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Research Article

Determination of Electrical Energy Cost of Decolorization of Reactive Red 120 via Heterogeneous Photocatalysis with TiO₂

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ABSTRACT

In this study decolorization of Reactive Red 120 (RR120) azo dye solution and synthetic dye-bath effluent of RR120 was investigated via heterogeneous photocatalysis with TiO₂ under UV light. Decolorization efficiency of synthetic dye-bath effluent was expected to be lower than that of RR120 solution. Electrical energy consumption was determined by figure of merit approach based on the requirement of electrical energy to reduce the concentration of a pollutant by one order of magnitude in 1 m^3 of contaminated water (E$_{EO}$) for low concentration of pollutant. Electrical energy consumption of synthetic dye-bath effluent was found higher than RR120 solution. Considering one order of magnitude treatment of RR120 the cost of electrical energy was found to be 1.23 and 7.73 € m^{-3} for decolorization of RR120 solution and synthetic dye-bath effluent, respectively. The applicability of solar light was evaluated, and it was found that solar driven photocatalysis is significantly efficient for decolorization of RR120.

KEYWORDS: Reactive Red 120; TiO₂; decolorization; figure of merit; the cost of electrical energy; solar light

INTRODUCTION

Since discovery of TiO₂ electrode by Fujishima and Honda to split water into H₂ and O₂, considerable researches on advanced oxidation processes (AOPs) have been conducted for air and water remediation. AOPs are based on the in situ generation of hydroxyl radical (OH·) which is a very reactive and nonselective oxidant towards chemical compounds with a standard redox potential of 2.8 V. OH· is capable of oxidizing a wide range of organic and inorganic compounds at ambient conditions [1-2]. More specifically, heterogeneous photocatalysis with TiO₂ has become increasingly prominent for the removal of hazardous pollutants such as pesticides, dyes, pharmaceuticals and NO present in water and air. When TiO₂ is illuminated with photon energy equal or larger than its band gap charge carrier species (e⁻ and h⁺) are generated. They either recombine or migrate to surface of TiO₂ on which photogenerated electrons (e⁻) reacts with dissolved oxygen to form superoxide anion radicals (O₂·⁻) and photogenerated holes (h⁺) reacts with adsorbed H₂O or OH· to form OH·. Once OH· is formed, pollutants are degraded through hydrogen abstraction and electron transfer. Fundamentals of heterogeneous photocatalysis with TiO₂ are well documented

[3-8]. The following equation is considered to define the overall process.

$$\text{Organic compounds} \xrightarrow{\ TiO_2/UV\ } CO_2 + H_2O + \text{mineral acids} \tag{1}$$
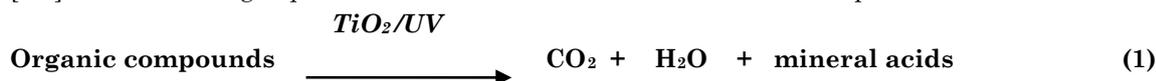
Textile industry consumes a large volume of water and a wide variety of chemicals such as dyes, detergents, salts and soda during manufacturing stages. Consequently, wastewater generated from textile industry is characterized by having intense color with unfixed dye, large volume and high COD and low BOD values. The problems associated with releasing such a colored wastewater into water bodies are non-aesthetic pollution, eutrophication, reduction of light penetration and formation of byproducts via chemical reactions occurred in the wastewater [9-11]. Reactive dyes extensively used to dye cotton, wool and polyamide fibers. Owing to low dye fixation rate and high hydrolysis tendency with OH^-, almost 50% of reactive dyes are lost in dyeing stage, resulting colored textile effluents. Reactive dyes mostly have an azo type chromophore group and azo dyes are hazardous to environment due to their toxic and nonbiodegradable nature. Therefore, removal of them from textile wastewater is of prime importance due to environmental concerns. Physical, chemical and biological treatment technologies have been used to eliminate them so far but they are either nondestructive or ineffective. Heterogeneous photocatalysis with TiO_2 is considered as an emerging technology for removal of azo dyes in recent years. Nonbiodegradable organic compounds can be mineralized into CO_2 and H_2O or degraded to biodegradable products by photocatalytic oxidation. Thus degradation of azo dyes using photocatalysis with TiO_2 under UV light [11-19] or solar light [20-24] has been extensively explored.

The selection of wastewater treatment technology is mainly depends on the technical and economic feasibility of the treatment. Since AOPs with UV are energy intensive processes, operating cost constitutes a significant part of cost of the processes. Therefore, determination of electrical energy cost of process concerned is an important and critical aspect. Determination of electrical energy consumption of AOPs has been defined by International Union of Pure and Applied Chemistry (IUPAC) considering two figures of merit. One is based on the requirement of electrical energy to remove 1 kg of the pollutant (E_{EM}) for high concentration of pollutant and the other is based on the requirement of electrical energy to reduce the concentration of a pollutant by one order of magnitude in 1 m^3 of contaminated water (E_{EO}) for low concentration of pollutant. Figure of merit approach renders a rapid determination of electrical energy cost of AOPs [25-27].

The objective of this study is to determine the electrical energy cost of decolorization of Reactive Red 120 (RR120) azo dye via heterogeneous photocatalysis with TiO_2 under UV light by using figure of merit approach. Besides, the decolorization of synthetic dye-bath effluent of RR120 was also considered.

MATERIALS AND METHOD
Materials
A commercially available RR120 (DyStar) was used as model compound. A gift sample of TiO_2-P25 powder was obtained from Degussa and used as received. According to the manufacturer's specifications, it is mainly in anatase form with an average particle size of 21 nm and a BET specific surface area of 50 $m^2\,g^{-1}$. H_2SO_4 (% 96 w/w) was purchased from Merck and NaOH was purchased from Sigma-Aldrich. All chemicals were analytically graded.

Experimental Procedure
Experimental studies were conducted in a pyrex glass cylindrical annular photoreactor. Details of experimental procedure are given in our previous study [28]. Actual solar radiation experiment was performed between 12:00 and 14:00 h in a sunny day in August at Inonu University in Malatya (38°19′ E, 38°21′ N), Turkey. In this study synthetic dye-bath effluent of RR120 was also used. It was prepared by mixing 0.02 dm^3 RR120 solution, 0.5 g dm^{-3} enzyme, 0.5 g dm^{-3} sequestering agent, 0.028 dm^3 30% w/w NaCl solution, 0.010 dm^3 20% w/w Na_2CO_3 solution and 0.034 dm^3 water. After dyeing process, the obtained effluent was used as a synthetic dye-bath effluent in photocatalytic experiment.

RESULTS AND DISCUSSION

Decolorization of Synthetic Dye-bath Effluent of RR120

Operating parameters influencing the decolorization of RR120 were evaluated in our previous studies [28-29]. We have shown that highest decolorization efficiency was obtained at pH 6 and decolorization efficiency was increased upon increasing TiO_2 concentration. Based on these results, in this study decolorization of synthetic dye-bath effluent of RR120 was investigated. Fig.1 represents the decolorization of RR120 solution and synthetic dye-bath effluent at pH=6 and 1 g dm^{-3} TiO_2 concentration under UV irradiation. After addition of TiO_2 to dye solution, the suspension was stirred for 30 min in dark to attain equilibrium. At the end 30 min 14.8% and 5.2% removal for RR120 solution and synthetic dye-bath effluent were obtained by adsorption, respectively. Almost complete decolorization was achieved within 240 minutes of reaction time for RR120 solution, while 59 % of decolorization efficiency was obtained after 300 minutes for synthetic dye-bath effluent, indicating that further reaction time was required.

Decolorization efficiency of synthetic dye-bath effluent was expected to be lower than that of RR120 solution. This is because a large amount of salts are added into dying medium due to low affinity of reactive dyes. CO_3^{2-} and Cl^- ions are known to be scavengers of generated OH^- and in the presence of these ions less reactive radicals are formed as given below in Eqs. 2-3 [30]. Thus, decolorization of synthetic dye-bath effluent was not easier as compared to for RR120 solution and required longer irradiation time.

$$Cl^- + OH^- \longrightarrow ClOH^- \tag{2}$$
$$CO_3^{2-} + OH^- \longrightarrow OH^- + CO_3^- \tag{3}$$

Determination of Electrical Energy Cost

Since low concentration of RR120 was studied in this study, electrical energy per order was considered (Eq.4).

$$E_{EO} = \frac{Pt1000}{V60log\frac{C_o}{C}} \tag{4}$$

where P is input power to the process (kW), t is the irradiation time (min), V is the volume of treated water (dm^3).

In general, photocatalytic oxidation of most organic contaminants obeys pseudo-first order kinetics. Experimental data were fitted well to pseudo-first order kinetic model given by Eq.5 for decolorization of RR120 in this study.

$$\ln\frac{C_o}{C} = k_{app}t \tag{5}$$

where C_o and C are initial and treated dye concentrations, k_{app} is apparent first-order rate constant and t is reaction time. Therefore, combination of Eq.4 and Eq.5. yields Eq.6.

$$E_{EO} = \frac{38.4P}{Vk_{app}} \tag{6}$$
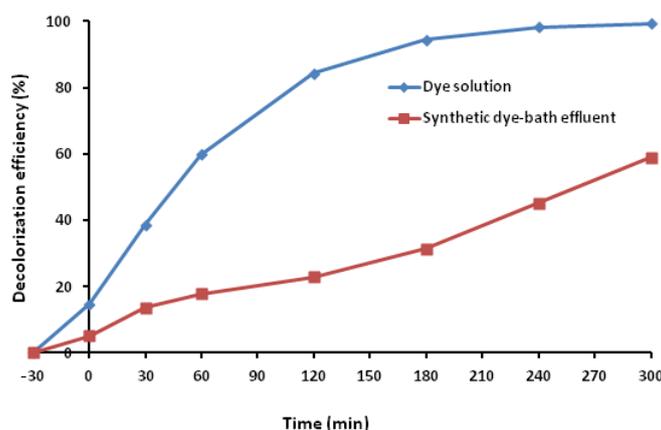
Fig.1: Decolorization of RR120 solution and synthetic dye-bath effluent
pH = 6, [TiO_2] = 1 g dm^{-3}

As is evident from Fig. 2, linear expressions were obtained with the plots of $ln (C_o/C)$ versus t for both RR120 solution at a concentration of 50 mg dm^{-3} and synthetic dye-bath effluent. From these plots, k_{app} values were found to be 0.0157 and 0.0025 min^{-1} for decolorization of RR239 solution and synthetic dye-bath effluent, respectively. The electrical energy consumptions were calculated using Eq.6. As can be seen in Fig. 3., one order of reduction in RR120

concentration in 1 m^3 treated water required 29.35 kWh electrical energy. In other words, to reduce the concentration of RR120 from 50 mg dm^{-3} to 5 mg dm^{-3} 29.35 kWh per m^3 treated water energy was involved. Electrical energy consumption of synthetic dye-bath effluent was much more higher than RR120 solution. This is an expected result because synthetic dye-bath effluent contains auxiliary chemicals in addition to dyes.

The cost electrical energy for decolorization of RR120 solution and synthetic dye-bath effluent was calculated taking the cost of electricity per kWh in Turkey as 0.0419 € kWh^{-1}. As can be seen in Fig.4, considering one order of magnitude treatment of RR120 the cost of electrical energy was found to be 1.23 and 7.73 € m^{-3} for decolorization of RR120 solution and synthetic dye-bath effluent, respectively.

Nonbiodegradable organic compounds can be either mineralized into CO_2 and H_2O or degraded to biodegradable products via heterogeneous photocatalysis with TiO_2. Therefore, heterogeneous photocatalysis can be applied alone or combining with other technologies as a pre- or post-treatment stage. Although biological treatments are generally preferred in wastewater treatment due to their low cost, they are inefficient in the case of nonbiodegradable organic compounds such as azo dyes. Since the operational cost of heterogeneous photocatalysis using UV lamps as a light source is high, this limitation could be overcome by considering combination of heterogeneous photocatalysis with biological treatments [31-32]. It can also be beneficial to use actual solar light.
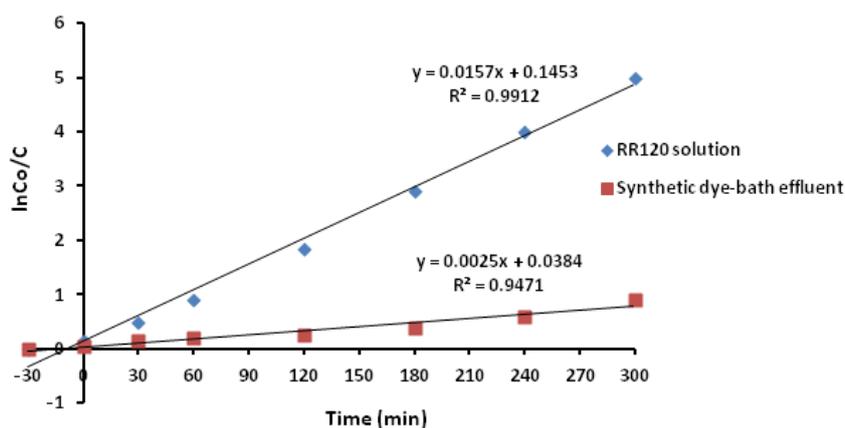

Fig.2. Kinetics of decolorization of RR120 solution and synthetic dye-bath effluent
[RR120] = 50 mg dm^{-3}, pH = 6, [TiO_2] = 1 g dm^{-3}
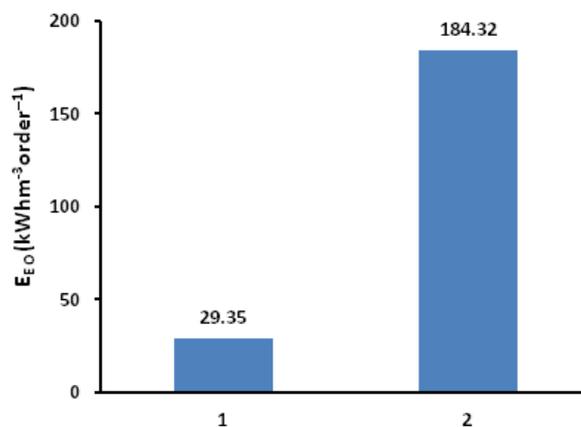

Fig.3: E_{EO} values for decolorization
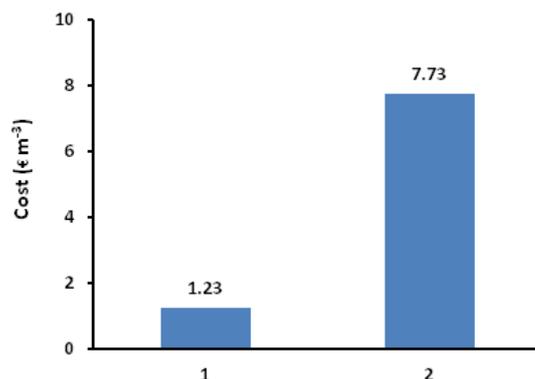**1. RR120 solution 2. Synthetic dye-bath effluent**

Fig. 4: Cost of electrical energy for decolorization
1. RR120 solution 2. Synthetic dye-bath effluent

Application of Solar Light

In order to determine the applicability of actual solar light in TiO_2 based photocatalysis, decolorization of RR120 solution was performed under sunlight irradiation. Fig.5 reveals the plot of decolorization efficiency versus irradiation time. 84% and 74% of decolorization efficiencies within 120 minutes of reaction time were obtained under irradiation with 24 W UV lamp

and actual solar light, respectively. This result is appreciable as Turkey has 3.6 kWh/m² yearly average solar radiation and 2610 h total yearly radiation period [33]. Owing to the considerable cost of electrical energy for decolorization of synthetic dye-bath effluent of RR120, solar driven photocatalysis could be an alternative treatment.
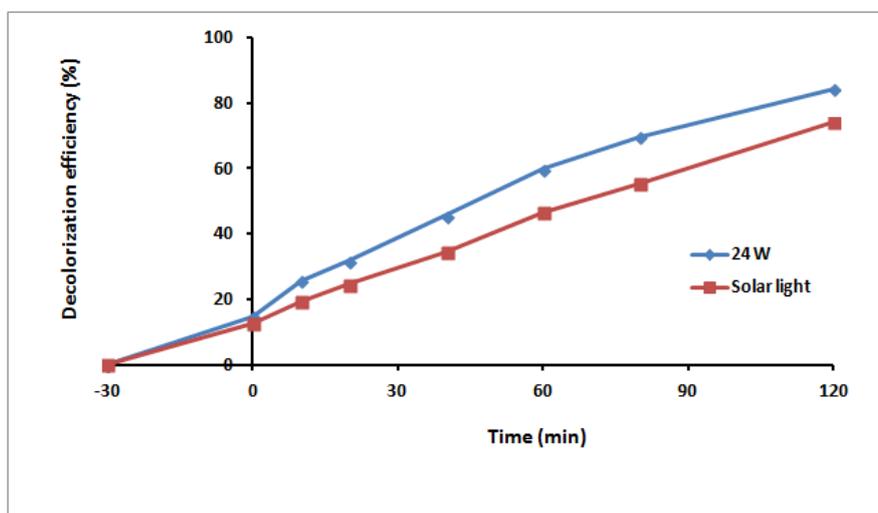

Fig.5. Decolorization of RR120 solution under solar light
[RR120] = 50 mg dm^{-3}, pH = 6, [TiO$_2$] = 1 g dm^{-3}

CONCLUSION

It was observed that almost complete decolorization of RR120 solution was achieved within 240 minutes of reaction time via TiO_2 based photocatalysis in the presence of UV light. However, decolorization of synthetic dye-bath effluent of RR120 was much slower than that of RR120 solution, with 59 % of decolorization efficiency after 300 minutes. Decolorization of RR120 followed by pseudo first order kinetics.

The electrical energy consumptions of RR120 dye solution and synthetic dye-bath effluent were determined by figure of merit approach based on electrical energy per order. One order of reduction in RR120 concentration in 1 m³ treated water required 29.35 kWh electrical energy. Considering one order of magnitude treatment of RR120 the cost of electrical energy was found to be 1.23 and 7.73 € m^{-3} for decolorization of RR120 solution and synthetic

dye-bath effluent, respectively. The results show that solar driven photocatalysis can be employed for the decolorization of RR120. The operating cost of the process can be reduced by combining TiO_2-assisted photocatalysis with biological treatment or using solar light.

ACKNOWLEDGEMENTS

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest in this research article.

REFERENCES

1. Lee SY, Park SJ. TiO_2 photocatalyst for water treatment applications. J Ind Eng Chem 2013; 19: 1761-1769.

2. Pelaez M, Nolan NT, Pillai SC, Seery MK, Falaras P, Kontos AG, Dunlop PSM, Hamilton JWJ, Byrne JA, O'Shea K, Entezari MH, Dionysiou DD. A review on the visible light active titanium dioxide photocatalysts for environmental applications. App Catal B 2012; 125: 331-349.

3. Binas V, Venieri D, Kotzias D, Kiriakidis G. Modified TiO_2 based photocatalysts for improved air and health quality. J Materiomics 2017; 3: 3-16.

4. Legrini D, Oliveros E, Braun AM. Photochemical processes for water treatment. Chem Rev 1993; 93(2): 671-696.

5. Ohtani B. Photocatalysis A to Z-What we know and what we do not know in a scientific sense. J Photoch Photobio C 2010; 11: 157-178.

6. Nakata, K, Fujishima A. TiO_2 photocatalysis: design and applications. J Photoch Photobio C 2012; 13: 69-189.

7. Chomg MN, Jin B, Chow CWK, Saint C. Recent developments in photocatalytic water treatment technology: A review. Water Res 2010; 44: 2997-3027.

8. Pattanaik P, Sahoo MK. TiO_2 photocatalysis: progress from fundamentals to modification technology. Desal WatTreat 2014; 52: 6567-6590.

9. Farouk HU, Raman AAA, Daud WMAW. TiO_2 catalyst deactivation in textile wastewater treatment: Current challenges and future advances. J Ind Eng Chem 2016; 33: 11-21.

10. Vilar VJP, Pinho LX, Pintor AMA, Boaventura RAR. Treatment of textile wastewaters by solar-driven advanced oxidation processes. Sol Energy 2011; 85: 1927-1934.

11. Konstantinou IK, Albanis TA. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations A review. Appl Catal Environ 2004; 49: 1-14.

12. Behnajady MA, Modirshahla N, Daneshvar N, Rabbani M. Photocatalytic degradation of an azo dye in a tubular continuous-flowphotoreactor with immobilized TiO_2 on glass plates, Chem Eng J 2007; 127: 167-176.

13. Rajeshwar K, Osugi ME, Chanmanee W, Chenthamarakshan CR, Zanoni MVB, Kajitvichyanukul P, Krishnan-Ayer R. Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media. J Photoch Photobio C 2008; 9: 171-192.

14. Akpan UG, Hameed BH. Parameters affecting the photocatalytic degradation of dyes using TiO_2-based photocatalysts: A review. J Hazard Mater 2009; 170: 520-529.

15. Soutsas K, Karayannis V, Poulios I, Rigad A, Ntampegliotis K, Spiliotis X, Papapolymerou G. Decolorization and degradation of reactive azo dyes via heterogeneous photocatalytic processes. Desalination 20010; 250: 345-350.

16. Dostanic J, Grbic B, Radic N, Stefanov P, Saponjic Z, Buha J, Mijin D, Photodegradation of an azo pyridone dye using TiO_2 films prepared by the spray pyrolysis method. Chem Eng J 2012; 180: 57-65.

17. Rajamanickam D, Shanthi M. Photocatalytic degradation of an azo dye Sunset Yellow under UV-A light using TiO_2/CAC composite catalysts. Spectrochim Acta A 2014; 128: 100-108.

18. Turkten N, Çınar Z. Photocatalytic decolorization of azo dyes on TiO_2: Prediction of mechanism via conceptual DFT. Catal Today 2017; 287: 169-175.

19. Miao J, Zhang R, Zhang L. Photocatalytic degradations of three dyes with different

chemical structures using ball-milled TiO_2. Mater Res Bull 2018; 97:109-114.

20. Muruganandham M, Shobana N, Swaminathan M, Optimization of solar photocatalytic degradation conditions of Reactive Yellow 14 azo dye in aqueous TiO_2. J Mol Catal A- Chem 2006; 246: 154-161.

21. Zayani G, Bousselmi L, Mhenni F, Ghrabi A. Solar photocatalytic degradation of commercial textileazo dyes: Performance of pilot plant scale thin film fixed-bed reactor. Desalination 2009; 246: 344-352.

22. Akpan UG, Hameed BH. Solar degradation of an azo dye, acid red 1, by $Ca–Ce–W–TiO_2$ composite catalyst. Chem Eng J 2011; 169: 91-99.

23. Ong SA, Min OM, Ho LN, Wong YS. Comparative study on photocatalytic degradation of mono azo dye Acid Orange 7 and Methyl Orange under solar light irradiation. Water Air Soil Poll 2012; 223: 5483-5493.

24. Rosu MC, Coros M, Pogacean F, Magerusan L, Socaci C, Turza A, Pruneanu S. Azo dyes degradation using TiO_2-Pt/graphene oxide and TiO_2-Pt/reduced graphene oxide photocatalysts under UV and natural sunlight irradiation. Solid State Sci 2017; 70:13-20.

25. Bolton JR, Bircher KG, Tumas W, Tolman CA. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems. Pure Appl. Chem 2001; 73: 627-637.

26. Buthiyappan A, Abdul Aziz AR, Daud WMAW. Degradation performance and cost implication of UV-integrated advanced oxidation processes for wastewater treatments. Rev Chem Eng 2015; 31(3): 263-302.

27. Muruganandham M, Selvam K, Swaminathan M. A comparative study of quantum yield and electrical energy per order (EEo) for advanced oxidative decolourisation of reactive azo dyes by UV light. J Hazard Mater 2007; 144: 316-322.

28. Turhan GD, Kartal OE. Photocatalytic degradation of C.I. Reactive Red 120 diazo dye by using TiO_2/UV process. In *Proceedings of* 8th National Congress on Environmental Engineering, Antalya Turkey, 12-14 November 2009, p 237-248.

29. Turhan GD, Kartal OE. Effect of operational parameters on the decolorization of C.I. Reactive Red 120 by advanced oxidation processes and investigation of kinetics. In *Proceedings of* 9th National Congress on Environmental Engineering, 5-8 October 2011, Samsun, Turkey, p 514-519.

30. Asghar A, Raman AAA, Daud WMAW. Advanced oxidation processes for in-situ production of hydrogenperoxide/hydroxyl radical for textile wastewater treatment: a review. J Clean Prod 2015; 87: 826-838.

31. Oller I, Malato S, Sanchez-Perez JA. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review. Sci Total Environ 2011; 409: 4141-4166.

32. Soares PA, Souza R, Soler J, Silva TFCV, Souza SMA, Boaventura RAR, Vilar VJP. Remediation ofa synthetic textile wastewater from polyester-cotton dyeing combining biological and photochemical oxidation processes. Sep Purif Technol 2017; 172: 450-462.

33. Sözen A, Arcakhoğlu E, Özalp M, Kanit EG. Use of artificial neural networks for mapping of solar potential in Turkey. Appl Energ 2004; 77: 273-286.