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Evaluation of the combination of Linear Alkylbezene Sulfonate (LAS) with emerging pollutants: an approach to aquatic ecotoxicity and Electron Beam treatment

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Abstract: The presence of surfactants and other emerging pollutants in water bodies has become a major environmental concern in several places around the world, since these pollutants cause adverse problems in aquatic ecosystems and compromise public health, regarding the supply of good quality water. These pollutants often originate from various sources, including industrial activities, pharmaceuticals, and personal care products. A critical aspect of this issue is that many of these pollutants and their mixtures are difficult to degrade in biological treatment processes, requiring auxiliary treatments. Electron beam technology has been applied in various environmental matrices to degrade these pollutants, helping not only to increase degradability, as also to reduce the toxicity of these compounds. The present work aimed to evaluate LAS surfactant single and combined effects with emerging pollutants (caffeine and ciprofloxacin antibiotic) to aquatic organism *Daphnia similis*. It was also evaluated the electron beam (EB) treatment for reducing toxicity of single compounds. The organisms were exposed to samples (non-irradiated and irradiated LAS and mixtures) for 48 hours and the observed effect was immobility. The toxicity was evaluated through EC50 (median effective concentration) calculations. The EC50 values showed a high toxicity level for surfactant LAS with EC50s below 9%. Caffeine and Ciprofloxacin EC50 data were higher than 20%. EC50% values of the mixtures were close to the values of the isolated compounds. After the EB treatment (5 kGy) about 70% acute toxicity reduction was obtained for LAS surfactant. The combined presence of surfactants and emerging pollutants in aquatic matrices requires a comprehensive approach to monitoring and mitigating their impacts to protect aquatic ecosystems and human health.

Keywords: Aquatic ecosystem, emerging pollutats, electron beam treatment, LAS.

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Avaliação da combinação do Linear Alquilbezeno Sulfonato (LAS) com poluentes emergentes: uma abordagem para ecotoxicidade aquática e tratamento por feixe de elétrons

Resumo: A presença de surfactantes e outros poluentes emergentes em corpos hídricos tem se tornado uma grande preocupação ambiental em diversos locais do mundo, uma vez que esses poluentes causam problemas adversos nos ecossistemas aquáticos e comprometem a saúde pública, no que diz respeito ao fornecimento de água de boa qualidade. Esses poluentes geralmente são advindos de diversas fontes, incluindo atividades industriais, farmacêuticas e produtos de higiene pessoal. Um aspecto crítico desta questão é que muitos destes poluentes e suas misturas são de difícil degradação em processos biológicos de tratamento, necessitando de tratamentos auxiliares. A tecnologia por feixe de elétrons vem sendo aplicada em diversas matrizes ambientais para degradação destes poluentes, auxiliando não só no aumento da degradabilidade, mas também na diminuição de toxicidade destes compostos. O presente trabalho teve como objetivo avaliar os efeitos isolados e combinados do surfactante LAS com poluentes emergentes (cafeína e antibiótico ciprofloxacina) no organismo aquático *Daphnia similis*. Assim como o tratamento por feixe de elétrons para redução da toxicidade dos compostos isolados. Os organismos foram expostos às amostras (não irradiadas e irradiadas de LAS e misturas) por 48 horas e o efeito observado foi imobilidade. a toxicidade foi avaliada através dos cálculos da CE50 (concentração efetiva mediana). Os valores de CE50 demonstraram elevada toxicidade do surfactante LAS com CE50 abaixo de 9%. Os dados de EC50 de cafeína e ciprofloxacina foram superiores a 20%. Os valores de CE50% das misturas foram próximos aos valores dos compostos isolados. Após o tratamento com feixe de elétrons (5 kGy) obteve-se cerca de 70% de redução da toxicidade aguda para o surfactante LAS. A presença combinada de surfactantes e poluentes emergentes em matrizes aquáticas exige uma abordagem abrangente para monitorizar e mitigar os seus impactos para proteger os ecossistemas aquáticos e a saúde humana.

Palavras-chave: Ecossistema aquático, irradiação por feixe de elétrons, LAS, poluentes emergentes.

1. INTRODUCTION

Linear Alkylbezene Sulfonate (LAS) is one of the most used anionic surfactants in industry, in cleaning and hygiene products, being frequently released in effluents in the aquatic environment. The global surfactant market data was more than USD 45.5 billion in 2023 [1].

In aquatic environments, surfactants are responsible for several changes in water quality, including foam formation, which reduces the biodegradation capacity of waterways. Additionally, surfactants can enhance the solubility of organic contaminants in aqueous solutions, thereby contributing to the depreciation of water quality [2,3]. Another important aspect to consider is the biodegradability of many surfactants, which is highly dependent on environmental conditions. Under aerobic conditions, linear alkylbenzene sulfonate (LAS) is biodegradable. However, under anaerobic conditions, LAS becomes more persistent and resistant to degradation [4,5].

Caffeine is the most consumed stimulant by humans. The literature report that the caffeine can be found in surface waters, groundwater and in drinking water. In Brazil, of a total of three hundred and twenty-nine (329) samples of surface waters collected in the São Paulo state, caffeine showed the highest frequency of detection (97% of samples) [6]. On the other hand, and concerning pharmaceuticals, ciprofloxacin is a fluoroquinolone antibiotic that has emerged as another major environmental pollutant currently. Over the past decades, this pollutant has been commonly detected in environmental matrices, posing high environmental risks to aquatic life [7,8].

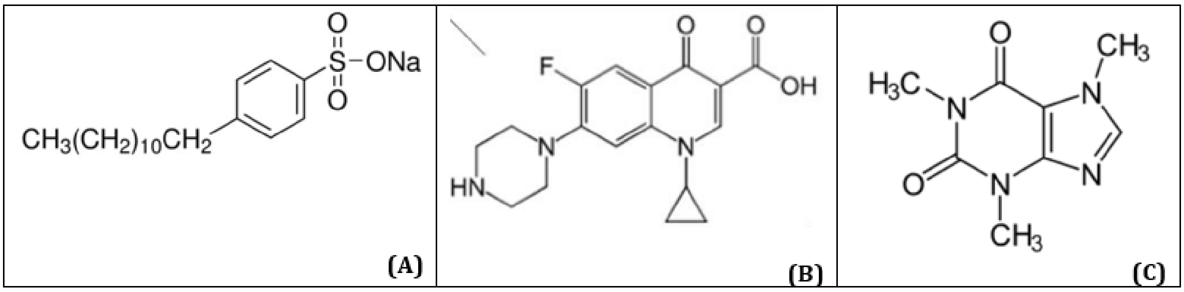
These critical factors highlight the necessity for integrated treatment processes to enhance the degradability of surfactants and other pollutants in wastewater. The electron beam irradiation has been applied in several environmental matrices, for the treatment of industrial and domestic wastewater and hazardous pollutants, e.g., textile dyes, pharmaceuticals, surfactants, tannery [9,10]. In this process, highly reactive intermediates (e.g. hydroxyl radicals) generated by water radiolysis and the radicals that form in radical transfer reactions induce the degradation of the target harmful organic pollutants, forming secondary radicals. Free radicals arising due to the ionization of water molecules interact chemically with each other or with molecules close to them. Among the main radicals formed in radiolysis, the hydroxyl radical (OH•) is the primary oxidant in the degradation of organic compounds. Also, hydroxyl radical is suggested to be the main reactive intermediate that induces the degradation of organic molecules [11].

In this context, the present study aimed to evaluate the individual and combined effects of the surfactant LAS, caffeine, and the antibiotic ciprofloxacin on the aquatic organism *Daphnia similis*. Additionally, the study assessed the potential of electron beam treatment to reduce the toxicity of these individual compounds.

2. MATERIALS AND METHODS

Linear Alkylbezene Sulfonate (LAS) surfactant (CH3(CH2)11C6H4SO3Na; CAS number: 25155-30-0; purity > 99%), ciprofloxacin (1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1ylquinoline-3-carboxylic acid; CAS number: 85721-33-1; purity >98%) and caffeine (C8 H10N4 O2 ; MM = 194.19 g mol−1; 1,3,7-Trimethylpurine-2,6-dione; CAS 58-08-2; purity >98%) were purchased from Sigma- Aldrich. The molecular structures of the compounds were presented at Figure 1.

Figure 1: Molecular structure: (A) Linear Alkylbezene Sulfonate; (B) Ciprofloxacin; (C) Caffeine



The assays performed for both LAS surfactant, caffeine and ciprofloxacin antibiotic, single and in mixture included acute toxicity assays with *Daphnia similis* cladoceran. The methodology was in accordance with Brazilian Technical Standard Methods [12]. The juvenile individuals (6–24 h) were exposed to the samples (LAS surfactant, caffeine and ciprofloxacin antibiotic, single and in mixture, non-irradiated and irradiated) for 48 h, with 20 organisms per concentration in each assay, which was realized in duplicate. A minimum of five concentrations were evaluated per assay and the concentrations were established after preliminary assays. Furthermore, a control only with natural water (the same used in the *D. similis* culture) was also carried out. The observed effect after the exposure was immobility. The acute toxicities of two binary mixtures were also evaluated herein: LAS surfactant + caffeine and LAS surfactant + ciprofloxacin antibiotic (1/1 ratio, w/w).

The toxicity data was expressed as EC50 (effect median concentration). The EC50 is an inversely proportional parameter to the toxicity. Statistics were applied according to Brazilian ABNT standard methods, with EC50 values obtained by the Trimmed Spearman-Karber method [13] and an analysis of variance (ANOVA) with a post hoc Dunnett's test was applied to verify the significance of differences between controls and experimental treatments values (significant differences, $p < 0.05$).

The samples were irradiated in an electron accelerator (Dynamitron model) at the Radiation Technology Center (CETER/IPEN). Parameters Applied: 1.4 MeV, fixed energy, batch system, conveyor speed of 6.72 m min^{-1} and variable electric current according to the required doses. The samples were irradiated at 5 kGy dose. The efficiency of irradiation in terms of toxicity reduction (TR%) after EBI treatment was obtained from the EC50 values, transformed into toxicity units (TU), as follow equation 1:

$$TU = 100/_{EC50} \quad TR\ (\%) = (TU_0 - TU_{irrad}/TU_0) \times 100 \qquad \text{(equation 1)}$$

Where: TU_0 = Toxicity Units before irradiation and TU_{irrad} = Toxicity Units after irradiation.

3. RESULTS AND DISCUSSIONS

Acute toxicity effects, expressed by EC50, of LAS surfactant, caffeine and ciprofloxacin antibiotic and binary mixtures to *D. similis* are reported in Figure 2. While EBI efficiency regarding toxicity of individual compounds (LAS; caffeine and ciprofloxacin) is summarized in Figure 3.

Figure 2: Acute toxicity (EC50%) data to *Daphnia similis* exposed to LAS surfactant, caffeine and ciprofloxacin antibiotic and binary mixtures

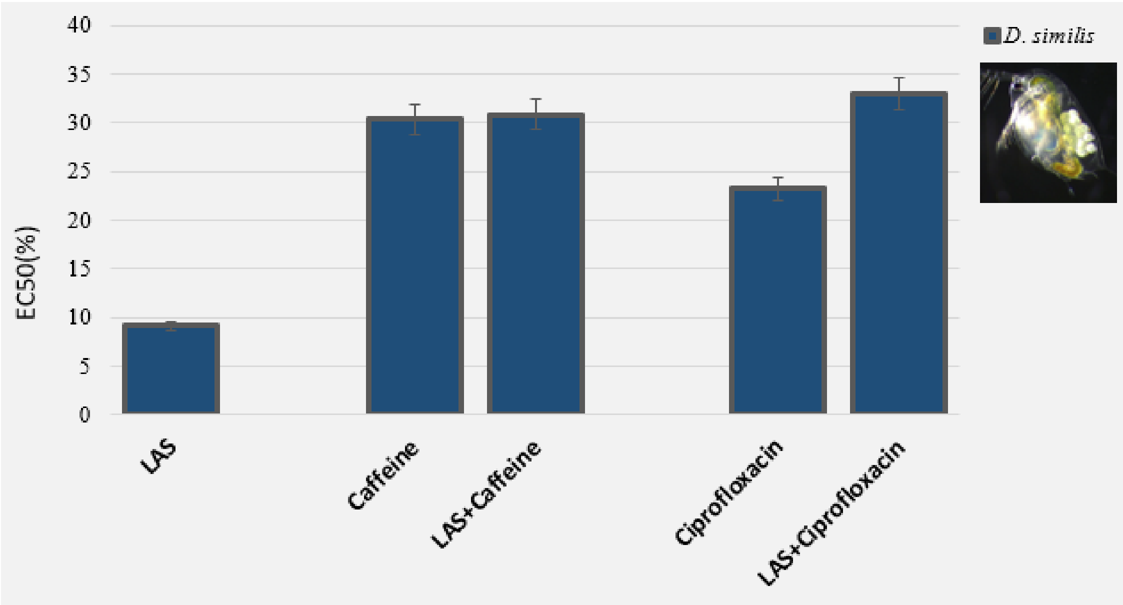
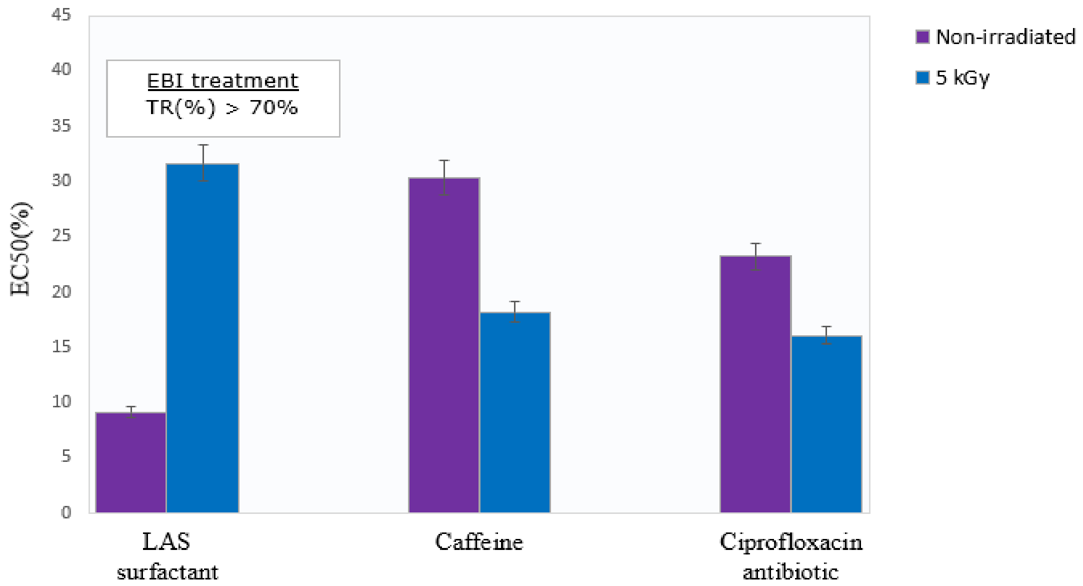


Figure 3: Acute toxicity of LAS surfactant, caffeine and ciprofloxacin and applied EBI dose (5kGy)



The EC50 values displayed in Figure 2 showed a high toxicity level for surfactant LAS, with EC50 values below 9%. In contrast, the EC50 values for caffeine and ciprofloxacin were above 20%. The EC50 data for the mixtures were similar to those of the individual compounds. Regarding the results obtained after the EBI treatment (Figure 3), considering 5 kGy as a suitable dose for acute toxicity removal, about 70% acute toxicity reduction was obtained for LAS surfactant. While no significant improvement in toxicity reduction was observed for the other compounds following EBI treatment.

Concerning LAS, similar results were obtained with 88% reduction in acute effects for *D. similis* following treatment at 3 kGy [14]. Regarding the removal of surfactants from effluents treated with electron beam, recent study has reported the removal of non-ionic surfactants from laundry effluent after exposure to a 3 kGy dose [15], and an 89.1% removal of LAS following a 10 kGy dose [16].

Previous studies have reported LAS toxicity to aquatic biota, highlighting biochemical, physiological and metabolic alterations, in addition to the decreased resistance of several species to environmental stress [2]. Concerning acute effects, literature data showed the high toxicity for organisms to distinct trophic level: *Hyallela azteca* (anfípode) EC50 = 0.91 mg/L; *Daphnia magna* (crustacean) EC50= 6.31 mg/L; *Danio rerio* (fish) EC50 = 6.6 mg/L [17].

Regarding surfactants mixtures, Garcia et al., 2024 [18], demonstrated that binary mixtures were very toxic for *Daphnia similis*. The EC50 for the anionic + fatty alcohol ethoxylate nonionic surfactant was 4.09 ± 0.69 and for anionic + alkylene oxide nonionic surfactant mixture was 3.34 mg/L. This study demonstrates that surfactants alone are very toxic to aquatic biota, which poses a great environmental concern, including when it comes to mixing them with other contaminants.

The presence of caffeine in aquatic environments is an increasing concern due to its widespread use and subsequent release into water bodies. Although the acute toxicity of caffeine to some aquatic organisms is generally considered moderate, with EC50 values typically exceeding 20%, its interaction with other pollutants can substantially enhance its toxic effects. Studies indicate that caffeine disrupts physiological and behavioral processes in aquatic organisms. For instance, in *Daphnia magna*, high concentrations of caffeine have been shown to reduce reproduction rates and alter larval development [19, 20].

A recent study has reported mixtures response of surfactants and other pollutants. In evaluation of the effects of caffeine and LAS effects on *Daphnia magna,* the mixture resulted in inhibition of the offspring and molting index. Furthermore, a significant decrease in the total offspring produced was observed, with the extent of the effect varying depending on the concentrations of caffeine and LAS in the analyzed scenarios [21].

Regarding ciprofloxacin, although its toxicity is relatively low for certain aquatic organisms, its interaction with other pollutants, such as surfactants, may potentially amplify its toxic effects. Ciprofloxacin has been shown to interfere with bacterial populations in aquatic ecosystems, potentially disrupting microbial communities and the processes they regulate. Studies indicate that ciprofloxacin, when combined with surfactants like LAS, can exhibit synergistic toxic effects, leading to greater harm to aquatic organisms, affecting their reproduction and development [22, 23]. The increased cell permeability caused by surfactants may facilitate the absorption of ciprofloxacin, exacerbating its toxicity.

4. CONCLUSIONS

Due the complexity of interactions between aquatic pollutants, integrated approaches are essential to assessing ecological risks. Future studies should focus on the mechanisms of toxic interactions between caffeine and surfactants, as well as other pollutant combinations. Effective waste management and effluent treatment policies are essential to minimize the release of these compounds into aquatic environments. The implementation of stringent regulations, along with the development of advanced water treatment technologies can mitigate the negative impacts of these substances.

Ecotoxicological assays and the evaluation of ionizing radiation technology for the treatment of surfactants provide relevant information about these hazardous pollutants, with a possible reduction of toxic loads and can be associated with management plans to minimize the impact of surfactants and other emerging pollutants on aquatic ecosystems.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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