settings [28] but also in marine environments [5], sediments from both environments are required to perform the degradation assays. Using sediments from marine origin has systematically been ignored in previous experiments evaluating the fate of other CECs.

To assess the anaerobic degradation of LAS using the OECD 308 guidelines, the following specific objectives were pursued: a) performing sampling campaigns in freshwater and marine settings to find sediments that fulfill the requirements in OECD 308, b) monitoring the concentrations of LAS in spiked water/sediment microcosms, and c)

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