IWA 17th SWWS AND 9th ROS
10th–14th November, 2024
Curitiba-Brazil

Redox mediator and microaeration as engineering approaches to enhance the biotransformation of linear alkylbenzene sulfonate (LAS) in anaerobic reactors

Oliveira, M.G.*, Queiroz, G.A.R.*, Vasconcelos, S.R.F.* da Silva, V.E.P.S.G.* and dos Santos, A.B.*

*Department of Hydraulic and Environmental Engineering, Federal University of Ceará, Fortaleza, Ceará, Brazil.

Highlights:

- AQS provides a higher LAS removal for the anaerobic treatment.
- Microaeration has no significant influence on LAS removal.
- AQS accelerated electron transfer and increased the removal of organic matter.

Keywords: Mediator redox; Linear alkylbenzene sulfonate; Microaeration.

INTRODUCTION

Linear alkylbenzene sulfonate (LAS) is the most prevalent surfactant in the laundry industry. LAS consists of a linear chain with length ranging from 10 to 14 carbon atoms (C10 to C14). LAS concentrations in municipal wastewaters range from 2 to 21 mg/L (Motteran et al., 2018). However, in wastewater from detergent and textile industries, these levels can reach worrying peaks of up to 1024 mg/L. The direct release of groundwater containing high levels of LAS could potentially harm aquatic and terrestrial ecosystems (Luo et al., 2023).

The biodegradation of LAS under anaerobic conditions remains a topic of debate. LAS has been identified as an inhibitor of anaerobic processes. Furthermore, despite its lower biodegradation rate, the anaerobic biodegradation of LAS has been studied in different design and operational conditions (Askari et al., 2021). In these studies, the degradation rates in UASB reactors ranged between 13% and 85%, with hydraulic retention times (HRT) of 6-48 h. A common operational HRT was around 12-24 h due to the recalcitrance of LAS (Okada et al., 2013).

Therefore, it is necessary to adopt strategies that increase LAS removal in anaerobic systems, especially those designed to operate with short hydraulic retention times (HRT), generally between 6 and 8 hours. Recent research indicates that introducing low oxygen concentrations (microaeration) into anaerobic systems could enhance the initial breakdown of recalcitrant compounds (Buarque et al., 2019). Furthermore, soluble quinone-based compounds, such as anthraquinone-2-sulfonate (AQS), have functioned as redox mediators, expediting anaerobic biotransformations (Silva et al., 2020).

Thus, this study evaluated various engineering strategies, including the incorporation of AQS and microaeration, to enhance the conversion of LAS in anaerobic reactors operated with a short hydraulic retention time (HRT) of 8 h. Furthermore, the operational stability of the system and the evolution of its microbial community under microaerobic conditions were evaluated.

METHODOLOGY

The synthetic wastewater consisted of an aqueous solution containing LAS (10 mg/L), sucrose (1 gCOD/L), basal medium (macro and micronutrients) and sodium bicarbonate (1 g/L), to maintain the pH close to 7.0. All reagents were used as purchased, without additional purification.

The experiment consisted of four reactors with a useful volume of 3.25 L. Two reactors were operated under the 8-hour HRT (R1 and R2), commonly used in the design of UASB reactors treating sanitary wastewater. The R1 reactor functioned as a traditional UASB reactor. Reactor R2 were built with the same dimensions and material as reactor R1, but were micro-aerated with synthetic air at their base through a flow controller mass. The microaeration air dose used was 0.2 $Lo_2./L_{feed}$, corresponding to 1.5 mL_{air}/min.

The experiment was divided into two phases. In Phase I, the reactors were fed with the synthetic influent described above. In Phase II, the AQS (50µM) was added to the influent. The performance of reactors was investigated during the 112 days of continuous operation including a short period without LAS between the Phase I and II.

COD, pH, and total alkalinity (TA) were determined by APHA (2012). The quantification of methane in biogas was determined by gas chromatography with ionization detection by dielectric barrier discharge, as used by Oliveira et al. (2021). The determination of LAS follows the methodology described by Silva et al. (2016) using high-performance liquid chromatography.

RESULTS AND CONCLUSIONS

The pH of the reactors' effluent remained alkaline throughout the experiment, with values that did not impair anaerobic digestion and indicating that there was no accumulation of VFAs. The maintenance of the pH of the R1 and R2 effluents above 7 probably occurred due to the production of AT during the anaerobic digestion process. In both reactors, it was observed great stability in terms of pH and AT, which also influenced the stability in the removal of organic matter.

Table 1 – Means and standard deviations of the COD removal, pH, Total Alkalinity, and methane production analyzed in the UASB reactors.

	Phase I		Phase II	
	R1	R2	R1	R2
$COD_{Removal}$ (%)	65.7 ± 12.3	77.6 ± 6.8	89.0 ± 5.9	87.6 ± 4.9
pH	7.6 ± 0.2	7.7 ± 0.2	7.7 ± 0.2	7.7 ± 0.2
Total Alkalinity	450.4 ± 148.6	437.1 ± 124.7	522.4 ± 110.8	549.0 ± 116.2
$LCH_4/gCOD_{app}$	2.0 ± 1.2	1.5 ± 0.5	2.0 ± 0.3	1.6 ± 1.7

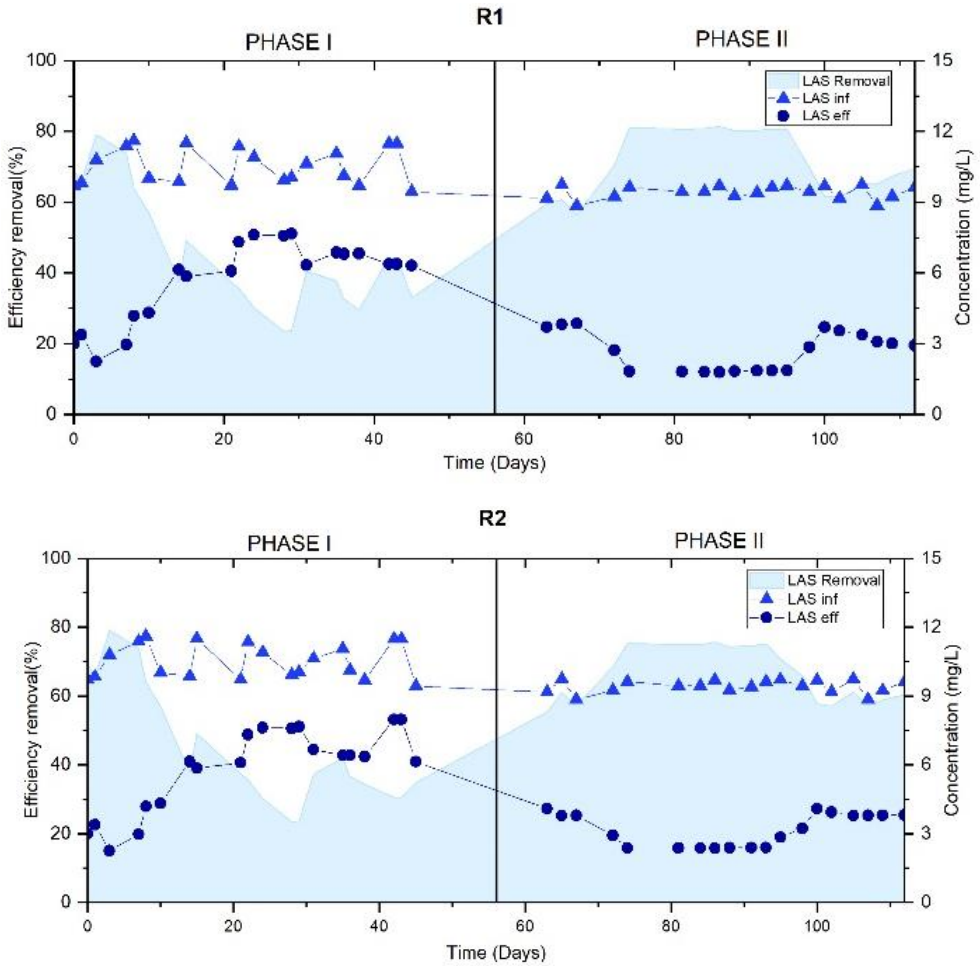
The COD concentration of the influent remained stable at around 1 g/L throughout the process. In Phase I, the average COD of effluents were 343.1 ± 123.4 mg/L and 223.8 ± 67.4 mg/L, for R1 and R2, respectively, corresponding to a COD removal efficiency of 65.7 ± 12.3% and 77.6 ± 6.8%, respectively. In Phase II, the average COD of effluents were 131.1 ± 71.4 mg/L and 143.3 ± 45.2 mg/L, for R1 and R2, respectively, corresponding to a COD removal efficiency of 89.0 ± 5.9% and 87.6 ±

4.9%, respectively. Therefore, AQS accelerated organic matter conversion to methane and increased the COD removal in the systems.

There was no difference in methane production between the phases for both reactors (Table I). It is worth mentioning that although the methane content in the biogas also decreased when the reactor was microaerated, this was only a consequence of biogas dilution by air (an oxygen source), whose N_2 content is very high (80%), This behavior was similar to other studies on the effect of microaeration in anaerobic systems (Oliveira et al., 2021). Thus, there was no inhibition of methanogenesis since methane production was not impaired.

There was no significant difference in the removal of LAS between the reactors R1 and R2 in both phases I and II (Phase I: R1 – 44.6 ± 17.2%, R2 – 44.3 ± 14.7%; Phase II: R1 – 66.1 ± 7.9%, R2 – 71.2 ± 9.0%) (Figure 1).

Figure 1 – LAS removal efficiency of reactors during the experiment.



The reductive biotransformation of pollutants is generally impaired under aerobic conditions, even with the presence of redox mediators, since oxygen acts as a much more efficient electron acceptor. In addition, some microorganisms can use the reduced redox mediator as an electron donor in aerobic

respiration. Therefore, the introduction of oxygen into anaerobic reactors can compromise this biotransformation process. Under microaerobic conditions, instead of acting as a final electron acceptor, oxygen is used only by microorganisms that produce monooxygenases to hydroxylate organic compounds, facilitating their subsequent anaerobic biotransformation (Silva et al., 2020).

However, the addition of AQS provided greater removal of LAS. The degradation of sulfonated compounds, such as LAS, can be complex, since the oxidation state of this element can vary from -2 to +6, and is subject to both chemical and biological transformations. Quinone-based compounds can act as redox mediators, accelerating the reductive biotransformation of several pollutants. Thus, their application in anaerobic reactors with short HRT can be an effective strategy to enhance biotransformation. Thus, the notable positive effect of AQS on the anaerobic biotransformation of LAS suggests that it may have overcome a possible limitation in electron transfer.

According to the literature, the reductive biotransformation of pollutants in the presence of a redox mediator occurs in two distinct steps: first, the mediator is biologically reduced during the oxidation of organic substrates and, then, it is chemically reoxidized during the reduction of the target pollutant (electron acceptor).

ACKNOWLEDGMENTS

The authors would like to thank the support obtained from the following Brazilian institutions: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq); Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Instituto Nacional de Ciência e Tecnologia em Estações Sustentáveis de Tratamento de Esgoto – INCT ETEs Sustentáveis.

REFERENCES

APHA, 2012. Standard Methods for the Examination of Water and Wastewater, 22nd ed. American Public Health Association, Washington.

Askari, A., Vahabzadeh, F., & Mardanpour, M. M. (2021). Quantitative determination of linear alkylbenzene sulfonate (LAS) concentration and simultaneous power generation in a microbial fuel cell-based biosensor. *Journal of Cleaner Production*, *294*. https://doi.org/10.1016/j.jclepro.2021.126349

Buarque, P. M. C., De Lima, R. B. P., Vidal, C. B., De Brito Buarque, H. L., Firmino, P. I. M., & Dos Santos, A. B. (2019). Enhanced removal of emerging micropollutants by applying Microaeration to an anaerobic reactor. *Engenharia Sanitaria e Ambiental*, *24*(4), 667–673. https://doi.org/10.1590/s1413-4152201920190030

Luo, Y., Jin, X., Xie, H., Ji, X., Liu, Y., Guo, C., Giesy, J. P., & Xu, J. (2023). Linear alkylbenzene sulfonate threats to surface waters at the national scale: A neglected traditional pollutant. *Journal of Environmental Management*, *342*. https://doi.org/10.1016/j.jenvman.2023.118344

Motteran, F., Nadai, B. M., Braga, J. K., Silva, E. L., & Varesche, M. B. A. (2018). Metabolic routes involved in the removal of linear alkylbenzene sulfonate (LAS) employing linear alcohol ethoxylated and ethanol as co-substrates in enlarged scale fluidized bed reactor. *Science of the Total Environment*, *640–641*, 1411–1423. https://doi.org/10.1016/j.scitotenv.2018.05.375

Okada, D. Y., Delforno, T. P., Esteves, A. S., Sakamoto, I. K., Duarte, I. C. S., & Varesche, M. B. A. (2013). Optimization of linear alkylbenzene sulfonate (LAS) degradation in UASB reactors by varying bioavailability of LAS, hydraulic retention time and specific organic load rate. *Bioresource Technology*, *128*, 125–133. https://doi.org/10.1016/j.biortech.2012.10.073

Oliveira, M. G. de, Mourão, J. M. M., Silva, F. S. S., dos Santos, A. B., & Pereira, E. L. (2021). Effect of microaerophilic treatment on swine wastewater (SWW) treatment: Engineering and microbiological aspects. *Journal of Environmental Management*, *299*. https://doi.org/10.1016/j.jenvman.2021.113598

Silva, J. da S. do N., Araújo, Maria Helena Peres Santos, A. B. dos, Silva, M. E. R. da, & Firmino, P. I. M. (2020). Redox mediator, microaeration, and nitrate addition as engineering approaches to enhance the biotransformation of antibiotics in anaerobic reactors. *Journal of Hazardous Materials*, *August*. https://doi.org/10.1016/j.jhazmat.2020.123932

Silva, R. F., Silva, G. L., Silva, P. T. S., & Silva, V. L. (2016). Identificação e quantificação de contaminantes emergentes em estações de tratamento de esgoto. *Revista Virtual de Quimica*, *8*(3), 702–715. https://doi.org/10.5935/1984-6835.20160053