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EFFECTS OF HIGH ENERGITIC RADIATION ON THE REMOVAL AND DETOXIFICATION OF CATIONIC DYE ASTRAZON BLUE FGRL

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YÜKSEK ENERJİLİ RADYASYONUN KATYONİK ASTRAZON MAVİSİ FGRL BOYAR MADDESİNİN ARINDIRILMASI VE DETOKSİFİKASYONU ÜZERİNE ETKİSİ

Abstract:

Decolorization and degradation of textile dye wastewater are performed by high energitic rays and affected by various factors such as pH, dye concentration, toxicity, COD, BOD_5 and absorbed dose. Cationic/basic dye of Astrazon Blue FGRL was treated using ionizing radiation and degree of decolorization at air and O_2 saturated and H_2O_2 conditions were discussed. The biodegradability (BOD_5/COD) of the dye solutions was enhanced after 1 kGy, 3 kGy, and 3 kGy irradiations for air, O_2 saturated and 2.6 mmol L^{-1} H_2O_2 solutions, respectively. However, optimum irradiation conditions for complete mineralization and decoloration of Astrazon Blue FGRL solutions were found to be 2 kGy pH 8 for air, 7 kGy pH 5 for O_2 saturated, 7 kGy pH 5 for 2.6 mmol L^{-1} H_2O_2 solutions, respectively. After irradiaiton at optimum conditions, the biorefractory organic compounds of Astrazon Blue FGRL were converted into smaller and biodegradable compounds by radiation technology.

Özet:

pH, boya konsantrasyonu, toksisite, KOİ, $BOİ_5$ ve absorplanan doz gibi bazı faktörlerden etkilenen tekstil boya atık suyunun renk giderimi ve arıtılması yüksek enerjili ışınlar vasıtasıyla gerçekleştirilir. Astrazon mavisi FGRL'nin katyonik / bazik boyası iyonlaştırıcı radyasyonla etkileştirilerek, renklenme derecesi havada, O_2 ve H_2O_2 ortamında değerlendirildi. Boya çözeltilerinin biyolojik olarak bozunabilirliği ($BOİ_5$/KOİ), hava, O_2 ve 2.6 mmol L^{-1} H_20_2 çözeltileri için sırasıyla 1, 3 ve 3 kGy absorbe edilen doz değerlerinde arıtırıldı. Bununla birlikte, Astrazon mavisi FGRL çözeltilerinin tamamen mineralizasyonu ve renk giderimi için optimum ışınlama koşullarının, hava için 2 kGy-pH 8, O_2 için 7 kGy-pH 5, 2.6 mmol L^{-1} H_2O_2 çözeltileri için 7 kGy-pH 5 olduğu bulunmuştur. Optimum koşullarda ışınlandıktan sonra, Astrazon mavisi FGRL'nin biyo-refrakter organik bileşikleri radyasyon teknolojisi ile daha küçük ve biyolojik olarak bozunabilir bileşiklere dönüştürüldüğü görülmüştür.

Keywords: Astrazon, mineralization, decoloration, radiation, toxicity

Anahtar kelimeler: Astrazon, mineralizasyon, renk giderimi, radyasyon, toksisite

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1. Introduction

Dyes and pigments have been widely used as colorant in the textile dyeing industry since the ancient time. So many different types of dyes or pigments are present for different textile raw materials. In acrylic, nylon, silk, and wool dyeing, cationic/basic textile dyes have been widely used. Dye-contaminated effluent in a large volume is discharged in dyeing processes, and 10 – 15 % of the dye is disappeared with the discharge effluent (Zollinger, 1991). According to US EPA (1996) report, 1,000 mg L^{-1} of dye was used in a typical dye bath and 100 mgL^{-1} of dye was left in the spent dye bath. In addition, even at low concentration, the presence of dyes could be quite visible and undesirable in the effluent (Nigam et al., 2000). Textile dyes are relatively resistant to biodegradation due to their molecular structures (Yeşilada, Cing & Asma 2002) and the presence of metals in their structure. Cationic/basic dyes are accepted as one of the most toxic substances (US EPA, 1996). In this context, the detoxification and removal of dyes from effluent is a must. In general, physio-chemical processes are being used (Robinson, Chandran & Nigam 2002). In some of the treatment methods, oxidation processes are used, for example, Fenton reagent and ozone (Pak and Chang, 1999; Lin & Lin, 1993). On the other hand, radiolysis process has also been considered to be an alternative advanced oxidation process (AOP) for the treatment of contaminant (Getoff, 2002; Bural et al., 2010; Poster et al., 2004). Research studies on dye molecules are continued with the dye molecules in different structures to identify the short-lived transients and stable intermediates and to understand the reaction mechanism during degradation (Kim, Lee & Lee 2007; Wojnarovits & Takacs, 2008; Emmi & Takacs, 2008; Paul et al., 2011).

In the irradiation of a dilute solution, the molecular products and three short-lived intermediates as depicted in reaction 1 (hydroxyl radical ($HO^{\bullet}$), hydrogen atom ($H^{\bullet}$) and hydrated electron (e_{aq}^{-}) are formed. The $HO^{\bullet}$ radical is deliberated leading to degradation: (a) it interacts double-bonds in compounds with diffusion-controlled rate, (b) it is the only oxidizing species, (c) in oxygen atmosphere, the degradation occurs through the oxidation reactions producing intermediate products having higher oxygen to carbon ratios towards complete mineralization and (d) in air and the oxygen-saturated solutions, e_{aq}^{-} and $H^{\bullet}$ react with oxygen in fast reaction, and form the inert $O_2^{\bullet-}/HO_2^{\bullet}$ pair (2)–(4):

$$H_2O + \gamma \text{ rays} \rightarrow OH^{\bullet}\,(2.8),\ e_{aq}^{-}\,(2.7),\ H^{\bullet}\,(0.6),\ H_2\,(0.45),\ H_2O_2\,(0.7), \quad (1)$$

The values in brackets are the G values of these species in the pH range of 3-11.

$$e_{aq}^{-} + O_2 \rightarrow O_2^{\bullet-} \quad (2)$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \quad (3)$$

$$HO_2^{\bullet} + H_2O \leftrightarrow O_2^{\bullet-} + H_3O^{+} \quad (4)$$

The fish bioasssay which is the conventional acute toxicity test has been used extensively to determine the toxicity of samples. The principle of fish bioassay lies in the exposure of the fish of selected species to test for 96 hours. After recording of mortalities at 24, 48, 72 and 96 hours, the concentrations which kill 50 percent of the fish (LC_{50}) are determined. Anyhow, there is abundance of research study debating about the sensitivity of Microtox System compared to the conventional fish bioassay. Most of the available data indicate that the more complex the sample, the higher the rate of correlation between the common test species. However, none of the common test species found in the food chain tolerates toxicants as very

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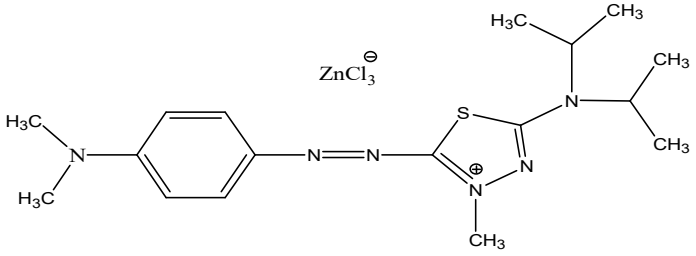
well. The Microtox organism, *Vibrio fischeri* (*P. phosphoreum*), was selected from other bioluminescent organisms because it demonstrated the highest sensitivity across a broad range of toxicants. When the applicability of these two methods are compared, it is known that the conventional method usually require 48 to 96 hours for testing, and need 10 hours of actual work. Therefore, it is accepted as a primary test for rapid determination of compounds yield containig certain risks for the aquatic environment (Lebsack et al., 1981).

In this research study, mineralization of basic/cationic dye Astrazon Blue FGRL and the degree of decoloration (DDC (%)) in aqueous solutions by gamma rays irradiation were investigated using chemical oxygen demand (COD), biological oxygen demand (BOD_5) measurements and by Ultraviolet–Visible spectroscopy to determine the role of the different reactive intermediates. In a wastewater treatment process, the determination of pH and toxicity are important in order to achieve the optimum decoloration conditions and discharge parameters in irradiation treatment.

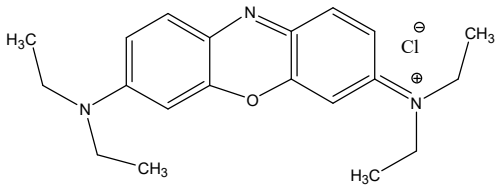
2. Materials and methods

2.1 Chemicals

Astrazon Blue FGRL is one of the basic/cationic dye and purchased from Dystar Thai Co., Ltd. It is a mixture of two compounds namely C.I. basic blue 159 and C.I. basic blue 3 (Figure 1). Their ratio is about 5:1 by weight, respectively. The net charge of both compounds is +1. Despite the Astrazon Blue FGRL is a mixture of those compounds, the results were evaluated as if it is a single dye. H_2O_2 used in this study was 30 % solution and supplied from Merck.



C.I. Basic Blue 159



C.I. Basic Blue 3

Figure 1. Chemical structure of Astrazon Blue FGRL.

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2.2 Irradiation and sample preparation

A number of studies were conducted by modifiying the H_2O_2 concentration to establish beneficial conditions to bio- compatibilize Astrazon Blue FGRL cationic dye solutions. 2.6 mmol L^{-1} H_2O_2 was found to be the most efficient H_2O_2 concentration to disintegrate the Astrazon Blue FGRL dye, to achieve the maximum decoloration and mineralization percentages by irradiation. Aqueous solutions were prepared at 100 mg L^{-1} and irradiated to 0, 1, 2, 3, 5, 7 and 9 kGy absorbed doses at three different conditions (air, O_2 saturated and 2.6 mmol L^{-1} H_2O_2). Then, pH, absorbans, toxicity, COD and BOD_5 analysis were conducted. Irradiations were carried out using Issledovatelj Px-γ-30 Russian made ^{60}Co irradiator at a dose rate of 1.714 kGy/h and at ambient temperature.

2.3 pH, colorimetric, COD and BOD_5 measurements

Orion 510 pH meter was used to measure the pH before and after irradiation. UV–Vis spectrophotometric measurements (ATI-Unicam 440 Spectrophotometer coupled with Vision32 software) were used to access the impact of gamma radiation on the persistent blue colour of the Astrazon Blue FGRL synthetically prepared wastewater. COD analyses were conducted with the standardized method of HACH and 0–1500 mg L^{-1} vials by using HACH CR/890 colorimeter. Five days BOD (BOD_5) analysis were performed with the standardized method of HACH using HACH Biotrak system and BOD incubator. Inoculum was supplied by the activated sludge unit of Ankara Municipal Wastewater Treatment Plant. Activated sludge collected from return sludge line was freed from residue organics in the bulk liquid before inoculation by aeration for one day and by washing two times with tap water.

2.4 Bioluminescent toxicity assay

The toxicity level of dye solutions was measured and denoted as EC-50 value meaning the test sample concentration reduced by 50 %. All tests were conducted using Modernwater Microtox 500 photometer. Microtox System® - Basic Test Protocol - 15 min exposure was followed for understanding the toxicity of the dye solutions by using Bacteria *Vibrio Fischeri*, which was supplied from Modernwater (Zwart & Sloof, 1983).

The toxicity, COD, BOD_5 and DDC measurements were conducted with minimal susceptibility to measurement errors. Average of three measurements were used in the calculations to minimize the experimental errors.

3. Results and discussion

The change of the DDC (%) in dye solutions were examined by spectrophotometrically. UV-Visible spectrum of the textile dye solutions were obtained in the spectral region of 200 – 900 nm using UV and Visible in order to determine the maximum absorbance wavelength. Absorbance spectrums showed a single peak in the visible region with a Absorbance spectrums at 602 nm. Three different solutions (air, O_2 saturated and 2.6 mmol L^{-1} H_2O_2) were prepared for investigation. The change of COD and BOD_5 were also followed for the irradiated and non-irradiated dye solutions as well as pH and toxicity to achieve the optimum discharge criteria.

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3.1 Change of absorpion spectra of Astrazon Blue FGRL aqueous solutions

Aqueous solutions of Astrazon Blue FGRL were irradiated in air, O_2 saturated and 2.6 mmol L^{-1} H_2O_2 by gamma rays under various doses and pH conditions. Strong absorption band in the visible region caused by the conjugation of hydrazyl unit. On the other hand, a weak triplet absorption band at UV region 231, 256 and 291 nm was dedected. Two shoulders of triplet band at 256 and 291 were due to the amine hyperconjugation with π band of aromatic ring and resulted with π– π* transition. Shoulder at 231 nm of the triplet peak was resulted from n- π* transition of imine group of the Astrazon Blue FGRL basic dye molecule. Those peaks were dissappered by irradiation and ring opening mechanism. Adsorption spectra of 100 mg L^{-1} (pH=7) dye solution versus to dose was shown in Figures 2-4 for irradiated sample in air, O_2 saturated and 2.6 mmol L^{-1} H_2O_2 solutions. As could be seen from Figures 2-4, the intensity of the singlet peak at 602 nm decreased by increasing the dose. Concentration of unirradiated and irradiated aqueous Astrazon Blue FGRL solutions was calculated and converted to DDC (%) by following the decreasement at 602 nm. Calculated DDC (%) values were graphed at Figure 5. Regarding to Figures 2-4, the intensity of the absorption bands were decreased by increasing the absorbed dose, and finally the absorbtion bands were dissappeared at 3, 7, and 7 kGy for air saturated, O_2 saturated and 2.6 mmol L^{-1} H_2O_2 solutions, respectively. At these dose values and pH (7), DDC (%) values were obtained as 98.5, 98, and 75 (Figure 5). As it is revealed in Figures 2-4, above mentioned behaviour can be attributed to the reactivity towards $HO^{\bullet}$ radicals of the primary water radiolysis product. Aromatic ring and also the azo group of the molecule are very sensitive to $HO^{\bullet}$ radicals (Roder et al., 1999). When the $HO^{\bullet}$ radical is added to the aromatic ring, a cyclohexadienyl radical is formed. Under these circumstances, the reactions between binary cyclohexadienyl radicals may be progressed by both disproportionation or/and dimerization.

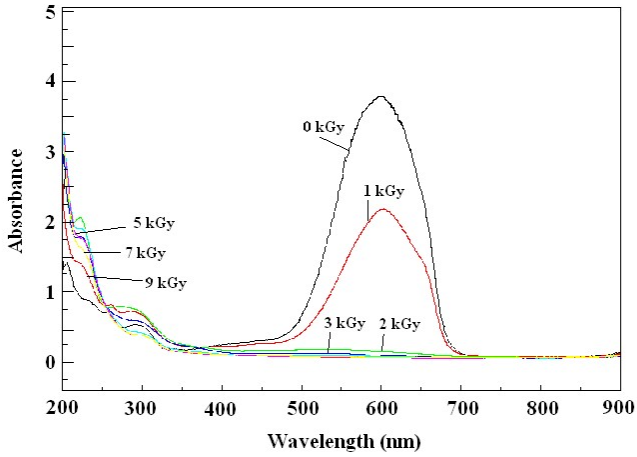

Figure 2. UV-Vis absorption spectra of 100 ppm Astrazon Blue FGRL irradiated at air saturated.

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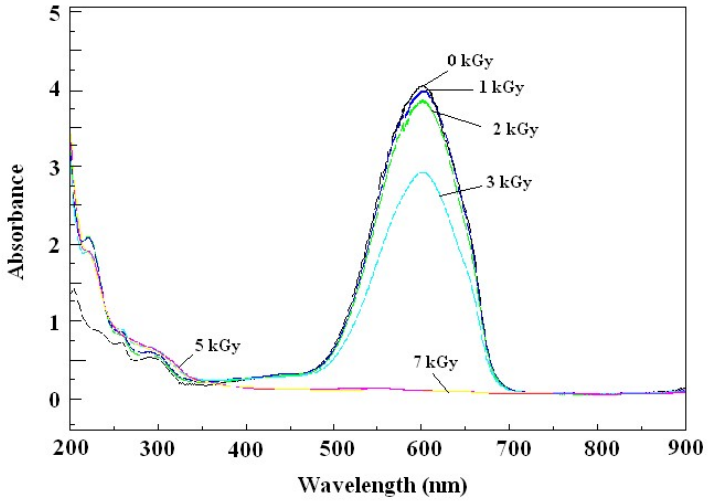

Figure 3. UV-Vis absorption spectra of 100 ppm Astrazon Blue FGRL irradiated at O_2 saturated.

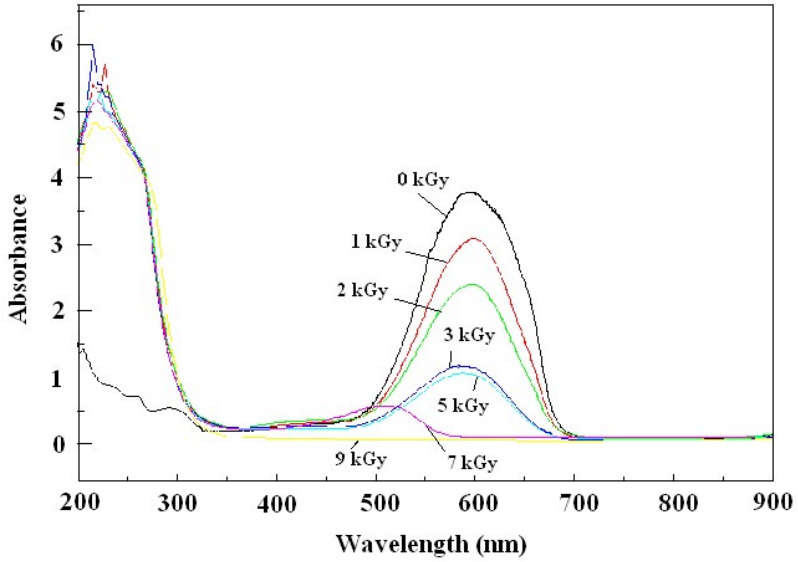

Figure 4. UV-Vis absorption spectra of 100 ppm Astrazon Blue FGRL irradiated at 2.6 mM H_2O_2.

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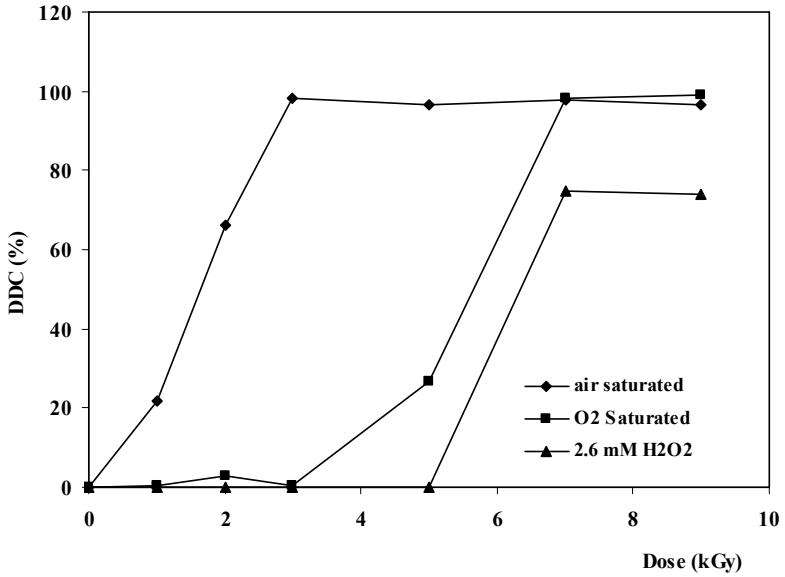

Figure 5. DDC (%) change versus dose irradiated at air saturated, O_2 saturated and 2.6 mM H_2O_2.

In the reaction of $HO^{\bullet}$ radicals with textile dye in air and O_2 saturated solutions, a competetive reaction could take place between $H^{\bullet}$ abstraction and addition of hydroxyl radicals to phenyl ring. However, in the O_2 atmosphere, some of e_{aq}^- and $H^{\bullet}$ are converted to the oxidative species of $O_2^{\bullet-}/HO_2^{\bullet}$ (Sharma et al., 2002). Therefore, some of $H^{\bullet}$ atoms are used in this conversion reaction. In spite of observing relatively same DDC % values for both solutions, the absorbed dose needed to decolorize or mineralize for dye solution saturated with O_2 was higher than that for saturated with air. The difference in absorbed doses among O_2 and air saturated solutions for the decolorization and mineralization was attributed to conversion of the $H^{\bullet}$ atoms to oxidative species. In conjuction with, hydrated electrons and $H^{\bullet}$ atoms were used in the decoloration of aqueous dye molecules, whereas $HO^{\bullet}$ radicals were used in the mineralization.

3.2 Study on the mineralization

COD is a method for the determination of oxygen concentration needed for the complete oxidation of compound(s) of interest. The COD test is commonly employed to indirectly measure the quantity of organic compounds in aquatic environment. In Table 1, the dose dependence of the COD value in a number of irradiated solutions in air, O_2 saturated and 2.6 mmol L^{-1} H_2O_2 solutions was shown. The COD values of aqueous solution prepared at 100 mg L^{-1} was measured as 130, 128, 120 mg/L for air, O_2 saturated and 2.6 mmol L^{-1} H_2O_2, respectively. COD % removal efficiency after irradiation was calculated and found to be 92, 94, and 85 % for air, O_2 saturated and 2.6 mmol L^{-1} H_2O_2, respectively. In the light of the results, the degradation of Astrazon blue FGRL dye is more pronounced at O_2 saturated solution in adverse to the decoloration results. From this result, 2 kGy is enough for air

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saturated solution, whereas 7 kGy is need to the mineralization of both other solutions. This was attributed to competition between the reaction of OH radicals with Astrazon Blue FGRL and H abstraction from Astrazon Blue FGRL as well as the addition of hydroxyl radicals to phenyl rings (Aleboyeh, Aleboyeh & Moussa, 2003). Addition of hydroxyl radicals to aromatic rings and the formation of cyclohexadienyl radicals were both generated (Wojnarovits et al., 2000). At the beginning of the radiolysis process, dissolved oxygen was reacted with these radicals, and aromatic rings decomposed to smaller molecules like, aldehydes, ketones and carboxylic acids in lower molecular weight. These decomposition by-products were responsible to the enhancement of BOD_5 and BOD_5/COD biodegradability ratio (Getoff, 1998; Getoff ,1999; Krapfenbauer et al., 2000).

Table 1. COD, BOD and BOD_5/COD ratio of dye solutions irradiated to 0 – 9 kGy.

Dose	Air			O_2			H_2O_2		
(kGy)	BOD_5	COD	BOD_5/ COD	BOD_5	COD	BOD_5/ COD	BOD_5	COD	BOD_5/ COD
0	40	130	0.31	42	128	0.33	34	120	0.28
1	45	70	0.65	21	61	0.35	27	76	0.35
2	7	10	0.70	20	60	0.34	25	64	0.39
3	<LOD	<LOD	<LOD	37	59	0.63	25	40	0.63
5	<LOD	<LOD	<LOD	30	45	0.62	26	42	0.62
7	<LOD	<LOD	<LOD	6	8	0.75	12	18	0.67
9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

LOD: Limit of dedection (1 mgL^{-1})

3.3 Study on the deviation of pH during radiolysis

pH is crucial in the complete decoloration and mineralization of textile effluents. In this regard, pH deviations were initially adjusted to 3 – 12, and measured after irradiation. Then, pH – DDC (%) relationship was followed (Figure 6 and Table 2) at fixed dose. As could be seen from Table 2, negligible pH deviations were observed before and after irradiation. As it was revealed at the curves of Figure 6, max. DDC (%) variation was evaluated at pH 8, 5, and 5 for air, O_2 saturated and 2.6 mmol L^{-1} H_2O_2, respectively. At these pHs, mineralization of the dye molecules following the smaller fragments were observed.

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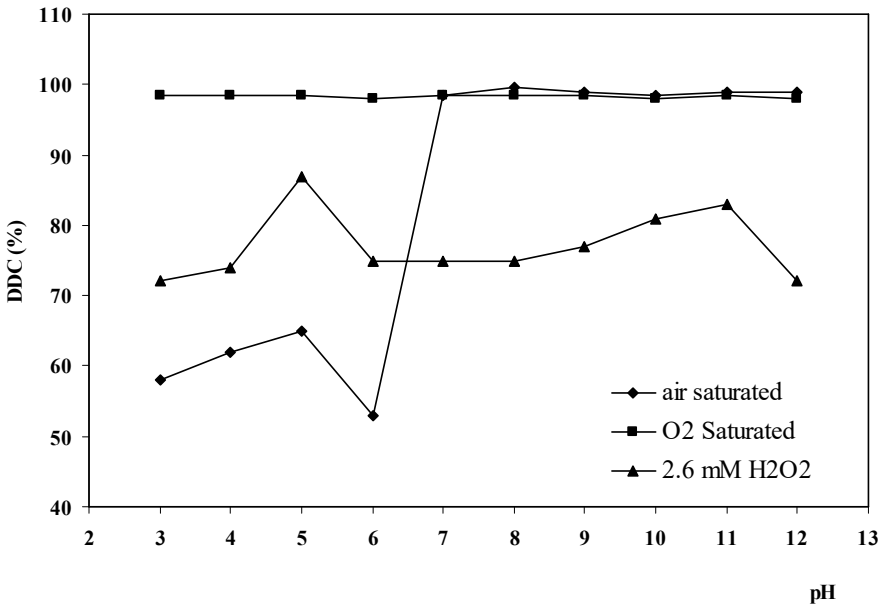

Figure 6. The pH effect on the DDC (%) at air saturated, O_2 saturated and 2.6 mM H_2O_2 at optimum dose.

Table 2. The pH and DDC (%) change of dye solutions at optimum doses.

pH (Bef. Irrad.)	pH (Aft. Irrad.); DDC (%)		
	Air (3 kGy)	O_2 (7 kGy)	H_2O_2 (7 kGy)
3.0	3.1; 58.0	3.3; 98.5	2.5; 72.0
4.0	4,3; 62.0	3.6; 98.5	3.6; 74.0
5.0	5.7; 65.0	4.7; 98.5	4.4; 87.0
6.0	5.9; 53.0	6.1; 98.0	5.6; 75.0
7.0	7.1; 98.5	7.4; 98.5	6.9; 75.0
8.0	8.1; 99.5	7.8; 98.5	8.4; 75.0
9.0	9.2; 99.0	8.6; 98.5	9.3; 77.0
10.0	9.6; 98.5	9.4; 98	10.5; 81.0
11.0	10.9; 99.0	9.8; 98.5	11.8; 83.0
12.0	11.9; 98.0	11.9; 98.0	11.9; 72.0

After dose and pH combination studies for complete decoloration and mineralization, concentration effects on DDC (%) versus dose were studied. In this regard, 10, 50, 75 and 100 mg L^{-1} at pH 8, 5, and 5 for air saturated, O_2 saturated and 2.6 mmol L^{-1} H_2O_2 solutions were

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irradiated at 3, 7, and 7 kGy, respectively. Absorption band of dye molecules at the visible region of 602 nm was quantified and converted to DDC (%) (Table 3 and Figure 7). Once solutions were irradiated, the effect of pH on the dye concentration and DDC wasn't differentiated. As depicted in Table 3 and Figure 7, DDC (%) of samples irradiated in 2.6 mmol L^{-1} H_2O_2 solutions decreased from 98 to 87 % by increasing the concentration. It was attributed to the increasement of the probability of radical-radical recombination at higher concentrations. However, pH was retained relatively the same for all solutions. Depending on the dye concentration, there was no significant change in the DDC (%) of air and O_2 saturated solutions, but completely decolorized. On the other hand, this result showed that the dye solutions in any concentration could be treated at optimum pH and also variation on the influent concentration in dyeing facility was independent from pH.

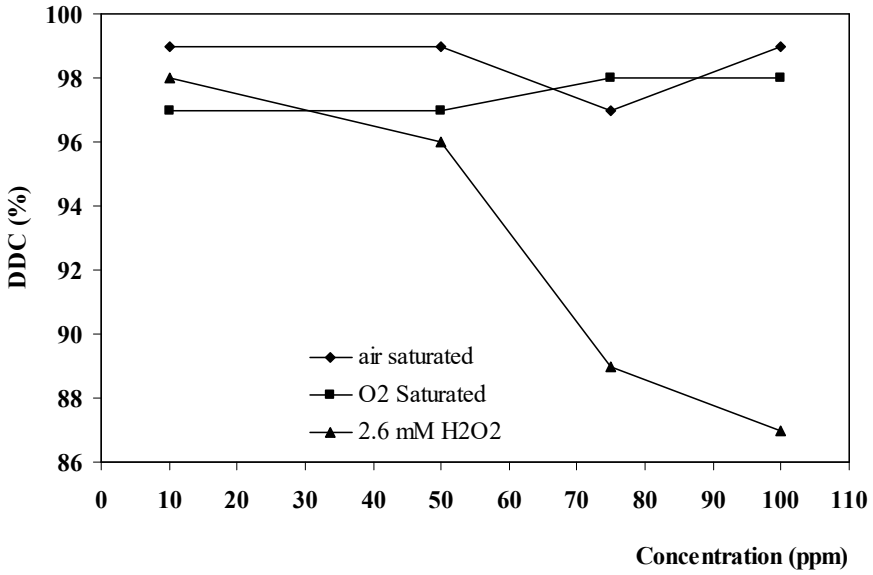

Figure 7. Concentration effect on DDC (%) at air saturated, O_2 saturated and 2.6 mM H_2O_2 at optimum dose.

Table 3. Concenration effect on pH and degree of decoloration (%) (DDC %) at optimum pH and dose.

Conc. (ppm)	Air (pH:8;3 kGy)	O_2 (pH:5;7 kGy)	H_2O_2 (pH:5;7 kGy)
	pH; DDC %	pH; DDC %	pH; DDC %
10	8.1; 99.0	5.0; 97.0	4.4; 98.0
50	7.7; 99.0	4.7; 97.0	4.6; 96.0
75	7.7; 97.0	4.7; 98.0	4.4; 89.0
100	8.1; 99.0	4.6; 98.0	6.0; 99.0

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3.4 Study on the variation of BOD_5 during radiolysis

A BOD_5 test is used in environmental monitoring in terms of stating the level of contamination in water. Therefore, COD and BOD_5 values are the most important parameters of the wastewater treatment process. Both determine the effluent characteristics, whether is suitable to discharge or is not. On the other hand, BOD_5/COD ratio is an indicator of biodegradability. The ratio of BOD_5/COD must be between 0.3 and 0.8 for untreated municipal wastewater. If this ratio is 0.5 or greater, the wastewater is easily biodegradable by microbiological means. But, when it is below than 0.3, the wastewater may contain some toxic compounds or the stabilization of the acclimated microorganisms may be needed (Tchobanoglous, Burton & Stensel, 2003; Garcia-Montano et al., 2006; Kantoğlu, 2017). In this context, the BOD_5/COD ratio of the 100 mg L^{-1} Astrazon Blue FGRL solutions was presented at different absorbed doses in Table 1. As revealed in Table 1, the BOD_5 and COD values were enhanced by increasing dose. In the unirradiated solutions, BOD_5/COD ratio was found to be 0.31, 0.33 and 0.28 for air, O_2 saturated, 2.6 mmol L^{-1} H_2O_2 conditions, respectively. These results indicated that all type of dye solutions were non-biodegradable. As seen from Table 1, the BOD_5 and COD decreased with increasing absorbed dose, and this decrease was attributed to new formation of excess biodegradable fragments upon the radiolysis process (Kim, Lee & Lee, 2007). It is shown in Table 1 that biodegradability of Astrazon Blue FGRL solutions was enhanced at 1, 3 and 3 kGy for air saturated, O_2 saturated, 2.6 mmol L^{-1} H_2O_2 solutions, respectively. However, as it is also revealed in Table 1, complete mineralization and decoloration of dye solutions during irradiation process can be obtained at 2, 7, and 7 kGy with increasing of BOD_5/COD ratio of 100 mg L^{-1} dye solutions to 0.70, 0.75, and 0.67 for air saturated, O_2 saturated, 2.6 mmol L^{-1} H_2O_2 solutions, respectively. It revealed that biodegradability was improved from non-biodegradable to biodegradable upon increasing the absorbed dose.

3.5 Bioluminescent Toxicity Assays

The toxicity of pollutant is generally tested by single cell green algae or fish. Wang and coworkers were surveyed the use of single cell green algae *Selenastrum capricornutum* as well as on *Pimephales promelas* on the toxicities of some textile dyes in the literature and published their findings as a table (Wang et al., 2002). The large error in EC_{50} due to the use of a small number of living organisims is the main disadvantages on fish and algae tests (Hao, Kim & Chiang, 2000). Therefore, bioluminescent toxicity test is recognised a pre-screening test method in worldwide, especially in USA, UK, Canada, Australia, Sweden, Germany.

The toxicity evaluation was conducted with both non-irradatied and irradiated samples (0, 1, 2, 3, 5, 7, 9 kGy) at pH 7. pH was measured and regulaed to 7 with an acid or base to comply toxicity basic test protocol. Dye solutions were analyzed by Microtox analyzer and obtained EC_{50} data was presented in Table 4. As revealed in Table 4, radiation effect on the reduction of toxicity was more pronounced in air saturated samples than O_2 and H_2O_2 added samples. In respect to toxicity results, H_2O_2 added samples were found to be more toxic than air and O_2 saturated solutions. 2, 7 and 7 kGy irradiation was needed to reach an efficent toxicity reduction for air saturated, O_2 saturated and 2.6 mmol L^{-1} H_2O_2 solutions, respectively. Based on the 15 min percentage toxicity reduction values, unirradiated and 2.6

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mmol L^{-1} H_2O_2 added samples with the value of 54.5 % could be expressed as the most toxic samples. In this context, the order of toxicity reduction efficiency after the same doses and irradiation conditions was also elucidated and obtained as Air > O_2 > 2.6 mmol L^{-1} H_2O_2 (Table 4). A deionized water sample subjected to air, oxygen saturation and H_2O_2 addition was prepared for blank analysis of toxicity test. It was observed that the effect of H_2O_2 and emitted light on the luminescent bacteria of *Vibrio fischeri* was found more pronounced than air and oxygen saturated solutions. Therefore, the higher toxicity values of H_2O_2 solutions in Table 4 were attributed to initial toxicity differences. On the other hand, the lower biodegradability index (<0.3) may also imply a toxicity (Kantoğlu, 2017). The higher toxicity and lower biodegradability index of unirradiated samples correlates with this phenomenon in this study.

Table 4. Toxicity level of irradiated and unirradiated Astrazon Blue FGRL solutions.

Dose (kGy)	EC50			TU			Toxicity Reduction (%)		
	Air	O_2	H_2O_2	Air	O_2	H_2O_2	Air	O_2	H_2O_2
0	7,6	7,9	5,1	13,2	12,7	19,6	0,0	0,0	0,0
1	14,6	29,3	6,9	6,8	3,4	14,5	47,9	73,0	26,1
2	33,2	45,1	8,1	3,0	2,2	12,3	77,1	82,5	37,0
3	30,4	52,1	10,1	3,3	1,9	9,9	75,0	84,8	49,5
5	32,1	55,4	11,8	3,1	1,8	8,5	76,3	85,7	56,8
7	31,6	58,3	12,6	3,2	1,7	7,9	75,9	86,5	59,5
9	29,8	53,9	11,2	3,4	1,9	8,9	74,5	85,3	54,5

4. Conclusion

2 kGy pH 8 at air saturated, 7 kGy pH 5 at O_2 saturated, 7 kGy pH 5 at 2.6 mmol L^{-1} H_2O_2 for Astrazon Blue FGRL were characterized as the ideal irradiation conditions for the complete mineralization, decoloration and detoxification. However, at 1, 3, and 3 kGy was enough for the enhancement of biodegradability (BOD_5/COD) ratio of Astrazon Blue FGRL in air saturated, O_2 saturated, 2.6 mmol L^{-1} H_2O_2 solutions, respectively. With this study, detoxification, decoloration and mineralization of basic/cationic Astrazon Blue FGRL textile dye solutions upon irradiation were studied and found to be easily decolored in air saturated solutions.

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