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# Decoloration and detoxification of effluents by ionizing radiation

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## HIGHLIGHTS

- 2.5 kGy was enough for decoloration and detoxification of S2 and S3.
- S1 effluents were very toxic and required at least 20 kGy for detoxification.
- Radiation processing reduced toxicity for 100% of treated samples.
- *V. fischeri* was the best tool for toxicity measurements.

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## ABSTRACT

Three distinct textile samples were investigated for color and toxicity (S1–chemical/textile industry; S2–final textile effluent; S3 - standard textile produced effluent–untreated blue). Radiation processing of these samples were carried out at Dynamitron Electron Beam Accelerator and color and toxicity removal were determined: color removal by radiation was 96% (40 kGy, S1); 55% (2.5 kGy, S2) and 90% (2.5 kGy, S3). Concerning toxicity assays, *Vibrio fischeri* luminescent bacteria demonstrated higher reduction after radiation than the other systems: removal efficiencies were 33% (20 kGy, S1); 55% (2.5 kGy, S2) and 33% (2.5 kGy, S3). *Daphnia similis* and *Brachionus plicatilis* fitted well for S3 effluents. Hard toxic volumes into biological treatment plant may be avoided if radiation would be previously applied in a real plant. Results reveled how indispensable is to run toxicity to more than one living-organism.



## 1. Introduction

The large production and wide usage of dyes make them an important environmental issue today as well as are the needs for saving water. Combined technologies may be successfully applied for wastewater treatment, allowing industrial reuse of waters. Ecological prejudices induced by textile effluents are also related to residual color (dyes and pigments into waters). Other negative effects to living organisms (toxicity and mutagenicity) are associated to the discharge of organic matter, detergents and metals and other chemicals in the effluents.

Since the seventies the possible use of ionizing radiation for degradation of dyes in aqueous solution have been published (Suzuki et al., 1978), including important reviews related to dyes solution degradation by Advanced Oxidation Processes (Wojnarovits and Takacs, 2008; Al-kdasi et al., 2004; Chen et al., 2003). Meanwhile few practical examples of pollutant degradation by Electron Beam (EB), were demonstrated by Han et al. (2002), through practical design installations in South Korea. The first mobile EB system was constructed at United State of America.

The objective of this paper was to apply electron beam accelerator for the removal of color and acute toxicity at three colored effluents. The samples were collected during the production of dyes, very hard color (a); at a textile industry, representing several colors, (b) and at a technical school laboratory–textile dyeing, (c), considered here as a standard blue effluent. Cotton is the main type of fiber produced in Brazil and reactive dyes are suitable for such type of product.

Ecotoxicity data was obtained in order to demonstrate the environmental risks related to the discharge of effluents to biota and to evaluate if EB irradiation is a technique able to remove acute toxicity while degrading the organic compounds in the effluents. It is important to demonstrate that irradiation does not result in any negative effect.

Biotechnology and combined processes for removing dyes from wastewaters were reviewed by Forgacs et al., 2004. Nonetheless the dozen of additional chemicals into a real textile effluent is not

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well understood, and the acute measured effects to living organisms may alert on the possible risks of such type of mixture, which is much more difficult to be treated. Adsorption processes are still being developed for special dyes (Fungaro et al., 2013). They also included toxicity assessments during feasibility studies. Chen et al. (2003) demonstrated the potential viability of aeromonas for decolorizing reactive blue 222.

The textile industrial effluents may contain several types of chemicals such as enzymes, starch, ammonia, disinfectants, soaps and surfactants, fats, waxes, anti-static agents, solvents, NaOH, dyes, chlorinated compounds, stearate and others (Allègre, et al., 2006). From 18 studied azo dyes, 11 compounds passed through the activated sludge process practically untreated. Others were adsorbed on the waste activated sludge (acid blue 113, acid red 151, direct violet 9 and direct violet 28 (Shaul et al., 1991).

Considering the potential of radiation for decolorizing dyes and the environmental benefits, the transference of this technology for real effluents would be supported once such a type of data is published. One possible way to evaluate effluents is through the acute toxicity measurements, also to their treatment technologies, mainly due to the diversity of contaminants present in textile effluents. The importance of textile manufacture justifies the possible use of radiation for the degradation of dyes and also the combined technologies. Reuse of such type of wastewater is needed.

One combined installation of EB irradiation followed by a biological treatment was demonstrated in South Korea by Han et al., 2002. The radiation source was a 1 MeV EB accelerator, 400 kW, which was applied for real dyes degradation.

Kinetic curves describing decoloration of dyes solutions by irradiation were shown during an important overview carried out by Wojnarovits and Takacs, 2008. The proposed mechanisms and the rate coefficients for the reaction of .OH, $e_{aq}$ and .H water radiolysis intermediates with the dye molecules and with model compounds were summarized. Additional studies are needed for real textile effluent where not only dozen of dyes may be present but several other chemicals (soda, surfactant, bleaching agents, enzymes, etc).

## 2. Material and methods

The ecotoxicology was applied to samples of real effluent from industrial dyeing processes, including the effluent of a chemistry industry, as a dye producer. Aiming to reduce acute toxicity effects from those effluents, an Electron Beam Accelerator was the radiation source used for reducing color and toxic effects from wastewaters. Liquid samples of colored effluents were submitted to EB irradiation, to whole toxicity evaluation and color determination.

### 2.1. Effluent sampling

Fifteen samples of real effluents were collected at chemical and textile manufacture and were nominated as S1, S2 and S3, according to the following industries they came from:

S1-effluents from chemical industry which manufacture the reactive dyes;
S2-final treated textile effluent (secondary biological treatment);
S3-raw effluent (after a cotton dyeing bath), always blue wastewater, containing the reactive blue 222 among several other chemicals. S3 effluent was considered as a standard effluent for studies purposes since all the processes were undertaken for dyeing cotton in a pre-industrial laboratory condition. All the components are known.

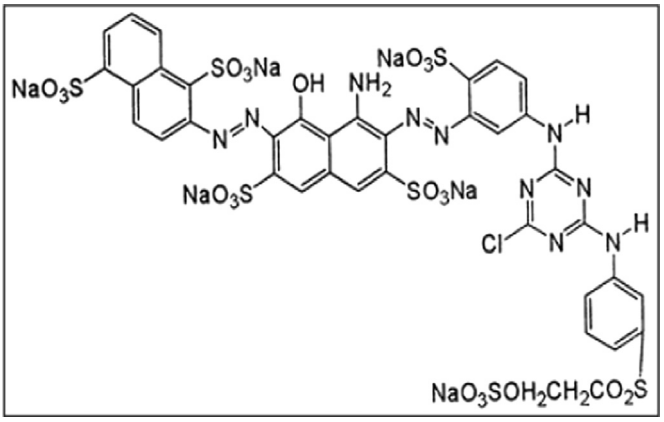


**Fig. 1.** Reactive blue-222–chemical structure (at S3 samples).

The color of S1 and S2 samples were different at each sampling, being S1 effluent very dark color. The molecular structure of blue-222 dye was presented at Fig. 1, once it is a component of S3 effluent.

### 2.2. Samples irradiation

Electron Beam Irradiation was carried out at a Dynamitron accelerator, 1.4 MeV fixed energy, variable current, and batch system. Samples pH were determined before irradiation and part of them were adjusted at $7.5 \pm 0.2$, before irradiation, by hydrochloric acid (1.0 M) addition (only sample S3). Before irradiation the samples were distributed in pyrex vessels (246 ml) to assure a 4 mm sample thickness, protected by plastic wrap. Dose measurements were performed for 5 kGy (1.4 MeV) together the experiments for wastewater and $< 5\%$ in dose variation was achieved (Perspex Harwell Red, Batch KZ-4034).

### 2.3. Toxicity measurements

Ecotoxicity assays were performed using serial dilution of the effluents (%) and the effective lethal concentration was the endpoint ($EC_{50}$), meaning the concentration at which 50% of the individuals reacted after a specified length of exposure: 48 h for *Daphnia similis* water fleas, 15 min for *Vibrio fischeri* luminescent bacteria and 48 h to *Brachionus plicatilis* rotifer. This last assay was applied only for the S3 samples.

All the methods carried out during toxicity assays were based on standard laboratory conditions. ABNT Brazilian Methods (ABNT, 2009, 2012), were followed during the cultivation of *D. similis*, and assays *D. similis* and *V. fischeri*, respectively). American Society for Testing Materials (American Society for Testing Materials, 1998) was applied for *B. plicatilis* rotifer assays (and cultivation). The statistics were applied according to the standard methods recommendation: Trimmed Sperman Karber for *D. similis* and for *B. plicatilis* and linear regression for *V. fischeri*. This last assay was carried at an M-500 Microtox Analyzer (luminescence measurements).

*D. similis* and *B. plicatilis* were rared at our laboratories. The use of *Brachionus plicatilis* (Fig. 2) in this study was relevant due to the spread of them in different aquatic environment. They are suitable for textile effluents once they survive at a wide spectra of salinity ($> 30\%$), which is common when tanking textile effluents into account.

*B. plicatilis* rotifer was measured (100 μm up to 360 μm) during the cultivation. They were kept at laboratory condition, at Instituto

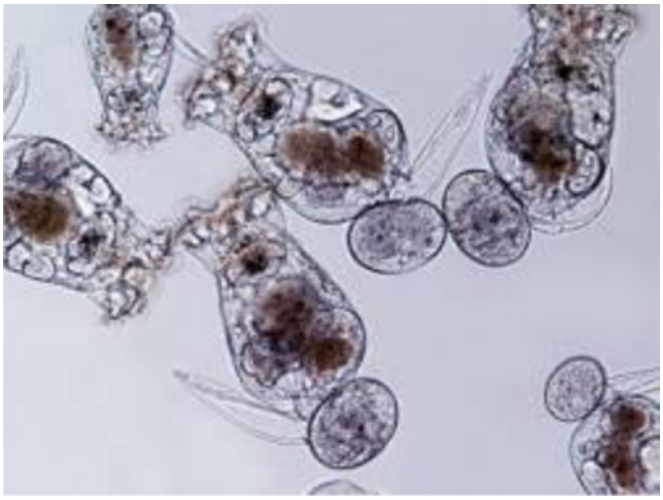

**Fig. 2.** *Brachionus plicatilis* rotifer rared at Fishing Institute for evaluation of toxic effects of samples S3 (Morais, 2015).

de Pesca de São Paulo (Fishing Institute) for the evaluation of toxicity of S3 samples irradiated and non irradiated. The samples were evaluated before and after treatment with EBI for toxicity tests over the specified living organisms and toxicity removal was calculated according to Eq. 1.

$$\text{Toxicity removal}(\%) = \left(EC50_0 - EC50_{irrad}\right) x\ 100/EC50_0 \quad (1)$$

where **EC50**$_o$ and **EC50**$_{irrad}$ are the effective average sample concentration before and after irradiation. Considering that lower the EC50 number, higher is the toxicity level.

Dissolved oxygen, pH, conductivity and salinity were measured by specific electrodes at each sample, before and after being submitted to toxicity assays (HQ 40d, Hach). Other laboratory equipments: incubation chambers (for photoperiod and temperature control). Varian Cary 50 for spectrophotometry. After abosorbance measurements, the same procedure (similar Eq. 1) was used for the calculation of color removal after radiation processing of effluents.

## 3. Results

The acute toxicity values obtained for S1 and S2 samples, before radiation processing, were presented at Table 1. The S1 values for *V. fischeri* and *D. similis* showed that this effluent was worst when compared to S2 effluent. For this last effluent (S2) we noticed that *V. fischeri* was more sensitive than *D. similis*.

Once we have considered S3 as a standard effluent, some other chemical parameters were determined (Table 2) as well a third

**Table 1**
Average acute toxicity of effluents S1 and S2 before radiation treatment and their 95% confidence range (EC50–sample %).

| Sample | *Vibrio fischeri* (15 min) | *Daphnia similis* (48 h) |
|---|---|---|
| S1 (1) | 0.15 (0.06–0.42) | 0.70 (0.52–0.70) |
| S1 (2) | 1.98 (1.72–2.29) | 0.16 (0.12–0.22) |
| S1 (3) | 1.91(1.05–3.95) | 4.38 (3.19–6.00) |
| S1 (4) | 6.12 (3.61–10.85) | 0.58 (0.38–0.89) |
| S1 (5) | 0.45 (0.38–0.53) | 1.00 (0.48–2.09) |
| **S1** $\bar{X} \pm S$ | **2.12** $\pm$ **5.87** | **1.36** $\pm$ **8.59** |
| S2 (1) | 23.44 (5.30–73.60) | 14.26 (11.69–17.39) |
| S2 (2) | 14.83 (10.74–27.80) | 42.44 (35.19–51.19) |
| S2 (3) | 29.12 (10.75–89.34) | 68.45 (61.42–76.41) |
| **S2** $\bar{X} \pm S$ | **22.46** $\pm$ **7.19** | **41.71** $\pm$ **27.10** |

**Table 2**
Chemical parameters determined for S3 effluent that directly affect toxicity.

| Sample | pH | Oxygen (mg $L^{-1}$) | Conductivity (mS $cm^{-1}$) | Salinity (g $L^{-1}$) |
|---|---|---|---|---|
| Untreated | 10.43 | 7.94 | 12.95 | 8 |
| Irradiated (2.5 kGy) | 7.64 | 7.75 | 14.69 | 8 |

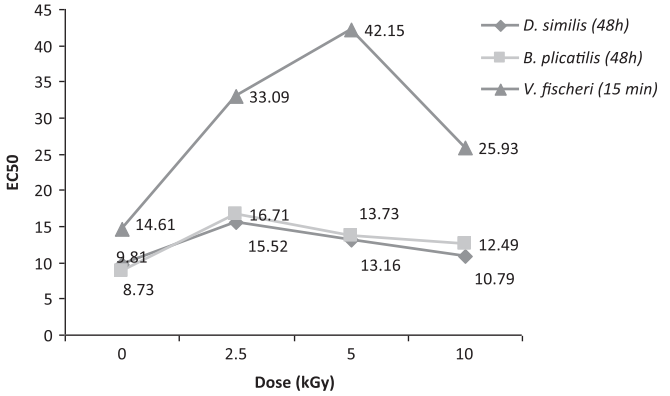


**Fig. 3.** Acute toxicity effect for the effluent S3 to three biological species versus dose.

biological assay was applied for acute toxicity measurements. *B. plicatilis* rotifer was the third living-organism exposed to S3 samples and they are suitable for monitoring textile effluents once they tolerate higher salinity than *D. similis*. The toxicity data obtained for S3 was presented at Fig. 3.

The radiation effects onto chemical parameters were observed mainly for pH and color reduction. Neutral pH is suitable for aquatic organisms and the 10.43 value at S3 is not in accordance to their needs and is out of regulations. After 2.5 kGy there was a reduction into pH value (7.64) that may be related to the partial decomposition of dye and surfactants. The degradation of organic compounds may decrease pH values due to the formation of organic acids (Suzuki et al., 1978). The concentration of salts in the effluent may influence toxicity through ion imbalance in biological cells, also associated to adverse effects of textile effluents. Salts and coloring agents in textile effluent result in a synergistic effect in freshwater ecosystem (Tigini. et al., 2011).

According to Fig. 3 it is possible to observe that before irradiation the EC50 values varied from 8.73 to 14.61. The *B. plicatilis* rotifer and *V. fischeri* bacteria exhibited very similar sensitivity. Nonetheless, after irradiation each biological assay resulted in different removal efficacy. At 2.5 kGy and 5 kGy the *V. fischeri* assay demonstrated that radiation substantially reduced toxicity. At 10 kGy the efficacy was diminished once decreasing EC50 was obtained. The dose dependence for toxicity removal may be related to several events induced by radiation such as partial degradation of organics compounds, pH reduction under biological limits, residual $H_2O_2$ and the formation of toxic by-products (Borrely et al., 2004). It is important to note that none of the doses resulted in higher toxicity if compared to the non irradiated samples.

Regarding the color of effluents, a typical curve was shown by Fig. 4, S3-blue effluent. At 0.5 kGy $>$ 70% of color was removed, while $>$ 90% was reduced by 2.5 kGy.

At Table 3 the average numbers for toxicity and color were presented. The first effluent (S1) was a very complex sample which required 20 kGy and 40 kGy. For textile samples (S2 and S3), treated at 2.5 kGy, color reduction induced by EB radiation was more effective than the reduction in toxicity.

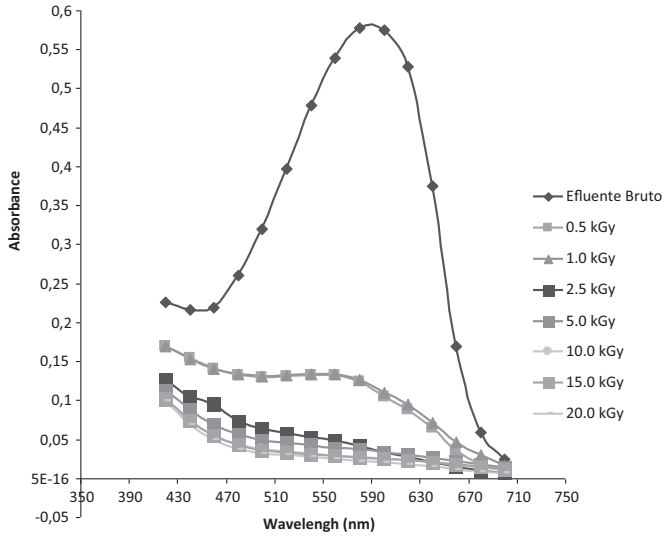


**Fig. 4.** Color removal at S3-effluent (blue dye 222) versus dose.

**Table 3**
Efficacy of EB irradiation for decolorization and toxicity removal to effluents S1, S2 and S3 (*V. fischeri*, 15 min).

| Effluent Sample | Dose (kGy) | Toxicity removal (%) | Color removal (%) |
|---|---|---|---|
| S-1 (chemistry-dyes)* | 20 | 33 | 47.5 |
| S-2 (treated textile) | 2.5 | 55 | 61 |
| S-3 (untreated - standard blue) | 2.5 | 33 | 90.60 |

* chemical effluent from dye manufactures and very dark color

## 4. Discussion

The toxicity of effluents is an important parameter to contribute for safety discharges of wastewaters into rivers, to avoid introduction of hard toxic volumes into biological treatment systems and to evaluate innovative techniques, such as Electron Beam Irradiation (EBI).

Although each effluent has peculiarities in their production processes, treatment with EBI proved to be effective in significantly decreased toxicity and color. $P < 0.0001$ was obtained for the sample treated by 2.5 kGy (S3). Toxicity is not directly related to the color of effluent, but to the other chemicals present in the samples. In the case of S3 previous results demonstrated the surfactant and sequestering agent much more toxic than the blue 222 dye (Morais, 2015). Similar results were obtained by Sharma et al. (2007) when they reported that chemicals products such as acids, heavy metals and salts in the textile effluent were considered responsible for the toxicity testing with fish *Gambusia affinis* and the duckweed *Lemna aequinoctialis*. Romanelli et al., 2004, obtained important degradation of anionic surfactants by EB.

According do Al-kdasi and co-authors, 2004, about 50% of 87 applied color are non-biodegradable, which is relevant not only for the intended needs of radiation for such a purpose but also for the election of *V. fischeri* and *B. plicatilis* during this study. The meaning of toxicity assays is to prevent toxic effect and such type of data is important for those who are in charge of treating or cleaning wastewaters. At municipal wastewater stations the level of toxicity will help during the equalization of entering industrial effluents into the biological system.

Regarding decoloration of effluents by radiation, the changes of the absorption spectrum in the visible region is observed when the intermediates formed in the reaction of the water radicals and the dye molecules reacts each other by re-establishing the conjugates system. However, the product molecules slightly differ from the starting molecules (Wojnarovits and Takacs, 2008). Some other authors demonstrated that the presence of $H_2O_2$ promoted markedly efficiency of decoloration of some dyes related to the degradation of them. Using electrons to apply 7 kGy Abdou et al., 2011, determined the following percent of decoloration for distinct classes of dyes (%): Direct azo (95.5%) > Reactive azo (95.3%) > Direct Anthraquinone (92%) > Reactive Anthraquinone (61.7%). Important is to mention that in general the daily industrial processing introduce more than dozens types of dye in their wastewaters.

If considering only the dyes, we are looking into the chromophore group, which is a color given and is represented by the radicals, which form a basis for the chemical classification of dyes when coupled with the chromogen. The importance of developing studies onto real effluents is to demonstrate that the technique may be feasible for chemical mixtures and to promote biodegradability, enhancing the possibilities for wastewater reuse in textile industries.

The results allow us to highlight that for the two textile samples (S2 and S3) 2.5 kGy was effective for decoloration and detoxification of effluents. The same dose was not enough to S1 sample, from chemical industry (Table 3). These results are good enough if irradiation is applied before biological treatment due to the reduced toxicity which is related to the starting-degradation of many compounds. Radiation processing reduced acute effects for all the treated samples. After 2.5 kGy, the decreasing pH at S3 effluents is a typical demonstration of organic acids being produced (Table 2).

## 5. Conclusion

The ecotoxicity data indicated 2.5 kGy for the textile studied effluents, which was efficiently able to reduce color (from 60% to > 90%). Combined technologies may guaranty a substantial improvement of wastewater and EB Irradiation applied as a first treatment step, before biological technology. Lower toxic charges are desirable for biological treatment systems as well as for discharged waters into environment. The *Vibrio fischeri* assay was the more sensitive and was a very good option since it is a fast assay, allowing us to get several results while running experiments at different environment and dose conditions.

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