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TOXICITY AND COLOUR REDUCTION FOR AZO DYES SUBMITTED TO ELECTRON BEAM IRRADIATION

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ABSTRACT

At present work, aqueous solutions of reactive azo dyes were treated with electron beam radiation (Reactive Black 5 (RB5) and Reactive Red 198 (RR198)). The efficiency of treatment was evaluated by colour alteration and toxicity of the azo reactive dyes. Different radiation doses were used (0.5 kGy to 10.0 kGy) and the textile dyes were tested at two concentrations (50 mg L^{-1} and 100 mg L^{-1}). The reduction of colour was determined by UV-vis spectrophotometer and the results showed that the samples lost the colour rapidly while the doses were incresead. The variation in acute toxicity for *Daphnia similis* was used to evaluate the efficiency of irradiation treatment (biological effects). The changes on pH values indicated presence of organic acids.

1. INTRODUCTION

Textile effluent is notoriously known to have a strong color, large amount of suspended solids, broadly fluctuating pH, high temperature and high chemical oxygen demand (COD) [4]. Synthetic textile dyes can be structurally different and a very low concentration of dyes in effluent is highly visible and undesirable [7]. Discharge of these dyes is undesirable not only for aesthetic reasons, but also because they may decrease the absorption of light by the water, plants and phytoplankton reducing photosynthesis and the oxygenation of water [9]. Many azo dyes and their intermediate products are toxic and mutagenic or carcinogenic to aquatic life and humans [6] and they may also contain levels of heavy metals that breach environmental standards [1]. Due to large scale production and extensive application they can cause considerable environmental pollution and are health risk factors [3].

Reactive textile dyes are extensively used for dyeing process in textile, and about 20-40% of these dyes are lost in the effluents. They exhibit a wide variability in chemical structure, primarily based on substituted aromatic and hetero cyclic groups. A large number of reactive dyes are azo compounds containing an azo bound (-N=N-). Since reactive dyes are highly soluble in water, their removal from wastewater is difficult by conventional coagulation and the activated sludge process [8, 13].

Actually several physical, chemical and biological technologies are being evaluated for the treatment of textile wastewater. Advanced oxidation processes (AOP) offer new routes for the oxidative degradation of organic compounds. Radiation technology (AOP process) has been recognized as a promising process for hazardous organic wastewater treatment. Free radicals are formed when water is irradiated with ionizing radiation, delivered from γ-rays or electron beam. The majorities of these radicals are hydroxyl radicals (●OH) and hydrated

electrons (e_{aq}), although smaller quantities of other radicals such as ●H are also formed [5, 10, 11, 12, 14]. These species are strongly oxidizing and capable of degrading aromatic compounds as textile dye.

The aim of the present study was to investigate the possibility of using electron beam irradiation to degrade reactive dyes. The efficiency of treatment for dyes in aqueous solution was evaluated by toxicity and colour reduction. Reactive Black 5 (RB5) and Reactive Red 198 (RR198) in water were irradiated with doses 0.5 to 10.0 kGy. The change of absorption spectra and pH value of solutions were analyzed as well as the degree of decoloration and reduction of acute toxicity.

2. EXPERIMENTAL

2.1. Materials

Remazol Black B 133% (C.I. Reactive Black 5 – RB5) and Remazol Red RB 133% (C.I. Reactive Red 198 – RR198) were obtained from Dyes manufacture (São Paulo) as a commercially available dye formulation and used without further purification. These dyes are diazo and monoazo type reactive dyes respectively, containing vinyl sulfonate reactive groups, as represented by the chemical structure in Figure 1.

2.2. Experimental Procedures

Distillated water was used to prepare the reactive dye samples with the concentration of 50 and 100 mg L^{-1}. The high voltage type electron accelerator in the Instituto de Pesquisas Energéticas e Nucleares (IPEN) was used as electron beam irradiation facility. The samples were irradiated with 1.5 MeV Dynamitron from Radiation Dynamics in a batch system, using Pyrex glass vessels and delivered doses were 0.5; 1; 2.5; 5; 7.5 and 10.0 kGy. The irradiation parameters of electron beam irradiation were 4.0 mm of sample thickness, a scan of 112 cm (94.1%) and conveyor velocity of 6.72 m/min.

The evaluation of the irradiation treatment efficiency was performed by analysis of the absorption spectra and absorbance (UV 1601 – Shimadzu), pH value and acute toxicity of the samples before and after irradiation.

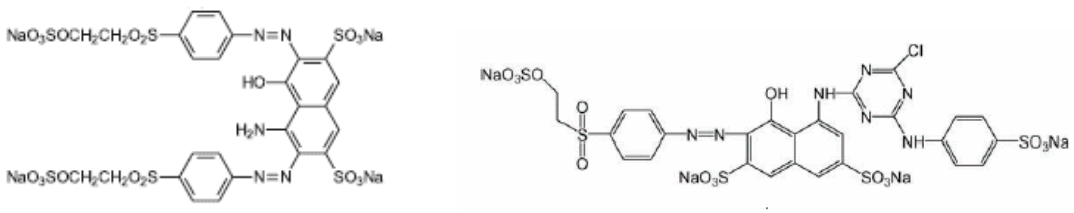

Figure 1. The structure of reactive black 5 (left) and reactive red 198 (right).

2.3. Calculation of Decoloration

The decoloration of dye solution was calculated as follows:

$$(A_0 - A_1) / A_0 \text{ x } 100\% \quad . \tag{1}$$

A_0 and A_1 are the maximum absorbance in visible area of the dye solution before an after irradiation.

2.4. Toxicity Measurements

The samples of reactive dyes were tested using 24 h born *Daphnia similis* at different dilution rates according to ABNT [1]. Toxicity tests were performed using twenty daphnids for concentration and 48 hours exposure at 20°C ± 0.5. At least five concentrations for each formula were analyzed. Results were expressed as daphnids immobilization percentage after 48 h exposition (EC 50 for 48 h). These values were transformed into Toxic Units (TU) for the calculation of the irradiation treatment efficiency (equation 2). For the maintenance of test-organisms: these organisms were feed with chlorela algae, photoperiod - 16 h light / 8 h dark, lighting with 1000 lux. The water hardness was adjusted and fixed to 46 mg L^{-1} $CaCo_3$, 7.5 pH and 20°C ± 0.5.

The acute toxicity evaluation was carried out for irradiated and unirradiated samples. The samples of reactive azo dyes (50 and 100 mg L^{-1}) irradiated with 1 kGy and 5 kGy respectively were chosen to evaluate the variation of acute toxicity.

$$UT = \frac{100}{EC50} \tag{2}$$

3. RESULTS AND DISCUSSION

3.1. Changes of Absorption Spectra and Decoloration

The absorption spectra of the aqueous solutions (RB5 and RR198 - 100 mg L^{-1}) under different radiation doses were presented at Figs. 2 and 3. Both RB5 and RR198 showed a strong absorption (visible band) at wavelength 597 nm and 515 nm, respectively. The characteristic peak value decreased rapidly with increasing dose from 0 to 0.5 kGy. The degree of decoloration was higher for RR198 than to RB5 at 100 mg L^{-1} solutions (86% and 76% respectively), but the same degree of decoloration was observed in solutions at 50 mg L^{-1} (97%).

The degree for dying removal is related to the chromoforous bound breakage that seems to be proportional to the radiation doses and concentration dependent. The RB5 molecule has two azo bounds and it was less sensitive for colour reduction than RR198. This last compound has only one azo bound. The sample concentration also seems to influence the decoloration degree and may be a factor for increasing the radiation dose. 1 kGy was enough for 50 mg L^{-1}

dye, accounting for 99% of colour reduction. To get the same effect at 100 mg L^{-1}, a higher dose was necessary. The highest values of absorbance in the UV region after irradiation can be related to the possible formation of intermediate compounds [2].

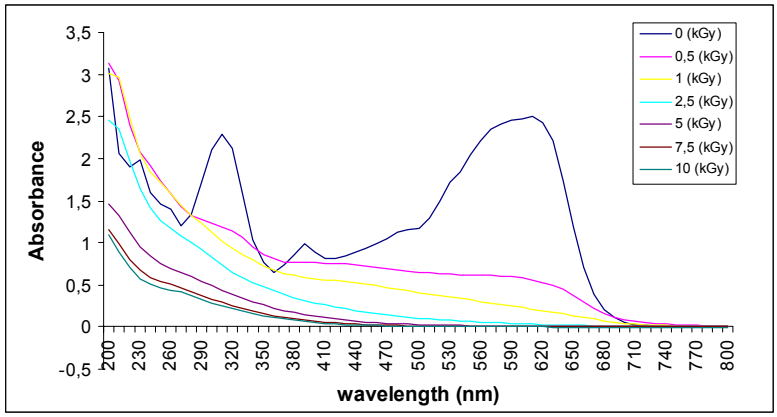

Figure 2. Absorbance spectra of RB5 (100 mg L^{-1}) versus radiation doses (kGy).

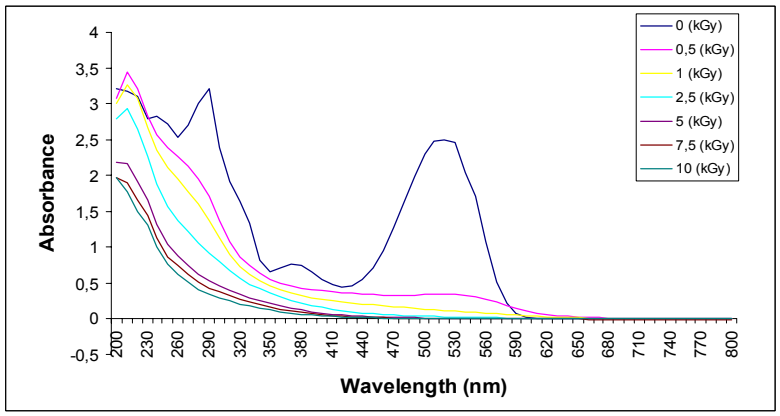

Figure 3. Absorbance spectra of RR198 (100 mg L^{-1}) versus radiation doses (kGy).

3.2. The Change of pH Value

Fig. 4 shows the change in pH values for RB5 and RR198 solutions under electron beam irradiation. The pH values of all dyes solution decreased dramatically after irradiation. The results suggest a direct relation between pH decreasing and increasing radiation doses. Organic acids are the main intermediate products during radiation degradation process [14, 15]. It also suggests a pattern for reactive azo dyes structure to initiate middle and small organic compounds (formic acids, acetic acids and benzoic compounds) [14]. According to Wang et al, if dye solutions continued to be irradiated by electron beam, the interim compounds react with active species as hydroxyl radicals to be degraded further to inorganic products.

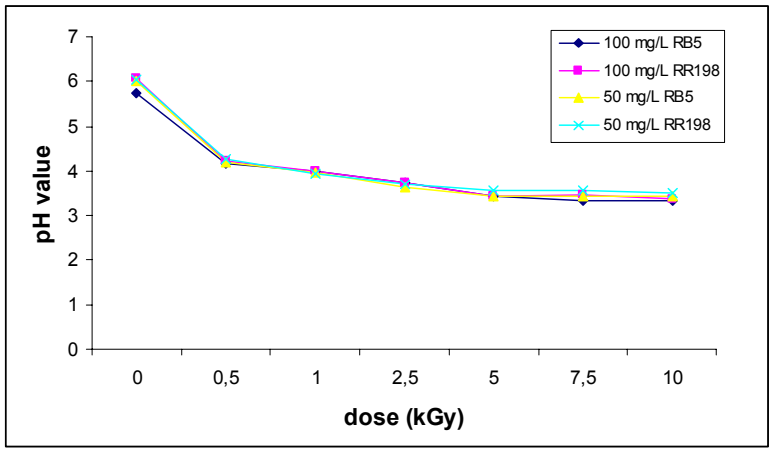

Figure 4. The change of pH value under electron beam irradiation of RB5 and RR198 solution.

3.3. Toxicity Results

Toxicity results as well as radiation efficiency are summarized in Table 1. Observing the toxic units (TU) it is possible to verify that RR198 was more toxic than RB5 for crustaceans. After irradiation the results show a decrease in the acute toxicity for RR198 samples and an increase for RB5 samples. The reactive azo dye RR198 (50 and 100 mg L^{-1}) irradiated with 1 and 5 kGy respectively reduced the acute toxicity in 77,31% and 84%. The intermediate formed chemical species may increase biological effect of RB5 samples after irradiation and need to be identified once they may enhance toxic effects to crustaceans.

Table 1. Effects of electron beam irradiation on acute toxicity

Samples	EC50 Untreated (48h; mg L^{-1})	EC50 Treated (48h; mg L^{-1})	TU Untreated (48h; mg L^{-1})	TU Treated (48h; mg L^{-1})	Removal (%)
RR198** (50mg L^{-1})	6.6	29.3	15.0	3.4	77.31%
RB5** (50mg L^{-1})	25.6	21.9	3.9	4.5	not removed
RR198* (100mg L^{-1})	4.0	24.9	25.0	4.0	84.0%
RB5* (100mg L^{-1})	34.0	17.8	2.9	5.6	not removed

** radiation dose 1 kGy
* radiation dose 5 kGy

3. CONCLUSIONS

Radiation can be applied successfully for reduction of colour for reactive azo dyes. The results show that the decoloration of dye solutions mainly depends on the molecular structure of dye and sometimes other more toxic compounds can be formed. Electron beam irradiation can effectively decompose dye molecules, but large absorbed dose is necessary to completely degrade dye molecules to inorganic forms.

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