J. Cosmet. Sci., 72, 91–98 (January/February 2021)

Fate of Alkyl Polyglucosides in the Environment

RACHNA RASTOGI, *Research and Development, Bregma Science LLP, Bangalore 560098, India (R.R.)*

Accepted for publication August 17, 2020.

Synopsis

Alkyl polyglucosides (APGs) belong to the class of green or natural surfactants synthesized from fatty acids and sugars. Growing concerns on toxicity of sulfates and ethoxylates has led to their popularity in personal and home care products. Increasing usage has resulted in higher concentrations in discharge sites or wastewater treatment plants. Studies show that APGs are readily biodegradable in laboratory settings; however, limited data are available on their effects on the environment. In this focused review, we discuss their biodegradation profile and toxicity of the parent compounds and metabolites in aquatic systems.

INTRODUCTION

With the increasing demand for natural and organic formulations, use of green surfactants is also on the rise. One such class of compounds, alkyl polyglucosides (APGs), derived from sugars (glucose) and long-chain fatty acids (coconut/palm), is now gaining traction because of easy availability, improved production methods, lower cost, and excellent skin compatibility as a replacement to conventional surfactants. APGs are also approved for use by ECOCERT, France, International Organic and Natural Cosmetics Corporation GmbH, BDIH, Germany, and COSMOS, Europe (1–4). Recently, APGs have also found applications in home care and institutional products because of their good cleaning abilities, a category dominated by ethoxylated and sulfated surfactants. Apart from their use in cleansing applications, APGs are also being used as emulsifiers in skin care products and stabilizers in drug delivery (3). Thus, as their usage increases, there is a renewed interest in understanding their impact on the environment.

Personal care and cleaning products post-use end up in wastewater treatment plants or directly let out into aquatic zones where decontamination facilities are not available. Because of their higher consumption, surfactants and their degradation products have been detected at various concentrations in surface waters, sediments, and sludge-amended soils (5). Because of their dissolution capability, surfactants tend to accumulate at the interfaces and can be toxic to the microbiota. If tolerated or after an acclimatization period, surfactants undergo biotransformation leading to loss of their surface activity.

Address all correspondence to bregmascience@gmail.com.

Depending on the by-products, the toxicity profile of the surfactants may change. This mineralization process beginning from the influent to final discharge into aquatic systems can last for days to months depending on environmental factors, microbiome distribution, and nutrient levels (1,5).

Environmental compatibility of surfactants and chemicals is determined by guidelines laid down by the Organisation for Economic Cooperation and Development (OECD). Environmental hazard assessment includes determination of potential effects on the aquatic (including sediment), terrestrial, and atmospheric zones along with accumulation in food chain and microbiological activity in sewage treatment systems (6,7). APGs have been classified as readily biodegradable and nontoxic in early research (8). Growing use of these surfactants as sulfated surfactant replacements and demand for natural and organic formulations warrants re-scanning of the available ecotoxicity data (9). This review aims at the general chemistry, degradation mechanisms, and toxicity of APGs and their metabolites in aquatic environment.

CHEMISTRY AND BIODEGRADATION PATHWAY

Surfactants are made of a hydrophobic tail and a hydrophilic headgroup. In case of APGs, the hydrophobic tail is derived from fatty alcohols of coconut and/or palm origin and a hydrophilic sugar, usually *D*-glucose from corn (Figure 1). These are linked together through glycosidic linkages at the anomeric carbon (carbon linked to two oxygen atoms) using strong acids as catalysts. The alkyl residues range from 6 to 18 carbon atoms, predominantly linear with the degree of polymerization (DP) of 1–3. Commercial grades of APGs usually are monoglucosides with a DP of 1.3–1.7 (1,3).

Figure 2 illustrates the two most common biodegradation mechanisms for APGs. One possible mechanism is APG hydrolysis to form glucose or saccharide units and

$$H\text{-}(C_6H_{10}O_5)_n\text{-}O\text{-}C_xH_{2x+1}$$

$$\text{Lauryl Glucoside: } H\text{-}(C_6H_{10}O_5)\text{-}O\text{-}C_{12}H_{25}$$

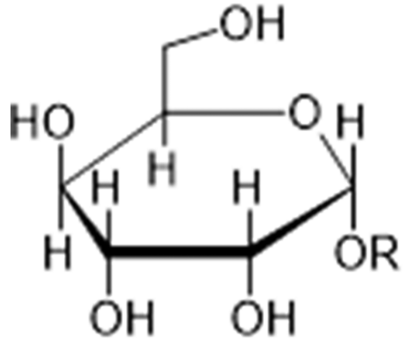

Figure 1. Empirical and structural formula of APGs, where n = average number of glucose units and x = number of carbon atoms in the alkyl chain. Example of lauryl glucoside or dodecyl—α-*D*-glucopyranoside, where $n = 1$ and $x = 12$; R = alkyl group.

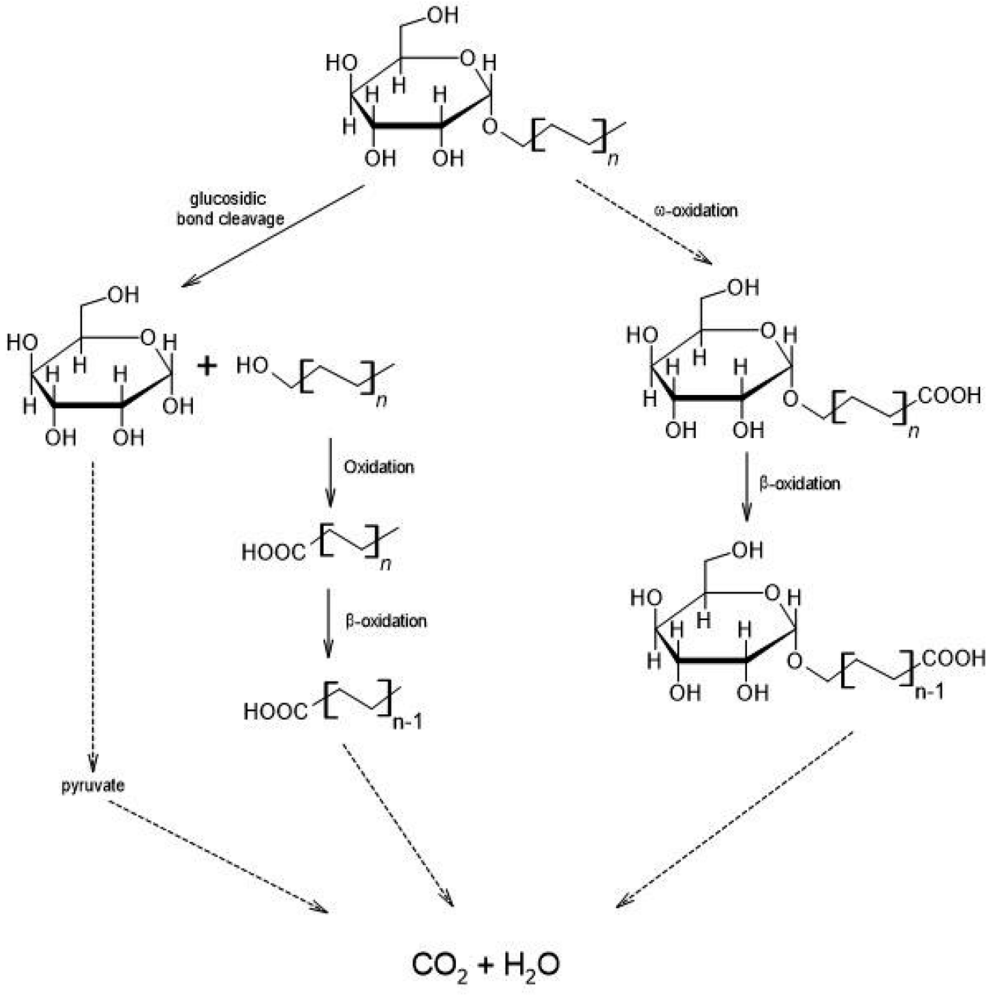

Figure 2. Biodegradation pathways for APGs. Based on chemical and spectroscopic analyses, the glucosidic bond cleavage is the predominant mechanism. Redrawn from Zgoła-Grześkowiak et al. (10); Eichorn and Knepper (11); Jurado et al. (13).

fatty alcohol. Glucose can then be metabolized *via* pyruvate cycle into carbon dioxide and water, whereas fatty alcohols undergo β-oxidation into fatty acids and metabolized intracellularly. This mechanism has been proven by using High Performance Liquid Chromatography (HPLC) and anthrone assay (10–13). Another proposed mechanism by Eichhorn and Knepper (11) is based on degradation of linear alkylbenzene sulfonates or alcohol ethoxylates, and involves ω-oxidation of the glucosides into corresponding alcohols, followed by breakdown into glucose and other by-products. However, in the Liquid Chromatography - Mass Spectroscopy (LC-MS) analysis of degraded samples, scientists failed to identify the corresponding alkanoic acid ions or adducts (11–13). Zhang et al. (14) report the ω-oxidation pathway such as sugar esters, based on degradation rates of linear and oxo-alcohol–derived APGs. The authors report that the longest and highly branched oxo $C_{14–15}$ APG had the slowest degradation

rate of ~80% compared with its linear counterpart which was more than 90% degraded in the same duration. The presence of highly complex and branched structure increased the time taken for the alkyl chain oxidation supporting the alkyl chain oxidation.

ARE APGS READILY BIODEGRADABLE?

Biotransformation or primary biodegradation is defined as a structural breakdown of a material such that it loses its inherent properties (9). Biodegradation profile under both aerobic and anaerobic conditions is important to establish the ultimate behavior of molecules in natural and wastewater environment. Low degradation rate in anaerobic conditions can potentially lead to surfactant accumulation in wastewater treatment plants and eventual soil contamination if used as a fertilizer. Ultimate biodegradation or mineralization is the conversion of the parent compound and its metabolites to carbon (9). In initial studies, Madsen et al. (15). have shown biotransformation of three APGs, namely, a linear, a branched and a monoester, and an alkyl ethoxylate in laboratory conditions. Ethyl glucoside esters, C_{10} and C_{12} ethyl glucoside esters, showed complete degradation in anaerobic conditions when exposed to three different innocula, freshwater sediment, marine, and digested sludge after typical lag periods of 3–4 weeks. Gas production was transiently inhibited in the early phase, but more than 75% of theoretical volume was achieved after 6 weeks (16). In another study, Jurado et al. (13) reported primary biodegradation pathways for $C_{8–16}$ glucoside, commonly known as coco glucoside from days 1 to 12 as hydrolysis of the APG into alcohol and polysaccharide.

Factors affecting the biodegradation rate: In isolated studies, various factors have been reported to affect the degradation rate.

i. Initial concentration: Using the anthrone method analysis, the effect of concentration has been demonstrated (13). Significant differences in degradation rates were noted as a function of initial concentration in aerobic conditions. Lower concentrations of 15 and 25 mg/L showed rapid degradation, whereas higher concentrations of 75 and 100 mg/L had an exponential decay curve with considerably lower degradation rates. Only 0.04% biotransformation in 50 h was noted for 100 mg/L compared with 62.09% for 15 mg/L (13). Starting concentration affected degradation rates; 100 mg/L APG dose in anaerobic testing conditions did not show complete degradation. Only 40.05% mineralization reached after 60 d for $C_{8–10}$, whereas longer chains showed less than 30% degradation in anaerobic conditions because of limited solubility (17). Thus, although APGs may be classified as readily biodegradable under aerobic conditions, their slower metabolism in the absence of oxygen can lead to eventual accumulation of parent molecules and their metabolites in anaerobic environments.
ii. Size of the hydrophobic residue: Biotransformation studies on linear and oxo derivatives of glucosides also confirm the effect of chain length on the degradation rate. Latency time of 0.5 d was noted for C_8 *versus* 2 d for C_{10} and above. After the primary degradation phase, the overall degradation rate was found to be similar for all chain lengths. The degradation rate was found to follow the following order: $C_8 > C_{10} \sim C_{12} > C_{14}$ (10,12). Similar observation had been previously reported for linear and branched glucosides and a monoester. The molecules showed higher degradation rates for lower alkyl chain length; branching may lead to increase in degradation time (12,13).

Increase in the alkyl chain length will lead to increase in hydrophobicity of the surfactant, causing higher cellular penetration rate and faster metabolism. However, cell death associated with toxicity may also increase, resulting in overall lower degradation rates. Furthermore, the initial concentration in the influent can lead to confounding outcomes because longer alkyl chain APGs have poorer aqueous solubility. Hence, a balance in cellular toxicity, concentration, and solubility needs to be achieved to draw an unbiased conclusion (17).

iii. Size of hydrophilic head: The effect of hydrophilic headgroup on the degradation rate has been reported in limited cases. Increase in the saccharide residues resulted in lower biodegradation rates due to increased hydrophilicity and lesser cellular penetrability (10). Mineralization studies are simulated in the laboratory as per the OECD 301 guideline under aerobic and anaerobic conditions (9). The eventual fate of an APG molecule is the conversion of primary degradation products, fatty alcohols, and glucose to carbon dioxide and water by the microbiome. Jurado et al. (18) have classified these reactions as stage 2 of degradation, lasting from days 13 to 21. Coco glucoside yielded a 99.20% total organic carbon (TOC) removal for the 15 mg/L (lowest test concentration) and a 45.21% TOC removal for the 100 mg/L (highest test concentration) within the 21-d test period in aerobic environment. Measurement of total Colony Forming Units showed initial reduction suggesting an acclimatization period for the microbiome.

For materials to be classified as readily biodegradable, the OECD 301 guideline recommends minimum of 60% CO_2 evolution or O_2 uptake in a 28-d test period with 10% in a 10-d window (9). The study by Madsen et al. (15) showed that all glycosides showed more than 60% CO_2 generation, except C_{12} monoester which failed to clear the 10-d window in aerobic conditions. Longer alkyl chain lengths and branching can lead to lower effective concentration for metabolism. In the anaerobic conditions, too, C_{12} monoester showed a higher degradation rate and can be compared with that of sodium benzoate, with 80% mineralization for the former compared with 86% of the latter in 28 d. Similar degradation time has been reported in other studies (12,19). Overall, APGs of chain lengths from C_8 to C_{14} continue to qualify as readily biodegradable with greater than 60% clearance in 28 d. However, in limited cases, they may not clear the 10-d window period (12,15,19).

DO APGS SHOW TOXICITY IN MARINE ENVIRONMENT?

Surfactants when dissolved in water are known to accumulate at interfaces. Although this property makes them active for formulations, it can also intensify their toxicity potential at cellular interface. Surfactants can dissolve the phospholipid cell membrane of bacteria, damage protein envelopes leading to cellular disruption, and death. Most laboratory experiments with activated sludge report biodegradation tests with a maximum of 40 mg/L of surfactant concentration to minimize cellular toxicity (1,2). In one study by Rios et al. (17), test concentrations of 100 mg/L have been reported. However, the researchers do not comment on the toxicity at such high concentrations.

C_8 glucoside showed least toxicity in three species, a microalga (*Raphidocelis subcapitata/ Kirchneriella subcapitata*), a plankton (*Daphnia magna*), and the zebrafish (*Danio rerio/ Brachydanio rerio*). *D. rerio* showed the highest sensitivity to APGs with an LC_{50} (lethal concentration at which 50% of the test organisms die) of 558 mg/L for C_8 and ~5 mg/L for $C_{12–14}$

also reconfirming the higher toxicity potential of longer alkyl chains as observed in activated sludge experiments (16). EC_{50} in *D. magna* also followed a similar pattern, suggesting nonspecific toxicity profile of APGs. Similar observations were reported by Garcia et al. (19) for *D. magna*. In luminescent bacteria (*Photobacterium phosphoreum*), toxicity decreased rapidly, and no toxic effects were detected after the third day correlating with the surfactant biodegradation rate. This study also showed that the toxic effects were mainly due to the parent molecule, and its elimination resulted in toxicity reduction.

In a separate experiment, caprylyl and decyl glucoside (C_8 and C_{10}), lauryl glucoside (C_{12}), and coco glucoside ($C_{8–16}$), and toxicity in Gram-negative bacteria (*Vibrio fischeri*) were found to be dependent on the initial concentration, chain length, and Hydrophilic-Lipophilic Balance (HLB). Shorter carbon chain and higher HLB in C_6 and C_{10} glucosides led to lower toxicity with EC_{50} (effective concentration at which 50% of test organisms show a response) of 29.05 (27.04–29.07) mg/L *versus* 13.81 (13.78–13.82) mg/L for $C_{8–10}$ in 15-min exposure (20).

Biodegradation of APG has shown to reduce dissolved oxygen levels in closed systems, suggesting that the process may impact water quality. In a first of its kind of a study, Sutton and Cohen evaluated the impact of APG at 0.1% and 1% concentration in low dissolved oxygen conditions using water columns in a blackwater pond in Georgia, USA. Concentration of dissolved oxygen was significantly reduced, and conductivity was higher than controls at both treatment levels. An overall decrease in all taxa was noted for the treatment, with predominant reduction in dominant species, *Chironomidae* and *Oligochaeta* in 14-d test period. Because APGs have shown >80% degradation in 21 d, it is possible that some undegraded surfactant might be present in the mesocosm. Whether the invertebrate species revived after the supposed APG degradation period or not was not captured as part of this study (21). In the second study, the research group has studied APG concentrations from 0.01 to 10 mg/L on plankton abundance and dissolved oxygen levels. APG concentrations of 2.5 and 5 mg/L showed 75% reduction in zooplanktons, especially copepods. No evidence of recovery was seen throughout the 1-mo study period. Dissolved oxygen levels were reduced in the first week but were seen to normalize by second and third weeks, except for 10 mg/L APG treatment where dissolved oxygen levels remained low throughout the study period. This change in the plankton community profile and overall distribution could have potential impact on the food cycle (22).

In a laboratory study, Duff et al. (23) have shown the effect of APG treatment on alga, *Chlorella*, in the presence of nitrogen and phosphorus as nutrients. The cell density was seen to decrease in the presence of APG alone. The presence of nutrients could not only reverse the impact of the surfactant; higher chlorophyll-a levels were noted in the APG + N treatment group, suggesting that the metabolites, glucose, and fatty alcohols were nontoxic as well as the increased algal biomass was a result of stress response to APG.

Although toxicity studies reported are limited and isolated, they do suggest that high concentrations of APGs may affect certain species in the food cycle. Usually, the chemical concentration is 10–100 times less in the discharge as compared with the influent, and the overall increase in the initial concentration can cause high levels in wastewater treatment plants (5,21). Linear alkylbenzene sulfonates, an example of the conventional surfactants used in the detergent industry, have been found up to 30.2 g/kg dry weight in treatment sludges, 1.09 mg/L in wastewater effluents, and 0.42 mg/L in discharge bodies (24–26).

CONCLUSION

As surfactants from renewable sources move to the forefront to cater to consumer demands for sustainable products, there is a parallel requirement of determining their impact on the aquatic environment. Biodegradability is of prime importance; laboratory experiments are suggestive and can forecast the degradation behavior of a compound in the environment. Our report shows that the actual scenario is much influenced by the starting concentration and chemistry of the molecule in question along with microbiome distribution and factors affecting their growth such as temperature, pH, and availability of organic matter. Although more nature-friendly than counterparts, these surfactants may not be eliminated in wastewater treatment plants, and their discharge in water bodies can lead to eventual changes in the food cycle over generations. Further research should include controlled actual test conditions along with simulated laboratory experiments.

REFERENCES

(1) D. Balzer and H. Lüders, *Nonionic Surfactants: Alkyl Polyglucosides* (Marcel Dekker, New York, NY, 2000), pp. 7–18.
(2) K. Hill, W. von Rybinski, and G. Stoll, *Alkyl Polyglycosides: Technology, Properties, and Applications* (VCH Publishers Inc., New York, NY, 1997), pp. 1–8.
(3) D. Geetha and R. Tyagi, Alkyl poly glucosides (APGs) surfactants and their properties: a review, *Tenside Surfactants Deterg.*, **49**, 417–427 (2012).
(4) COSMOS Standard, Raw Materials for COSMOS-Standard Cosmetics (2020), accessed April 5, 2020, http://www.cosmos-standard-rm.org/verifmp.ph.
(5) G.-G. Ying, Fate, behavior and effects of surfactants and their degradation products in the environment, *Environ. Int.*, **32**, 417–431 (2006).
(6) J. L. Berna, G. Cassani, C.-D. Hager, N. Rehman, I. Lopez, D. Schowanek, J. Steber, K. Taeger, and T. Wind, Anaerobic biodegradation of surfactants – scientific review, *Tenside Surfactants Deterg.*, **44**, 312–347 (2007).
(7) I. Effendi, S. Nedi, Ellizal, Nursyirwani, Feliatra, Fikar, Tanjung, R. Pakpahan, and Pratama, Detergent disposal into our environment and its impact on marine microbes. *IOP Conf. Ser. Earth Environ. Sci.*, **97**, 012030 (2017).
(8) U. Merrettig-Bruns and E. Jelen, Anaerobic biodegradation of detergent surfactants, *Materials*, **2**, 181–206 (2009).
(9) OECD, OECD Guidelines for the Testing of Chemicals (2006), accessed April 3, 2020. Revised Introduction to the OECD Guidelines for Testing of Chemicals, Section 3 Part 1: principles and Strategies Related to the Testing of Degradation of Organic Chemicals, Organisation for Economic Co-operation and Development (OECD), Paris, France.
(10) A. Zgoła-Grześkowiak, T. Grześkowiak, M. Frańska, A. Rzasa, and Z. Łukaszewski, Investigations on the biodegradation of alkylpolyglucosides by means of liquid chromatography–electrospray mass spectrometry, *Biodegradation*, **19**, 635–642 (2008).
(11) P. Eichhorn and T. P. Knepper, Investigations on the metabolism of alkyl polyglucosides and their determination in waste water by means of liquid chromatography–electrospray mass spectrometry, *J. Chromatogr. A*, **854**, 221–232 (1999).
(12) Y. Qin, G. Zhang, J. Zhang, Y. Zhao, and J. Zhao, Primary aerobic biodegradation of linear and oxo alcohol alkylpolyglucosides (APG), *J. Surfactants Deterg.*, **9**, 227–230 (2006).
(13) E. Jurado, M. Fernández-Serrano, J. Núñez-Olea, M. Lechuga, J. L. Jimenez, and F. Rios, Effect of concentration on the primary and ultimate biodegradation of alkylpolyglucosides in aerobic biodegradation tests, *Water Environ. Res.*, **83**, 154–161 (2011).
(14) J. Zhang, K. Xie, X. Dai, and G. Zhang, Differences between alkyl polyglucosides of natural alcohol and oxo-alcohol, *J. Surfactants Deterg.* **6**, 253–257 (2003).
(15) T. Madsen, G. Petersen, C. Seiero, and J. Torslov, Biodegradability and aquatic toxicity of glycoside surfactants and a nonionic alcohol ethoxylate, *J. Am. Oil Chem. Soc.*, **73**, 929–933 (1996).
(16) T. Madsen, H. B. Rasmussen, and L. Nilsson, Anaerobic biodegradation potentials in digested sludge, a freshwater swamp and a marine sediment, *Chemosphere*, **31**, 4243–4258 (1995).

(17) F. Ríos, A. Fernández-Arteaga, M. Lechuga, E. Jurado, and M. Fernández-Serrano, Kinetic study of the anaerobic biodegradation of alkyl polyglucosides and the influence of their structural parameters, *Environ. Sci. Pollut. Res.*, **23**, 8286–8293 (2016).
(18) E. Jurado, M. Fernández-Serrano, J. Núñez Olea, M. Lechuga, J. L. Jime´nez, and F. Rı´os, Acute toxicity of alkylpolyglucosides to *Vibrio fischeri*, *Daphnia magna* and microalgae: a comparative study, *Bull. Environ. Contam. Toxicol.*, **88**, 290–295 (2012).
(19) M. T. Garcia, I. Ribosa, E. Campos, and J. Sanchez Leal, Ecological properties of alkylglucosides. *Chemosphere*, **35**, 545–556 (1997).
(20) E. Jurado, M. Fernández-Serrano, J. Núñez-Olea, G. Luzon, and M. Lechuga, Acute toxicity and relationship between metabolites and ecotoxicity during the biodegradation process of non-ionic surfactants: fatty-alcohol ethoxylates, nonylphenol polyethoxylate and alkylpolyglucosides. *Water Sci. Technol.*, **59**, 2351–2358 (2009).
(21) K. T. Sutton and R. A. Cohen, APG-containing product reduces dissolved oxygen in freshwater pond mesocosms: implications for benthic macroinvertebrate abundance, *Fund. App. Lim.*, **180**, 291–298 (2012).
(22) S. F. Riera and R. A. Cohen, Alkyl polyglucoside compound influences freshwater plankton community structure in floating field mesocosms, *Ecotoxicol*, **25**, 1458–1467 (2016).
(23) J. A. Duff, M. N. Osier, S. Schwartz, and R. A. Cohen, Nutrient availability alters alkyl polyglucoside toxicity to the freshwater microalga *Chlorella* sp., *Fund. App. Lim.*, **190**, 173–181 (2017).
(24) J. L. Berna, J. Ferrer, A. Moreno, D. Prats, and F. R. Bevia, The fate of LAS in the environment, *Tenside Surfactants Deterg.*, **26**, 101–107 (1989).
(25) K. Fox, M. Holt, M. Daniel, H. Buckland, and I. Guymer, Removal of linear alkylbenzene sulfonate from a small Yorkshire stream: contribution to GREAT-ER project, *Sci. Total Environ.*, **251/252**, 265–275 (2000).
(26) M. S. Holt, K. K. Fox, M. Burford, M. Daniel, and H. Buckland, UK monitoring study on the removal of linear alkylbenzene sulphonate in trickling filter type sewage treatment plants. Contribution to GREAT-ER project #2, *Sci. Total Environ.*, **210/211**, 255–269 (1998).