Influence of linear alkylbenzene sulfonate (LAS) on the production and recovery of resources in an aerobic granulation system for wastewater treatment

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Highlights:

- Granular biomass remained stable with the presence of LAS;
- The presence of LAS increased the production of biopolymers;
- There was a high production of ALE.

Keywords: aerobic granular sludge; linear alkylbenzene sulfonate; resource recovery.

INTRODUCTION

Resource recovery in wastewater treatment plants has become a topic of great interest to the scientific community. Wastewater treatment systems are no longer seen just as a means of treating waste and are now being considered as factories for the recovery and use of resources (Santos et al., 2022). Carvalho et al. (2021) reported that the recovery of alginate-like exopolysaccharides (ALE) and other biopolymers from excess granular sludge began in 2016 at the Nereda® ALE extraction plant, which was built and patented as Kaumera Nereda®. Since then, the recovery of resources from excess sludge in sewage treatment plants has garnered the attention of the scientific community.

Frutuoso et al. (2023a) highlight that the main source of resources in wastewater treatment plants are extracellular polymeric substances (EPS), which are secreted by consortia of microorganisms present in the sludge and are mainly composed of proteins (PN) and polysaccharides (PS). In addition, EPS are also formed by nucleic acids, humic acids, lipids, ALE, and amino acids, such as tyrosine and tryptophan (TRY).

In this context, aerobic granular sludge (AGS) technology, which can simultaneously remove several types of pollutants, stands out for producing biopolymers in quantities greater than those found in other aerobic technologies (Rollemberg et al., 2018). Frutuoso et al. (2023a) highlight that this characteristic favors the formation of granules and their stability. Furthermore, it has advantages, such as reduction in electricity consumption and construction area, when compared to similar technologies, such as activated sludge (AS) (Rollemberg et al., 2018).

According to Wu et al. (2020), linear alkylbenzene sulfonate (LAS) is a low-cost surfactant, widely used in household detergents, which has seen a significant increase in its production and consumption over the years. This increase in consumption has been reflected in the concentrations of LAS present in sanitary sewage, which vary from 3 to 20 mg L^{-1}.

Cui et al. (2022) state that LAS concentrations of 0.3 to 10 mg L^{-1} already have a toxic effect on aquatic biota and can cause stress to biomass in aerobic wastewater treatment systems. Almeida et al. (2024) describe the importance of a controlled stress source in AGS systems for the production of biopolymers. Thus, the use of AGS to treat wastewater containing LAS appears to be an opportunity in the sanitation sector, since the stress caused by the presence of LAS can enhance the production of resources.

Studies evaluating the effect of LAS on the production and recovery of resources in aerobic granulation systems have not yet been reported. Therefore, this work investigated the production of

EPS, ALE, and tryptophan in an AGS reactor operated in the presence of LAS and evaluated the biomass stability in response to the stress caused by this pollutant.

METHODOLOGY

An 8-L AGS sequencing batch reactor (SBR) was operated with cycles of 6 h (20-min filling, 120-min anaerobic reaction, 214-min aerobic reaction, 5-min settling, and 1-min decanting), volumetric exchange ratio of 50%, and hydraulic detention time (HRT) of 12 h. Aeration was provided by a mini air compressor, and the air flow was kept constant (6 L min^{-1}) throughout the experiment.

The reactor was operated over two phases (without LAS and with LAS) that were carried out in sequence. The reactor was fed with synthetic sanitary sewage containing 1000 mg COD L^{-1} (propionic acid), 50 mg N-NH_4^+ L^{-1} (ammonium chloride), and 7 mg P-PO_4^{3-} L^{-1} (potassium phosphate). The medium was buffered with 2.5 g L^{-1} of sodium bicarbonate, and, in the second phase, a concentration of 10 mg L^{-1} of LAS was added to the feed.

Resource production was evaluated based on the production of biopolymers present in the sludge structure. EPS (PS and PN) was quantified according to Huang et al. (2017), whereas ALE and TRY were quantified according to Ferreira dos Santos et al. (2022). COD, N-NH_4^+, N-NO_3^-, N-NO_2^-, P-PO_4^{3-}, and VSS were determined according to APHA (2012). LAS concentration was determined using the adapted method by Silva et al. (2017).

RESULTS AND CONCLUSIONS

The addition of LAS favored the production of EPS and ALE. However, the same behavior was not observed for tryptophan, which had a reduction in production (Figure 1). EPS production remained constant immediately after the addition of LAS. However, after around 70 days, a significant increase in EPS production was observed, reaching stabilization with concentrations above 900 mg EPS g^{-1} VSS. The same behavior was observed for ALE, which presented concentrations similar to those presented by Santos et al. (2022). Frutuoso et al. (2023b) state that ALE is a fraction of EPS capable of forming hydrogels and, therefore, contributing to the stability of the biomass. It is possible that AGS remained stable in the presence of LAS due to the high production of ALE during the phase under stress caused by this surfactant.

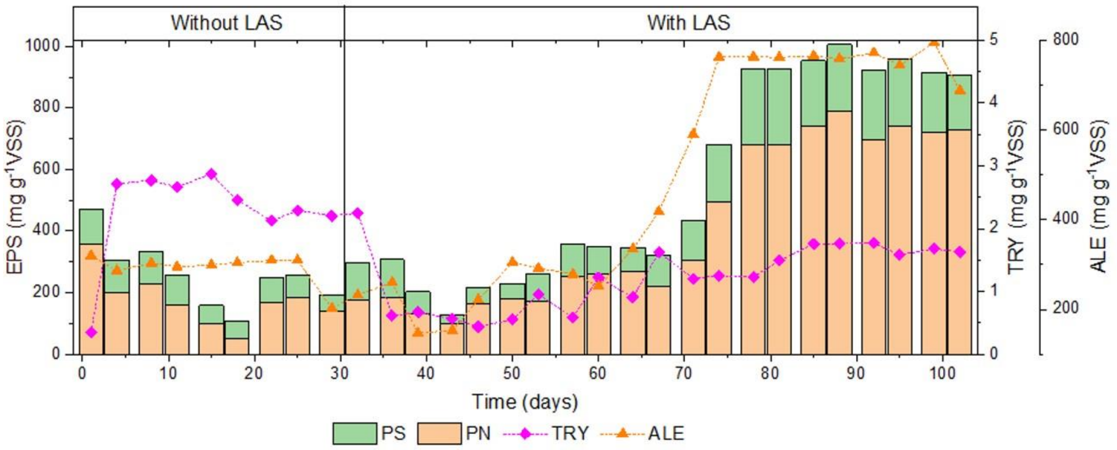

Figure 1. Production of extracellular polymeric substances (EPS) (in terms of polysaccharides, PS, and proteins, PN), tryptophan (TRY), and alginate-like exopolysaccharides (ALE).

Zahra et al. (2022) conducted a study on the main parameters and configurations that can enhance ALE production in sewage treatment systems and observed values ranging from 14.3 to 499.0 mg ALE g^{-1} VSS. This study obtained an average value of 756.5 ± 31.8 mg ALE g^{-1} VSS for the period after granulation, which is significantly higher than that reported in the literature. This high ALE production shows the potential of using AGS to treat LAS-containing effluents for resource utilization.

For tryptophan, a reduction in the production of this compound was observed shortly after the addition of LAS. It increased again after adapting to the new conditions with LAS, but remained below the initial values (Figure 1). Frutuoso et al. (2023a) presented similar concentrations in their work, reaching 3.5 mg TRY g^{-1} VSS. However, in the present study, TRY production in the presence of LAS reached an average of only 1.7 ± 0.1 mg TRY g^{-1} VSS, which is considered low.

Throughout the entire experiment, protein production was greater than polysaccharide, especially after the addition of LAS, which favored protein production in the EPS. Silva et al. (2023) state that high PN productions can facilitate the aggregation of granules, which may have prevented the loss of biomass that LAS can cause.

Finally, during the two phases, COD removal did not change significantly (93-94%). However, N and P removals increased after LAS addition, from 62% to 70% for N and from 14% to 20% for P. Concerning LAS removal, a very high efficiency could be reached (Table 1). Therefore, the presence of LAS increased the production of biopolymers in the AGS without compromising its performance. The large amount of these biopolymers in the sludge served as protection against the negative effects of LAS, showing how promising this technology is for treating the most diverse types of pollutants.

Table 1. Characteristics of influents, effluents and reactor performance.

Parameter	Without LAS	With LAS
COD_{inf} (mg L^{-1})	928 ± 98	972 ± 55
COD_{efl} (mg L^{-1})	43 ± 22	56 ± 18
COD_{rem} (%)	93 ± 4	94 ± 2
TP_{inf} (mg P-PO_4^{3-} L^{-1})	10,1 ± 0,3	11,2 ± 0,9
TP_{efl} (mg P-PO_4^{3-} L^{-1})	8,1 ± 0,9	8,0 ± 0,5
TP_{rem} (%)	13,8 ± 6,1	20,1 ± 9,5
TN_{inf} (mg N-NH_4^+ L^{-1})	47,7 ± 1,7	50,1 ± 3,4
N-$NH_4^+{}_{efl}$ (mg L^{-1})	0,5 ± 0,4	2,4 ± 2,9
N-$NH_4^+{}_{rem}$ (%)	99,0 ± 0,8	95,1 ± 6,1
N-$NO_2^-{}_{efl}$ (mg L^{-1})	2,3 ± 2,2	4,1 ± 1,9
N-$NO_3^-{}_{efl}$ (mg L^{-1})	15,4 ± 8,0	8,7 ± 2,5
TN (%)	61,8 ± 16,6	70,0 ± 4,5
LAS_{inf} (mg L^{-1})	-	10,9 ± 1,4
LAS_{efl} (mg L^{-1})	-	0,1 ± 0,1
LAS_{rem} (%)	-	99,1 ± 1,5

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REFERENCES

Frutuoso, F. K. A., Santos, A. F. dos, França, L. L. S., Barros, A. R. M., & Santos, A. B. dos (2023a). Influence of operating regime on resource recovery in aerobic granulation systems under osmotic stress. *Bioresource Technology*, *376*(128850), 128850.

Frutuoso, F. K. A., Santos, A. F. dos, França, L. L. S., Barros, A. R. M., & Santos, A. B. dos (2023b). Influence of salt addition to stimulating biopolymers production in aerobic granular sludge systems. *Chemosphere*, *311*(137006), 137006.

Carvalho, C. A. de, Santos, A. F. dos, Ferreira, T. J. T., Lira, V. N. S. A., Barros, A. R. M., & Santos, A. B. dos (2021). Resource recovery in aerobic granular sludge systems: is it feasible or still a long way to go? *Chemosphere*, *274*(129881), 129881.

Apha, AWWA, & Wef. (2012). *Standard methods for the examination of water and wastewater* (22º ed). American Public Health Association.

Cui, X., Ren, Q., Zhang, J., & Zhou, Y. (2022). Removal kinetics of linear alkylbenzene sulfonate in a batch-operated oxygen based membrane biofilm reactor treating greywater: Quantitative differentiation of adsorption and biodegradation. *The Science of the Total Environment*, *806*(150523),

Rollemberg, S. L. S., Barros, A. R. M., Firmino, P. I. M., & Santos, A. B. dos (2018). Aerobic granular sludge: Cultivation parameters and removal mechanisms. *Bioresource*

Santos, A. F. dos, Frutuoso, F. K. A., de Carvalho, C. A. de, Lira, V. N. S. A., Barros, A. R. M., & Santos, A. B. dos (2022). Carbon source affects the resource recovery in aerobic granular sludge systems treating wastewater. *Bioresource Technology*, *357*(127355), 127355.

Huang, X., Zheng, J., Liu, C., Liu, L., Liu, Y., & Fan, H. (2017). Removal of antibiotics and resistance genes from swine wastewater using vertical flow constructed wetlands: Effect of hydraulic flow direction and substrate type. *Chemical Engineering Journal (Lausanne, Switzerland: 1996)*, *308*, 692–699.

Almeida, F. D. P., Carvalho, C. B. de, Barros, A. R. M, Frutuoso, F. K. A., & Bezerra dos Santos, A. (2024). Aerobic granulation and resource production under continuous and intermittent saline stress. *Chemosphere*, *360*(142402), 142402.

Silva, L. G., Gavazza, S., Florencio, L., & Kato, M. T. (2017). Quantificação de alquilbenzeno linear sulfonato em estação de tratamento de efluentes e rios por cromatografia líquida de alta eficiência e extração em fase sólida. *Quimica nova*. https://doi.org/10.21577/0100-4042.20170007

Wu, P., Zhang, X., Wang, C., Liu, W., & Faustin, F. (2020). Feasibility of applying intermittent aeration and baffles for achieving granular nitritation in a continuous short-cut denitrifying phosphorus removal system. *The Science of the Total Environment*, *715*(137023), 137023.

Zahra, S. A., Abdullah, N., Iwamoto, K., Yuzir, A., & Mohamad, S. E. (2022). Alginate-like exopolysaccharides in aerobic granular sludge: A review. *Materials Today: Proceedings*, *65*, 3046–3053.