

Düzce Üniversitesi Bilim ve Teknoloji Dergisi

Araştırma Makalesi

Astrazon Red FBL Çözeltisinin Gama Işınlarıyla Renk Giderimi ve Detoksifikasyonu

i Ömer KANTOĞLU

^a TENMAK, Nuclear Energy Research Institute, Kahramankazan, 06980 Ankara, TÜRKİYE * Sorumlu yazarın e-posta adresi: omer.kantoglu@tenmak.gov.tr DOI: 10.29130/dubited.1069909

Öz

Bu çalışmada, Astrazon Red FBL boyasının sulu çözeltilerinin yüksek enerji ile etkileşimi sonrası renk giderimi ve detoksifikasyonu farklı deneysel koşullar altında (hava, doygun O₂, 2.6 mM H₂O₂) araştırılmıştır. Bu kapsamda renk giderme, mineralizasyon, detoksifikasyon, pH, KOİ ve BOİ₅ parametreleri takip edilmiştir. Biyobozunurluk (5 günlük biyolojik oksijen ihtiyacı/kimyasal oksijen ihtiyacı -BOD₅/COD-) oranı, tüm çözeltiler için 2 kGy ışınlamada artmıştır. Astrazon Red FBL çözeltilerinin mineralizasyonunu ve renk giderimini sağlamak üzere hava için 5 kGy ve pH 9, doygun O₂ için 5 kGy ve pH 11, 2.6 mM H₂O₂ için 7 kGy ve pH 11, optimum ışınlama koşulları olarak bulunmuştur. Yüksek enerjili ışınlarla muamele edilen Astrazon FBL çözeltilerinin toksisitesini ölçmek için microtox bioassay testi gerçekleştirilmiştir. Hava, doygun O₂ ve H₂O₂ çözeltileri için sırasıyla %81.2, %86.7 ve %56.3 oranlarında 5, 5 ve 7 kGy'de toksisite azalması sağlanmıştır. Çalışmanın sonucu olarak, Astrazon Red FBL tekstil boyasının ışınlama teknolojisi ile arıtımının gerçekleştirilebileceği tespit edilmiştir.

Anahtar Kelimeler: Astrazon, radyasyon, renk giderimi, toksisite, mineralizasyon, KOİ, BOİ5

Decoloration and Detoxification of Astrazon Red FBL Solution Using Gamma Rays

ABSTRACT

In this study, decoloration and detoxification of Astrazon Red FBL dye solutions using gamma rays have been examined at different environments (air, O_2 saturated, 2.6 mM H_2O_2). In this context, the decoloration, mineralization, detoxification, pH, COD and BOD₅ parameters were followed. Biodegradability (5 days of biological oxygen demand/ chemical oxygen demand -BOD₅/COD-) ratio has been improved up on 2 kGy irradiation for all solutions. Optimum irradiation conditions were found to be 5 kGy pH 9 for air, 5 kGy pH 11 for O_2 saturated, 7 kGy pH 11 for 2.6 mM H_2O_2 to provide mineralization and decoloration of Astrazon Red FBL solutions. Microtox bioluminescent test was conducted to measure the toxicity of Astrazon FBL solutions treated with high energetic rays. Toxicity reduction has been achieved at 5, 5 and 7 kGy in the range of 81.2, 86.7 and 56.3 % for air, O_2 saturated and H_2O_2 solutions, respectively. As a result of study, it is found that Astrazon Red FBL dye could be treated by irradiation technology.

Keywords: Astrazon, radiation, decoloration, toxicity, mineralization, COD, BOD₅

I. INTRODUCTION

Rapid growth of agricultural and industrial worldwide in connection with the increase in the world populations, accumulated the global concerns in the field of waste management such as remediation of industrial and municipal liquid and solid wastes. Textile industry is one of the main pollution contributors by producing of high volume of effluent. In last three decades, both the public and government encourage to improve and to replace current technologies with the new emerging technologies [1].

In this context, conventional techniques, such as electrochemical, ultrafiltration, Fenton, biological and enzymatic, sonochemical, coagulation, adsorption, supercritical water oxidation and reverse osmosis, are mostly applied to the removal of textile dyes containing wastewater. Generally, effluent of textile industries contains wide range of organic contents and color to gather with surfactants and additives, which are non-biodegradable and they don't meet the regulations by activated sludge treatment, which in turn results with considerably important environmental and health problems. In this context, decolorization of textile wastewater takes considerable of attention, whether for the potential toxicity of dye stuffs or coloration of the water resources [2-9]. Biological treatment is accepted as cost-effective, cheap and simple to apply regarding to other treatment methods [10, 11]. The conventional methods have some disadvantages and are not effective for total mineralization of recalcitrant species in wastewater [12]. In addition, low BOD₅/COD ratio for colored pollutants indicates that mineralization of these kind of pollutants would be difficult by the common used treatment methods such as activated sludge processes, chemical coagulation and may cause serious aquatic problems in the environment [13-15]. In this context, researches have been begun to focus on new technologies and processes. Advanced oxidation processes (AOPs) are commonly used for the mineralization and for the enhancement of the biodegradability containing refractory and/or non-biodegradable contaminants. Radiation technology as a part of AOPs has been adopted for the treatment of the textile industry effluents [16]. •OH radicals with a high electrochemical oxidation potential are mainly used as oxidizing agents in these AOP methods and activate a set of reactions, which would destruct the high molecular weight dye molecules into smaller and less toxic compounds. Hydroxyl radicals can also be created by using plasma, UV radiation, gamma radiation, and electron beam radiation. Number of studies have been performed by radiation technology for the removal of colorants and mineralization of textile dyes such as disperse and reactive dyes [17-22]. Astrazon classified dyes are quite resistant to microbial disintegration. However, some dyes can be treated by anaerobic microorganisms. But those microorganisms may be affected by aromatic amine groups of the dye molecules in terms of their toxicity and carcinogenity. In last three decades many studies have shown that radiation could be used for the decolorization of dyes and is promising for the treatment of dyeing wastewater.

One of the important criteria of treated and untreated wastewater is the toxicity. Toxicity tests help to understand which of the chemicals are toxic for living organisms and to determine the level of below the LOD of the analytical techniques for many toxic substances [23]. Toxicity test can be an indicator for toxic substance, which cannot be detected by any analytical system. In this context, some rapid test methods have been developed and standardized to better identify the toxicity level of contaminants available in wastewater. These rapid test methods are accepted as rapid screening methods by several countries. The rapid Microtox test, using the luminous marine bacteria *Vibrio fischeri*, is one of these test methods that is used world-wide and there are an extensive number of related scientific publications [24].

In this study, the possibility of discoloration (DDC (%)) and detoxification as well as mineralization of Astrazon Red FBL dye solutions by irradiation was investigated. Aqueous solutions of Astrazon Red FBL were evaluated for decoloration and mineralization as changing the absorbed dose between 0 and 9 kGy in air, O_2 saturated and 2.6 mM H₂O₂ solutions. The variation in pH, toxicity, COD and BOD₅ of the Astrazon Red FBL dye solutions were also studied.

II. EXPERIMENTAL

Astrazon Red FBL (C.I. Basic Red 46) (Figure 1) was donated by Dystar Thai Co., Ltd (Singapore). Hydrogen peroxide was purchased from Merck (Germany). Solution samples were prepared at 200 ppm (Astrazon Red FBL) by using deionized water and irradiated to 0, 2, 5, 7 and 9 kGy doses under different experimental conditions (air, O₂ saturated and 2.6 mM H₂O₂). Decolorization of aqueous solution of Astrazon Red FBL was determined by the evaluation of absorption spectra with respect to applied doses and concentrations. The mineralization of dye was followed by pH and COD values. The biodegradability was followed in BOD₅ value, as well the changes in BOD₅/COD ratio. On the other hand, dve solutions were subjected to bioluminescent toxicity test to better understanding of influent and effluent toxicity characteristics. Samples were irradiated at the dose rate of 1.714 kGy/h at room temperature using Issledovatel Px-y-30 Russian made ⁶⁰Co gamma rays irradiator. The pH of the solutions was determined using Orion 510 pHmeter before and after irradiation. Absorbance measurements were performed by using Ati-Unicam 440 UV-Visible spectrophotometer operated with Vision32 software. COD was measured with the standard method of HACH and vials for COD 0 - 1500mg/L by using HACH CR/890 colorimeter. BOD₅ analyses were performed with the standard method of HACH by using HACH Biotrak system and HACH BOD₅ incubator. Inoculum used freshly for BOD₅ tests was supplied by Ankara Municipal Wastewater Treatment Plant. Before using, activated sludge was first aerated for one day and then washed two times with tap water to remove remaining organics in the bulk liquid.



Figure 1. Chemical structure of Astrazon Red FBL (C.I. Basic Red 46.)

The degree of decoloration of dye solutions can be calculated by the following equation.

DDC (%) = (($A_0 - A_i$)/A0) x 100

 $A_0 \mbox{ and } A_i$ are the maximum absorbance (530 nm) in visible area of the dye solution before and after irradiation.

Toxicity tests of Astrazon Red FBL dye solutions were performed with lyophilized luminescent bacteria reagent *Vibrio fischeri*, reconstitution solutions by using Microtox 500 Toxicity analyzer (Modernwater). Test was performed according to the supplier's protocol using basic test mode [25]. The test allows the interaction between organisms and dye solutions and measures the percentage of bioluminescence light reduction at 5 and 15 min. The data obtained were EC_{50} value, which is defined as the effective concentration of a wastewater sample that is a reduction in the emitted light of luminescent bacteria by a factor of 50 %. The results are expressed in terms of toxicity unit (TU). The TU is the inverse of its EC_{50} value [25]. All values given in the text are an average of at least three measurements.

III. RESULTS and DISCUSSION

Synthetic textile wastewaters used in this study were prepared by using Astrazon Red FBL (200 ppm). The change of DDC (%) of dye solutions were examined by UV-Visible spectroscopy. All samples were

scanned between 200 - 900 nm for the determination of maximum absorbance wavelength. UV-Vis absorption spectrum of Astrazon Red FBL mainly shows single absorption peak in the visible region ($\lambda_{max} = 530$ nm). It arises due to the conjugation through hydrazyl unit. There is also a weak peak at 291 nm appeared because of the amine hyperconjugation of the π bond of aromatic ring on Astrazon Red FBL chemical structure, in turn leading to π - π^* transition. This peak disappeared with ring opening mechanism after irradiation.

3.1 Effect of radiation on the absorpion characteristic of Astrazon Red FBL in aqueous solutions

Aqueous solutions of Astrazon Red FBL were irradiated at different experimental conditions, namely air, O_2 saturated and 2.6 mM hydrogen peroxide by gamma rays at various doses and pHs. Absorption spectra of 200 ppm dye solution versus irradiation doses and conditions are demonstrated in Fig. 2. As seen at Fig.2, the singlet peak at 530 nm decreased with increasing doses. From Fig. 2, concentration of unirradiated and irradiated aqueous Astrazon Red FBL solutions was calculated and converted to DDC (%) by following the decrement at the absorption band of 530 nm and the results were graphed at Fig. 3.

Regarding to results in Figs. 2 and 3, the intensity of absorption band was decreased with increasing the absorbed doses, and finally disappeared at 5, 5, 7 kGy for air, O_2 saturated and 2.6 mM H₂O₂ solutions, respectively. Results showed that the DDC (%) is almost identical for air and O_2 saturated solutions. As seen in Figure 2a, there is still an absorption peak at 5 kGy. However, considering this DDC value, it is negligible. While the DDC value is 93.7 at 5 kGy, it is 95.2 at 7 kGy. The 1.5 percent difference is considered insignificant because of the 2 kGy to be gained from dose reduction in the industrial treatment of dyestuffs. The 2 kGy reduction in dose significantly reduces the treatment cost. At the same time, the obtained treatment efficiency is sufficient for discharge. For this reason, considering the operating cost and treatment quality, it is considered that it would be more feasible to apply a 5 kGy dose instead of a 7 kGy dose. A similar result is also valid in Figure 2c, and it was evaluated that it would be more feasible to administer a dose of 7 kGy instead of 9 kGy there.



Figure 2. UV-Vis spectra of Astrazon Red FBL dye solution under irradiation at (a) air, (b) O_2 saturated and (c) 2.6 mM H_2O_2 .



Figure 3. DDC (%) variation as a function of absorbed dose at air, O_2 saturated and 2.6 mM H_2O_2 .

Addition of hydrogen peroxide enhances the decoloration reaction. It interacts rapidly with hydrated electrons and leads to the formation of •OH radical. In this context, it is attributed to increment in •OH radical that the increase in the DDC. However, the increase of DDC (%) by addition of 2.6 mM H_2O_2 is rather low than air and O_2 saturated solutions. Regarding to this result, dye chromophore groups are destructed further more by the •OH radical than the hydrated electrons despite of a part of the •OH radicals are scavenged by the excess hydrogen peroxide. Therefore, DDC value of dye solution with H_2O_2 is lower than air and O_2 saturated solutions. In addition, hydrogen, •OH radicals and hydrated electrons react with the textile dye molecules with the diffusion controlled processes. During irradiation process, oxygen molecule reacts with the hydrogen atoms and hydrated electrons, which produces superoxide radical anions and peroxy radicals as defined below, respectively.

$$\mathrm{H}^{\bullet} + \mathrm{O}_2 \to \mathrm{HO}_2^{\bullet} \tag{1}$$

and

$$e_{aq} + O_2 \to O_2^{\bullet}$$
(2)

Thus dye molecule interaction with the hydrated electrons and hydrogen atoms is limited. During irradiation, hydroxyl radicals may generate the meaningful reduction in the red dye molecules. Both the addition reaction of hydroxyl radicals to phenyl rings at Astrazon Red FBL dye molecule (Figure 1) or H• abstraction from phenyl rings compete with each other [1]. The cyclohexadienyl type of radical was occurred by addition reaction of hydroxyl radicals to the phenyl rings at the Astrazon Red FBL [26]. These radicals (cyclohexadienyl type) attacked to dissolved oxygen and then, converted to CO_2 and H_2O as shown in the following reaction [27-29].

$$Dye + OH^{\bullet} \rightarrow Cyclohexadienyl type radical \rightarrow CO_2 + H_2O$$
 (3)

3.2. Change in COD

The COD test is most widely used test to indirect measurement of the organic contents in

water/wastewater. The chemical oxygen demand (COD) is an indicative measure of the amount of oxygen that can be consumed by reactions in a measured solution. The initial COD values of aqueous dye solution of 200 ppm was measured as 279, 289, 210 mg/L for air, O₂ saturated and 2.6 mM H₂O₂, respectively. They were subjected to gamma ray irradiation and measured values were shown in Table 1. When samples were exposed to gamma rays, a decrease in COD, or in other words, an increase in percent COD removal, was observed as a function of dose increment. COD % removal efficiency was calculated and found to be 94, 96, and 82% for air, O₂ saturated and 2.6 mM H₂O₂, respectively. It is attributed to the dependency of COD removal efficiency to the absorbed dose. The COD removal characterisitic has similiar trend with the decoloration of dye molecules. Decoloration is merely discreminated by the disintegration of color centes on the conjugated electron structure of dye molecules. Post-irradiation after decoloration, aromatic ring is disintegrated to smaller molecules. At the beginning of the radiolysis, decomposition of Astrazon Red FBL molecules into the smaller molecules was initiated and it finally resulted with CO2 and H2O upon excess irradiation. It was revealed at Table 1 that the reduction in COD increased as a function of applied dose. In addition, it is also noteworthy that the COD reduction against dose was observed a similar behaviour as in the case of DDC (%) versus dose. In this context, the disintegration of color centers in the molecules was responsible for the main cause of the discoloration. However, COD reduction mainly rely upon the complete mineralization of the dye stuffs by irradiation dose. The color center groups of molecule could be degraded by a low dose application in the initial stage of the decolorization process. But, this is going to be cause an incomplete mineralization of the dye molecule by the formation of smaller molecular weight intermediates upon incomplete degradation process. However, the partial mineralization at the beginning of the irradiation was turned to complete mineralization at 5, 5, and 7 kGy for air, O_2 and H₂O₂ solutions, respectively.

Dose	Air				O ₂ satu	rated	2.6 mM H ₂ O ₂		
(kGy)	COD	BOD ₅	BOD ₅ / COD	COD	BOD ₅	BOD ₅ /COD	COD	BOD ₅	BOD ₅ / COD
0	279	81	0.29	289	78	0.27	210	67	0.25
2	158	55	0.35	123	44	0.36	114	57	0.33
5	18	14	0.78	11	8	0.72	33	34	0.37
7	14	11	0.77	11	8	0.70	11	7	0.62
9	14	10	0.75	11	7	0.68	6	4	0.63

Table 1. COD, BOD₅ and biodegradability index of Astrazon Red FBL solution under irradiation.

3.3. Change in pH

The change in pH was studied in two phases. First, pH before and after irradiation was monitored. Second, pH – DDC (%) relationship was followed at constant irradiation dose. Results of both studies are presented at Table 2. In the determination of pH variation during irradiation, pH of the solutions was fixed between 3 and 12, and dose was kept constant for each experimental conditions. After sample preparation, pH was immediately measured and irradiated to 0 - 9 kGy (Fig. 4). Then, pH was measured again. As depicted in Table 2 and Fig. 4, a negligible pH difference was observed. Only pH 9 of air and O₂ saturated conditions were deviated from the linearity. After irradiation, pH reduced to 7.1 and 7.3 by releasing or decomposing of some acidic group(s) from Astrazon Red FBL and it caused a shift of pH from basic to neutral (20). As it was seen from the curves of Fig. 5, maximum DDC (%) variation was found at pH 9, 11, and 11 for air, O₂ saturated and 2.6 mM H₂O₂, respectively. Based on these pHs, dye was disintegrated to intermediate molecules and then were decolorized.

nH (Bef Irrad) —	pH (Aft. Irrad.) ; DDC (%)						
pii (bei: iiiuu.)	Air (5 kGy)	O ₂ (5 kGy)	H ₂ O ₂ (7 kGy)				
3.0	3.0;90	3.04;92	3.21;55				
4.0	4.6;94	4.50;91	4.96;62				
5.0	5.1;97	5.37;88	5.13;60				
6.0	5.6;97	5.80;89	6.19;63				
7.0	6.3;93	6.80;84	7.06;47				
8.0	6.7;96	6.95;81	7.46;50				
9.0	7.1;99	7.27;88	8.74;65				
10.0	9.1 ; 99	9.29;91	9.58 ; 89				
11.0	10.3;99	10.26;96	10.61;96				
12.0	12.0;98	11.86;96	11.32;97				

Table 2. The variation of pH and DDC (%) at optimized dose.



Figure 4. The change in pH before and after irradiation.



Figure 5. The pH effect on the DDC (%) at air (5 kGy), O_2 saturated (5 kGy) and 2.6 mM H_2O_2 (7 kGy).

The DDC (%) is accepted to be a crucial parameter in the treatment of both dyeing and finishing effluents. Variation in the DDC (%) of the solution in various concentrations (10, 50, 100 and 200 ppm) at optimized irradiation conditions (air: pH=9, 5 kGy; O_2 saturated: pH=11, 5 kGy and 2.6 mM H₂ O_2 : pH=11, 7 kGy) presented in Table 3. As seen in Table 3, pH is relatively the same with the initial pH adjustment for O_2 saturated and 2.6 mM H₂ O_2 conditions. As observed in pH analysis, pH of aerated solutions was also dropped from 9 to 7 by irradiation. Some acidic release from dye might cause this pH deviation. However, DDC (%) of air saturated solutions is quite similar with O_2 saturated, but higher than the dye solution containing 2.6 mM H₂ O_2 . The decoloration has no pronoun dependence on pH and dye concentration. As a results under these treatment conditions, irradiation is an effective treatment process for the achievement of decoloration at any substrate concentration.

Conc. (ppm)	Air (pH:9;5 kGy)	O2 (pH:11;5 kGy)	H ₂ O ₂ (pH:11;7 kGy)		
	pH ; DDC %	pH ; DDC %	рН ; DDC %		
10	7.1;99	10.7;86	11.3 ; 88		
50	7.1;99	10.8;96	11.8 ; 94		
100	7.4;97	10.6 ; 94	11.6 ; 94		
200	7.2;98	10.7;93	11.1 ; 95		

Table 3. Concentration effect on pH and DDC % at optimized pH and absorbed dose.

3.4. Change in BOD₅

BOD₅ is the amount of dissolved oxygen consumption by microorganisms to decompose the organic matters under aerobic conditions at 20 °C in five-days period. COD and BOD₅ values are a key element in the characterization of wastewater treatment process. They determine the effluent characteristics, whether they are suitable or are not to discharge. On the other hand, BOD₅/COD is an indicator for biodegradability of wastewater where their ratio is smaller than 0.3 or higher than 0.8, it means that the effluent has a biodegradability problem, which is caused by different effects in nature [30, 31]. The BOD₅/COD ratio (biodegradability index) of the 200 ppm dye solutions was summarized as a function of absorbed doses in Table 1. As could be seen from Table 1, the biodegradability index of the unirradiated 200 ppm Astrazon Red FBL solutions was measured to be 0.29, 0.27 and 0.25 for air, O₂ saturated, 2.6 mM H₂O₂ conditions, respectively. Regarding to this result, it indicates that all the solutions prepared under different conditions are non-biodegradable. Table 1 shows that biodegradability index of 200 ppm solution was increased from 0.29 to 0.35 at 2 kGy; and at 9 kGy, it was become to 0.75. The results suggest that the non-biodegradable dye solutions are become biodegradable just expose to 2 kGy dose for each experimental conditions and their biodegrability are enhanced with increasing dose.

3.5. Bioluminescent toxicity test

Sterile deionized water and saturated air and oxygen as well as H_2O_2 were used in the preparation of samples. Vibrio fischeri is severely affected by H_2O_2 and emitted light less than samples saturated with air and oxygen solutions. Toxicity results as well as radiation efficiencies are summarized in Table 4. Observing the toxicity units (TU), it is possible to verify that Astrazon Red FBL was more toxic prepared in H_2O_2 solution than air and O_2 saturated solutions. The reason was assumed to be initial toxicity differences. After irradiation, the results show a dramatically decrease in acute toxicity for all solutions irradiated up to 9 kGy. As could be seen from Table 4, the dose of 5, 5 and 7 kGy is required to detoxify the dye solutions for air, O_2 and 2.6 mM H_2O_2 solutions, respectively. In addition, the lower biodegradability index (<0.3) means that aqueous sample solution may also contain some toxic species [22]. This higher toxicity values of unirradiated samples may also be another factor that cause the increse in toxicity. When the detoxification rate was compared, toxicity reduction was found to be in the order of Air $\geq O_2 > H_2O_2$ solutions.

	EC ₅₀			TU			Toxicity Reduction (%)		
Dose (kGy)	Air	O_2	H_2O_2	Air	O_2	H_2O_2	Air	O_2	H_2O_2
0	5.2	5.2	3.1	19.2	19.2	32.3	0.0	0.0	0.0
2	9.1	12.3	3.9	11.0	8.1	25.6	42.9	57.7	20.5
5	27.6	39.2	4.9	3.6	2.6	20.4	81.2	86.7	36.7
7	28.6	38.2	6.5	3.5	2.6	15.4	81.8	86.4	52.3
9	28.1	36.9	5.7	3.6	2.7	17.5	81.5	85.9	45.6

Table 4. Toxicity of Astrazon Red solutions under irradiation.

As it was observed in decoloration studies, the toxicity characteristic of aerated and O_2 saturated solution was quite similiar. The above studies encourage the high energy induced treatment method for decoloration and detoxification of dye influents coming from textile industries.

IV. CONCLUSION

Decoloration, detoxification and mineralization of Astrazon Red FBL in aqueous solutions exposed to ionizing radiation has been studied. In this context, aqueous solutions of Astrazon Red FBL were irradiated at various doses in different experimental conditions, namely air, O_2 saturated, 2.6 mM H₂O₂. Dose, pH, decoloration, toxicity, COD and BOD₅ removal have been followed to determine optimum irradiation conditions. Dose and pH were optimized to be 5 kGy pH 9 at air, 5 kGy pH 11 at O₂ saturated, 7 kGy pH 11 at 2.6 mM hydrogen peroxide for Astrazon Red FBL. In addition, an enhancement on the biodegradability (BOD₅/COD) index was observed at 2 kGy for Astrazon Red FBL in all irradiation conditions.

In this study, the decoloration, detoxification and mineralization of cationic Astrazon Red FBL dye under irradiation was experienced and the dye is found to be easily decolored. In the achievement of decoloration, detoxification and mineralization for textile dyes, it was revealed that irradiation process itself or irradiation process combined by air, oxygen or hydrogen peroxide could be used successfully. When it is compared in terms of the irradiation efficiency and the feasibility, irradiation at air has advantages like low dose applications, and chemical consumptions as well as less auxilary equipment requirements. As a final conclusion, dose of 5, 5 and 7 kGy is sufficient for the complete decoloration, detoxification and mineralization of Astrazon Red FBL dye in air, O_2 saturated and 2.6 Mm H_2O_2 solutions, respectively.

<u>ACKNOWLEDGEMENTS</u>: The author thanks to both Turkish Energy, Nuclear and Mining Research Agency (A4.H1.F12) and International Atomic Energy Agency (IAEA-TUR/8/017) for financially support.

V. REFERENCES

[1] A. Aleboyed, H. Aleboyeh, and Y. Moussa, "Decolorisation of acid blue 74 by ultraviolet/ H₂O₂," *Environmental Chemistry Letters*, vol. 1, no. 3, pp. 161–164, 2003.

[2] S.F. Kang and H.M. Chang, "Coagulation of textile secondary effluents with Fenton's Reagent," *Water Science and Technology*, vol. 36, no. 12, pp. 215–222, 1997.

[3] H.Y. Shu and M.C.J. Chang, "Pre-ozonization coupled with UV/H2O2 process for the decolorization and mineralization of cotton dyeing effluent and synthesized C.I. Direct Black 22 wastewater," *Journal of Hazardous Materials*, vol. B121, no. 1-3, pp. 127–133, 2005.

[4] F. Zidane, P. Drogui, B. Lekhlif, J. Bensaid, J. Blais, S. Belcadi and K.J. Kacemi,"Decolourization of dye-containing effluent using mineral coagulants produced by electrocoagulation," Journal of Hazardous Materials, vol. 155, pp. 153-163, 2008.

J.H. Mo, Y.H. Lee, J. Kim, J.Y. Jeong and J. Jegal, "Treatment of dye aqueous solutions using [5] nanofiltration polyamide composite membranes for the dye wastewater reuse," Dyes and Pigments, vol. 76, pp. 429–434, 2008.

S. Souza, E. Forgiarini and A. Souza, "Toxicity of textile dyes and their degradation by the [6] enzyme horse radish peroxidase (HRP)," Journal of Hazardous Materials, vol. 147, pp. 1073-1078, 2007.

C. Wu, "Decolorization of C.I. reactive red 2 in O₃, Fenton-like and O₃/Fenton like hybrid [7] Systems," Dyes and Pigments, vol. 77, pp. 24-30, 2008.

M. Panizza and G. Cerisola, "Removal of colour and COD from wastewater containing acid [8] blue 22 by electrochemical oxidation," Journal of Hazardous Materials, vol. 153, no. 1-2, pp. 83-88, 2008.

[9] G.J. Brunner, "Near and supercritical water. Part II: oxidative processes, review," Supercritical Fluids, vol. 47, pp. 382–390, 2009.

J.L. Morias and P.P. Zamora, "Use of advanced oxidation process to improve the [10] biodegradability of mature landfill leachate," Journal of Hazardous Materials, vol. B123, pp. 181-186, 2005.

T.H. Kim, C. Park, J. Lee, E.B. Shin and S. Kim, "Pilot scale treatment of textile wastewater by [11] combined process (fluidized biofilm process-chemical coagulation-electrochemical oxidation)," Water Research, vol. 36, pp. 3979–3988, 2002.

M. Noorjahan, M. Pratap Reddy, V. Durga Kumari, B. Lave' drine, P. Boule and M. [12] Subrahmanyam, "Photocatalytic degradation of H-acid over a novel TiO₂ thin film fixed bed reactor and in aqueous suspensions," Journal of Photochemistry and Photobiology A: Chemistry, vol. 156, pp. 179-187, 2003.

I. Arslan and I.A. Balcioglu, "Degradation of commercial reactive dye stuffs by heterogenous [13] and homogenous advanced oxidation processes: a comparative study," Dyes and Pigments, vol. 43, pp. 95–108, 1999.

M. Koch, A. Yediler, D. Lienert, G. Insel and A. Kettrup, "Ozonation of hydrolyzed azo dye [14] reactive yellow 84(CI)," Chemosphere, vol. 44, pp. 109-113, 2002.

G.M. Shaul, C.R. Dempsey and K.A. Dostal, "Fate of water soluble azo dyes in the Activated [15] Sludge Process," United State Environmental Protection Agency, Water Engineering Research Laboratory, USA, Project summary no. EPA/600/S2-88/30, 1988.

B. Han, J. Kim, Y. Kim, J.S. Choi, I.E. Makarov and A.V. Ponomarev, "Electron beam treatment [16] of textile dveing wastewater: Operation of pilot plant and industrial plant construction," Water Science and Technology, vol. 52, no. 10-11, pp. 317-324, 2005.

N. Getoff, "Radiation chemistry and the environment," Radiation Physics and Chemistry, vol. [17] 54, pp. 377–384, 1999.

N.M. Mahmoodi, N.Y. Limaee, M. Arami, S. Borhany and M.J. Mohammad-Taheri, [18]

"Nanophotocatalysis using nanoparticles of titania. mineralization and finite element modelling of solophenyldyede colorization," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 189, pp. 1–6, 2007.

[19] A. Doubla, L.B. Bello, M. Fotso and J.L. Brisset, "Plasmochemical decolourisation of bromothymol blue by gliding electric discharge at atmospheric pressure," *Dyes and Pigments*, vol. 77, pp. 118–124, 2008.

[20] M. Wang, R. Yang, W. Wang, Z. Shen, S. Bian and Z. Zhu, "Radiation-induced decomposition and decoloration of reactive dyes in the presence of H₂O₂," *Radiation Physics and Chemistry*, vol. 75, pp. 286–291, 2006.

[21] T. Ting and N. Jamaludin, "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*, vol. 73, pp. 76–80, 2008.

[22] Ö. Kantoğlu, "Decoloration and mineralization of aqueous solution of cationic (basic) dye Astrazon Black FDL by using gamma rays," *Radiochimica Acta*, vol. 105, no. 3, pp. 241-248, 2017.

[23] D. De Zwart and A.J. Folkerts, "Monitoring the toxicity of organic compounds dissolved in Rhine water," *Hydrobiology Bulleetine*, vol. 24, no. 1, pp. 5-12, 1990.

[24] M.E. Lebsack, A.D. Anderson, C.M. Degraeve, and H.L. Bergman, "Comparison of Bacterial luminescence and fish bioassay result for fossil –fuel process waters and phenolic constituents," *Aquatic Toxicology and Hazard Assessment: Fourth Conference*, 1981, pp 348-356.

[25] Basic Test, Azur Environmental Ltd, Microtox User Manual, pp. 23-33, 1998.

[26] L. Wojnarovits, T. Palfi, E. Takacs, and S.S. "Emmi, Reactivity differences of hydroxyl radicals and hydrated electrons in destructing azo dyes," *Radiation Physics and Chemistry*, vol. 74, pp. 239–246, 2005.

[27] S. Hammami, N. Bellakhal, N. Oturan, M.A. Oturan, and M. Dachraoui, "Degradation of acid orange 7 by electrochemically generated OH radicals in acidic aqueous medium using a boron-doped diamond or platinum anode: a mechanistic study," *Chemosphere*, vol. 73, pp. 678–684, 2008.

[28] J. Yang, J. Dai, C. Chen, and J. Zhao, "Effects of hydroxyl radicals and oxygen species on the 4-chlorophenol degradation by photoelectrocatalytic reactions with TiO₂-film electrodes," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 208, pp. 66–77, 2009.

[29] J. Paul, K.P. Rawat, KS.S. Sarma, and S. Sabharwal, "Decoloration and degradation of Reactive Red-120 dye by electron beam irradiation in aqueous solution," *Applied Radiation and Isotopes*, vol. 69, pp. 982-987, 2011.

[30] J. Garcia-Montano, F. Torrades, J.A. Garcia-Hortal, X. Domenech, and J. Peral, "Combining photo-Fenton process with aerobic sequencing batch reactor for commercial hetero-bireactive dye removal," *Applied Catalysis B: Environmental*, vol. 67, pp. 86–92, 2006.

[31] Ö. Kantoğlu, "Effects of high energitic radiation on the removal and detoxification of cationic dye Astrazon Blue FGRL," *Turkish Journal of Nuclear Sciences*, vol. 33, no. 1, pp. 1-14, 2021.