Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.698822

48 (2012) 261–266
October

Photocatalytic decolorization of ethyl orange at various buffer solutions using nano-titanium dioxide: a kinetic investigation

Morteza Montazerozohori*, Sajjad Mojahedi Jahromi

Department of Chemistry, Yasouj University, Yasouj 7591874831, Iran
Tel./Fax +98 7412223048; Mobile +98 9177411674; email: mmzohory@yahoo.com; mmzohori@mail.yu.ac.ir

Received 1 December 2011; Accepted 18 April 2012

ABSRACT

Photocatalytic decolorization of an azo dye, ethyl orange in the presence of nano-titanium dioxide (99.9% anatase) suspensions at various buffer pHs 2, 5, 7, 9 and 11 under 400 W high pressure mercury lamp illumination under aerobic condition is described. Some important parameters such as nano-photocatalyst dosage, photoreaction time, buffer pH effect and initial concentration of dye in photo-reactor cell have been evaluated. Kinetics investigations are in agreement with pseudo-first-order kinetic for dye degradation at all considered buffer pHs. Accordingly observed rate constant (k_{obs}), photodegradation rate (k_r) and adsorption constant K_A are reported for all media based on Langmuir–Hinshelwood model. Finally spectrophotometric monitoring suggests that nearly complete degradation at pH 2 and 9 within considerable shorter reaction time than other used buffer pHs.

Keywords: Ethyl orange; Nano-titanium dioxide; Photocatalytic; Illumination; Kinetics; Decolorization

1. Introduction

Azo compounds are compounds bearing the functional group R–N=N–R′, in which R and R′ can be either aryl or alkyl. The azo compound class accounts for 60–70% of all dyes. Some azo dyes are toxic and may cause the carcinogenic effects [1,2]. On the other hand, these dyes have widely been used with textile, cosmetic, food colorants, printing, and pharmaceutical industries [3–5]. Therefore, organic pollutants including azo dyes are very harmful from the environment and health points of view. In recent years, environmentally and health friendly researcher have introduced a variety of methods for removal or elimination of non-pleasant chemical matter involving physical adsorption [6], advanced oxidation processes [7–9], biosorption [10,11]. Adsorption methods transfer the pollutants to other media leading to secondary pollution. Chemical oxidation methods are generally not economic due to the reagents that are used. On the other hand, biological based methods have been found that are ineffective in some reports [12–14]. Therefore, developing the methods that minimize these disadvantages are in demand yet. Photocatalytic degradation is a good candidate for this mean. Some advantages of photocatalytic degradation with respect to other methods are cheapness and reusability, chemically and biologically inert, high efficiency, operating at ambient temperature and finally ideal to treat trace level pollutants. Because of these advantages, photocatalytic process as an effective and economic method has been used for complete mineralization of many organic dyes [15–20]. Among various semiconductors acting as photocatalyst, titanium dioxide due to chemical stability, non-toxic nature, suitable band gap, high efficiency and low cost is preferred with respect to other ones [21]. To the best of our knowledge,

---

*Corresponding author.

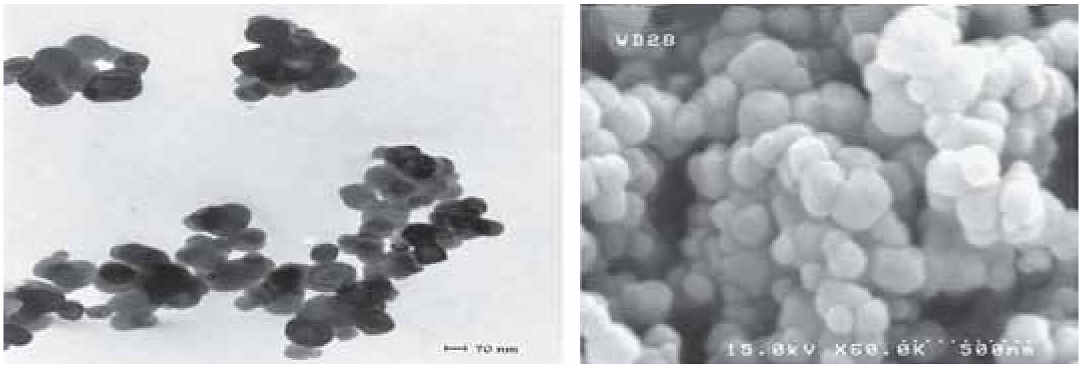

Fig. 1. TEM and SEM of the used nano-titanium dioxide.

despite many reports on photocatalytic degradation of methyl orange under different conditions [22–26], except a report on degradation of its sodium salt [27], there is no report on photocatalyzed decolorization of non-salted ethyl orange (EO) at buffer media using nano-titanium dioxide. In this work, in continuation of previous reports on photodegradative removal [28–31], photocatalyst promoted EO decolorization in various buffer solutions using nano-titanium dioxide in a photoreactor under 400 W high pressure mercury lamp illumination is described and decolorization kinetics based on Langmuir–Hinshelwood model is presented.

2. Materials and methods

2.1. Chemicals and instuments

Chemicals such as NaOH, HCl and KCl (Merck company); K_2HPO_4 and KH_2PO_4 (Fluka company); $Na_2B_4O_7 \cdot 10H_2O$ and EO (Sigma–Aldrich company) were used as purchased. Nano-titanium dioxide, 70–140 nm (anatase) with surface area of 20–25 m^2/g, and purity 99.9% (from Sigma–Aldrich) was applied as photocatalyst. SEM and TEM of titanium dioxide were recorded on instruments of Hitachi Japan-S4160 and Philips CM-10 TEM microscope operated at 100 kV, respectively (Fig. 1). Photodegradation experiments were carried out at a photoreactor set involving 400 W high pressure mercury lamp. Dye concentration following was performed by employing a JASCO V-570 UV–Visible spectrophotometer. A centrifuge was used for separation of photocatalyst from suspension. Buffer pH control was made by F60 pH-meter.

2.2. General photodecolorization experiment

A volume of 20 mL buffer solution (pH = 2, 5, 7, 9 and/or 11) of EO with known concentration and a desired amount of nano-titanium dioxide as well as air bubbling through it, was placed in photoreactor cell and subjected to a 400 W high pressure mercury lamp. The reactor on the mixer was placed in the dark for 10 min to reach sorption–desorption equilibrium on catalytic surface. The concentration of EO and decolorization percent of EO at each time was measured by use of UV–Visible spectrophotometer and by aid of calibration curves (Fig. 2) that are easily available from drawing of absorbance–concentration plots using prepared standard buffer solutions of EO with pH 2, 5, 7, 9 and 11 at relative maximum wavelengths at those pHs that are 508, 478, 472, 472 and 470 nm, respectively. (The ethyl orange is also known as 4-[[4-(diethylamino)phenyl]azo] benzenesulfonic acid. It belongs to the weak organic acids and therefore is sensitive to pH meaning that it has various forms (acidic, neutral and anionic) that leads to different absorbance of EO at various pHs).

3. Results and discussion

3.1. The effect of catalyst

For optimization of catalyst dosage at each buffer pH, a solution of EO at that pH was irradiated by high pressure 400 W mercury lamp at room temperature. Fig. 3

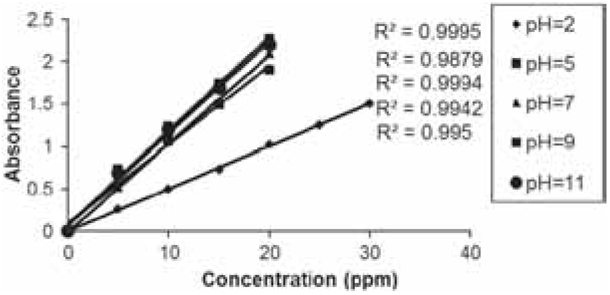

Fig. 2. Calibration curves of EO at various buffer solutions.

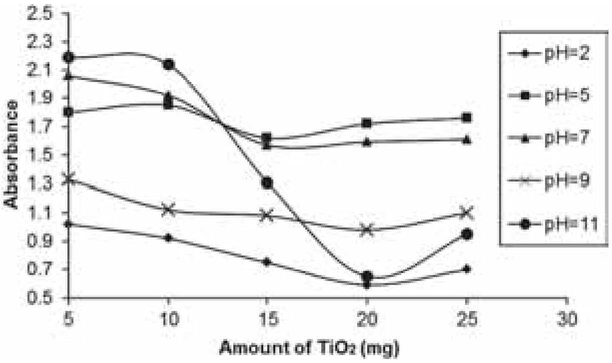

Fig. 3. Effect of the dosage of photocatalyst on the residual absorbance of EO after 1.5 h irradiation.

illustrates the effect of catalyst dosage on photocatalytic decolorization at various buffer pHs after a constant irradiation time of 1.5 h. It is well seen that the absorbance of EO is decreased with an increase of photocatalyst amount and reached a minimum at 15 mg for buffer pH 5 and 7; and 20 mg as optimum amounts of photocatalyst at pH 2, 9 and 11, respectively. The reason of this observation may be due to the fact that an increase of TiO_2 leads to more availability of active sites affecting decolorization of EO, while the additional higher quantities of TiO_2 would not have more effect on the decolorization efficiency due to increased opacity of the suspension in large amount of catalyst leading to lower decolorization of dye [32,33].

3.2. Irradiation time effect

Fig. 4 depicts EO absorbance versus irradiation time. As the irradiation time increases the residual absorbance of solution was found to be decreased to reach nearly total decomposition for pH 2 and 9 after 6 and 7 h. Decomposition percents at pH 5, 7, 11 were found to be 69.56%, 74.69% and 52.07% after 14, 16 and 18 h, respectively.

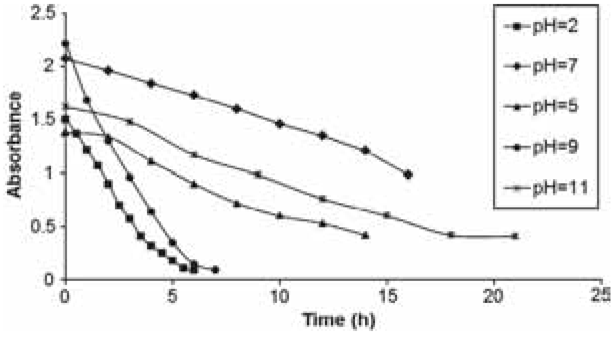

Fig. 4. Effect of irradiation time on photodecomposition of EO.

3.3. Effect of pH

Wastewater containing organic dyes may have different pHs; therefore it is important to study the role of pH on decolorization of dye. To study the effect of pH on the decolorization efficiency, experiments were performed at various buffer pH values, ranging from acidic to basic media for constant dye concentration. pH has an important role on photocatalytic process due to its effects on catalyst surface charge. The surface charge of photocatalyst is variable in different pH condition. The investigation of all aspects of pH effects on the photocatalytic decomposition process is not possible because of its multiple roles. First, it is related to the acid–base property of photocatalyst surface so that in acidic solution TiO_2, surface is positive and in basic solution is negative while zero point charge for TiO_2 surface is widely reported at 6.25–6.90 [34,35]. Also acid–base equilibrium constant of dye is affected by pH leading to dye adsorption on catalyst surface and finally on photocatalytic degradation. Also medium pH controls production of oxidizing agents. Fig. 5 illustrates a competition between degradation percentages of EO after 5 h in the presence of optimum amount of catalyst at each pH. As can see in this figure the highest degradation percents; 95% and 93.25% are related to pH 2 and 9. In addition to pH effects on surface charge changes as mentioned above, it is to be noted that in acidic pH, the higher amount of oxygen is adsorbed on the surface of photocatalyst and therefore the higher concentration of hydrogen peroxide is generated (Scheme 1). The hydrogen peroxide molecules can be converted to hydroxyl radicals as oxidizing agents under irradiation. On the other hand in basic media, high concentration of hydroxyl radial due to oxidation of hydroxide anions by (h^+(VB)) are responsible for dye decomposition.

These explanations may be the reason for high efficiency of photocatalytic degradation at pH 2 and 9.

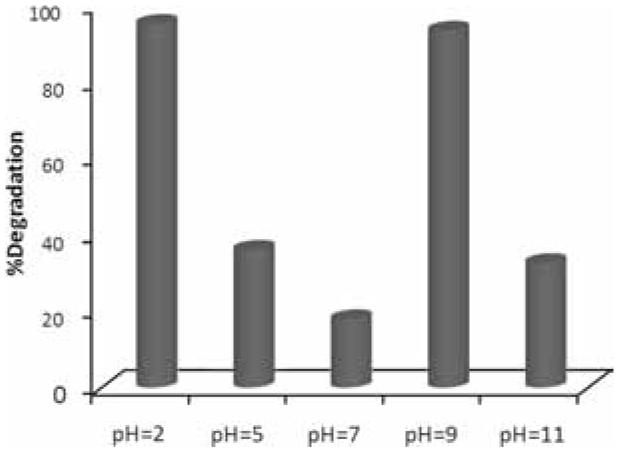

Fig. 5. The effect of buffer pH on % photodegradation of EO.

3.4. Kinetic investigation

Fig. 6 shows plots of Ln(C_0/C_t) of EO versus irradiation time (in which, C_0 and C_t are initiated and concentration at time t, respectively) for acidic (pH =2 and 5), neutral (pH = 7) and basic (pH = 9 and 11) media that found to be linear. Therefore, degradation of EO in buffer solutions can be approximately modeled as pseudo-first-order kinetics similar to many other reports [36–40].

The observed rate constants (k_{obs}) of photocatalytic process can be easily obtained from the slopes of Fig. 6 plots. These evaluated rate constants have been collected and presented in Table 1. Among these rate constants, the highest values of k_{obs} are related to pH 2 and 9, respectively. This is in agreement with explanations of pH effects on degradation percent in previous section. More kinetic investigation was performed based on Langmuir–Hinshelwood (L–H) kinetic model modified to accommodate the reaction occurring at a solid–liquid interface. The related surface catalytic reaction rate [41,42] can be expressed by:

$$1/R = 1/k_r K_A[C_0] + 1/k_r$$

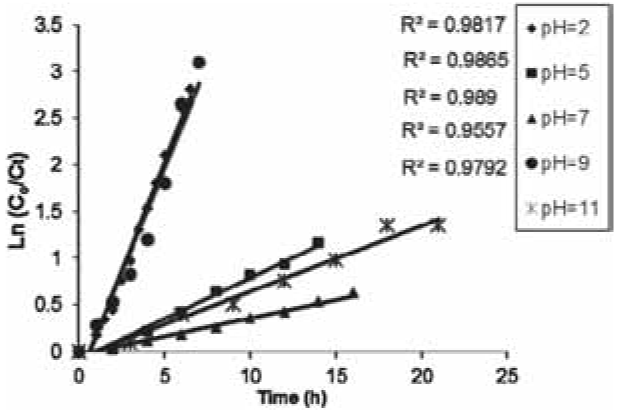

Fig. 6. Plots of Ln(C_0/C_t) of EO versus irradiation times at various buffer pHs.

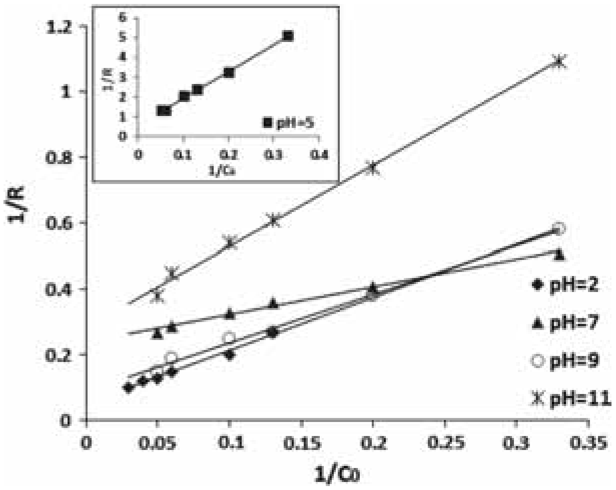

Fig. 7. The plots of 1/R vs. 1/C_0 at various pHs (Langmuir–Hinshelwood kinetics model).

where, k_r is apparent rate constant at catalyst surface and K_A equilibrium adsorption–desorption constant. If the diagram of 1/R versus 1/C_0 at various buffer pHs (R = reaction rate and C_0 is initial concentration) (Fig. 7) being drawn and found to be linear, the L–H kinetic model can be considered and therefore K_A and k_r can be extracted from the slope and intercept of plots. These parameters have been evaluated and summarized in Table 1. The maximum of k_r values are related to pH 2 and 9, respectively.

4. Conlcusion

In this work, photocatalytic decompositon of EO by nano-titanium dioxide in buffer solutions under irradiation by 400 W high pressure mercury lamp has been reported. The effect of photocatalyst amount, buffer pHs and irradiation time on photocatalytic process were studied. Optimum amounts of photocatalyst were found to be 15 mg per 20 mL for pHs 5 and 7; and 20 mg per 20 mL for pH 2, 9 and 11. The dye was efficiently degraded within 6 and 7 h in pHs 2 and 9; and 14, 16

Table 1
Kinetic and thermodynamic parameters in photodegradation of EO at various buffer pHs

EO	pH = 2	pH = 5	pH = 7	pH = 9	pH = 11
K_A (L.mg^{-1})	4.37×10^{-2}	4.72×10^{-2}	2.9×10^{-1}	6.0×10^{-2}	1.16×10^{-1}
k_{obs} (h^{-1})	4.68×10^{-1}	8.74×10^{-2}	3.91×10^{-2}	4.49×10^{-1}	7.05×10^{-2}
k_r (mg min^{-1} L$^{-1)}$	16.29	1.57	4.15	11.26	3.51
$t_{1/2}$ (h)	1.48	7.93	17.23	1.54	9.83

and 18 h in pHs 5, 7 and 11, respectively. Kinetic study of dye photocatalytic degradation at various buffer pHs 2, 5, 7, 9 and 11 was performed. Pseudo-first-order rate constants at various pHs were evaluated that are placed in the range of 3.91×10^{-2}–4.68×10^{-1} h^{-1}. Ultimately, L–H parameters including K_A (adsorption constant) and k_r (degradation rate constant at surface) were extracted from related plots for above buffer pHs that were in the spans of 4.37×10^{-2}–2.9×10^{-1} L mg^{-1} and 1.57–16.29 mg min^{-1} L^{-1}, respectively.

Acknowledgement

The authors wish to thank the Yasouj University for financial supporting this work.

References

[1] L. Sztandera, A. Garg, S. Hayik, K.L. Bhat and C.W. Bock, Mutagenicity of aminoazo dyes and their reductive-cleavage metabolites: a QSAR/QPAR investigation. Dyes Pigments 59 (2003) 117–130.

[2] N. Mathur, P. Bhatngar and P. Bakre, Asingse mutagenicity of textile dyes from pali(Rajasthan) using ames bioassay. Appl. Ecol. Environ. Res., 4 (1) (2005) 111–118.

[3] Y. Gao, C. Li, J. Shen, H. Yin, X. An and H. Ji, Effect of food azo dye tartrazine on learning and memory functions in mice and rats, and the possible mechanisms involved. J. Food Sci., 76 (2011) T125–T129.

[4] M.A. El-Kashouti, M.M. El Molla, H.S. Elsayad, K.A. Ahmed, M.H. Helal and G.H. Elgemeie, Synthesis of several new pyridine-2(1H) thiones containing an arylazo function and their applications in textile printing. Pigment Resin. Technol., 2008 (38) 80–86.

[5] H.M. Pinheiro, E. Touraud and O. Thomas, Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters. Dyes Pigments, 61 (2004) 121–139.

[6] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review. J. Bioresour. Technol., 97 (2006) 1062–1070.

[7] S.A. Abo-Farha, Comparative study of oxidation of some azo dyes by different advanced oxidation processes: fenton, fenton-like, photo-fenton and photo-fenton-like. J. Am. Sci., 6 (10) (2010) 128–142.

[8] F. Fu, Q. Wang and B. Tang, Effective degradation of C. I. Acid Red 73 by advanced Fenton process. J. Hazard. Mater., 174 (2010) 17–22.

[9] N.K. Daud, U.G. Akpan and B.H. Hameed, Decolorization of Sunzol Black DN conc. in aqueous solution by Fenton oxidation process: effect of system parameters and kinetic study, Desal. Water Treat., 37 (2012) 1–7.

[10] A.-H. Chen and S.-M. Chen, Biosorption of azo dyes from aqueous solution by glutaraldehyde-crosslinked chitosans, J. Hazard. Mater., 172 (2009) 1111–1121.

[11] Z. Qi, G. Wenqi, X. Chunanxin, L. Yubia, B. Cuping and C. Shaohua, Biosorption of methylene blue from aqueous solution on spent cottonseed hull substrate for Pleurotus ostreatus cultivation. Desal. Water Treat., 29 (2011) 317–325.

[12] B.Z. Li, X.Y. Xu, and L. Zhu, Catalytic ozonation-biological coupled processes for the treatment of industrial wastewater containing refractory chlorinated nitroaromatic compounds. J. Zhejiang Univ. Sci. B, 11 (3) (2010) 177–189.

[13] Y. Li and D.L. Xi, Decolorization and biodegradation of dye wastewaters by a facultative-aerobic process. Environ. Sci. Poll. Res., 11 (6) (2004) 372–377.

[14] R. Russ, J. Rau and A. Stolz, The function of cytoplasmic flavin reductases in the reduction of azo dyes by bacteria. Appl. Environ. Microbiol., 66 (2000) 1429–1434.

[15] M.H. Ehrampoush, G.H.R. Moussavi, M.T. Ghaneian, S. Rahimi and M. Ahmadian, Removal of Methylene Blue dye from textile simulated sample using tubular reactor and TiO_2/UV-C and photocatalytic process. Iran. J. Environ. Health. Sci. Eng., 8 (1) (2011) 35–40.

[16] A.E. Si and E.K. Ma. Treatment of ink wastewater via heterogeneous photocatalytic oxidation. Desal. Water Treat., 7(3) (2009) 1–5.

[17] M. Ghanbarian, R. Nabizadeh, A.H. Mahvi, S. Nasseri and K. Naddafi, Photocatalytic degradation of linear alkylbenzene solfunate fromaquous solution by TiO_2 nanoparticles. Iran. J. Environ. Health. Sci. Eng., 8 (2011) 309–318.

[18] U. Akpan and B. Hameed, Parameters affecting the photocatalytic degradation of dyes using TiO_2-based photocatalysts: a review. J. Hazard. Mater., 170 (2009) 520–529.

[19] B.H. Hameed, U.G. Akpan, Keng Poh Wee, Photocatalytic degradation of acid red 1 dye using ZnO catalyst in the presence and absence of silver. Desal. Water Treat., 28 (2011) 1–6.

[20] M. Nasr-Esfahani and M.H. Habibi, A comparative study on physicochemical properties and photocatalytic behavior of two different nanostructure composite TiO_2 films coated on glass substrate. Desal. Water Treat., 3 (2009) 64–72.

[21] U.I. Gaya and A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. J. Photochem. Photobiol. C: Photochem. Rev., 9 (1) (2008) 1–12.

[22] M.N. Rashed and A.A. El-Amin, Photocatalytic degradation of methyl orange in aqueous TiO_2 under different solar irradiation sources. Int. J. Phys. Sci. 2 (3) (2007) 073–081.

[23] W. Wang and S. Yang, Photocatalytic degradation of organic dye methyl orange with phosphotungstic acid. J. Water Res. Prot., 2 (2010) 979–983.

[24] Z. Zainal, C.Y. Lee, A. Kassim, M.Z. Hussein and N.A. Yusof, Photoelectrochemical degradation of methyl orange using TiO_2/Ti films prepared via sol–gel technique. Acta Chim. Slov., 54 (2007) 166–174.

[25] M.H. Habibi and E. Askari, The effect of operational parameters on the photocatalytic degradation of C.I. Reactive Yellow 86 textile dye using manganese zinc oxide nanocomposite thin films. J. Adv. Oxid. Technol., 14 (2) (2011) 190–105.

[26] M. Nasr-Esfahani and M.H. Habibi, Silver doped TiO_2 nanostructure composite photocatalyst film synthesized by sol–gel spin and dip coating technique on glass. Int. J. Photoenergy, ID 628713 (2008) 1–11.

[27] A.B. Prevot, D. Fabbri, E. Pramauro, C. Baiocchi and C. Medana, High-performance liquid chromatography coupled to ultraviolet diode array detection and electrospray ionization mass spectrometry for the analysis of intermediates produced in the initial steps of the photocatalytic degradation of sulfonated azo dyes. J. Chromatogr. A, 1202 (2) (2008) 145–154.

[28] M. Montazerozohori, B. Karami and M.H. Habibi, Photodegradation kinetics of some thiols and thiones in aqueous suspension of zinc oxide, Ann. Chim., 96 (5–6) (2006) 285–292.

[29] M. Montazerozohori, M.H. Habibi, S. Joohari and V. Khodadostan, The effects of some operational parameters in photodegradation of benzylamine and aniline and their kinetics in aqueous suspension of TiO_2 and Pt-loaded TiO_2. Ann. Chim., 97 (10) (2007) 1015–1026.

[30] M. Montazerozohori, M. Nasr-Esfahani, S. Nezami and S. Mojahedi, Kinetic studies of photocatalytic decomposition of eriochrome black T in buffer solutions at various pHs under high pressure mercury lamp irradiation, Fresen. Environ. Bull., 20 (2011) 1836–1840.

[31] M. Montazerozohori, S. Nezami and S. Mojahedi, A kinetic study of photocatalytic degradation of tolonium chloride under high pressure irradiation in aquatic buffer systems. E-J. Chem., 8 (S1) (2011) S19–S26.

[32] L. Yang, L.E. Yu and M.B. Ray, Degradation of paracetamol in aqueous solutions by TiO_2 photocatalysis. Water Res., 42 (2008) 3480–3488.

[33] J. Saien and A.R. Soleymani, Degradation and mineralization of Direct Blue 71 in a circulating upflow reactor by UV/TiO_2 process and employing a new method in kinetic study. J. Hazard. Mater., 144 (2007) 506–512.

[34] N. M. Mahmoodi, and M. Arami, Bulk phase degradation of Acid Red 14 by nanophotocatalysis using immobilized titanium(IV) oxide nanoparticles. J. Photochem. Photobiol. A-Chem., 182 (2006) 60–66.

[35] X. Zhang, Y. Wang and G. Li, Effect of operating parameters on microwave assisted photocatalytic degradation of azo dye X-3B with grain TiO_2 catalyst. J. Mol. Catal. A-Chem., 237 (2005) 199–205.

[36] N. Guettai and H.A. Amar, Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension. Part I: Parametric study. Desalination, 185 (2005) 427–437.

[37] N.M. Mahmoodi, M. Arami, N. Yousefi Limaee and N.S. Tabrizi, Kinetics of heterogeneous photocatalytic degradation of reactive dyes in an immobilized TiO_2 photocatalytic reactor. J. Coll. Interf. Sci., 295 (2006) 159–164.

[38] T.E. Doll and F.H. Frimmel, Kinetic study of photocatalytic degradation of carbamazepine, clofibric acid, iomeprol and iopromide assisted by different TiO_2 materials-determination of intermediates and reaction pathways. Water Res., 38(4) (2004) 955–964.

[39] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard and J.-M. Herrmann, Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania. Appl. Catal. B: Environ., 39 (1) (2002) 75–90.

[40] H. Yang, G. Li, T. An, Y. Gao and J. Fu, Photocatalytic degradation kinetics and mechanism of environmental pharmaceuticals in aqueous suspension of TiO_2: A case of sulfa drugs. Catal. Today, 153 (2010) 200–207.

[41] I. Langmuir, The mechanism of the catalytic action of platinum in the reactions. Trans. Faraday Soc., 17 (1921) 621–654.

[42] R.W. Matthews, Photocatalytic oxidation and adsorption of methylene blue on thin films of near-ultraviolet illuminated. J. Chem. Soc. Farad. Trans. 1, 85 (1989) 1291–1302.