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Degradation of high concentrations of nonionic surfactant (linear alcohol ethoxylate) in an anaerobic fluidized bed reactor

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HIGHLIGHTS

- The reactor was adequate for LAE removal, even at high surfactant concentrations.
- The LAE did not affect the organic matter removal and was used as a carbon source.
- Sucrose affected the volatile fatty acid production and the microbial diversity.

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ABSTRACT

The removal and degradation of the nonionic surfactant linear alcohol ethoxylate (LAE)Genapol® C-100 in an anaerobic fluidized bed reactor were evaluated with 4.7 mg LAE/L to 107.4 mg LAE/L added to the synthetic substrate (535 ± 121 mg/L to 882 ± 126 mg/L of organic matter). High removal efficiencies of the COD (chemical oxygen demand) (88%) and LAE (98%) were observed even at high surfactant concentrations during the 492 days of operation. The absence of sucrose in the synthetic substrate modified the microbial community. Similarity coefficients between the phases with sucrose and without sucrose were 74% and 59% for the Archaea and Bacteria domains, respectively. The higher LAE removal (98%) was obtained for the 97.9 mg LAE/L influent in the absence of the co-substrate, as well as the greater diversity of volatile fatty acid. At the end of the reactor operation 2.05 mg of LAE was adsorbed in the biomass and 98.5% was biodegraded.

1. Introduction

Surfactants comprise a large group of chemical compounds with tensoactive properties, which makes them useful for employment as an essential ingredient in household and industrial detergents, personal care products, pesticide formulations and other applications (Ying, 2006). Nonionic surfactants are being used in increasing amounts as components of cleaning agents because their effectiveness is not affected by water hardness, the foaming can be adjusted highly accurately and they are preferable to anionic surfactants for industrial and household uses (Hera, 2009). These surfactants contain no electric charge in their molecular structure, e.g. alcohol ethoxylates (AEs) which are used in a wide variety of applications (household cleaning products, personal care and industrial applications).

AEs are known for their low toxicity, high biodegradability, varying degrees of ethoxylation and excellent cleaning performance (Myers, 1999). Therefore, they are also perceived as ideal replacements for alkylphenol ethoxylates (APEOs), which are nonionic surfactants consisting of a branched chain in which its metabolic degradation products might be able to mimic hormones (Warhurst, 1995). Besides, they are also endocrine disruptors being different from LAE that generates short chain metabolites and has low lipophilicity and therefore less toxic (Roberts 1991; Newsome et al., 1995).

The AE can be derived from natural or synthetic sources (fatty alcohol ethoxylate) and can be notably hydrophilic due to the presence of the polyethylene glycol chain (Hera, 2009). The chosen surfactant for this study was the linear alcohol ethoxylate (LAE) which consists of a long aliphatic alkyl chain and an alcohol, thus forming the hydrophobic portion of the molecule that is connected to a chain with several units of ethylene oxide (EO), which is characterized as the hydrophilic fraction (Mösche, 2004). The LAE (Genapol® C-100) is used as a wetting

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agent, an emulsifier and a cleaning agent in detergents, personal products and industrial applications.

The LAE is commercially significant (Mezzanotte et al., 2002) and for this reason, is thrown into water bodies by industrial wastewater and sewage in bulk. For instance, 23–141 mg/kg and 0.9–15.6 mg/L of LAE were found in the sludge from a biological wastewater treatment system (Mösche, 2004; Berna et al., 2007) and in a wastewater treatment system, respectively (Morrall et al., 2006). The presence of LAE was also recorded in environmental samples: e.g. river sediments (160–1600 μg/kg); marine sediment (37–1300 mg/kg); and silt from rivers (171–919 mg/kg) (Cavalli et al., 2000; Petrovic and Barcelo, 2004; Dyer et al., 2006).

The monitoring of nonionic surfactants in the aquatic environments has indicated that these compounds could be present in concentrations known to cause acute and chronic effects in sensitive organisms, such as crustacean and fish (Ferrara et al., 2005; Roberts et al., 2007). Accordingly, possible sources of LAE, as well as better analytical methods must be developed to determine and treat them when present in the environment.

The nonionic surfactants can be removed by wastewater treatment processes, such as biological oxidation, advanced methods of treatment (e.g., ozonation), activated sludge or adsorption monoreticulated resins (Mezzanotte et al., 2002). The LAE is considered biodegradable under aerobic, anoxic (Hera, 2009) and anaerobic conditions (Mösche, 2004), nevertheless, high rates of instabilities in the biological processes may occur in anaerobic treatment of wastewater containing these surfactants (Mösche and Meyer, 2002).

In anaerobic screening tests Berna et al. (2007) cite that LAE are biodegradable with efficiencies above 70%. Wagener (1987) observed an LAE removal efficiency of 90% for 1 g/L of the surfactant influent in fix bed reactor. In batch reactor Huber et al. (2000) observed that LAE was totally degraded for 40 mg/L influent in 22 days. However, there is a lack of information about the LAE degradation rate in anaerobic continuous systems. The anaerobic fluidized bed reactor (AFBR) has been widely studied for anionic surfactant (linear alkylbenzene sulfonate — LAS) removal (Oliveira et al., 2010), nevertheless, still not studied for LAE degradation. An advantage of the AFBR is the adherence of microorganisms to the support material, which promotes a large specific surface area and leads to high biomass concentrations and reaction rates; therefore, the required reactor volume is smaller (Encina and Hidalgo, 2005). The recirculation rate applied to the reactor promotes a high mixing degree in the system facilitating the mass transfer and aiding in the dilution of toxic compounds. This fact increases the availability of the surfactant for the microorganisms, which makes it better for its removal efficiency compared to other reactor configurations (Oliveira et al., 2010).

Accordingly, the LAE (Genapol® C-100) removal and degradation were evaluated in a continuously operated AFBR filled with biomass immobilized on sand as the support material, which makes this a novel study, even more so considering the high concentrations of the nonionic surfactant employed and the evaluation of the microbiological aspects involved in this degradation.

2. Materials and methods

2.1. Fluidized bed reactor

The fluidized bed reactor was constructed in acrylic (1.256 L) as a cylinder 100 cm tall with a diameter of 4 cm. Sand was used as the support material (306 g) with a diameter between 1.4 mm and 1.7 mm and a density of 2300 g/L. The bed height and volume expansion were 25.7 cm and 8.2%, respectively (Fig. 1). The support material was submitted to a treatment with 10% fluoridric acid to enhance the surface roughness (Barros et al., 2010). The reactor was operated in a continuous system, with a hydraulic retention time (HRT) of 18 h at 30 °C. The recirculation flow applied to the reactor was 106 L/h.

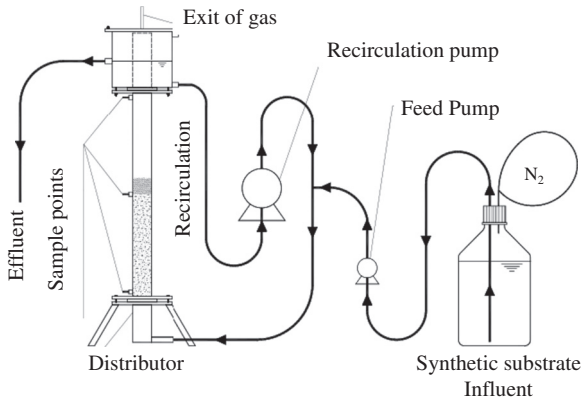

Fig. 1. Schematic representation of the anaerobic fluidized bed reactor. Adapted from Oliveira et al. (2010).

2.2. Inoculum

The inoculum was obtained from sludge coming from a full-scale UASB reactor used in the treatment of swine manure, situated in the Department of Agricultural Engineering, University Estadual Paulista — UNESP, Jaboticabal (Brazil). The inoculation of the reactor was performed by adapting the biomass to the synthetic substrate without adding the surfactant LAE. The system was kept in a closed circuit for 19 days at a controlled temperature of 30 °C with a COD average of 534.9 ± 121 mg/L.

2.3. Synthetic substrate and phases of operation

The synthetic substrate used in the feeding of the reactor consisted of sucrose (80 mg/L), yeast extract (500 mg/L), sodium bicarbonate (400 mg/L), 0.5 mL of salt solution (50.0 g/L of NaCl, 1.4 g/L of $MgCl_2 \cdot 6H_2O$ and 0.9 g/L of $CaCl_2 \cdot 2H_2O$) (Duarte et al., 2008 adapted from Torres, 1992) and nonionic linear alcohol ethoxylate — LAE (Genapol® C-100 from Sigma-Aldrich®, St. Louis, USA).

The nonionic surfactant used was derived from coconut oil, which is a mixture of alkyl chains of C_{12} and C_{14} with an average of 10 ethoxy units. This surfactant has a molecular weight of 627 g and a critical micelle concentration (CMC) of 0.075 mM; its solubility is 1 g/10 mL of water.

All phases of the reactor operation were fed with synthetic substrate, in the Phases I to V, nonionic linear alcohol ethoxylate (LAE — Genapol® C-100) was added besides the synthetic substrate. In the last phase (Phase V) only the sucrose was removed from the feeding system (Table 1).

2.4. Analytical methods

Physicochemical analyses of COD, pH, alkalinity and total solids were performed by standard methods for examination of water and wastewater (APHA–AWWA–WPCF, 2005) and volatile organic acids (Penteado et al., 2013).

The quantification of LAE (Genapol® C-100) was performed by high performance liquid chromatography (HPLC — Shimadzu system) following the method of Matthijs et al. (2004), which was adapted in this study. The following organic solvents were used in preparing the samples: methanol, acetonitrile, cyclohexane and dichloromethane, all with high purity (99%).

The derivatives used were 1-naphtoyl and 1-chloride-methylimidazole (Sigma-Aldrich®, St. Louis, USA). A column of solid phase extraction (SPE) high performance SampliQ® (Inc., Palo Alto, CA, USA) filled with an alumina of 5 × 6 mL from Agilent Technologies® (Inc., Palo Alto, CA, USA) (0.5 g/6 mL) was used and coupled to the