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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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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. Furthermore, surfactants can increase the solubility of organic contaminants in aqueous, which contribute to depreciation of water quality [2,3]. Another aspect to be considered is that biodegradability of many surfactants which depends on environmental conditions: under aerobic conditions, LAS is degradable. However, under anaerobic conditions LAS becomes persistent and difficult to degrade [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, caffeine detection was 97%, in surface waters samples, in São Paulo state [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 aspects confirm the need for combined treatment processes for better 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, the electron beam can promote the decomposition of organic contaminants as a result of their reactions with highly reactive species from water radiolysis [11].

In this context, the present study aimed to evaluate the single and combined effects of LAS surfactant, caffeine and ciprofloxacin antibiotic to aquatic organism *Daphnia similis*. Furthermore, it was evaluated the electron beam treatment potential for reducing toxicity of single compounds.

2. Methodology

Chemical compounds

Linear Alkylbezene Sulfonate (LAS) surfactant ($CH_3(CH_2)_{11}C_6H_4SO_3Na$; 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 ($C_8H_{10}N_4O_2$; 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 structure of the compounds were presented at Fig. 1.

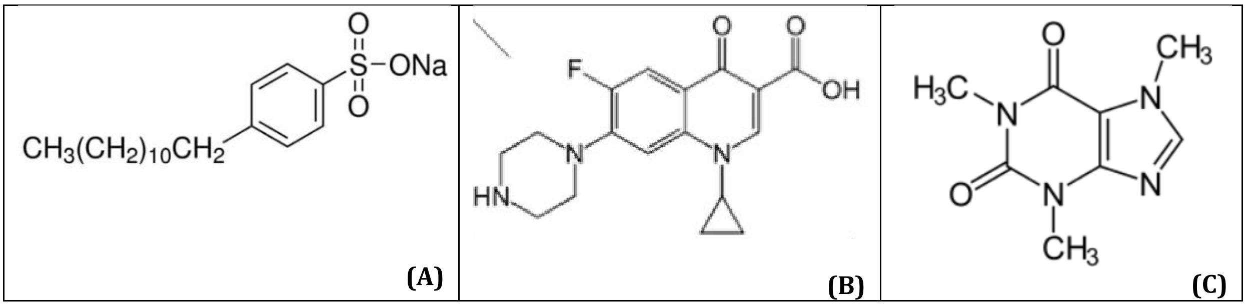

Figure 1: Molecular structure: (A) Linear Alkylbezene Sulfonate; (B) Ciprofloxacin; (C) Caffeine.

Ecotoxicity assay

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 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, $p < 0.05$).

Electron Beam Irradiation (EBI) treatment

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 (RT%) 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: TUo = Toxicity Units before irradiation and TUirrad = Toxicity Units after irradiation

3. Results and Discussion

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

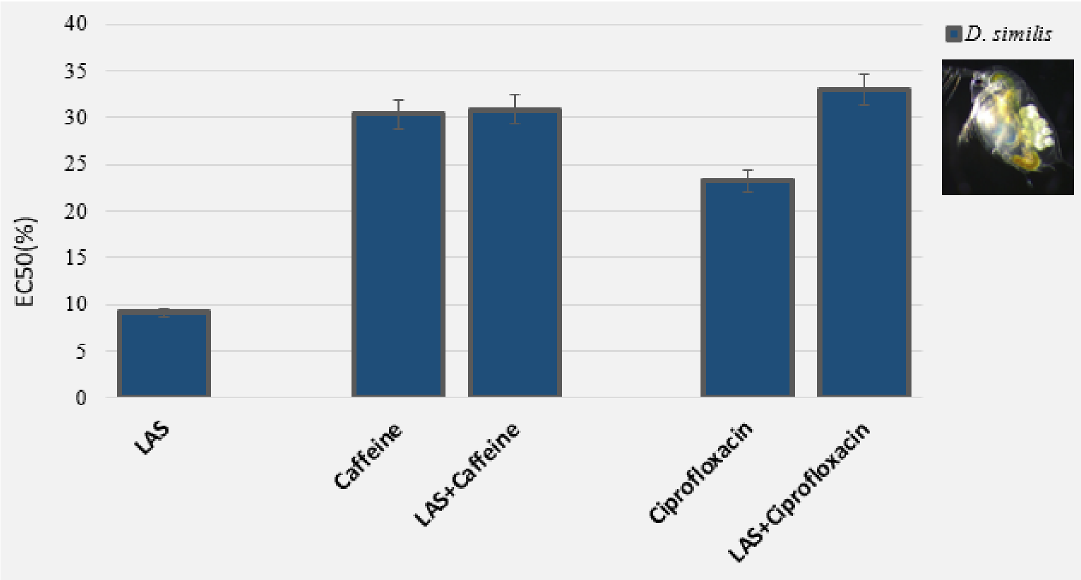

Figure 2: Acute toxicity (EC50%) data to *Daphnia similis* exposed to LAS surfactant, caffeine and ciprofloxacin antibiotic and binary mixtures.

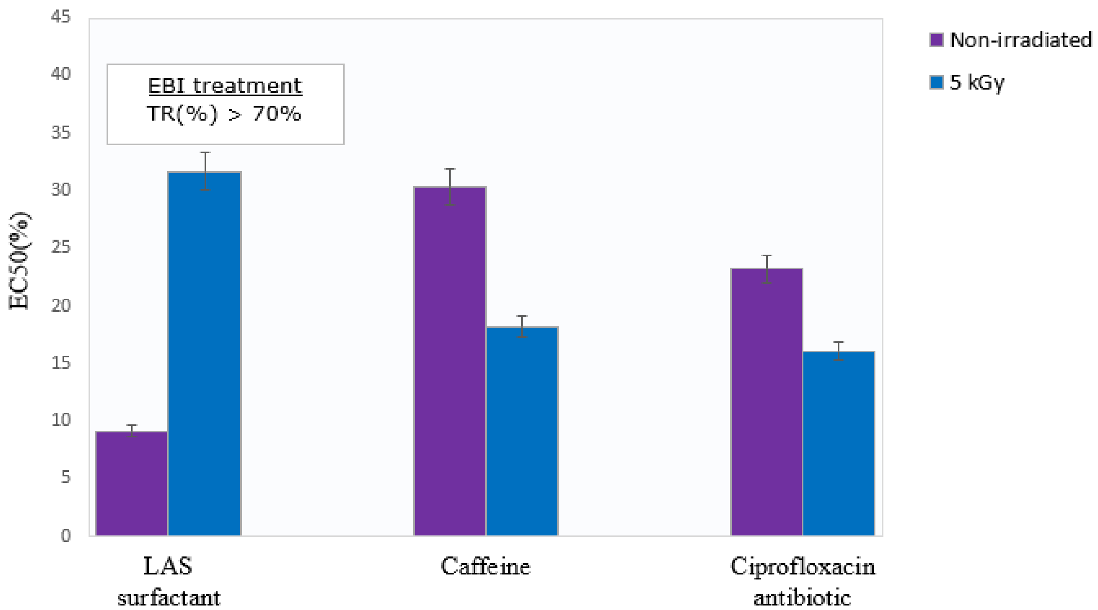

Figure 3: Acute toxicity of LAS surfactant, caffeine and ciprofloxacin and applied EBI dose (5kGy).

The EC50 values displayed in figure 2 showed a high toxicity level for surfactant LAS with EC50s below 9%. Caffeine and Ciprofloxacin EC50 data were higher than 20%. The EC50% values of the mixtures were close to the values of the isolated 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 for the other compounds no improvement was observed in relation to the toxicity reduction after EBI treatment.

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 [14]. A recent study has reported mixtures response of surfactants and other pollutants. In evaluation of caffeine and LAS effects on *Daphnia magna*, the mixture caused in *Daphnia magna* an inhibition on offspring index and molting index, furthermore a significant decrease in the total offspring produce, depending on the scenario analyzed in relation to caffeine and LAS concentrations [15].

4. Conclusions

Ecotoxicological assays and the evaluation of ionizing radiation technology for the treatment of surfactants provide relevant information about these hazardous pollutants. Such information allows treatments 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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