# ECOTOXICOLOGICAL APPROACH OF SURFACTANTS TREATED BY IONIZING RADIATION

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## Abstract
Removing surfactants from liquid effluents has been a fundamental issue since they are found in several industrial effluents, hospitals, restaurants, and even homes. When disposed into aquatic environmental, surfactants can implicate in significant changes, including several adverse effects to aquatic organisms. The present study was developed to assess the ecotoxicological effects of surfactants (anionic and nonionic) to aquatic organisms *Vibrio fischeri* bacteria, *Daphnia similis* crustacean. The ionizing radiation (Electron Beam Irradiation - EBI) was applied as a possible technology for the treatment of these contaminants in order to reduce acute toxic effects. The obtained data showed that the surfactants were toxic for both organisms, and the nonionic were more toxic than anionic. EB irradiation reduced surfactants toxicity by 40% acute toxic effects for nonionic surfactant and more than 70% for anionic, for both exposed organisms classes.

## Introduction
The surfactant market is estimated to reach US$ 39.86 billion by 2021, an increase of 5.4% between 2016 and 2021. Surfactants are the single most important ingredients in laundry and household cleaning products, comprising from 15 to 40% of formulation of these products. Furthermore, they are used in several industrial processes, such as in the textile, pharmaceutical, tannery, paper, chemistry industries [1,2].
Despite the importance of surfactants in daily life and industry processes, they are one of the main hazardous pollutants in wastewater and water bodies. Beyond the visual aspect of foam, the impacts of detergents on rivers are very critical. Practically the entire biota can be affected, with a significant loss of biodiversity. The biodegradation capacity of the water body is reduced due to the depreciation of the dissolved oxygen level in water. As a consequence of surfactants residues we have also the flowering of algae, which often releases toxins into the water bodies. Previous studies have been reported toxic effects of surfactants to different aquatic organisms including algae, daphnids, and bacteria, with data of effect concentrations (EC) lower than 0.5 mg $L^{-1}$ to *Vibrio fischeri* bacteria, for example [3,4]. Moreover, these contaminants can interfere in energy metabolism and transport of nutrients and oxygen; compromising the enzymatic activities and normal physiological function of organisms. Linear alkylbenzene sulphonate (LAS) in liver and internal organs of rainbow trout showed rapid absorption into systemic circulation [5,6].
Important concentrations of surfactants have been detected in surface waters and effluents in different regions of the world. For anionic surfactants: in Brazil, it was detected in surface waters concentrations between 14 and 155 μg $L^{-1}$; in India, the levels in surface and ground water system are ranging from 2 to 62 μg $L^{-1}$; in Nile river (Egypt) in surface water ranged between 0.07–2.45 mg $L^{-1}$ [7,8,9].

Regarding surfactants characterization, analytical and assessment techniques to achieve effective identification and quantification of several surfactants in different environmental matrices have been developed, with appropriate extraction, purification, and preconcentration. In this sense, several techniques such as spectrophotometry, titrimetry, and chromatography have been used [10,11].

Due the capability to specifically identify surfactant types, chromatographic techniques (mainly HPLC-MS and GC/MS) are the most common methods usually adopted to analyse various surfactants (anionic, cationic, non-ionic, amphiprotic, and semi-polar surfactant groups) and their degraded products, mainly when the surfactant is a component of an environmental matrix. Although relatively simpler techniques, such as spectrophotometric, can be applied if the surfactant is present as a single component [11].

The chemical characteristics, the low biodegradation, high toxicity of surfactants, confirm the needs for combined treatment processes for better degradability and in this regard, a possible technology may be ionizing radiation. The electron beam irradiation has been applied in several environmental matrices, for the treatment of industrial and domestic wastewater and hazardous pollutants [12,13].

In this context, the aim of the present study was to assess the acute toxicity of surfactants in aquatic organisms from distinct trophic levels, as well as electron beam treatment efficiency for toxicity reduction.

## Experimental

### Samples

The present study evaluated the surfactants nonionic (Alkyl aryl ethoxylated and aromatic sulphonate) and anionic (Sulphonated Dodecylbenzene) in an aqueous solution. The maximum concentration evaluated in acute assays was 1g $L^{-1}$.

### Electron beam irradiation

The liquid effluents were irradiated using a Dynamitron Electron Beam Accelerator and applying the following parameters: 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 distributed in pyrex vessels, ensuring 4 mm sample thickness, and the vessels were protected by plastic wraps. The samples were irradiated at 2.5 kGy dose.

### Acute toxicity assays

Acute toxicity assays with *Daphnia similis* were carried out in accordance with NBR 12713: 2016 [14]. A minimum of five concentrations and a negative control with natural water (the same used in the *D. similis* culture) were evaluated per assay. Twenty organisms per concentration, at least 6–24 h, were exposed to the samples for 48 h. The observed effect after the exposure period was immobility. The results were expressed as EC50, the median concentration to observe an effect for 50% of all exposed organisms. Statistics were applied according to the standard methods recommendation, obtained by the Trimmed Spearman-Karber method.

The assays with *Vibrio fischeri* bacteria were performed in Microtox®, M-500, Microbics system. The bacteria luminescence was analyzed before and after 15 min of exposure to the samples; toxicity was evidenced by loss of luminescence. The assays were performed in triplicate, with a minimum of four concentrations, with a dilution factor of 2. The negative control with diluent solution (NaCl 2%) and a positive control with phenol were also performed. The methodology was in accordance with Brazilian Technical Standard Methods NBR

15411:2012 [15]. The EC50 values were obtained from a statistical procedure based on the gamma effect (γ) and the sample concentration (C%), using linear regression.
For both data, sample toxicity removal (%) after EBI treatment as calculated from EC 50 values, transformed to toxicity unit (UT), before and after irradiation.

**Results and discussion**

Acute toxic effects and EBI treatment values are reported in Table 1, Figure 1 and 2, respectively.

**Table 1.** Acute toxicity (EC50 values) and confidence limits (CL) of anionic and nonionic surfactants samples.

| Aquatic organism | Surfactant | EC50 (mg $L^{-1}$) | CL 95% (mg $L^{-1}$) |
|---|---|---|---|
| *D. similis* | Anionic | 19.7 | (15.8-24.6) |
| | Nonionic | 11.0 | (9.2-13.2) |
| *V. fischeri* | Anionic | 64.4 | (23.7-74.6) |
| | Nonionic | 2.3 | (0.6-8.0) |

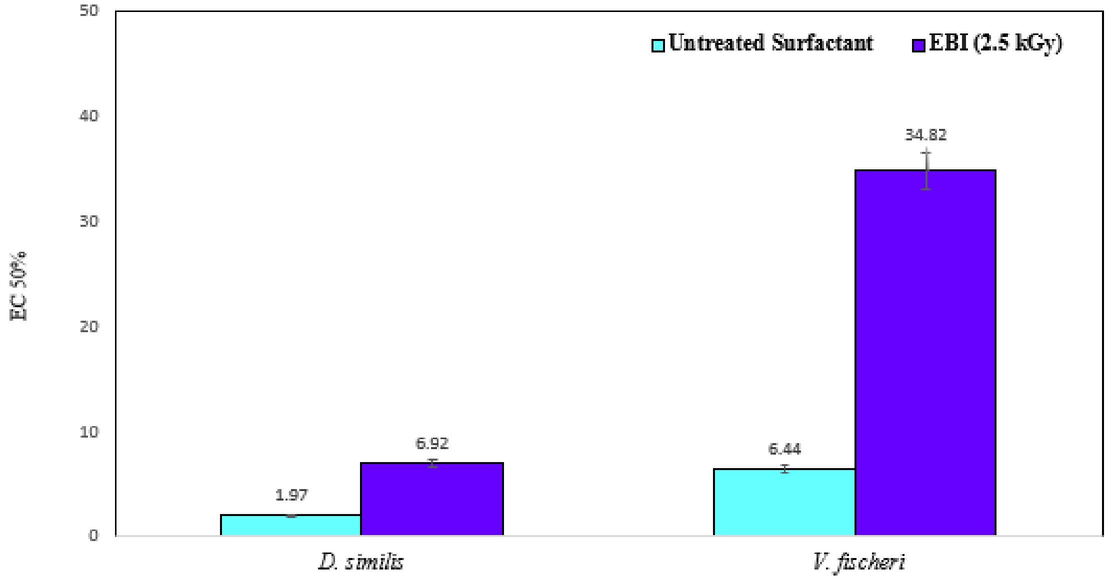


**Figure 1.** Acute toxicity (EC50% values) of anionic surfactant versus applied EBI dose.

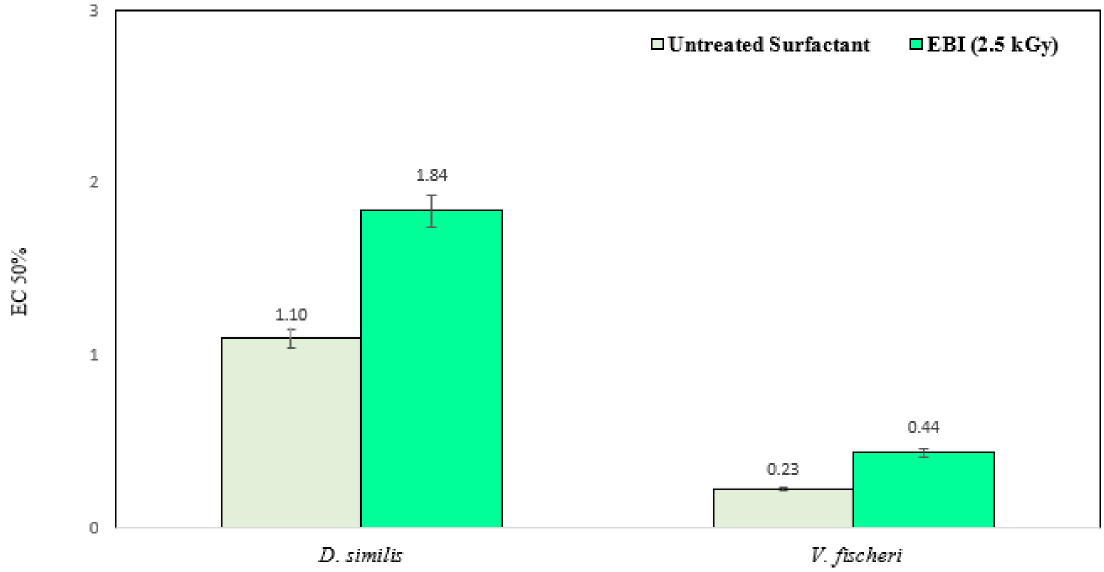


**Figure 2.** Acute toxicity (EC50% values) of nonionic surfactant versus applied EBI dose.

The acute effects data obtained herein showed that the surfactants were toxic for both organisms, which nonionic are more toxic than anionic, with EC50 lower than 11 mg $L^{-1}$ (Table 1).

Previous studies reported acute toxic effects of surfactants to different aquatic organisms including algae, daphnids, and bacteria. For *V. fischeri*, were described values of EC50 = 0.35mg $L^{-1}$ (sodium dodecyl sulfate) and 1.92 (amine-oxide-based surfactant AO-R12) [3,4]. For several algae species exposed to cationic surfactants, median growth inhibition concentration ranged between 0.55-10.6 mg $L^{-1}$, with deleterious effects for photosynthetic activity [16]. While exposure to fish (*Clarias gariepinus*) LC50 (mg $L^{-1}$) values for anionic surfactants were 10.57-15.16 and for nonionic between 16.88-22.61 [17].

Regarding the results obtained after the EBI treatment (Figure 1 and 2), considering 2.5 kGy as a suitable dose for acute toxicity removal, about 40% acute toxicity removal were obtained for nonionic surfactant for both organisms. While the reduction was better for anionic, approximately 70% removal of acute effects for *D. similis* and 80% for *V. fischeri*.

## Conclusion

The surfactants are critical issues for aquatic environmental and the present study showed that they were very toxic to both organisms. The proposal of this study was also to evaluate the toxicity reduction of the samples after treatment by electron beam. This technology has been obtaining promising results in the treatment of several organic compounds. In fact, in this study, the electron beam technology was effective in reducing the toxicity of the surfactants, even that the low, the effects reduction was considerable.

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