



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. 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 for reducing color of the effluent, starting from 0.5 kGy. EB irradiation may be proposed as an alternative treatment for the final effluent from textile processing, mainly for reuse purposes.

Key-words: Electron beam irradiation, surfactant, textile effluents, toxicity.

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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 m³ of water. For the processing of 1500-2000 kg/day of yarn, the volume of effluent generated is 100-200 m³/d, approximately [3].

These effluents contain high amount of dyes (azoic, indigo and aniline), bleaching agents, salts, acids, alkalis, metals, suspended solids; some of these with low biodegradability and high solubility, for example surfactants, 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 *Danio 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; Borrely *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 the 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. MATERIALS AND METHODS

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 in this effluent. Both samples were submitted to electron beam irradiation in order to evaluate toxicity and color removals. Irradiated colored samples were submitted to the UV-VIS spectrophotometer analysis.

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 (non-ionic, ethoxylated) was analyzed at the concentration of 1 g.L^{-1} , the same used for fiber processing.

2.2. Acute Toxicity

Two organisms were selected, the *Daphnia similis* microcrustacean and *Vibrio fischeri* marine bacteria, and both tests followed the recommendations and methodologies of the Brazilian Technical Standard Methods (ABNT-NBR). Rearing organisms and assays were performed at Radiation Technology Center (IPEN/SP).

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 sample toxicity. Results were expressed by EC50, which means the median concentration of effect obtained during exposure. The calculation was based on the value of the gamma effect (γ), 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). The observed effect is the immobility of exposed organisms [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 (Figure 1). 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.



Figure 1: Electron beam scanner system during liquid samples irradiation.

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 follows:

 $(A_{o} - A_{i})/A_{o} * 100\%$

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 2: Acute toxicity for <u>D. similis</u> and <u>V. fischeri</u> of the yellow effluent after treatment with electron beam irradiation.



EC 50% values (1.74 up to 2.02) demonstrated that yellow effluent was very toxic, even after irradiation. The same pattern was confirmed with *V. fischeri*. Relatively low reduction (17.77%) was achieved after 2.5 kGy.

Radiation processing of blue effluents (C.I. Blue 222) was more effective for toxicity than this present data: 34.5% reduction for *D. similis* and 47.8% for *B. plicatilis* at a dose of 2.5 kGy, Borrely *et al.* [14]. The toxicity for two reactive dyes was evidenced by Pinheiro [15]: the vinylsulfone form of the Remazol Black dye that was toxic EC $50_{(15min)} = 6.23 \text{ mg.L}^{-1}$, for *V. fischeri* and Remazol Orange 3R was toxic to *D. similis* (EC 50= 0.54 mg.L⁻¹). The irradiated samples obtained a reduction of 59.52% of acute toxicity for *V. fischeri* to R. Black B; 82.95% for Orange 3R (*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 H₂SO₄), bases (N₂O SiO₂), salt (NaNO₂), heavy metals (Cu), are highlighted by high toxic power [4]. Tigini *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.

Color reduction during radiation processing of textile effluent is very effective as can be observed in Figure 3.

Figure 3: Effluent color removal versus dose.



Based on the UV-VIS spectrophotometry analysis, it was observed that the removal of color of the effluent was obtained even at 0.5 kGy (90% removal at 10 kGy). Most of the papers highlighted the efficacy of irradiation at relatively low doses (13-15; 18).

The evaluation of acute toxicity for *D. similis* and *V. fischeri* of the surfactant is shown in Figure 4. The values are also compared at 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 4: EC50 (%) for <u>D. similis</u> and <u>V. fischeri</u> exposed to the surfactant (non-ionic ethoxylated).

Due to the chemical of surfactants they can interact with the major components of the cell membrane, proteins and lipids, destruction of membrane systems and weakening the protective structures of organisms [19]. Other possible effects to living-organisms: growth, reproduction and motility of aquatic organisms; root suppression in plants; death and shoot inhibition are also cited by Rebello *et al.* [20].

Romanelli *et al.* [21] demonstrated important toxicity values for the main surfactants used in the industry: sodium dodecyl sulfate (SDS) EC 50% $_{(15min)}$ 1.92 ± 0.40 for *V. fischeri* and EC 50% $_{(48h)}$ 11.81 ± 4.64 for *D. similis*; Linear alkylbenzene sodium (LAS), 13.49 ± 4.54 (*V. fischeri*) and 4.56 ± 1.44 (*D. similis*). Few comparative data on toxicity to several organisms was presented at Table 1.

Surfactant	Organism-test	EC50 (mg.L ⁻¹)	Reference
Sodium dodecyl sulfate	V. fischeri*	1.92 ± 0.40	21
	D.similis**	11.81 ± 4.64	
Linear alkylbenzene sodium	V. fischer*	13.49 ± 4.54	21
	D.similis**	4.56 ± 1.44	
Docusate sodium	P. subcapitata***	39.5	22
	V. fischeri*	74.5	
Perfluorooctanoic acid	P. subcapitata***	96.2	22
	V. fischeri*	524	
Non-ionic ethoxylated	V. fischeri*	42.70 ± 2.1	Present paper
	D.similis**	4.40 ± 0.22	

Table 1: Relative toxicity of surfactants among species assessed by effective concentration (EC50).

Legend: * 15 min.; ** 48 h; ***96h.

4. CONCLUSION

The yellow effluent was very toxic for both organisms, even after irradiation. These results reinforce the needs for better improvement of effluents before discharging them into water bodies. EB irradiation was effective for color reduction of the studied effluent. Concerning surfactant, it was also a very toxic compound, which is used during the dyeing processing.

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