

# ELECTRON BEAM IRRADIATION OF TEXTILE EFFLUENTS AND NON-IONIC ETHOXYLATED SURFACTANT FOR TOXICITY AND COLOR REMOVAL

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## ABSTRACT

Textile industry has an expressive scenario in the world economy and Brazil is the 5th in the textile production. By 2015, Brazilian textile production represented US \$ 39.3 billion, accounting for more than 1.8 million tons of fabric (ABIT, 2017). The effluents from textile industry are highlighted by quantity of wastewater discharged and variety of substances (dyes, bleaching agents, surfactants, salts, acids, among others). Such compounds often prove to be toxic to aquatic biota. This present study aims to assess toxicity of whole effluents, before and after irradiation (by electron beam accelerator, EBI). In addition, the reduction of the effluent color after irradiation is also very important. *Daphnia similis* and *Vibrio fischeri* were the biological systems applied for toxicity evaluations. Previous results demonstrated the surfactant as the main toxic compound, in the untreated and irradiated forms, EC 50 = 0.44 ppm  $\pm$  0.02 (untreated); EC 50 = 0.46 %  $\pm$  0.07 (irradiated). The irradiation was effective in reducing the color of the effluent, starting from 0.5 kGy. EB radiation may be proposed as an alternative treatment for the final effluent from textile processing, mainly for reuse purposes.

## 1. INTRODUCTION

The textile industry annually handles approximately US\$ 330 billion in exports and US\$ 308 billion in imports. In this scenario, Asia is the world leader in production with 2/3 of the total manufactured, Brazil ranks 5th in world production of textiles, with 2.4% of the total, earning approximately US\$ 39 billion [1,2].

The textile production of one tonne of cotton yarn requires approximately 10 m<sup>3</sup> of water. For the processing of 1500-2000 kg/day of yarn, the volume of effluent generated is 100-200 m<sup>3</sup>/d, approximately [3].

These effluents contain high amount of dyes (azoico, indigo and aniline), bleaching agents, salts, acids, alkalis, metals, suspended solids; some of these with low biodegradability and high solubility, for example the surfactant, which makes them difficult to remove by conventional effluent treatment. In addition, high Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are verified in these effluents [4,5].

Toxicity in textile effluents affects several organisms in the food chain and some of them may be cited: induction of genotoxicity and general alterations for *D. rerio* [6]; alteration in the hematopoietic system in

albino rats (male) [7]; alterations in the reproductive system of swiss albino rats and mice, with a reduction in body weight of up to 25% and of the reproductive organ of up to 48% [8]; behavioral changes in different aquatic organisms exposed to such effluents [9]; high toxicity, EC50 (%) between 2 and 7, of the cotton reactive bath, for the organisms *D. magna*, *L. sativum*, *P. subcapitata* and *C. sativus*, [10]. In addition, studies have shown that textile effluents as well as their compounds may be carcinogenic, mutagenic or teratogenic to a number of organisms [5, 11, 12].

Due to the wide variety of compounds, the textile effluent usually requires a combination of treatments, and within these stand out AOPs (Advanced Oxidative Processes), such as electron beam irradiation, which have been shown to be an effective methodology for the reduction of toxicity and effluent color removal.

Several studies have studied electron beam irradiation as an alternative treatment for textile effluents: Kim *et al.* [13] shows a decrease in the color of the textile effluent, around 75%, with a dose of 1.0 kGy, and a significant decrease, in the order of 30 to 40%, of parameters such as TOC, BOD and COD in the same effluent; Borrelly *et al.* [14], obtained a reduction in color of more than 90% from the 2.5 kGy dose and a decrease in acute toxicity of more than 30% for reference organisms, such as *D. similis* and *B. plicatilis*, at the same dose. Pinheiro [15] demonstrated at the dose of 10 kGy color removal efficiency of more than 95% for Remazol Black B and Remazol Orange 3R, a reduction of more than 50% in acute toxicity was also observed, for *V. fischeri* and *D. similis*, for both dyes from 10 kGy.

The objective of this study was to evaluate efficiency of electron beam irradiation for toxicity and color removal from textile effluents and one of the compounds used in the fiber processing which is a non-ionic ethoxylated surfactant.

## 2. METHODOLOGY

The evaluation of the acute toxicity and color removal efficiency was performed in the textile effluent and in one sample of surfactant once it is an important compound of the studied effluent. Both samples were submitted to electron beam irradiation in order to evaluate reduction of toxicity and removal of color. For the later analysis, the irradiated colored samples were submitted to the UV-VIS spectrophotometer.

### 2.1. Preparation of samples

The effluent was obtained by simulated processing in the textile chemistry laboratory of the Senai (National Service of Industrial Learning). This effluent represents the complete cotton processing (bleaching, dyeing and washing of the fiber); as dye, for fiber dyeing, Reactive dye Yellow 160 was used.

The surfactant (Goldpal TMZ, non-ionic, ethoxylated) was analyzed at the concentration of 1 g.L<sup>-1</sup>, the same used for fiber processing.

### 2.2. Acute Toxicity

Two test organisms were selected for the tests: the microcrustacean *Daphnia similis* and the marine bacteria *Vibrio fischeri*, both tests followed the recommendations and methodologies of the Brazilian Technical Standard (ABNT-NBR). Organ cultures and tests were performed in Radiation Technology Center of the Energy and Nuclear Research Institute (IPEN).

The acute toxicity test with *Vibrio fischeri* followed the method proposed in NBR 15411 [16], with microtox system, model M-500 of Microbics. In order to determine the toxic effect of the sample, after 15 minutes of exposure of the bacteria to the sample is analyzed if there was loss of luminescence, which is indicative of toxicity of the sample. The test result is expressed by EC50, which means the median concentration of effect obtained during exposure. The calculation based on the value of the gamma effect (Y), which is the quotient between the light emitted and the remaining light, was used for the calculation of EC50.

The *Daphnia similis* assay is based on the exposure of young individuals to various concentrations of the test substance over a period of 48 hours, allowing the determination of the concentration of the toxic agent that causes acute effect to 50% of organisms. The result of the acute toxicity test is expressed by the EC50 (median effective concentration), with the immobility of organisms being observed [17].

All toxicity assays were performed in triplicate for improved reliability of results. The results were exposed from the mean values obtained in the tests.

### 2.3. Electron beam irradiation

The effluent and surfactant samples were irradiated in the CTR/IPEN at the electron accelerator (Dynamitron model) with energy fixed at 1.4 MeV, varying the current of the electronic beam. For the effluent, doses ranging from 0.5 kGy to 20 kGy were used, and for the surfactant the fixed dose was 2.5 kGy.

### 2.4. Color analysis

Spectrophotometry was used in the color analysis of irradiated and non-irradiated effluents. The Konica Minolta brand UV-VIS spectrophotometer, model CM-3600d (SENAI Laboratory) was used. The absorbance reading was taken at 430 nm.

The decoloration removal were calculated as follow:

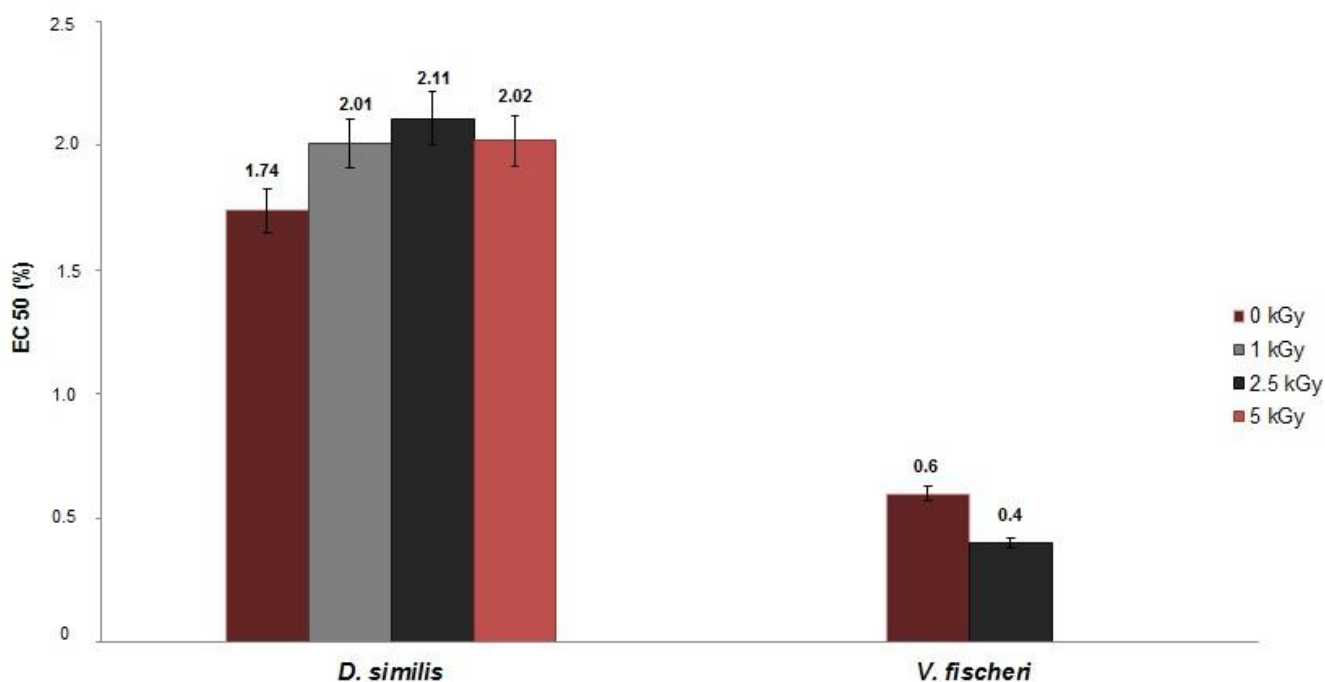
$$(A_o - A_i) / A_o * 100\%$$

$A_o$ = absorbance of effluent solution before irradiation

$A_i$ = absorbance of effluent solution after irradiation

## 3. RESULTS AND DISCUSSION

The results for the acute toxicity of the yellow effluent (with Remazol Reactive Yellow 160) before and after electron beam irradiation are shown in figure 1. The values are shown in table 1.



**Figure 1: Acute toxicity for *D. similis* and *V. fischeri* of the yellow effluent after treatment with electron beam irradiation.**

**Table 1: EC50 values (%) for organisms *D. similis* and *V. fischeri*, exposed to samples of interest before and after irradiation with electron beam.**

<b>Surfactant</b>		
Dose (kGy)	<i>D. similis</i> EC 50% <sub>(48h)</sub> , I.C., S. D.	<i>V. fischeri</i> EC 50% <sub>(15min)</sub> , I.C., S. D.
0	0.44 (0.38 – 0.50), ± 0.02	0.27 (0.23-0.31), ± 0.03
2,5	0.46 (0.41 – 0.53), ± 0.07	N.R.
<b>Yellow Effluent</b>		
Dose (kGy)	<i>D. similis</i> EC 50% <sub>(48h)</sub> , I.C., S. D.	<i>V. fischeri</i> EC 50% <sub>(15min)</sub> , I.C., S. D.
0	1.74 (1.49-2.01), ± 0.53	0.6 (0.22-1.99), ±0.29
1	2.01 (1.67-2.40), ±0.09	N.R.
2,5	2.11 (1.80-2.46), ±0.40	0.4 (0.11-1.51), ±0.10
5	2.02(1.66-2.44), ±0.32	N.R.

**Legend:** EC 50(%) = Median Effective Concentration - values referring to the average of three tests. I.C.: Interval de Confidence. S.D.: Standard Deviation. N.R.: Not Realized.

Note that for the yellow effluent, there was a slight reduction of toxicity after irradiation, with EC 50% between 1.74 and 2.02 for *D. similis*. The values demonstrate effluent toxicity reduction efficiency for *D. similis* of 13.36% in the dose of 1 kGy; 17.77% with 2.5 kGy and 13.89% in the dose of 5 kGy. Even with this improvement, it should be noted that the effluent is still extremely toxic to the organism, since the parameter of EC 50% is inversely proportional to toxicity. The same pattern, in relation to electron beam irradiation, was not observed for *V.fischeri*.

Confirming the data presented in the present study, Borrely *et al.* [14] in dye effluent analysis C.I. Blue 222 highlights high toxicity of textile effluents to aquatic organisms: *D. similis* EC50% = 11.66; *V. fischeri* = 5.25; *B. plicatilis* = 13.26. With electron beam treatment, the author observed an improvement in toxicity with 34.55% efficiency for *D. similis* and 47.83% for *B. plicatilis* at a dose of 2.5 kGy. For *V. fischeri* the dose of 5 kGy gave a better result with an efficiency of 57.29%.

The toxicity for two reactive dyes was evidenced by Pinheiro [15]: the vinylsulfone form of the Remazol Black dye that was toxic EC 50%<sub>(15min)</sub> = 6.23 mg L<sup>-1</sup>, for *V. fischeri* and Remazol Orange 3R, in the same manner, which was toxic to *D. similis* (EC 50% = 0.54 mg L<sup>-1</sup>). A reduction of 59.52% of acute toxicity for *V. fischeri* to R. Black B and for R. Orange 3R reduction of 82.95% (*V. fischeri*) and 71.26% (*D. similis*), both at 10 kGy.

The toxicity in textile effluents may reach different organisms of the trophic chain when discharged at the environment. Few example of such type of studies: with aquatic plants such as *Lemna aequinoctialis* revealed fragmentation, root loss and reduction (50-70%) in size. In the effluent, pollutants such as acids (HCl and H<sub>2</sub>SO<sub>4</sub>), bases (N<sub>2</sub>O SiO<sub>2</sub>), salt (NaNO<sub>2</sub>), heavy metals (Cu), are highlighted by high toxic power [4]. Tigrini *et al.* [10] revealed high toxicity during the processing of cotton fiber (cotton reactive bath) to: *D. magna* CE50 7.2%; *L. sativum* EC50 2.8%; *C. sativus* EC50 4.4% and *P. subcapitata* EC50 2.2%.

From exposure to untreated textile effluent in mammals (Swiss albino rats and mice), significant changes were observed in total proteins (14-70%), cholesterol (14-91%) and total lipids (10-30%) of the reproductive organs and spermatozoa of these organisms. Histopathological studies revealed altered spermatogenesis, with higher sperm abnormalities, reduced sperm count (10-59%), and altered motility (14-56%). In addition, complete sterility is emphasized in albino rats [8]. Sharma, Kalpana [7], has shown, for example, red cell size decrease (13-27%), indicating microcytic anemia, and their modified form (Poikilocytosis) in swiss albino rats.

Another proposal of the present study was the reduction of the effluent color after electron beam irradiation, through UV-VIS spectrophotometry analysis. The values obtained are organized in figure 2 and in table 2. The figure 2 shows the percentage of color removal efficiency from different irradiation doses, it's noted that with increasing irradiation dose the percentage of staining removal increases. The table 2 relates the doses used in the effluent samples, the absorbance values obtained and the percentage of color removal efficiency for each dose.

With the increase of the irradiation doses, the effluent color decreases, which can be proven by the absorbance values presented in table 2.

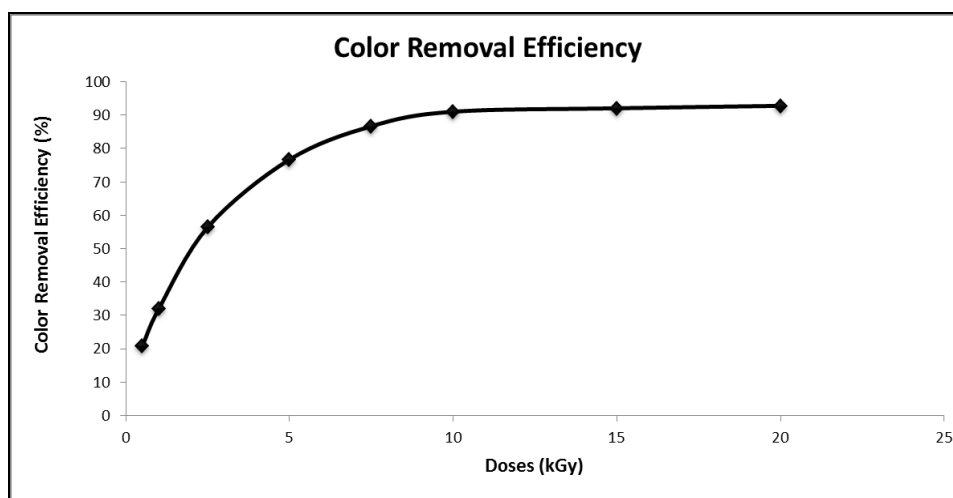


Figure 2: Effluent color removal versus dose.

Table 2: Absorbance values (430nm) and removal efficiency of yellow textile effluent submitted to different doses of irradiation.

Dose	ABS (430nm)*	Color Removal Efficiency (%)
0.5	1.2068	20.82
1.0	1.0378	31.91
2.5	0.6636	56.46
5.0	0.3553	76.68
7.5	0.2029	86.68
10.0	0.1370	91.01
15.0	0.1212	92.04
20.0	0.1100	92.78

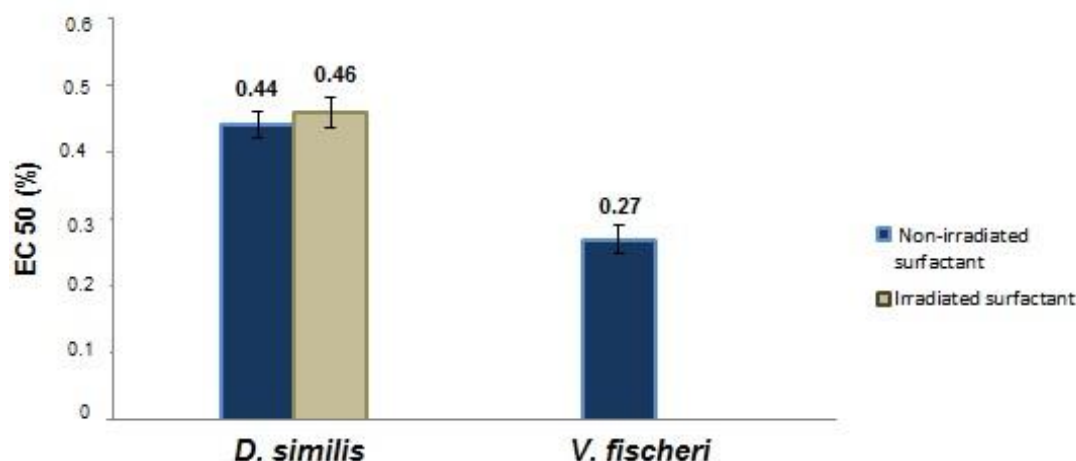
Legend: ABS (430nm)\*: The values refer to the average of three readings. S.D.: Standard deviation.

Based on the UV-VIS spectrophotometry analysis, it was observed that the removal of color of the effluent was already possible from the 0.5 kGy dose, with a removal efficiency greater than 90% from the 10 kGy dose.

These values are confirmed by the literature: Borrelly *et al.* [14] points out a reduction of more than 90% in color from the dose of 2.5 kGy for effluent containing Reactive Blue 222. Pinheiro [15] demonstrated that at the dose of 10 kGy the removal efficiency of the color was higher than 95% for the dyes Remazol Black B and Remazol Orange 3R. Kim *et al.* [13] highlight the decrease of the color of the textile effluent around 75% with treatment of electron beam in the dose of 1 kGy. Wojanárovits & Takács [18], highlight the efficiency of the process of ionizing radiation in the discoloration of textile dyes, already at the dose of 3.0 kGy.

The evaluation of acute toxicity for *D. similis* and *V. fischeri* of the surfactant is shown in figure 3. The values are also found in table 1. It is observed that both the untreated and the treated with electron beam irradiation

were very toxic for both organisms, with EC 50 lower than 1%, concluding that there was no reduction of the surfactant toxicity after the treatment with electron beam.



**Figure 3: Mean of EC 50 (%) for *D. similis* and *V. fischeri* exposed to the surfactant, with respective standard deviations.**

In water bodies, the formation of foams, besides causing visual pollution and inhibiting the purification processes of the receptor bodies and photosynthesis, also acts in the reduction of the gas exchanges between the atmosphere and the surface of the water, contributing to the decrease of the oxygen rates Dissolved in the waters. Due to their chemical nature, surfactants can interact with the major components of the cell membrane, proteins and lipids, de-structuring membrane systems and weakening the protective structures of organisms [19]. Changes such as: growth, reproduction and motility of aquatic organisms; root suppression and death and shoot inhibition are also cited by Rebello *et al.* [20].

Romanelli *et al.* [21] indicates important toxicity values for the main surfactants used in the industry: sodium dodecyl sulfate (DSS) EC 50%<sub>(15min)</sub>  $1.92 \pm 0.40$  for *V. fischeri* and EC 50%<sub>(48h)</sub>  $11.81 \pm 4.64$  for *D. Similis*; Linear alkylbenzene sodium (LAS),  $13.49 \pm 4.54$  (*V. fischeri*) and  $4.56 \pm 1.44$  (*D. similis*).

Importants values of surfactant toxicity to aquatic organisms are reported by Santos *et al.* [22]: EC 50 (%) *D. similis*: 9.62; *H. azteca*: 19.29%; *V. fischeri*: 0.94%. In the present work, it was also verified high toxicity to the organisms exposed to the surfactant: EC 50 (%)<sub>(48h)</sub> *D. similis*: 0.44 and for *V. fischeri* EC 50<sub>(15min)</sub>: 0.27, which corroborates with the other studies that evidenced the high toxicity of the compound.

According to data obtained in the present study, Hodges *et al.* [23], highlight toxicity in EC50%<sub>(48h)</sub> of LAS surfactant for *D. Magna* between 0.67% and 53% and Rosal *et al.* [24], highlight high toxicity of the surfactant docusate sodium: EC 50 (mg L<sup>-1</sup>) for *V.fischeri* of 74.5, and for *Pseudokirchneriella subcapitata* 39.5.

Regarding the proposed with electron beam irradiation, although the present study did not identify an improvement in irradiated surfactant toxicity, Romanelli *et al.* [21] obtained an improvement over 17% in relation to the LAS surfactant toxicity for *D. similis*, and greater than 50 % for DSS; already for the organism *V. fischeri*, the EC 50 before the irradiation of the DSS surfactant was 1.92% and after it reached 19.55%; and for LAS of 13.49% it was to 19.83%, after irradiation.

#### 4. CONCLUSIONS

The yellow effluent was also toxic for both organisms with EC 50% lower than 2.11%, both in the untreated and electron beam irradiated form. With these results, it is shown the concern in analyzing them and controlling them when discarded in the water bodies. The surfactant as well as the yellow effluent were toxic to the analyzed organisms. The surfactant as the main toxic compound, in the untreated and irradiated forms, EC 50 =  $0.44 \text{ ppm} \pm 0.02$  (untreated); EC 50 =  $0.46\% \pm 0.07$  (irradiated) for *D. similis* and 0.27% for *V. fischeri*.

Electron beam irradiation is a good treatment alternative, mainly in the reduction of the coloring of the textile effluent, due to a reduction of coloration of more than 90% in the dose of 10 kGy, with the possibility of reuse of this in the industry itself, generating economic gains And environmental issues.

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