Council for LAB/LAS Environmental Research

LAS ANAEROBIC BIODEGRADATION

Anaerobic biodegradation refers to biodegradation under oxygen-free (anoxic) conditions. The requirement for anaerobic biodegradation of the cleaning agents (surfactants) used in laundry and cleaning products has been a part of ecolabel programs in Europe, which attempt to identify "environmentally preferred" ingredients. The anaerobic biodegradation criteria are based on laboratory tests that model anaerobic digesters, typical components of municipal wastewater treatment plants (WWTPs). It has been known for some time that there is no measurable reduction in LAS levels in sludge (bio-solids) treated in WWTP anaerobic digesters. Consistent with this observation, LAS does not pass laboratory tests for biodegradation that model anaerobic digesters. However, anaerobic biodegradation is not relevant to environmental safety for substances such as LAS that rapidly and completely biodegrade under aerobic conditions, which predominate in the real-world environment. For instance, while there are no measurable reductions in LAS levels in anaerobic digesters, the LAS remaining after anaerobic digestion does not impact the environment as the bio-solids are typically applied to agricultural lands as a soil conditioner or fertilizer. Under the aerobic conditions of sludge-amended soil, any residual LAS undergoes rapid and complete biodegradation, with no unreasonable risk to crops or soil organisms.

LAS in bio-solids may also reach freshwater and marine sediments, where conditions, especially in deep layers, may once again become anaerobic. The European Commission Scientific Committee on Health, Environment and Emerging Risks (SCHEER) reviewed the results of a University of Cadiz study conducted using pristine sediment/water samples (OECD 308 Guideline method) and concluded "negligible anaerobic degradation in freshwater and degradation only under certain conditions in marine waters may lead to accumulation of LAS and thus may present an issue of relevant environmental concern." However, risk assessments of LAS levels in sediments generally indicate that LAS levels are low, below no-effect levels for aquatic and sediment organisms, indicating no unreasonable risk to the environment. Indeed, studies are available suggesting that LAS undergoes anaerobic biodegradation in non-pristine (impacted) marine sediments and in bio-reactors, vessels designed to facilitate wastewater treatment. There are still many unknowns regarding the factors that influence LAS anaerobic biodegradation, including the factors which limit anaerobic biodegradation in WWTP anaerobic digesters but allow LAS anaerobic biodegradation in bio-reactors, and that allow LAS anaerobic biodegradation in certain marine sediments but not in others. Nonetheless, the available data indicate that eco-label program requirements for anaerobic biodegradation are not supported by the available science, and do not identify environmentally preferred products.

- Anaerobic biodegradation is not relevant to environmental safety for substances such as LAS that are rapidly and completely biodegraded under aerobic conditions, which predominate in the real world environment.[(1)] Anoxic conditions are encountered in

anaerobic digesters used in sewage (wastewater) treatment. The LAS remaining in the sludge (bio-solids) after anaerobic digestion does not impact the environment as the bio-solids are typically applied to agricultural lands as a soil conditioner or fertilizer, where any residual LAS undergoes rapid and complete biodegradation. For other methods of sludge disposal, such as landfilling or incineration, biodegradation is not relevant.

- As noted in the HERA Project report[1], this conclusion has been affirmed by the Scientific Committee on Health and Environment Risks (SCHER), a committee of experts who serve an advisory role within the European Commission. SCHER, in an opinion on the environmental risk posed by detergent surfactants, such as LAS that are poorly biodegradable under anaerobic conditions, concluded "A poor biodegradability under anaerobic conditions is not expected to produce substantial modifications in the risk for freshwater ecosystems as the surfactant removal in the STPs seems to be regulated by its aerobic biodegradability" (SCHER, 2005[2]). This statement was again confirmed by SCHER in its opinion of 2008: 'The LAS-HERA report of 2004 contained no recent publications which affected the conclusion of SCHER in its opinion of 2005. Similar recent publications, later than 2004 (Garcia et al., 2005; Garcia et al. 2006a and b; references cited in LAS-HERA report of 2007), did not give grounds for any change of that opinion" (SCHER, 2008[3]). As a consequence, the requirement of ultimate biodegradability under anaerobic conditions cannot be considered an effective measure for environmental protection.

- LAS undergoes anaerobic biodegradation in selected marine sediments. Lara-Martin et al.[4,5,6] demonstrated that LAS biodegrades in anoxic marine sediments impacted by wastewater treatment plant effluents. Laboratory experiments performed on marine sediments spiked with 10-50 ppm of LAS showed that degradation is feasible, reaching a value of 79% in 165 days, with a half-life time of ca. 90 days. Anaerobic biodegradation was also observed with marine sediments sampled at anoxic depths in the sedimentary column. LAS concentrations in pore waters decreased sharply while biodegradation intermediates (SPC) increased. An anaerobic biodegradation pathway for LAS has also been demonstrated. The initial step in LAS anaerobic biodegradation (fumarate addition) is similar to the initial step of anaerobic biodegradation of simple compounds widely found in the environment (long-chain alkanes), structurally similar to the alkyl chain of LAS.

- More recently, anaerobic biodegradation of LAS has been examined in pristine freshwater and marine sediments in a University of Cadiz study[7] using a standard test method, the OECD 308 Guideline.[8] LAS anaerobic biodegradation was observed only in sandy, low-organic carbon marine sediments (63% biodegradation over 160 days). SCHER, now re-named the Scientific Committee on Health, Environment and Emerging Risks (SCHEER) reviewed the results as the test was conducted in response to the 2008 SCHER request for a study on LAS anaerobic biodegradation using a standard test method such as the OECD 308 method. As expected in reviewing the data, SCHEER concluded: 1) in marine waters anaerobic degradation of LAS may occur only under

particular conditions (e.g. sandy sediment with low organic carbon content); 2) the potential for anaerobic degradation of LAS is negligible in freshwater, and 3) the conditions in which some anaerobic degradation has been observed may be atypical for sites impacted by wastewater, where muddy and organic sediments may be encountered more frequently.(9) The SCHEER concluded: "Considering that LAS are compounds that are produced in very high volumes and that they are continuously released in sites impacted by wastewater, it is the opinion of the SCHEER that negligible anaerobic degradation in freshwater and degradation only under certain conditions in marine waters may lead to accumulation of LAS and thus may present an issue of relevant environmental concern."

- CLER provided detailed comments on the SCREER opinion to which the SCHEER WG provided responses that were adopted on 18 June by the plenary members.(10) In responding to the CLER comments, SCHEER clarified:
    - The Opinion is "mainly based on the study of the University of Cadiz, although recent scientific evidence should also be taken into account."
    - Noting CLER's statement that 'additional published studies provided evidence of LAS anaerobic biodegradation in marine sediments, including sewage-impacted sediments,' the SCHEER states "this agrees with the conclusions of the SCHEER Opinion, as well as those of the Cadiz study that accept the possibility of anaerobic biodegradation in the marine environment, only under specific conditions."
    - The statement that LAS may present 'a problem of relevant environmental concern' "is a general statement, not a risk characterization."

- LAS anaerobic biodegradation has been demonstrated in 18 studies using batch and flow-through bio-reactors, vessels designed to facilitate treatment of wastewater by microorganisms.(11) Analytical methods specific for the detection of LAS were used to ensure sensitive and accurate measures of biodegradation. The biodegradation observed was primary biodegradation (removal of parent material (LAS)) but complete biodegradation (mineralization) was documented in one study using radiolabeled LAS. Anoxic conditions were confirmed by use of resazurin oxygen-indicator dye, by linking biodegradation with anaerobic processes such as denitrification and by demonstrating that the predominant microorganisms present are only compatible with anoxic conditions. Anaerobic biodegradation was observed with a wide variety of sludges, including anaerobic digester sludge, indicating that digester sludge has the capacity to anaerobically biodegrade LAS. Rapid and efficient LAS anaerobic biodegradation is possible, with approximately 50% biodegradation observed in a recent study (flow-through reactors at 30 C with 35-37 hour hydraulic residence times).(12)

- Factors that potentially explain the observation of LAS anaerobic biodegradation under some conditions but not others include: 1) competition with other, more easily biodegraded organic substances (anaerobic digesters digesting bio-solids vs. bio-reactors treating LAS as the main carbon source) and 2) the limited microbial populations present

in pristine sediments (OECD 308 Guideline study) versus the more robust microbial populations observed in impacted marine sediments.

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