2019 International Nuclear Atlantic Conference - INAC 2019
Santos, SP, Brazil, October 21-25, 2019
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-08-3

Agência Brasileira do ISBN
ISBN 978-85-99141-08-3

Toxicity and color reduction of reactive dyestuff RB21 and surfactant submitted to electron beam irradiation

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ABSTRACT

There is an unwelcome reaction between the coloring and the water during the dyeing procedure, a portion of the coloring agent is lost in the bathing and it will compose the final whole effluent. The high absorbance index is related to lost dyes and they also contribute with the toxic effects to the aquatic biota. In addition, these effluents contain large quantity of surfactants applied during dyeing baths, which also contribute to the high toxicity in these samples. The objective of this study was to evaluate electron beam irradiation technology, applied in samples of the Color Index Reactive Blue 21 (RB21) dye and in samples of surfactant nonionic and in order to reduce toxicity for both and for RB21, color reduction. Among the objectives of the study there are the dye exhaustion degree, and some physic-chemical parameters. The acute toxicity assays were carried with *Daphnia similis* microcrustacean and the results for of dyestuff solution were: the irradiated samples with concentration of $0.61 g.L^{-1}$ did not present significant results, the EC 50(%) value was to 58.26 for irradiated sample with 2.5kGy and EC 50(%) 63.59 for sample irradiated with 5kGy. The surfactant was more toxic than RB 21, with EC 50(%) value at 0.42. The color reduction reached 63.30% for the sample of the lowest concentration of effluent. There was a reduction of pH during irradiation.

1. INTRODUCTION

The water is a vital resource for the human consumption, and for keeping health biota (fauna and flora), and also agricultural and industrial suitable production. However, water is becoming more and more scarce even after hundreds of regulations. There is a huge need for rational use of water, avoiding the wastes and the pollution, which is related not only environmentalists, but also governmental institutions and its productive processes. Many persons (1/6 of world population) have no access to clean water [1].

The textile sector demands a high amount of water in its production chain, producing high quantity of residual water. Primary and secondary part of textile processing require more water due to dyeing of a given substract [2]. The cotton fiber stands out as the most consumed by the clothing sector, and more than half of its production is dyed with reactive coloring agents. The molecules of such dyeing are reacting to the fibers in alkaline pH, through Hydrogen Bonds, Van der Waals Force and, also, through Covalent Bonds [3]. However, as wells as the reaction between dye and fiber, it also generates the reaction between dye and the water used in the bathing, known as hydrolyzed dye.

The dyes hold lengths of eletromagnetic waves that fluctuate from 400 to 720 mm, a range known as visible spectrum. They can be rated by its chemical structure, its application, according to the fiber used in the dyeing, or by its commercial trademark [4].

The commercial name of a dye is contained in the base of the International Color Index (single and global classification system of colors), and can be identified through the CAS number with respect to the registration of a particular chemical compound available in the Chemical Abstracts Service database. The dye used in this study was the C.I. Reactive Blue 21 (RB21): molecular mass equal to 1079.53g mol^{-1}, nº CAS $12236\text{-}86^{-1}$, Homofunctional, reactive group Vinylsulphone and chromophore group Phthalocyanine. It is employed in colors with shades of green water, green flag and turquoise. Its structure is shown in Figure 1.

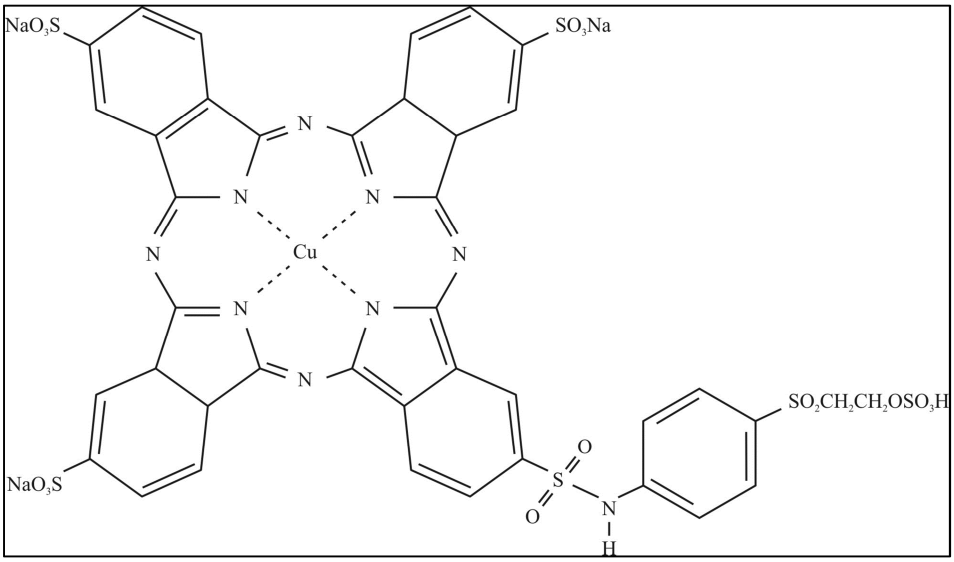

Figure 1: Molecular Structure of the RB21 dye

The textile effluents contain high amount of dyes, 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. These compounds can interact and change the major components of the cell membrane, proteins and lipids of organisms. In aquatic organisms, alterations in growth, reproduction and motility were observed and correlated to textile pollution [5; 6].
The variation of color from the derived effluent is substantial, generating absorptiometrics units in the range of 420nm to 600nm [7; 8]. Due to strong staining and high solubilization of dyes even low concentrations. They reduce light penetration into aquatic systems. Therefore, there is a need to review, in addition to the absorptiometrics index, other valuation parameters such as dissolved oxygen concentration in water, and the possible induction of toxicity to the aquatic organism.

According to M.A. Rauf e S. Salman Ashraf [9], the Advanced Oxidation Processes (AOP) are a set of techniques that normally uses a strong oxidant that makes a sequence of reactions, spliting the macromolecule into smaller and less harmful substances. Moreover, they argue that the degradation of the dyes starts, exclusively, by the attack of OH• in places rich in eletcrons from the dye molecules. The radical OH• formed is the main reactive kind that degrade the dye, destroying or changing the structure of its chromophore group [10].

The ionizing radiation, by electron beams, appeared as an option to the advanced oxidation process for the effluent treatment through important reactive kinds for the oxidation of organic contaminants [11].

The identification of possible biological damage to the environment can be made through standard toxicity tests, in which sensitive organisms are submitted to a certain toxic compound with the aim of establishing level of effects, whether lethal or sub-lethal. The acute toxicity tests, for example, allow us, in a short period of time, to evaluate part of life cycle of the organism; immobility or mortality, influence on biochemical reactions, among other effects [12].

2. OBJECTIVES

The objective of this study was to evaluate electron beam irradiation technology, applied in samples of Reactive Blue 21 (RB21) and surfactant nonionic in order to analyze the toxicity, color reduction, exhaustion degree, and the pH.

3. METHODOLOGY

The methodology of this work consisted in analyzing RB21 dye submitted to Electron Beam Treatment, in order to evaluated the toxicity, and other parameters, such as Absorptiometric Decay, the Dye Exhaustion Level and the pH obtained after treatment. Acute toxicity of non-ionic surfactant, before and after the irradiation, was evaluated.

3.1. Preparation of the samples

The reactive dye and surfactant aqueous solution were prepared at LEBA (Environmental and Biological Assays Laboratory) as described follow.

* **Dyestuff RB 21:** the concentration $0.61 g.L^{-1}$ was used on the basis of the study developed by Rosa *et al*. [13], assessing the exhaustion degree to RB21 dye, with standard concentration of $1.5 g.L^{-1}$ in the manufacturer dye. This study determined that only 59.29% of the dye migrated to the fiber that is 40.71% of the dye remained in the dyeing bath. Therefore, it was interesting to analyze the fact that, stemming from the initial concentration of dye, $0.61 g.L^{-1}$ stayed in the effluent.

***Surfactant (nonionic):** was analyzed at the concentration of $1 g.L^{-1}$, the same used for cotton fiber processing.

3.2. Irradiation of the samples

The EBI of samples was carried out at an Industrial Electron Beam Accelerator, Dynamitron, at Centro de Tecnologia das Radiações/IPEN-CNEN/SP. The irradiations were performed at batch processing; samples constained in glass pyrex and covered with plastic film. The speed of the conveyer belt was 6.72m min^{-1}, variable current and 1.4MeV fixed energy.

The doses applied during this study were: 2.5kGy and 5 kGy for dye solutions and 2.5kGy for surfactant samples.

3.3. Ecotoxicological Assays

The acute toxicity was evaluated with microcrustacean *Daphnia similis*, in accordance with the NBR 12713/2016 [14]. The criteria applied for choosing this organism was its high sensibility to chemical agents, and its bioavailability, and relatively simple maintenance in laboratory standard conditions. *D. similis* were taken from LEBA proper culture for acute toxicity measurements.

The assays were based on the exposition of young organisms (between 6 to 24 hours - young), for a period of 48 hours, for determining the concentration of the toxic agent that caused immobility or mortality to 50% of exposed organisms (EC50). Preliminary and definitive assays were carried.

3.3.1. Statistical Analyses

EC50 values were based on immobility raw data and Trimmed Spearkman-Karber method analysis [15]. The validation of these assays were based on a negative control. Furthermore, according to the recommendations of ABNT standard procedure, the sensitivity of organisms for Potassium Chloride was measured as a reference substance.

3.3.1.1. Toxic Unit

As EC50 values are an inversely proportional parameter, it is common to use the Toxic Unit calculation. The Toxic Unit (TU) express a direct value, namely, the higher its numeric value, the higher will be the toxicity of the analyzed sample. It can be obtained through the following sequence [16].

$$\mathrm{TU} = \frac{100}{EC50} \qquad (1)$$

3.4. Absorptiometric Decay

The absorptiometric decay (AD) that involve the level of color reduction was determined by using acrylic buckets with thickness of 1.0cm through the visible spectrophotometer (Konica Minolta, CM-3600d model), in the SENAI/SP facilities. It was made a reading of lenght ranging from 400m to 700m, with the raw and irradiated samples. The calculation of AD was obtained by the equation:

$$A_{\mathrm{D}} = \left[\frac{A_{0} - A_{f}}{A_{0}}\right] \mathrm{x}\, 100 \qquad (2)$$

A_0= Initial absorbance;
A_f = Final absorbance.

3.5. Exhaustion Degree

The exhaustion degree consists in quantifying the concentration of the dye existing in the solution. The calculation has its base through the preparation of a solution with concentration 0.61gL^{-1} of RB21 and, in the sequence, this solution was diluted in 10 samples with a reduction of 10% each until the final concentration.

The absorbance of all samples were evaluated through the visible spectrophotometer, under an illuminant D65, 10º (Konica Minolta CM-3600d model) and, with the values obtained and its concentrations, a theoretical adjustment curve was drawn, in addition to an equation base to calculate the dye concentration in the sample after the irradiation.

4. RESULTS AND DISCUSSION

The toxicity results of *Daphnia similis* exposed to samples of RB21 dye and no-ionic surfactant were organized in table 1. Very similar data was obtained to all samples of reactive RB21 dye before and after irradiation 2.5 and 5kGy. On the other hand, the surfactant was very toxic for *D. similis* and much more toxic if compared to RB-21 dye. After 2.5kGy the toxic units were reduced (Table 1).

In addition to the toxicity analysis, we evaluated color of the samples in relation to the absorbed dose. The Figure 2 represents the reading of the absorbance of RB 21 dye, at 400nm to 700nm. From Fig. 2 it is possible the observation of significant decrease of absorbance of irradiated sample. It was possible to verify a degree of discoloration of 19.55% in the irradiated sample with 2.5kGy and 24.60% in the irradiated sample with 5kGy.

Table 1: Values of EC50 and TU in raw and irradiated samples

Sample	$EC50_{48h}$ (%)	TU
RB21 - 0.61g.L^{-1} (0kGy)	61.12 (53.17 - 70.26)	1.64
RB21 - 0.61g.L^{-1} (2.5kGy)	58.26 (55.87 - 60.75)	1.72
RB21 - 0.61g.L^{-1} (5kGy)	63.59 (61.30 - 65.96)	1.57
Surfactant - 1.0g.L^{-1} (0kGy)	0.42	238.09
Surfactant - 1.0g.L^{-1} (2.5kGy)	0.46	217.39

He *et al.* [17] applied EBI as support in the biodegradability of textiles effluents. The results showed that irradiation after biological process can increase the biodegradability up to 224%. Borrely *et al.* [18] investigated three textile samples regarding its color and toxicity. After the EBI, 80% toxicity removals were obtained for *V. fischeri*, *D. similis* and *B. plicatilis*.

Regarding the pH values from the irradiated samples, it is shown a decrease: for RB21 dye initial pH of 5.90 decrease to 4.92 (2.5kGy), and then to 4.76 (5kGy). This acidity increase due to the formation of organic acids coming from the organic compounds degradation [19].

In this study, high toxicity to *D. similis*, EC50 (mg/L) was determined for surfactants. From other authors, Romanelli *et al*. [20] indicates important toxicity values for sodium dodecyl sulfate EC 50% 1.92 to *V. fischeri* and EC 50% 11.81 to *D. similis*. For Linear alkylbenzene sodium, 13.49 (*V. fischeri*) and 4.56 (*D. similis*) were reported. To the same surfactant, Hodges *et al*. [21] found values from 0.67%.

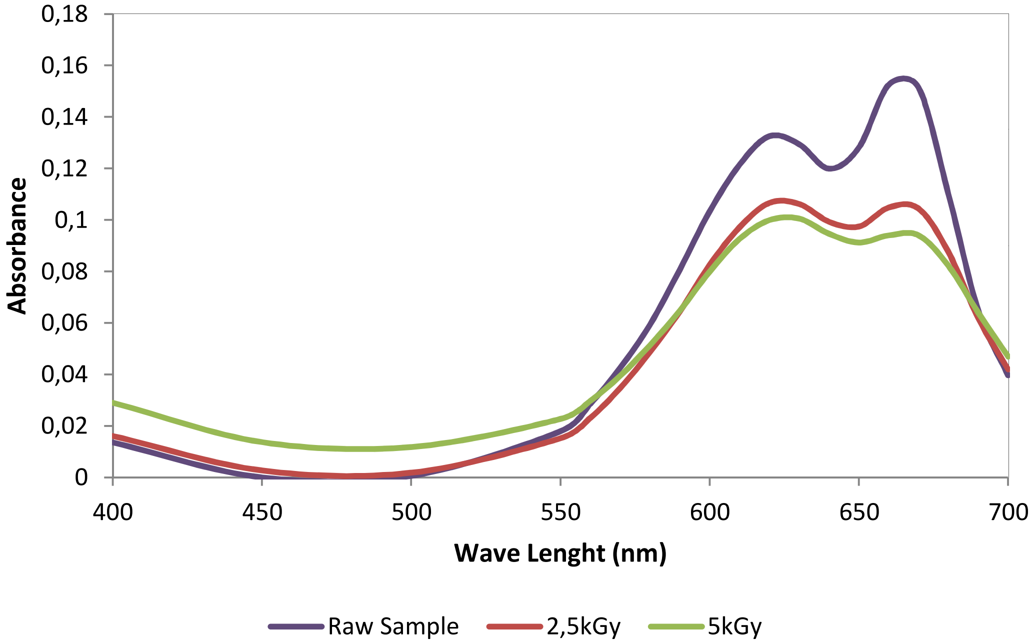

Figure 2: Reading of concentration sample 0.61g.L^{-1} absorbance

It is known that many materials have their coloration altered when exposed to ionizing radiation, and the figure below allows us to verify that the effect of ionizing radiation on the dye solution promoted, in addition to color reduction, a change of the same. The interaction between the radiation and the solution led to the modification of the optical properties of the dye structure [22]. Treatments by adsorption have been used for the dye remotion, like Vanaamudan, Chavada e Padmaja [23], who studied the adsorption in hydrotalcite, obtaining the values of 226 mg.g^{-1}, that are ideal to the RB21 absorption in pH 2.0. Sohrabi *et al.* [24] obtained 95% of RB21 removal in aqueous solution through the adsorption of iron compounds.

Correlating the absorbance data with the dilution concentrations, a theoretical calibration curve allowed us to calculate the concentration of dye present in the sample after irradiation. For this work, with the base of the calibration curve, the following equation was obtained:

$$RB21_n = \frac{Abs_n + 0{,}2501}{6{,}6333} \qquad (3)$$

In table 2 it is possible to observe the values of final concentration of RB21 after irradiation, based in correlating the absorbance data with the dilution concentrations, these values were obtained with equation 3. The results demonstrated the reduction to final concentration of Reactive Blue 21

Table 2: Final concentration of RB21 after irradiation

Initial Concentration ($g.L^{-1}$)	Dose (kGy)	Final Concentration ($g.L^{-1}$)
$0.61 g.L^{-1}$	2.5	0.0538
$0.61 g.L^{-1}$	5	0.0528

5. CONCLUSIONS

Electron beam irradiation was effective for the discoloration of aqueous solutions of the RB21 dye, with 24.60%. Regarding the toxicity, the surfactant solution showed a low value of EC50 and can be rated as highly toxic product. In this regard no improvement was obtained by irradiation. If comparing acute toxic effects the surfactant was much more toxic than the RB 21 dye. Irradiation-based technology may be feasible once several organics may be reduced at the same time and with relatively low dose.

ACKNOWLEDGMENTS

We would like to thank Faculdade de Tecnologia SENAI Antoine Skaf and Instituto de Pesquisas Energéticas e Nucleares. Both provided necessary resources to the development of this work. Our thanks also to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), by the financial assistance granted.

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