MORTEZA MONTAZEROZOHORI*, MASOUD NASR-ESFAHANI*, SHIVA JOOHARI**

PHOTOCATALYTIC DEGRADATION OF AN ORGANIC DYE IN SOME AQUEOUS BUFFER SOLUTIONS USING NANO TITANIUM DIOXIDE: A KINETIC STUDY

Photocatalytic degradation of an organic dye, emerald green, on nano titanium dioxide (anatase 99.5%) at basic buffer pH of 7, 8 and 9 has been investigated. The effects of various operating parameters such as initial concentration of dye, catalyst dosage, bufferic pH and irradiation time on photocatalytic degradation have been studied in a photoreactor cell containing high pressure mercury lamp to obtain the optimum conditions. COD removal was found to be 65–71% confirming considerable mineralization. The photodegradation of the dye obeyed a pseudo-first order kinetics according to the Langmuir–Hinshelwood model at all used buffer pH. The observed rate constants (k_{obs}) of photocatalytic degradation were 3.3×10^{-2} min^{-1}, 7.09×10^{-2} min^{-1} and 1.32×10^{-1} min^{-1} at buffer pH of 7–9 respectively. Furthermore, the Langmuir–Hinshelwood rate constants, k_r and adsorption constants, K_A are reported for current process at various buffer pH.

1. INTRODUCTION

A literature survey shows that nearly 20% of dyes are left during the dyeing processes leading to produce a large amount of wastewaters containing these dyes as pollutant. Aromatic rings in dye molecular structure cause toxicity and mostly biodegradability resistance so that the dyes are becoming a highlighted source of non-pleasant pollutions [1]. The existence of very low amounts of dyes is clearly detectable and considerably affects water quality [2, 3] thus it is advisable to develop green technologies that present efficient decomposition of them. In this direction, photocatalytic degradation process as a practical method is of interest. Heterogeneous photocatalysts such as titanium dioxide and zinc oxide have been extensively used for the photocatalytic decontamination and deodorization of wastewater [4–9] due to their properties

_____

*Department of Chemistry, Yasouj University, Yasouj, 75914-353, Iran; corresponding author M. Montazerozohori, e-mail: mmzohori@mail.yu.ac.ir; mmzohory@yahoo.com

**Department of Basic Science, Yasouj Branch, Islamic Azad University, Yasouj, Iran.

like photostability, low costs, nontoxicity and applicability at ambient conditions [4–11]. Emerald green also named as brilliant green is one of the important dyes in the paper printing, textile, rubber and plastic industries [12], wood and silk materials. It is often used for some other purposes such as biological stain, dermatological agent, veterinary medicine, and as an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus [13]. This dye is toxic and hazardous through eye and skin contact, inhalation and ingestion. Various reported researches on removal of this water pollutant [14–18] obviously reveal importance of subject. In continuation of our previous reports on photodegradation processes [19–22], in this work we report photocatalytic degradation of emerald green on nano titanium dioxide at aqueous buffer of pH 7, 8 and 9. The effect of some operating parameters and kinetics study of its photodegradation at each pH are described.

2. MATERIALS AND METHODS

Reagents. All compounds were purchased from Merck and Aldrich. Cationic dye of emerald green with C.I number of C.I. 42040 with 90% purity produced by Sigma-Aldrich was applied as target dye (Scheme 1). Nano titanium dioxide (anatase 99.5% with particle size of 70–100 nm) was analytical grade. The pH of solution was adjusted using diluted aqueous buffers that were prepared by the following compounds: KH_2PO_4, Na_2HPO_4, NaOAc, HOAc, $Na_2B_4O_7$, HCl, H_2SO_4 and NaOH. In all experiments doubly distilled water was used.
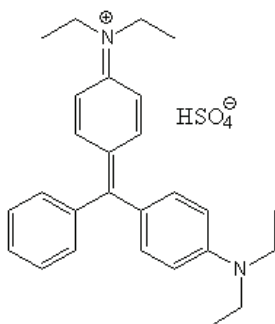
Scheme 1. Structure of emerald green

Apparatus. Photochemical set containing 400 W high pressure mercury lamp was used for photodegradation experiments. UV-VIS spectrophotometer, JASCO-V570, was used for spectral monitoring and analyses of dye concentrations. A parsazma SH-12 model of centrifuge was used for separation of photocatalysts from solution. Metrohm-620 model of pH-meter was applied for controlling of buffer solution pH.

Analytical determinations. Spectrophotometric method was used for determination of concentration of dye via calibration curves at λ_{max} = 624 nm for buffer pH of 7, 8 and 9. For this mean, the absorbance of the dye buffer solutions (with concentrations of 10, 20, 30, 40, 50 and 60 mg/dm³) vs. concentration was plotted. Chemical oxygen demand, COD, was estimated by using standard methods [23]. COD removal was evaluated by following equation:

$$\text{COD removal} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100\% \tag{1}$$

General procedure for photodegradation process. The photodegradation experiments were performed by irradiation of 20 cm³ of 40 mg/dm³ buffer solution of emerald green (oxygenated for 5 min) as well as considered amounts of photocatalysts (125, 250, 500, 1500 and/or 500 mg/dm³) in a photoreactor cell under irradiation of 400 W high pressure mercury lamp at room temperature. After requested time for photodegradation, the photocatalyst was separated by centrifugation and the photolyte was analyzed by the UV-Vis spectrophotometric method. In each photodegradation process, percentage of degradation progress was calculated as follows:

$$\text{Photodegradation} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{2}$$

Blank experiments (BE). A series of competitive parallel photodegradation reactions were performed for investigation of role of the effective agents including catalyst, irradiation and oxygen. The results are summarized in Table 1. The blank experiments were: BE1– 20 cm³ solution of dye (40 mg/dm³) without nano titanium dioxide irradiated under argon gas at pH of 7, 8 and 9; BE2 – similar to BE1 only under oxygen instead of argon; BE3 – 20 cm³ solution of dye (40 mg/dm³) with optimum amount of nano titanium dioxide (500, 1500 and 500 mg/dm³ for pH of 7, 8 and 9, respectively) with irradiation and argon gas at pH of 7, 8 and 9; BE4 – similar to BE3 with oxygen instead of argon.

Table 1

Residual concentrations in mg/dm³ in parallel
blank reactions under various conditions

pH	Time [min]	UV/Ar	UV/O₂	UV/TiO₂/Ar[a]	UV/TiO₂/O₂[a]
7	30	38	33.24	33.10	14.75
8	20	29	23.48	23.12	9.85
9	20	22.20	16.98	16.8	3.38

[a]Optimum amount of catalyst (500, 1500 and 500 mg/dm³
for pH of 7, 8 and 9 respectively) were used in blank experiments.

3. RESULTS AND DISCUSSION

The mechanism of photocatalytic degradation of dye molecules using nano titanium dioxide as photocatalyst in presence of UV irradiation has been reported in the literature [24]. Accordingly under UV illumination, one electron is transferred from conduction band to the valence band of TiO_2 generating electron/hole (e^-/h^+) pair. The e^-/h^+ pairs can produce active species such as hydroxyl radicals, superoxide anion radicals and hydrogen peroxide via redox reaction that they degrade dye molecules (D) to decomposed products (P).

The role of some effectual parameters in photocatalytic degradation of dye and the kinetics model of the process will be discussed in the next sections. By designing the blank experiments as in materials and methods section and regarding Table 1, it was found that residual concentrations after photocatalytic degradation in the presence of photocatalyst, oxygen and irradiation simultaneously were considerably lower than those reactions when one of them is absent. Therefore optimization of photodegradation was carried out in the presence of photocatalyst, oxygen and upon irradiation.

3.1. CALIBRATION CURVES FOR THE STANDARD SOLUTIONS

Electronic spectra of emerald green in the range of pH from 7 to 9 are similar and exhibit λ_{max} at 624 nm. Therefore standard solutions containg 0–60 mg/dm^3 of the dye at pH of 7, 8 and 9 were prepared and the absorbances vs. concentration at λ_{max} were plotted. The diagrams are linear and in agreement with the Lambert–Beer law.

3.2. OPTIMIZATION OF CATALYST DOSAGE ON PHOTOCATALYTIC PROCESS

Photodegradation of organic compounds takes place both on active surface of the catalyst particles and in bulk solution by means of phocatalytically generated active oxidant species. Therefore the photocatalyst dosage plays an important role in photodegradation processes. In our experiments, the effect of the catalyst doses has been examined by evaluating the residual concentration of emerald green at each pH after photocatalytic degradation using various dosages of nano titanium dioxide within the same reaction times. The plots of residual concentration of emerald green vs. various doses of catalysts and pH have been sketched in Fig. 1. As seen in this figure, the amounts of 500, 1500 and 500 mg/dm^3 were found to be optimum doses of catalyst at pH of 7–9, respectively for effective degradation of dye. Exceeding the optimum amount, suspended photocatalyst particles scatter UV light and therefore reduce the formation of electron/hole pairs and active sites [8, 24–26], leading to lower efficiency in photodegradation. It is to be noted that in our conditions, dispersion of TiO_2 at

pH = 8 is lower than at two other pH, so that the higher amount of photocatalyst is an optimum dose at this pH.
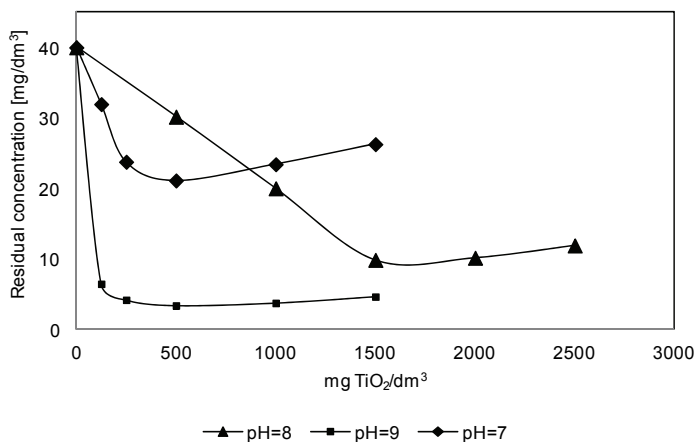

Fig. 1. The effect of catalyst dosage on residual concentration
after irradiation (20 min, V = 20 ml) at various buffer pH

3.3. THE EFFECT OF pH

Photocatalytic degradation of emerald green is affected by pH of the solution. Figure 2 shows that maximum of dye degradation occurrs at pH = 9. This result can be explained based on adsorption characteristic with respect to pH of the solution.
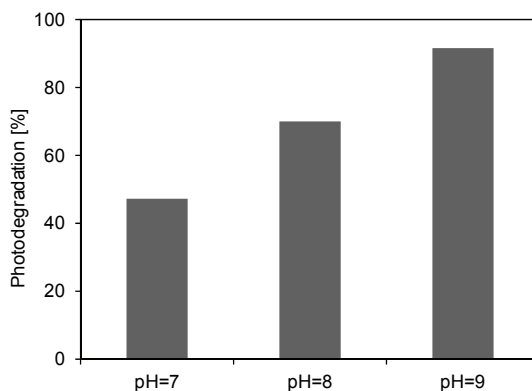

Fig. 2. The effect of pH on photodegradation; TiO_2 – 500 mg/dm^3 (pH = 7 and 9)
and 1500 mg/dm^3 (pH = 8); V = 20 ml, irradiation time = 20 min

TiO_2 usually has an isoelectric point of charge at ca. pH = 6.8 which means that its surface has a positive charge at pH lower than 6.8 via protonation and a negative

charge at pH higher than 6.8 via deprotonation. At pH = 9, more negative charges at the photocatalyst surface cause more dye adsorption or migration of dye near to the catalyst surface due to electrostatic interaction between cationic emerald green dye (under basic medium) and catalyst surface. Therefore, the target dye is more susceptible to photodegradation [27, 28] at more basic solution. On the other hand, in more alkaline solution $^{\bullet}$OH is easier to be generated by oxidizing of more hydroxide ions available on photocatalyst surface that diffuse to bulk solution leading to more effective photodegradation in the order of pH = 9 > pH = 8 > pH = 7 [10]. Solutions of pH other than 7–9 were not investigated because there is no a suitable absorption wavelength for spectrophotometric monitoring and analysis.

3.4. KINETICS STUDY

The plots of residual concentration vs. time for dye degradation using optimum amount of nano titanium dioxide at each pH are shown in Fig. 3. As shown in this figure for pH of 8 and 9, the dye residual concentration reached very low values after ca. 30 and 50 min while at pH = 7 it occurred after 150 min.
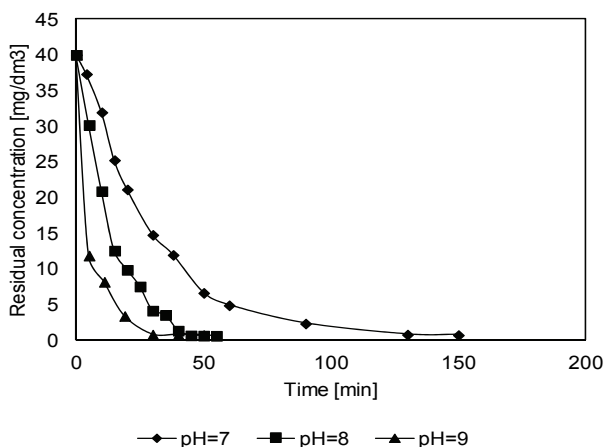

Fig. 3. Plots of residual concentration versus time for photodegradation
of emerald green at various buffer pH by use of optimum dosage of nano TiO$_2$:
500 mg/dm^3 (pH = 7 and 9) and 1500 mg/dm^3 (pH = 8); V = 20 ml

The photodegradation of the dye obeys the pseudo-first order kinetics:

$$-\frac{dC}{dt} = k_{\mathrm{obs}}C \qquad (3)$$

where C is the concentration of emerald green and k_{obs} is the observed first-order rate constant. From the integration of this equation, the concentration–time equation of

$\ln(C_0/C_t) = k_{obs}t$ will be derived. A plot of $\ln(C_0/C_t)$ vs. time leads to a linear diagram so that its slope equals the observed first-order rate constant of photodegradation k_{obs}.
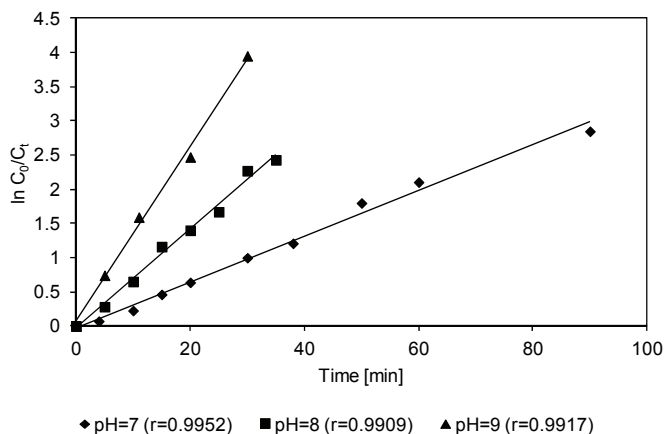

Fig. 4. Kinetics of the emerald green degradation ($\ln(C_0/C_t)$ vs. t)
at various buffer pH by use of optimum dose of nano TiO$_2$: 500 mg/dm^3
(pH = 7 and 9) and 1500 mg/dm^3 (pH = 8); V = 20 ml

Table 2

Kinetic parameters in photocatalytic degradation
of emerald green at various pH[a]

Parameter	pH = 7	pH = 8	pH = 9
k_{obs} (min^{-1})	3.30×10^{-2}	7.09×10^{-2}	1.32×10^{-1}
$t_{1/2}$ (min)	30	14.10	7.58
K_A (l·mg^{-1})	3.73×10^{-2}	8.60×10^{-3}	7.27×10^{-4}
k_r (mg·min^{-1}·l^{-1})	1.57	6.15	70.42

[a]Optimum dose of TiO$_2$ – 500 mg/dm^3 for
pH = 7 and 9 and 1500 mg/dm^3 (pH = 8); V = 20 m.

The emerald green adsorption on the photocatalyst surface can be explained by the Langmuir–Hinshelwood (L-H) kinetic model [29–33], modified to accommodate the reaction occurring at a solid–liquid interface. In this model, the reaction rate is proportional to the surface coverage θ:

$$\theta = \frac{KC_0}{1 + KC_0 + K_s C_s} \tag{4}$$

where K and K_s are the adsorption coefficient of the substrate (dye) and the solvent; C_0 and C_s are the initial concentrations of the substrate and solvent.

The apparent photodegradation rate R at catalyst surface (k_r) can be expressed as a single-component L-H kinetic rate expression:

$$R = -\frac{dc}{dt} = k_r \theta = k_r \frac{KC_0}{1 + KC_0 + K_s C_s} \tag{5}$$

If K_A defined as:

$$K_A = \frac{K}{1 + K_s C_s} \tag{6}$$

will be introduced, we obtain:

$$R = k_r \frac{K_A C_0}{1 + K_A C_0} \tag{7}$$

and eventually after simple transformation we arrive at:

$$\frac{1}{R} = \frac{1}{k_r K_A C_0} + \frac{1}{k_r} \tag{8}$$

The linear plots of $1/R$ vs. $1/C_0$ for emerald green at various pH have been shown in Fig. 5, which tests the validity of the L-H model. In the current investigated range of concentration, linear plots show that photodegradation kinetic is in accordance with the L-H model.
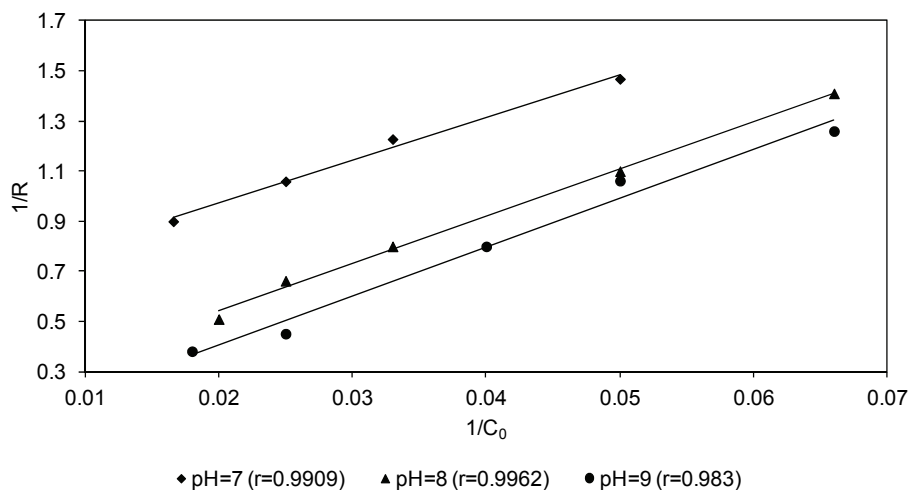

Fig. 5. The plots of $1/R$ vs. $1/C_0$ at various pH (Langmuir–Hinshelwood kinetics for degradation of emerald green) by use of optimum dose of nano TiO_2: 500 mg/dm^3 (pH = 7 and 9) and 1500 mg/dm^3 (pH = 8); V = 20 ml

As seen in Table 2, observed photodegradation rate constant, k_{obs} (related to total reaction) and apparent photodegradation rate constant, k_r increase while dye degradation half time $t_{1/2}$ decreases upon increasing pH of the solution.

3.5. MINERALIZATION EVALUATION OF PHOTODEGRADATION

Chemical oxygen demand indicates the extent of degradation or mineralization of organic matter. For this mean, the percentage of reduction in COD was studied for emerald green according to literature [23]. The COD removal of 40 mg/dm^3 of dye solutions after complete photocatalytic decolourization at optimum conditions are illustrated in Fig. 6.
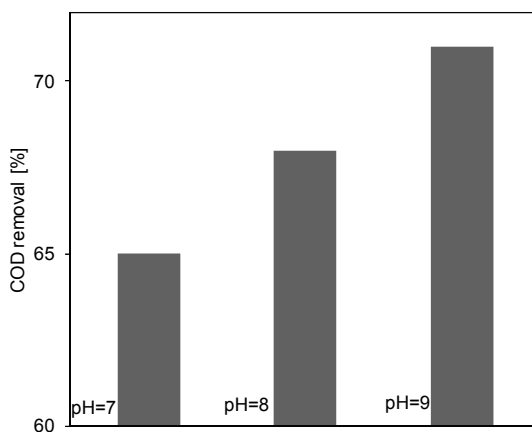

Fig. 6. COD removal of 40 mg/dm^{3}of dye at various buffer pH by use of optimum
amount of TiO$_2$: 500 mg/dm^3 (pH= 7 and 9) and 1500 mg/dm^3(pH = 8);
time: 150, 50 and 50 min for pH of 7, 8 and 9 respectively; V = 20 ml

Under optimum conditions COD removal was 65% in 150 min for the dye at pH = 7 with 500 mg/dm^3, 72% in 50 min for dye at pH = 8 with 1500 mg/dm^3 and ultimately 78% in 50 min for dye at pH = 9 with 500 mg/dm^3. The COD removal is lower than the photodegradation measured by the spectrophotometric method which may be due to the formation of uncoloured products during the photoprocess. Therefore, probably, complete mineralization of dyes is achieved after longer irradiation times at each pH.

4. CONCLUSION

In this study, photocatalytic degradation of emerald green has been investigated in the presence of some effectual agents such as photocatalyst dose, pH and irradiation time. The results exhibited nearly complete photodegradation after 150, 50 and 30 min

by use of optimum doses of nano TiO$_2$ at various pH. Observed photocatalytic degradation rate constants of dye at various basic media were 3.3×10^{-2} min^{-1}, 7.09×10^{-2} min^{-1} and 1.32×10^{-1} min^{-1} for pH of 7, 8 and 9, respectively. Finally, the L-H rate constant, k_r, adsorption–desorption constant, K_A and dye degradation half times, $t_{1/2}$ were evaluated at some basic pH.

REFERENCES

[1] KONSTANTINOU I.K., ALBANIS T.A., Appl. Catal. B: Environ., 2004, 49, 1.
[2] GRZECHULSKA J., MORAVISKI A.W., Appl. Catal., 2002, 36, 45.
[3] LEDAKOWICZ S., SOLECKA M., ZYLLA R., J. Biotechnol., 2001, 89, 175.
[4] KATOH M., AIHARA H., HORIKAWA T., TOMIDA T., J. Colloid Interface Sci., 2006, 298, 805.
[5] WANG G., WU F., ZHANG X., LUOC M., DENG N., J. Hazard. Mater., 2006, 133, 85.
[6] WANG W.-Y., KU Y., Water Res., 2006, 40, 2249.
[7] ANANDANA S., VINUB A., VENKATACHALAM N., ARABINDOO B., MURUGESAN V., J. Mol. Catal. A: Chem., 2006, 256, 312.
[8] HASNAT M.A., UDDIN M.M., SAMED A.J.F., ALAM S.S., HOSSAIN S., J. Hazard. Mater., 2007, 147, 471.
[9] SO C.M., CHENG M.Y., YU J.C., WONG P.K., Chemosphere, 2002, 46, 905.
[10] HASNAT M.A., SIDDIQUEY I.A., NURUDDIN A., Dyes Pigments, 2005, 66, 185.
[11] TAIXING W., GUANGMING L., JINCAI Z., HISAO H., NICK S., J. Phys. Chem., B 1999, 103, 4862.
[12] GUPTA G.S., SHUKLA S.P., PRASAD G., SINGH V.N., Environ. Technol., 1992, 13, 925.
[13] ZOLLINGER H., *Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments*, VCH Publishers, New York, 1987, p. 92.
[14] NANDI B.K., GOSWAMI A., PURKAIT M.K., Appl. Clay. Sci., 2009, 42, 583.
[15] ASADULLAH M., ASADUZZAMAN M., KABIR M.S., MOSTOFA M.G., MIYAZAWA T., J. Hazard. Mater., 2010, 174, 437.
[16] MANE S.V., MALL I.D., SRIVASTAVA V.C., Dyes Pigments, 2007, 73, 269.
[17] NANDI B.K., GOSWAMI A., PURKAIT M.K., J. Hazard. Mater., 2009, 161, 387.
[18] MANE V.S., MALL I.D., SRIVASTAVA V.C., J. Environ. Manage., 2007, 84, 390.
[19] HABIBI M.H., ZEINI ESFAHANI A., MOHAMMADKHANI N., MONTAZEROZOHORI M., Monat. Chem., 2004, 135, 1121.
[20] HABIBI M.H., KHALEDISARDASHTI M., MONTAZEROZOHORI M., Ann. Chim., 2004, 94, 421.
[21] MONTAZEROZOHORI M., KARAMI, B., HABIBI M.H., Feres. Environ. Bull., 2007, 16 (1), 44.
[22] MONTAZEROZOHORI M., HABIBI M.H.JOOHARI S., KHODADOSTAN, V., Ann. Chim., 2007, 97 (10), 1015.
[23] *Standard Methods for the Examination of Water and Wastewate*r, 20th Ed., American Public Health Association, 1998.
[23] WU T., LIN T., ZHAO J., HIDAKA H., SERPONE N., Environ. Sci. Technol., 1999, 33, 1379.
[24] AUGUGLIARO V., PALMISANO L.SCHIAVELLO M., SCLAFANI A., MARCHESE L., MARTRA G., MIANO F., Appl. Catal., 1991, 69, 323.
[25] ZHAO M.Y., CHEN S.F., TAO Y.W., J. Chem. Tech. Biotechnol., 1995, 64, 339.
[26] BEKBOLET M., OZKOSEMEN G., Water Sci. Technol., 1996, 3, 189.
[27] KONSTANTINOU I.K., ALBANIS T.A., Appl. Catal. B: Environ., 2004,49, 1.
[28] AHMAD R., KUMAR R., J. Korean Chem., Soc., 2010, 54 (1), 125.
[29] JUNNY B., PICHAT P., Langmuir, 1991, 7, 947.

[30] LANGMUIR I., Trans. Faraday Soc., 1921, 17, 621.
[31] MATTHEWS R.W., J. Chem. Soc. Farad. Trans., 1, 1989, 85, 1291.
[32] EL-EKABI H., SERPONE N., J. Phys. Chem., 1988, 92, 5726.
[33] CHAN Y.C., CHEN J.N., LU M.C., Chemosphere, 2001, 45, 29.