

Toxicity and color reduction of a textile effluent containing reactive red 239 dye by electron beam irradiation

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ABSTRACT

Textile effluents are a mixture of dyestuff, surfactants, dispersants, acids, alkalis and bleaching agents, among other compounds, and some of these are highly soluble and relatively recalcitrant. Suitable improvement of textile effluents may require combined treatment processes, such as Conventional Treatments and Advanced Oxidative Process (AOPs). Electron beam irradiation (EBI) has been proposed as a possible technology for the treatment of textile effluents. In this context, the aim of the present study was to evaluate the efficiency of an Electron Beam treatment applied to toxicity and color reduction of a textile effluent containing reactive Red 239 dye. Effluent COD and TOC were also evaluated. The assessed effluents were submitted to EBI treatment at doses ranging from 0.5 to 15 kGy. *Vibrio fischeri* bacteria and *Daphnia similis* crustaceans were exposed to both irradiated and non-irradiated effluents, the toxicity was evaluated through EC50 (median effective concentration) calculations. EB irradiation successfully reduced effluent toxicity and color. The EC50 for *D. similis*_(48h) were of 6.31% ± 3.19 (non-irradiated) and 27.56% ± 9.31 (10 kGy), and for *V. fischeri*_(15min), of 7.41% ± 1.52 (non-irradiated) and 31.89% ± 10.99 (10 kGy), respectively. Approximately 70% toxicity reduction was obtained for both organisms, while 95% color reduction was obtained by applying 5 kGy.

1. Introduction

Despite the extreme importance of textile manufacturing for the Brazilian economy, the environmental aspects of this sector can still be improved. Effluents from the textile industry are critical, as they contain numerous contaminants, such as surfactants, dyes, peroxides, salts, acids, metals, suspended solids and organic compounds, as well as other additives. The high solubility, residual color and low biodegradability of many of these compounds require additional efforts for suitable cleaning. In this regard, combined processing emerge as a possibility, where activated sludge systems and Advanced Oxidative Processes (AOPs) may enhance organic degradation efficiency.

About 72 toxic chemicals have been identified in textile effluents, and it is estimated that approximately 200 billion liters of effluents are produced annually worldwide by the textile industry (Kant, 2012). Many negative effects have been identified due to the hundreds of contaminants diluted in aquatic systems, affecting dissolved oxygen, turbidity, color, temperature and, consequently, aquatic organisms. In this regard, the potential relationship between effluent toxicity and chemical oxygen demand has been discussed by Liang et al. (2018). Furthermore, highly toxic products can be generated even after

biodegradation, confirming the need for measuring whole acute effects after AOPs applications whenever possible.

Several negative effects of industrial pollutants on different living organisms due to dyes and textile effluent exposure have been evidenced. For example, *Danio rerio* fish have displayed genotoxicity induction, enzymatic alterations, oxidative stress and decreased swimming embryo activity (Abe et al., 2018; Meireles et al., 2018), while many toxic effects of textile effluents containing reactive dye Blue 222 have been evidences for *D. similis*, *V. fischeri* and *B. plicatilis* (Borrely et al., 2016). In addition, physiological changes and behavioral symptoms involving the heart, kidneys, lungs and intestinal epithelium were detected, as well as cell degeneration, renal tubule epithelial cell necrosis and alveolar emphysema have been reported in *Rattus norvegicus* (Akhtar et al., 2018).

The importance and scarcity of water today indicate the need for combined treatment processes. A possible technology in this regard is ionizing radiation using accelerated electrons. During this process, highly reactive intermediates (e.g. hydroxyl radicals) generated by water radiolysis are the primary oxidants in the reaction, leading to organic dye degradation. Besides radiation, other frequently used methods employed for the oxidation of organic compounds include UV-

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peroxide, ozonation, the photo-Fenton process, photocatalysis, and sonolysis (Wojnárovits and Takács, 2008).

Radiation efficacy concerning color removal and biodegradability of real industrial wastewater, as well as organic pollutant removal, using doses lower than 10 kGy have been reported in several studies. For example, two different industrial textile complexes demonstrated that this technology, alongside biological treatment processes, significantly improve effluent degradability and decolorizing. In China, EB irradiation enhanced effluent biodegradability up to 224% (3 kGy) (Kim et al., 2011; Han et al., 2002; He et al., 2016; IAEA, 2017).

In this context, the aim of the present study was to assess electron beam treatment efficiency in the toxicity and color reduction of a textile effluent containing the reactive dye Red 239. Sublethal effects of the effluents on *Daphnia similis* were observed during 21 days. Physico-chemical analyses, such as COD, TOC and pH were also determined in effluent samples.

2. Material and methods

2.1. Preparation of samples

The effluents were obtained by cotton dyeing during textile processing in a pre-industrial textile laboratory, representing the complete cotton coloring process (bleaching, dyeing and washing). The reactive Red 239 dye (Fig. 1) was applied and all compounds in the assessed effluents are known (Table 1).

2.2. Electron beam irradiation

The liquid effluents were irradiated at the Radiation Technology Center (CETER/IPEN/SP-Brazil), 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. Sample pH was determined before irradiation, with mean pH of 7.84 ± 0.45.

The samples were distributed in pyrex vessels (246 ml), ensuring 4 mm sample thickness, and the vessels were protected by plastic wraps. Doses were determined using a Perspex Harwell Red Batch KZ-4034 dosimeter, with less than 5% variation. The effluent samples were irradiated with doses ranging from 2.5 to 10.0 kGy, and 0.5, 1.0 and 15.0 kGy were included for color analyses.

2.3. Toxicity assays

• Acute Toxicity:

Acute toxicity assays using the crustacean *Daphnia similis* (ABNT NBR 12713: 2016) and bacteria *Vibrio fischeri* (ABNT NBR 15411:2012) followed Brazilian Technical Methods standards.

The *Daphnia similis* assay comprised exposure of juvenile individuals to the effluent samples for 48 h. Organisms immobility was the measured end point. The acute toxicity assay with *Vibrio fischeri* was performed in M-500 microtox Microbics system. Bacteria luminescence was analyzed before and after 15 min of exposure to the effluents. Loss of luminescence was indicative of toxic samples. Nine assays per sample

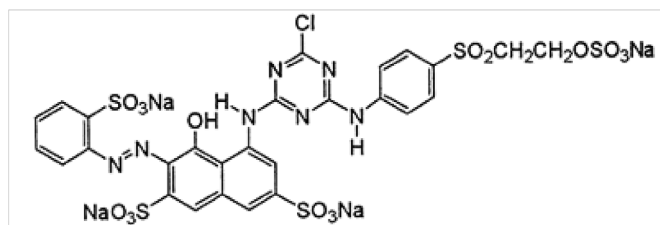


Fig. 1. C. I. Reactive Red 239 - chemical structure.

Table 1

Chemicals used in the cotton dyeing fiber process.

Catalase enzyme (g L ⁻¹)	0.50
Anionic Dispersant agent	1.00
Anionic Sequestering agent	1.00
Sodium carbonate	0.50
Sodium chloride	50.00
Sodium hydroxide	1.00
Sodium metasilicate	0.50
Nonionic Ethoxylate Surfactant	1.00
Reactive dye Red 239	15.00
Acetic acid (mL L ⁻¹)	1.00
Hydrogen peroxide	2.00
Sulfuric acid	0.15

were performed for each organism.

Results were expressed as EC50%, an inversely proportional parameter, i.e. the median concentration to observe an effect for 50% of all exposed organisms for exposure at standardized conditions. Statistics were applied according to the standard methods recommendation, using the Trimmed Sperm Karber analysis for *D. similis* and linear regression for *V. fischeri*.

Sample toxicity removal (%) after EBI treatment as calculated as follows (Eq. (1)):

$$TR(\%) = \left(\frac{TU_0 - TU_{\text{irrad}}}{TU_0} \right) \times 100; TU = \frac{100}{EC50\%} \quad (1)$$

Where: TU₀ = Toxicity Units before irradiation and TU_{irrad} = Toxicity Units after irradiation, and EC50% = median concentration of effect.

• Sublethal effects:

Sublethal textile effluent effects on *Daphnia similis* were also determined, during 21 days. Exposure concentrations were based on acute toxicity assays (triplicate), and, thus, lower than those applied in the acute effect assays. Image analyses were carried out using a Leica MZ95 magnifier (3.2×), Leica DFC 295 camera and the Leica Application Suite V4.12.0 software.

2.4. Physico-chemical parameters

Color: Absorbances were determined at 520 nm on a 1800 UV-VIS Shimadzu spectrophotometer and assessed using the UV-Probe Ver. 2.7 software. Color removal was calculated as follows (Eq. (2)):

$$CR(\%) = \left(\frac{A_0 - A_{\text{irrad}}}{A_0} \right) \times 100 \quad (2)$$

Where: A₀ = absorbance of the effluent solution before irradiation and A_{irrad} = absorbance of the effluent solution after irradiation.

Total Organic Carbon (TOC); Chemical Oxygen Demand (COD) and pH: The TOC analyses were performed using a Shimadzu TOC-5000A equipment, and the results were based on total carbon and inorganic carbon values. COD was assessed by a colorimetric method using a spectrophotometer. TOC and COD removals (%) obtained by the EBI method were calculated using values before and after irradiation, by applying equations similar to (1) and (2). For these analyzes, the effluent samples were irradiated at doses ranging from 2.5 to 15 kGy. Effluent pH values were determined by using a specific electrode (Micronal B474) for the untreated and irradiated samples (2.5–10 kGy).

3. Results and discussion

3.1. Toxicity reduction performance by EB irradiation

Aquatic organism toxicities of the textile effluent containing the reactive dye Red 239 irradiated with EBI were determined herein.

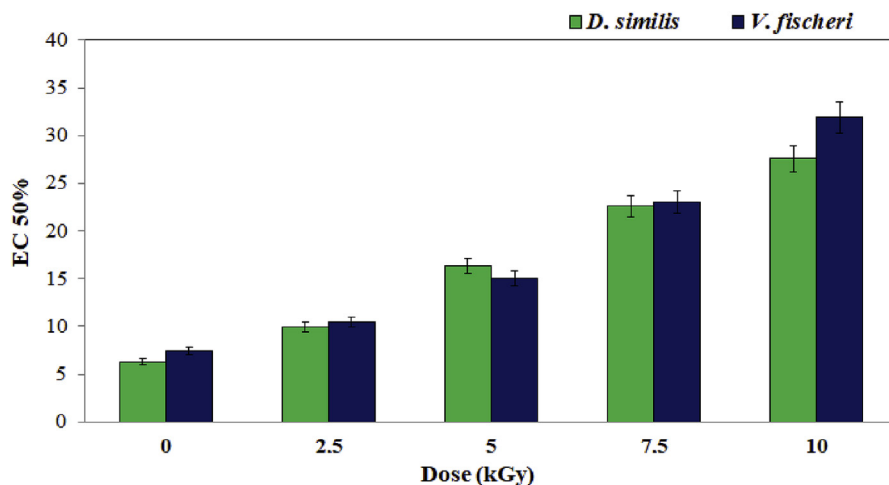


Fig. 2. Acute toxicity (EC50% average values) of a textile effluent containing RR239 versus applied EBI doses.

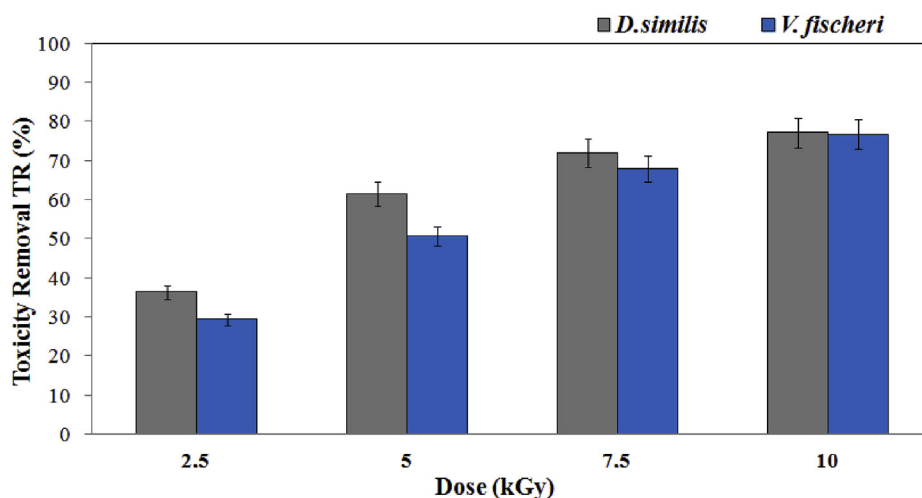


Fig. 3. Textile effluent toxicity removal (TR) (%) after EBI treatment.

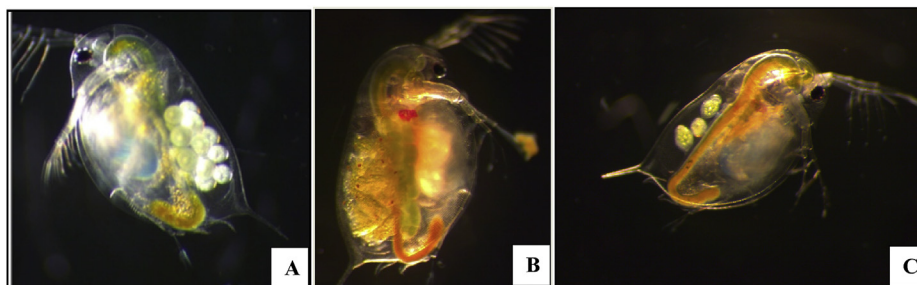


Fig. 4. *D. similis* exposed to textile effluent under different conditions. A. Control. B. Organism exposed to the raw effluent. C. Organism exposed to the treated effluent at 5 kGy.

Acute toxic effects and EBI efficiency regarding toxicity are reported in Figs. 2 and 3, while sublethal daphnid effects are summarized in Fig. 4.

Regarding the EC50 values displayed in Fig. 2, high toxicity level were observed for non-irradiated samples, very toxic for both assessed organisms, with EC50s below 7.5%. As EC50 is an inversely proportional parameter, higher EC50 values indicate that higher concentrations of treated samples are required to achieve effective median concentrations (EC50%), evidencing lower effects on the assessed organisms after irradiation. The obtained toxicity removal values (TR, %), displayed in Fig. 3, confirm that acute effect removal was enhanced from 2.5 up to 10 kGy for both organisms.

For example, at 5 kGy and 10 kGy, EC50 = 16.36% \pm 5.37 (5 kGy) accounted 61.43% toxicity removal for *D. similis* and 50.73% for *V. fischeri* (EC50 = 15.04 \pm 2.48), while 10 kGy resulted > 70% acute effects removals for both exposed organisms, at EC50 values of 27.56 \pm 9.31 for *D. similis* and 31.89 \pm 10.99 for *V. fischeri*.

Concerning acute textile effluent effects, several published reports demonstrate significantly toxic effects for different organisms before treatment, corroborating data from the present study, such as those reported by Sharma et al. (2007), EC50 = 0.7% for *L. aquinoctialis* when assessing textile wastewater in India and Liang et al. (2018), EC50 = 1.7% for *V. fischeri* when evaluating textile wastewater in

China. For daphnids, EC values of 4.58% for *D. similis* exposed to a mixture of reactive RB 222, RR 239, RY145 dyes and 10.40% for *D. magna* exposed to an effluent containing the reactive dye Red 120 have been reported (Darsana et al., 2015; Rosa et al., 2019).

Regarding the results obtained after the EBI treatment, considering 5 kGy as a suitable dose for acute toxicity removal, about 61% and 51% acute toxicity removal were obtained, while efficiencies of 34.55% for *D. similis* and 47.83% *B. plicatilis* (2.5 kGy) and *V. fischeri* 57.29% (5 kGy) were observed by Borrely et al. (2016) for an effluent containing the RB222 dye. On the other hand, a lower efficiency was obtained for real effluents containing the reactive dye Yellow 160, of approximately 18% at 2.5 kGy (Borrely et al., 2019).

Daphnid sublethal effects and reproduction effects were assessed after exposure to effluent samples for 21 days. Neonate assessments were carried out every other day. The negative control (Fig. 4A) corresponds to the ideal number of incubated eggs for a female 21-day old daphnid exposed only to natural water under the same conditions as those exposed to the effluent samples. Daphnid reproduction rates were reduced after exposure to untreated effluents, where the dye entered the eggs and filtering system, also leading to egg malformations (Fig. 4B). On the other hand, less dye deposition was noted for organisms exposed to the treated effluent at 5 kGy (Fig. 4C). In this case, although reproduction rates were lower when compared to the control, no egg malformations were observed.

Concerning different classes of organisms, biochemical alterations in zebrafish embryos, as well as alterations in swimming activity and toxic cell effects, such as enzyme changes and oxidative stress, have been previously reported (Abe et al., 2018; Meireles et al., 2018). In another case, Sharma et al. (2007), reported dye deposition in gills and internal organs, body darkening, eye whitening and mucus secretion in *Gambusia affinis* fish specimens. Regarding mammals, *Rattus norvegicus* specimens exposed to textile wastewater exposed has been associated to several physiological changes and behavioral symptoms, and sub-chronic exposure led to the renal tubule epithelial cell degeneration and necrosis, as well as hepatocyte necrosis (Akhtar et al., 2018).

The importance of toxicity measurements is clear, as it includes the interaction of most pollutants contained in raw effluents, not only dyes. However, physicochemical parameters alone are not enough for the evaluation of effectiveness of the proposed treatments for removing hazardous compounds.

3.2. Removal of organic pollutants by EB irradiation

Color and organic compounds were also determined in the investigated effluents, displayed in Figs. 5 and 6 and Table 2.

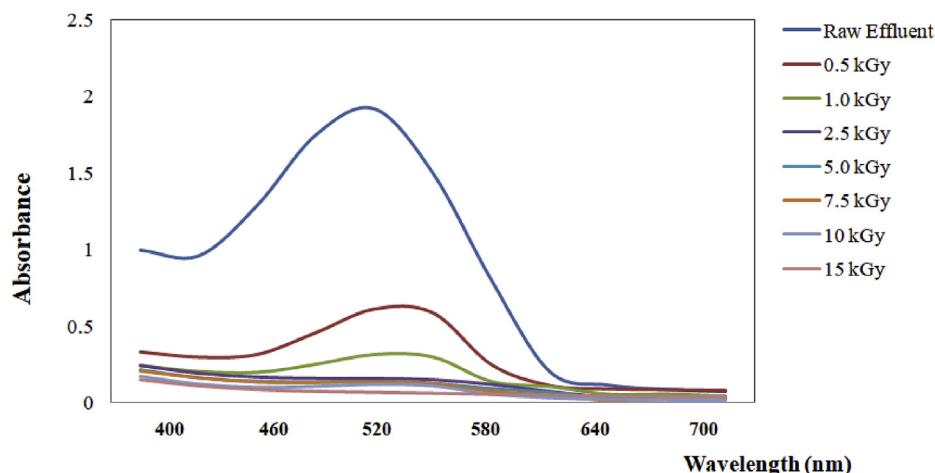


Fig. 5. Color removal of the investigated effluent versus applied EBI. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

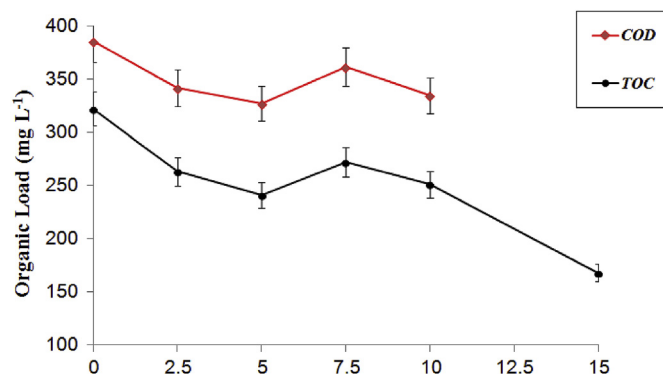


Fig. 6. COD and TOC values of the investigated textile effluent versus applied EBI.

Table 2

Efficiency of EBI technology for color, COD and TOC removal in textile effluents.

Effluent Samples Dose (kGy)	Color Removal CR (%)	COD Removal (%)	TOC Removal (%)
2.5	94.00	11.28	18.33
5.0	95.60	15.17	25.22
7.5	95.64	6.22	15.54
10.0	96.15	13.22	22.12
15.0	98.00	–	47.81

Concerning textile effluent decoloration after EBI treatment, an applied dose of 5 kGy led to 95% color removal compared to raw samples, while 0.5 kGy accounted for 80% color removal. Considering dye solution decoloration and textile effluent treatment by radiation, similar results have been demonstrated when applying ionizing radiation, as follows: Direct Black 22, 100% color removal at 6 kGy (Vahdat et al., 2010); Reactive azo (95.3% removal) and Direct azo (95.5% removal), at 7 kGy (Abdou et al., 2011); Reactive Blue 222, 90% removal at 2.5 kGy (Borrely et al., 2016); while dye mixtures from textile industries presented 61% removal at 0.5 kGy (Ting and Jamaludin, 2008).

The mean COD concentration in the raw effluent was of 385.5 mg L^{-1} . The best result after EBI treatment was obtained at a 5 kGy, of 327.0 mg L^{-1} . Similar COD values in raw textile effluents have been reported by He et al. (2016), of 316 mg L^{-1} , and of 309 mg L^{-1} after the application of a 6 kGy.

After effluent sample EBI treatment, TOC values decreased (Fig. 6)

from 322.3 mg L⁻¹ in the raw effluent to 241 mg L⁻¹ after a 5 kGy and 168.2 mg L⁻¹ after a 15 kGy, indicating EBI efficiency concerning TOC removal, of approximately 25% and 48% for both doses, respectively. Similarly, Liang et al. (2018) reported that a TOC value for untreated textile wastewater from an industrial complex in China of 320 mg L⁻¹. Applying ionizing radiation, in aqueous solution with remazol Black 5 dye, 45% TOC removal with 5 kGy was reported by Abdou et al. (2011).

Concerning pH, no significant change was noted comparing the raw effluent samples (7.84 ± 0.45) with samples treated with 5 kGy (8.53 ± 0.69) and 10 kGy (8.36 ± 0.58).

Relatively low irradiation doses have been reported as a possible and feasible target for EBI by several authors as an advanced process to contribute with other technologies for the improvement and reuse of industrial effluents.

4. Conclusions

The toxicity results reported herein represent the effects of several contaminants present in textile effluents. Both acute and sublethal effects decreased after EB irradiation. The assessed textile effluent was very toxic, with an EC 50 average of 6.31 for *D. similis* and 7.41 for *V. fischeri*. EBI was effective for toxicity removal, resulting in > 70% acute effects. Sublethal *D. similis* effects when exposed to effluents samples for 21 days, were also detected. After the application of a 5 kGy, less dye deposition was noted in the daphnid filtering system, and no egg malformation was observed. Textile effluent irradiation improved both acute and sublethal effects and is a promising technique for textile effluent treatment.

Other benefits were also observed after irradiation at 5 kGy, such as over 95% decoloration, 15.17% COD removal and 25% TOC removal. The degradability of such type of contaminants may be improved by combining processes.

Therefore, the aforementioned negative biological effects comprise a strong motivation for searching for innovative technologies in order to improve the treatment of different classes of contaminants.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Abdou, L.A.W., Hakeim, O.A., Mahmoud, M.S., El-Naggar, A.M., 2011. Comparative study between the efficiency of electron beam and gamma irradiation for treatment of dyes solutions. Chem. Eng. J. 168, 752–758. <https://doi.org/10.1016/j.cej.2011.01.071>.

- Abe, F.R., Soares, A.M.V.M., Oliveira, D.P., Gravato, C., 2018. Toxicity of dyes to zebrafish at the biochemical level: cellular energy allocation and neurotoxicity. Environ. Pollut. 235, 255–262. <https://doi.org/10.1016/j.envpol.2017.12.020>.
- Akhtar, M.F., Ashraf, M., Javed, A., Anjum, A.A., Sharif, A., Saleem, M., Mustafa, G., Ashraf, M., Saleem, A., Akhtar, B., 2018. Association of textile industry effluent with mutagenicity and its toxic health implications upon acute and sub-chronic exposure. Environ. Monit. Assess. <https://doi.org/10.1007/s10661-018-6569-7>. 190–179.
- Associação Brasileira de Normas Técnicas, ABNT, 2016. Ecotoxicologia aquática, Toxicidade Aguda- Método de ensaio com *Daphnia spp* (Crustacea, Cladocera). ABNT, Rio de Janeiro (NBR12713).
- Associação Brasileira de Normas Técnicas, ABNT, 2012. Ecotoxicologia aquática, Determinação do efeito inibitório de amostras de água sobre a emissão de luz de *Vibrio fischeri*. ABNT, Rio de Janeiro (NBR15411).
- Borrely, S.I., Silva, L.G.A., Del Sole, S.V., Garcia, V.S.G., Boiani, N.F., Rosa, J.M., 2019. Electron Beam Irradiation of textile effluents and non-ionic ethoxylated surfactant for toxicity and color removal. Braz. J. Radiat. Sci. 7–2A, 1–10. <https://doi.org/10.15392/bjrs.v7i2A.702>.
- Borrely, S.I., Morais, A.V., Rosa, J.M., Badaró-Pedroso, C., Pereira, M. da C., Higa, M.C., 2016. Decoloration and detoxification of effluents by ionizing radiation. Radiat. Phys. Chem. 124, 198–202. <https://doi.org/10.1016/j.radphyschem.2015.11.001>.
- Darsana, R., Chandrasehar, G., Deepa, V., Gowthami, Y., Chitrikha, T., Ayyappan, S., Goparaju, A., 2015. Acute toxicity assessment of reactive red 120 to certain aquatic organisms. Bull. Environ. Contam. Toxicol. 95, 582–587. <https://doi.org/10.1007/s00128-015-1636-z>.
- Han, B., Ko, J., Kim, J., Kim, Y., Chung, W., Makarov, I.E., Ponomarev, A.V., Pikaev, A.K., 2002. Combined electron-beam and biological treatment for dyeing complex wastewater. Pilot plant experiments. Radiat. Phys. Chem. 64, 53–59. [https://doi.org/10.1016/S0969-806X\(01\)00452-2](https://doi.org/10.1016/S0969-806X(01)00452-2).
- He, S., Sun, W., Wang, J., Chen, L., Zhang, Y., Yu, J., 2016. Enhancement of biodegradability of real textile and dyeing wastewater by electron beam irradiation. Radiat. Phys. Chem. 124, 203–207. <https://doi.org/10.1016/j.radphyschem.2015.11.033>.
- IAEA. International Atomic Energy Agency, 2017. China's First Wastewater Plant Using Radiation Opens. Radiation Science & Technology. <https://www.iaea.org/sites/default/files/publications/magazines/bulletin/bull58-1/5810809.pdf>, Accessed date: 30 August 2019.
- Kant, R., 2012. Textile dyeing industry and environmental hazard. Nat. Sci. 4, 22–26. <https://doi.org/10.4236/ns.2012.41004>.
- Kim, Y., Kim, J., Han, B., 2011. Application of an electron accelerator for the treatment of wastewater from textile dyeing industries. J. Kor. Phys. Soc. 59, 3489–3493. <https://doi.org/10.3938/jkps.59.3489>.
- Liang, J., Ning, X., Sun, J., Song, J., Lu, J., Cai, H., Hong, Y., 2018. Toxicity evaluation of textile dyeing effluent and its possible relationship with chemical oxygen demand. Ecotoxicol. Environ. Saf. 166, 56–62. <https://doi.org/10.1016/j.ecoenv.2018.08.106>.
- Meireles, G., Daam, M.A., Sanches, A.L.M., Zannoni, M.V.B., Soares, A.M.V.M., Gravato, C., Oliveira, D.P., 2018. Red disperse dyes (DR 60, DR 73 and DR 78) at environmentally realistic concentrations impact biochemical profile of early life stages of zebrafish (Danio rerio). Chem. Biol. Interact. 292, 94–100. <https://doi.org/10.1016/j.cbi.2018.07.007>.
- Rosa, J.M., Garcia, V.S.G., Boiani, N.F., Melo, C.G., Pereira, M.C.C., Borrely, S.I., 2019. Toxicity and environmental impacts approached in the dyeing of polyamide, polyester and cotton knits. J. Environ. Chem. Eng. 7, 102973. <https://doi.org/10.1016/j.jece.2019.102973>.
- Sharma, K.P., Sharma, S., Sharma, Subhasini, Singh, P.K., Kumar, S., Grover, R., Sharma, P.K., 2007. A comparative study on characterization of textile wastewaters (untreated and treated) toxicity by chemical and biological tests. Chemosphere 69, 48–54. <https://doi.org/10.1016/j.chemosphere.2007.04.086>.
- Ting, T.M., Jamaludin, N., 2008. Decolorization and decomposition of organic pollutants for reactive and disperse dyes using electron beam technology: effect of the concentrations of pollutants and irradiation dose. Chemosphere 73, 76–80. <https://doi.org/10.1016/j.chemosphere.2008.05.007>.
- Vahdat, A., Bahrami, S.H., Arami, M., Motahari, A., 2010. Decomposition and decoloration of a direct dye by electron beam radiation. Radiat. Phys. Chem. 79, 33–35. <https://doi.org/10.1016/j.radphyschem.2009.08.012>.
- Wojnárovits, L., Takács, E., 2008. Irradiation treatment of azo dye containing wastewater: an overview. Radiat. Phys. Chem. 77, 225–244. <https://doi.org/10.1016/j.radphyschem.2007.05.003>.