Radiation processing of detergents and possible environmental benefits*

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Abstract. Detergents at waters inducing negative changes for biological degradability and water general quality. Some authors have evidenced a considerable amount of anionic surfactant and toxic effects into natural water and effluents related to detergents. The objective of the study was to apply electron irradiation for reducing toxicity, and for degradation of surfactants. To quantify surfactant LAS determination as MBAS (methylene blue active substances) was applied. The capacity of radiation to reduce surfactants was evidenced for real effluent and for water solution containing sodium dodecyl sulfate, linear alkylbenzene sulfonate (LAS), separately. An electron beam accelerator (EBA) 1.5 MeV was the radiation source. Anionic surfactant solutions as well as real effluents resulted in less toxic samples after irradiation. Toxicity was evaluated for *Vibrio fischeri* and *Daphnia similis*. An important decline of total anionic surfactant was observed after irradiation to doses: 6.0 kGy and 20 kGy (surfactant in water solutions and effluents, respectively). To conclude, EBA irradiations accounted for 88% to 96% less toxic surfactants solutions and effluents and 68% to 96% for MBAS compounds decomposition.

Key words: EB irradiation • anionic surfactants • effluent • *Vibrio fischeri* • *Daphnia similis*
authors evidenced a considerable amount of surfactant and toxic effects in natural waters and effluents [6, 10]. Bigard et al. reported 754.3 kg of anionic surfactant/day in a Brazilian wastewater treatment plant [4]. These findings reinforced the search for advanced alternatives to improve industrial effluents.

Ionizing radiation has been studied as a pretreatment for especial kind of effluents with surfactants [10, 13]. These authors used an electron beam accelerator, EBA for their purposes, although the first publication on surfactant degradation applied gamma radiation [12].

The present paper shows the efficiency of electron beam irradiation for the reduction of acute toxicity caused by anionic surfactants. The degradation of anionic surfactants induced by electron irradiation was also considered. Two acute toxicity assays were applied with the luminescent bacteria Vibrio Fischeri and with the freshwater microcrustacean Daphnia similis.

**Material and methods**

Ionizing radiation from EBA was applied in order to reduce the level of surfactants from real effluents and from cleaned waters. Sodium dodecyl sulfate and sulfate linear alkylbenzene were irradiated in water solutions. The radiation effects were evaluated considering the surfactants degradation as well as acute toxicity reduction.

**Samples and anionic surfactant determination**

Part of the samples were collected at a municipal wastewater treatment plant at Suzano, São Paulo, Brazil. A second collection of samples were prepared at the Laboratory by diluting individually SDS and LAS with distilled water. The surfactant initial concentrations of the prepared samples were 100 mg/L.

To quantify the anionic surfactants the methylene blue active substances method (MBAS) was applied and the organic blue phase was photometrically measured at 652 nm [3].

**Irradiation**

The samples were exposed to electron beam irradiation at Instituto de Pesquisas Energéticas e Nucleares (IPEN), with a Dynamitron Electron Beam Accelerator (EBA) from RDI Inc. The machine energy was fixed at 1.4 MeV and the electric current was varied up to 25 mA. The radiation doses applied to surfactants as water solution varied from 3.0 kGy to 12 kGy and the radiation doses applied to real effluents were 10, 20 and 50 kGy.

**Table 1.** Mean surfactant concentration for irradiated and unirradiated samples and percentage of the surfactant removal by EBA irradiation (at 6.0 kGy)

<table>
<thead>
<tr>
<th>Surfactant concentration (mg/L)</th>
<th>LAS solution</th>
<th>SDS solution</th>
<th>Real effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated sample</td>
<td>99.12 ± 0.81</td>
<td>99.29 ± 1.48</td>
<td>3.21–41.24</td>
</tr>
<tr>
<td>Irradiated sample</td>
<td>6.81 ± 4.92</td>
<td>4.49 ± 3.63</td>
<td>0.21–13.28</td>
</tr>
<tr>
<td>% removal</td>
<td>93%</td>
<td>96%</td>
<td>68–93%</td>
</tr>
</tbody>
</table>

For material irradiation, the volume of samples was controlled in order to guarantee ideal dose distribution in the water (4 mm thickness). Pyrex vessels contained the samples during irradiation which was carried out in batch conditions. Samples were protected by a single plastic cover.

**Toxicity assays**

Two acute toxicity assays were carried out in order to correlate the surfactant degradation with the reduction of biological effects. The test-organisms applied for toxicity measurements were the Daphnia similis cladocera and Vibrio fischeri bacteria. For the first assay, young organisms were exposed to different concentrations of surfactant and/or wastewater samples, for 48 h, according to the standard method [2]. From the number of immobile organisms, it was calculated the concentration that caused immobilization for 50% of the exposed organisms, EC50(%) for D. similis. Acute toxicity assay with the bioluminescent bacteria V. fischeri was performed with a Microtox®, M-500 (Microbics). The organisms were exposed to different concentrations of the samples for 15 min. The statistical method was a linear regression that calculates the EC50(%) based on the reduction of light as far as the sample concentration increased [1].

**Evaluation of the irradiation process efficiency**

The EC50(%) obtained values were transformed into toxic units (TU = 100/EC50). The percentage of the reduction toxicity was calculated comparing the TUs from unirradiated and irradiated samples. Similar comparison was used for surfactant contents related to its degradation induced by EBA irradiation.

**Results and discussion**

For the starting irradiation of SDS surfactant (C₀ = 100 ppm), the following concentrations were obtained (ppm): 9.75, 4.03, 2.28 and 1.88 for the doses 3, 6, 9 and 12 kGy, respectively. The obtained data as radiation degradation of surfactants is shown in Table 1 for both types of samples, water solution and wastewater, while the toxicity effects of surfactants on living organisms are presented in Tables 2 and 3. The data presented in these tables are those to be suggested as the proper for each type of sample, i.e. 6.0 K Gy.

The prepared samples with LAS and SDS and real effluent showed a significant reduction on the surfactant concentration after the irradiation process (Table 1). For the prepared samples (LAS and SDS in distilled
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The removal of surfactant was 93% and 96% with 6.0 kGy. On the other hand, when irradiating real and complex effluent doses of 20.0 kGy up to 50.0 kGy were required to satisfactorily reduce surfactant and toxicity.

Several authors demonstrated the capability of radiation to reduce organic and microbial contamination of water, wastewater and sewage sludge [5, 8, 9]. Nonetheless, very few data is available concerning surfactants or detergents decomposed by ionizing radiation [10, 11, 13].

Regarding toxicity of surfactants, the results showed that both Daphnia and the luminescent bacteria were sensitive to toxic effects of these surfactants. The EC50 and TUs values obtained are shown in Tables 2 and 3. The higher doses required for real effluents are related to the complexity of samples and solids content. The 20 and 50 kGy dose were very efficient for removing surfactant and toxicity from the real effluent. This means that a substantial part of the biological effect (toxicity) is related to surfactants.

When Romanelli et al. studied radiation effects on SDS, it was noticed that pH values decreased substantially after radiation due to production of acid compounds [13].

When the surfactants were submitted to the irradiation process, the degradation of the molecules occurs by the attack of oxidizing species that are produced during water radiolysis. Podzorova et al. [11] detected from 0.2 up to 13.25 mg/L of a surfactant in municipal wastewater. This contaminant was completely removed by radiation process using doses from 4.0 to 5.0 kGy [11]. The results obtained for real effluents must be emphasized as well as the efforts made to bring such a technology to contribute to real environmental solutions.

**Conclusion**

Results obtained for acute toxicity reduction from 88 to 96% and from 68 to 96% concerned the percentage of surfactant removal even for the worst situation (hard industrial effluents). This study showed that electron beam irradiation can be an important tool for the reduction of acute toxicity caused by surfactants in waters. The process can be applied as advanced oxidation process for treating effluents, especially the ones daily produced by surfactants manufacturing.

**References**