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Degradation of diethyl phthalate (DEP) in aqueous solution using TiO_2/UV process

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ABSTRACT

Diethyl phthalate (DEP) has been classified as an endocrine disruptor pollutant. The degradation of DEP $C_{12}H_{14}O_4$, in aqueous solution by TiO_2-UV process was optimized using high pressure mercury lamp. Effects of TiO_2 dosage and type, and pH values on the degradation of DEP by TiO_2/UV process were investigated. The optimal TiO_2 dosage and pH value for the DEP degradation were 1 g l^{-1} and 7.0, respectively using TiO_2 P25. The degradation rate of DEP by TiO_2/UV process under optimal conditions reach 78.6% and could be fitted first-order kinetics.

Keywords: Diethyl phthalate DEP; Photocatalytic degradation; TiO_2; Hydroxyl radical; Endocrine disruptor

1. Introduction

Phthalate esters (PAEs) represent a class of chemical compounds used most widely as plasticizers for polyvinyl chloride (PVC) resins and cellulose film coating. To a minor extent they have also found application in cosmetics, insect repellents and propellants [1]. Phthalates are easily transported to the environment during manufacture, disposal and leaching from plastic materials, in which they are bonded non-covalently to allow the required degree of flexibility [2]. The short-chained phthalates, dimethyl phthalate (DMP) and diethyl phthalate (DEP) are among the most frequently identified phthalates in diverse environmental samples including surface marine waters, freshwaters and sediments [1,3]. Epidemiological studies with humans have shown that phthalates induce adverse health effects such as disorders in male reproductive tract, breast and testicular cancers and neuro-endocrine system disruption [4]. DEP, the phthalate that we focus on this study, has been found to have diverse acute and chronic toxic effects on several species at different trophic levels, as well as endocrine-disrupting properties [3,5]. The most common method for PAEs removal from wastewater is biological treatment, which is based on the metabolic degradation of PAEs by microorganisms [6]. However, the biodegradation process is time-consuming; the degradation rate ranged from several days to a few months [3].

Since DEP is hard to be biodegradable and other treatment cost is too high; there is a need to search for better treatment methods for the pollutants. Advanced oxidation processes (AOPs) have been successfully utilized to treat highly contaminated and toxic wastewater with organic pollutants (especially persistent organic pollutants (POPs)) [7–10]. In fact, several studies have examined the elimination of DEP using advanced oxidation processes (AOPs) involving the generation of the hydroxyl radical ($OH^\bullet$), such as UV/H_2O_2 [11], UV/H_2O_2/Fe^{2+} [1] and Fe(III)/solar light [12]. These studies

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agree that the reaction of DEP with $OH^{\bullet}$ is dominant for the removal of DEP, indicating that AOPs are effective processes for removing DEP from water. The maximum degradation percentage (75.8%) of DEP was observed within 120 min at pH 3 in the $UV/H_2O_2/Fe^{2+}$ system, with original H_2O_2 and Fe^{2+} concentrations of 5.00×10^{-4} and 1.67×10^{-4} mol l^{-1}, respectively [11]. However, few studies related to the use of titanium dioxide in the photocatalytic degradation of PAEs. In fact, heterogeneous photocatalysis through illumination of UV on TiO_2 surface is an attractive advanced oxidation process to treat aqueous organic compounds. One of the advantages of photocatalysis is that aliphatic and aromatic compounds can be completely mineralized under controlled conditions [13,14]. Moreover, titanium dioxide (TiO_2) is widely used as photocatalyst, since it is well known to be capable of oxidizing various pollutants, non-toxic, chemically stable, and commercially available [6,7,9,10,13,15–19]. The disadvantage is the slow electron transfer from TiO_2 to O_2 and that mineralization requires longer time [20]. However, there is a lack of reports on DEP removal by TiO_2/UV system and its photocatalytic degradation. In this study, we focus on the degradation of DEP using TiO_2-UV process from aqueous phase. The effect of various parameters such as contact time, initial catalyst dosage, photocatalyst type and operation pH has been investigated. The kinetic data on photocatalytic degradation studies are processed.

2. Experimental methods

2.1. Diethyl phthalate

The DEP (CAS N° 84-66-2) has as formula $C_{12}H_{14}O_4$. Its molecular weight is 222.24 g l^{-1} has a boiling point of 298–299°C and aqueous solubility of 1.1 g l^{-1} (at 25°C). The structure of DEP is shown in Fig. 1.

DEP is stable in aqueous solution. No degradation was observed in the dark at room temperature after 1 mo. The UV–Visible spectrum (Fig. 1) comprises two maxima, a weak one at 276 nm ($\varepsilon_{276} = 1480$ l mol^{-1} cm^{-1}) and a more intense one at 228 nm ($\varepsilon_{228} = 7880$ l mol^{-1} cm^{-1}).

2.2. Reagents

All chemicals were of reagent grade and used without further purification. The DEP $C_{12}H_{14}O_4$, was purchased from Across Organics (99%). All the DEP solutions were prepared in distilled water. P25 from Degussa was used as photocatalysts in this study. P25 consists of 75% anatase and 25% rutile with specific BET surface area of 50 m^2 g^{-1}. Hombikat UV 100 consists of 100% pure anatase with a specific BET surface area of 250 m^2 g^{-1}.

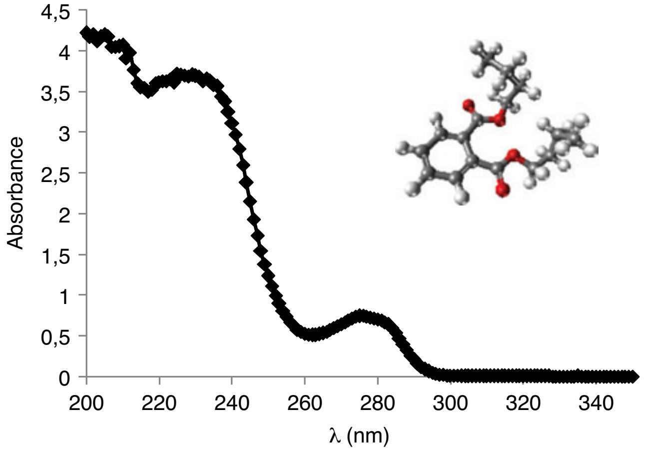

Fig. 1. UV–Visible spectrum of an aqueous solution of DEP.

2.3. Experiments

Before photocatalysis experiments, suspensions of TiO_2 in the DEP solution were stirred 30 min in the dark at 25 ± 1°C, a sufficient time to reach DEP equilibrium concentration. Assuming that adsorption–desorption of substrate and reaction intermediates is relatively slow in comparison to the recombination rate of electron–hole pairs, we suppose that the oxidation reactions to adsorption onto TiO_2 surface of the DEP is limited [21]. After mixing DEP solution with a predetermined amount of TiO_2 particle in a glass reactor, the mixture was maintained in suspension by a magnetic stirrer. The pH values of the suspensions were adjusted to the desired values using 0.1 M HCl or NaOH. Measurements were made using WTW Multi 197i pH meter. The total volume of the suspension in the photoreactor was 1 l for all cases. The samples were withdrawn at given time intervals, and immediately filtered through 0.45 μmTeflon syringe filters to minimize any continuing adsorption of DEP after sampling. UV-visible spectra and analytical determination of DEP remaining in solution was done calorimetrically using UV-visible spectrophotometer (Thermospectronic UV1) and quartz cell. The wavelength of 230 nm, in the visible spectrum of DEP (Fig. 1), was selected to monitor the disappearance of the molecule [11]. The calibration graph of the absorbance versus concentration obeyed a linear Beer–Lambert relationship under operational conditions.

2.4. Photocatalytic degradation experiments

Stock solutions of DEP containing the desired concentrations were prepared in water. The photocatalytic degradation experiments were carried out in a laboratory-scale cylindrical annular Pyrex photoreactor as

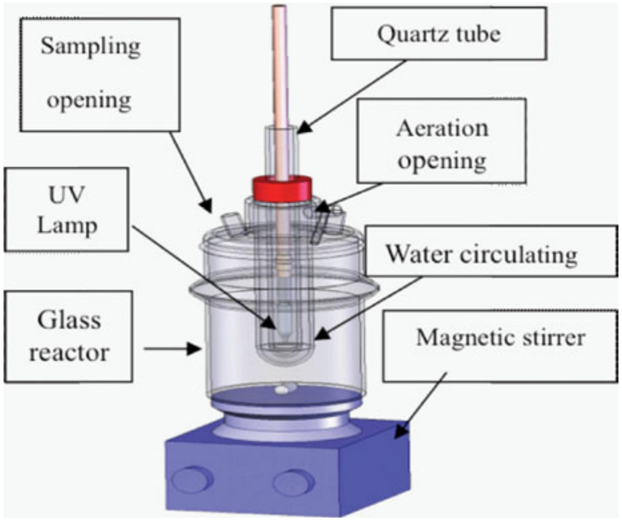

Fig. 2. Photo-reactor with mercury UV lamp [13].

shown in Fig. 2. The photochemical reactor was made of glass with a plain quartz tube (through which the UV lamp is entering) equipped with a magnetic stirring bar, a water-circulating jacket and two openings for aeration. The photoreactor was equipped with a high pressure mercury lamp (Cathodeon HPK 125 W; λ > 253 nm).

For the irradiation experiments 1 l of the desired solution were filled into the reactor. The required amount of photocatalyst was added and the solution was stirred for at least 30 min in the dark to allow equilibration of the system. Samples were collected before and in regular intervals during the irradiation and immediately filtered through 0.45 µmTeflon syringe filters before analyses.

3. Results and discussion

3.1. Adsorption of DEP on TiO_2

The adsorption experiments were conducted to study the adsorption behavior of DEP on TiO_2 particles at pH 3.0, 7.0 and 9.0. The initial concentration of DEP used in all the experiments was 150 mg l^{-1}. After 30 min, the adsorption amounts of DEP by TiO_2 particles (1 g l^{-1}) at pH 3, 7 and 10 were 8.1%, 12.5% and 10.6%, respectively. The results showed that neutral pH favored the adsorption of DEP on TiO_2 particles. This is because TiO_2 particles at the point of zero charge (isoelectric point, about pH 6.2–7.5) [18,22] could adsorb more DEP molecules. When pH is below isoelectric point of the P25 TiO_2, the surface of TiO_2 particles is electropositive, which does not favor the adsorption of DEP molecules. On the contrary, when pH is above isoelectric point, the surface of TiO_2 particles is electronegative, which does also not favor the adsorption of DEP molecules.

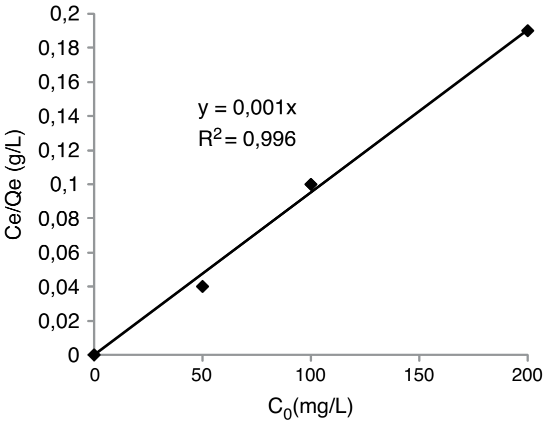

Fig. 3. Adsorption isotherm obtained with TiO_2 Degussa P 25 (1 g l^{-1}), at pH 7.

The adsorbed DEP per unit weight of the catalyst TiO_2 (mg g^{-1}) at equilibrium (Q_e) were calculated from Eq. (1):

$$Q_e = V\left(C_i - C_e\right) / M \tag{1}$$

where C_i and C_e is the initial and equilibrium DEP concentration in the dark (g l^{-1}); V is the solution volume (l); and M is the photocatalyst mass (g). Fig. 3 represents an example of the adsorption isotherm of DEP on TiO_2 (1 g l^{-1}) at pH 7 and showed that the adsorption isotherm fitted the Langmuir–Hinshelwood equation [19,23,24].This behavior is considered as indicative of well shaken adsorption system and fast chemical ion surface attachment [16,21].

3.2. Effect of TiO_2 dosage on the degradation of DEP

DEP is soluble in water with a reported maximum of solubility of approximately 1000 mg l^{-1} [12]. DEP is stable in aqueous solution. No degradation was observed in the dark at room temperature. In general, DEP exhibits weak absorption of light at λ higher than 300 nm. The UV–VIS spectrum comprises only a weak maximum absorption at 276 nm (ε_{276} = 1480 l mol^{-1} cm^{-1}). The experimental results showed that the degradation of DEP did not occur after 3 h irradiation using mercury UV lamp (Cathodeon HPK 125, λ > 253 nm) which indicated that DEP was extremely inert and difficult to be degraded. However, the concentration of DEP continuously decreased when photocatalyst TiO_2 was added into DEP solution under UV irradiation. The effect of catalyst weight (TiO_2-P25) on the percentage removal of DEP was investigated from 0 to 2 g of the catalyst per liter, using the DEP concentration stable at 150 mg l^{-1}, effect of TiO_2 dosage on the degradation of DEP is shown in Fig. 4.

It can be seen that the addition of photocatalyst is markedly improving the degradation of the model

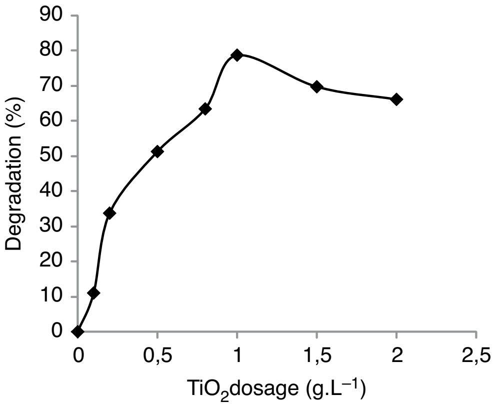

Fig. 4. Effect of TiO_2 dosage on the photocatalytic degradation of DEP in aqueous solution. $[DEP]_0$ = 150 mg l^{-1}, pH = 7, and irradiation time = 180 min.

pollutants itself as well as its mineralization in comparison to direct photolysis, that is 0 g l^{-1} photocatalyst concentration. The degradation efficiency of DEP increased with increasing amounts of TiO_2 up to 1 g l^{-1}. Then, the degradation efficiency kept decreasing slowly with the enhanced amount of the catalyst. The increase in the degradation efficiency of DEP was because of the increase in the total surface area of the catalyst, namely number of active sites, available for the photocatalytic reaction as the dosage of catalyst increased [27,29]. However, when the dosage of TiO_2 was overdosed, the number of active sites on the TiO_2 surface would become almost constant due to the decreased light penetration, the increased light scattering and the loss in surface area occasionally by agglomeration at high solid concentration [1]. Therefore, 1 g l^{-1} of TiO_2 was chosen as the optimal amount for the later photocatalytic degradation of DEP.

3.3. *Effect of type of photocatalyst*

The influence of the substrate concentration on the degradation kinetics of DEP was investigated for two commercially available titanium dioxide powders: Degussa P25 (1 g l^{-1}) and Sachtleben Hombikat UV 100 (1 gl^{-1}). The degradation rate of DEP is shown in Fig. 5 for both employed photocatalysts. The degradation efficiency decreases according time to reach 78.6% and 52.5% respectively for TiO_2 P25 and TiO_2 UV100.

While both materials qualitatively exhibit a similar behavior on the degradation of DEP, relatively higher rate was obtained when Degussa P25 was used as a photocatalyst for the removal of the DEP.

3.4. *Effect of pH on the degradation of DEP*

The pH value of the solution was another important parameter affecting photocatalytic degradation of organic pollutant since the amphoteric behavior of most semiconductor oxide affects the surface charge of the photocatalyst. Therefore, role of initial pH on the degradation of DEP was investigated, as illustrated in Fig. 6.

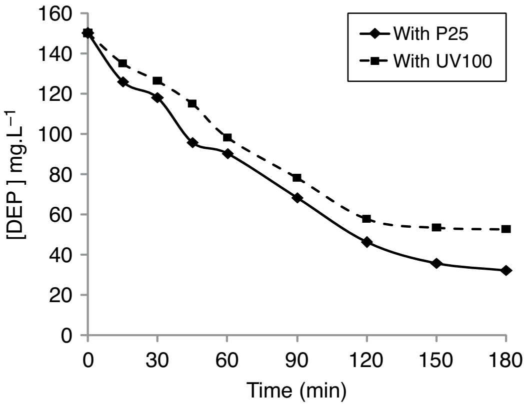

Fig. 5. Effect of TiO_2 type on the photocatalytic degradation of DEP in aqueous solution. $[DEP]_0$ = 150 mg l^{-1}, pH = 7, and irradiation time = 180 min.

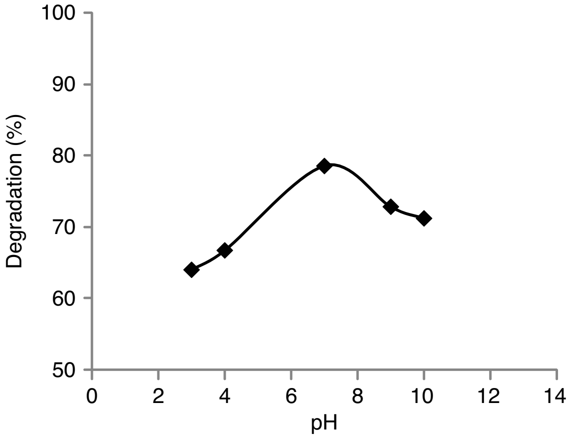

Fig. 6. Effect of pH on the photocatalytic degradation of DEP in aqueous solution. $[DEP]_0$ = 150 mg l^{-1}, $[TiO_2]$ = 1 g l^{-1}, and irradiation time = 180 min.

The efficiency DEP degradation increased when pH value increased from 3 to 7. When pH value was above 7, the degradation efficiency kept nearly constant with increase in pH value. The pH value of zero point charge of TiO_2 is about pH (6.2–7.5) [25]. It is considered that, in alkaline solution (pH > 8), the positively charged DEP is likely adsorbed on negatively charged TiO_2 particle surface, and in acidic solution (pH < 6), the negatively charged DEP is likely adsorbed on positively charged TiO_2 particle surface [18]. It should also be pointed out that high concentration of OH^- ions in the medium might trap CO_2 generated by degradation of DEP, and as a result, bicarbonate and carbonate were formed in the alkaline medium, which would limit degradation rate

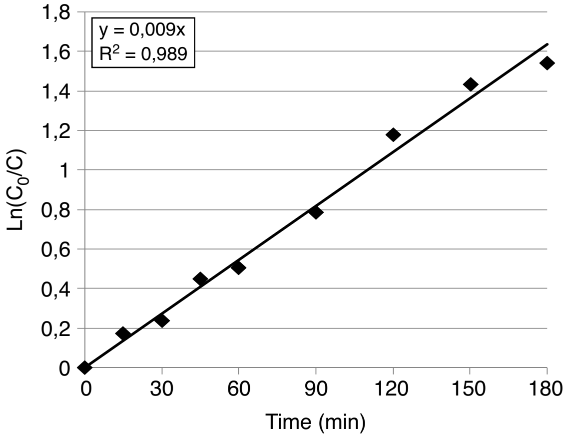

Fig. 7. Kinetic of the photocatalytic degradation of DEP in aqueous solution. $[DEP]_0$ = 150 mg l^{-1}, $[TiO_2]$ =1 g l^{-1}, and irradiation time = 180 min.

of DEP because bicarbonate and carbonate are efficient scavengers of hydroxyl free radicals [1]. Therefore, pH 7 was selected as the optimal experimental condition and there was no need for a neutralization process.

3.5. *Kinetic of photocatalytic degradation of DEP*

In this study, the photocatalytic degradation of DEP at the identified optimum conditions corresponds to a first-order kinetics model, which is described by Eq. (2):

$$C = C_0 e^{-kt} \tag{2}$$

where C_0 is the initial concentration of the DEP (mg l^{-1}); C is the concentration of DEP at time t (mg l^{-1}); t is the irradiation time, and k is the reaction rate constant (min^{-1}). The photocatalytic degradation rates were reproducible with R^2 (0.989) for the plots of natural log of DEP concentration versus time (Fig. 7). The rate constant of photocatalytic degradation of DEP at 150 mg l^{-1} in the presence of 1 g l^{-1} TiO_2 was 0,009 min^{-1}, and $t_{1/2}$ was around 77 min. The degradation half-life of DEP by microbial anaerobic degradation was 15.4 d [17]. From the results, it is indicated that the degradation efficiency of photocatalysis was faster than that of microbial degradation.

4. Conclusions

In this paper, an advanced oxidation process, TiO_2/UV system was utilized to degrade aqueous DEP, which was among endocrine disrupting compounds and priority pollutant in environment.

Authors studied a few design parameters such as effect of temperature, light density, UV type (UVA, UVB and UVC), but design parameters such as pH, photocatalyst and the amount of TiO_2 have been shown to be important variables during TiO_2 photocatalysis of DEP. This study showed their impact on the system and the optimal concentrations of TiO_2 and pH were examined. The maximum degradation percentage (78.86%) of DEP was observed within 3 h at pH 7 in the TiO_2/UV system, using TiO_2 Degussa P25 and a high pressure mercury lamp ($\lambda > 253$ nm), with optimal TiO_2 dosage and pH value 1 g l^{-1} and 7, respectively. Under optimum conditions, the degradation of DEP $C_{12}H_{14}O_4$, in aqueous solution by TiO_2-UV process, is following pseudo first-order kinetic. Pseudo kinetic constant equal to 0.009 min^{-1} is obtained and are superior to 0.866 and 0.1588 min^{-1} obtained using respectively: ozonation in the presence activated carbon at pH = 7.2, and photochemical degradation with UV/H_2O_2 system (initial concentration DEP 1.04 mg l^{-1}, UV intensity 133.9 µ cm^{-2}, initial concentration H_2O_2 = 30 mg $^{-1}$) [11,26]. The use of photocatalytic process and its combination with other process for DEP contaminated wastewater degradation can be interesting option to be investigated.

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References

[1] X.-R. Xu, S.-X. Li, X.-Y. Li, J.-D. Gu, F. Chen, X.-Z. Li and H.-B. Li, Degradation of *n*-butyl benzyl phthalate using TiO_2/UV, J. Hazard. Mater., 164 (2009) 527–532.

[2] G.-P. Yang, X.-K. Zhao, X.-J. Sun and X.-L. Lu, Oxidative degradation of diethyl phthalate by photochemically-enhanced Fenton reaction, J. Hazard. Mater., 126 (2005) 112–118.

[3] V. Matteo, M. Guidotti, G. Macilenti and C. Cremisini, Phthalate esters in freshwaters as markers of contaminants sources—a site study in Italy, Environ. Int., 23(3) (1997) 337–347.

[4] C.A. Staples, D.R. Peterson, T.F. Parkerton and W.J. Adams, The environmental fate of phthalate esters: a literature review, Chemosphere 35 (1997) 667–749.

[5] A. Kapanen, J.R. Stephen, J. Brüggemann, A. Kiviranta, D.C. White and M. Itävaara, Diethyl phthalate in compost: ecotoxicological effects and response of the microbial community, Chemosphere 67 (2007) 2201–2209.

[6] B.V. Chang, T.H. Wang and S.Y. Yuan, Biodegradation of four phthalate esters in sludge, Chemosphere, 69 (2007) 1116–1123.

[7] S. Adishkumar and S. Kanmani , Treatment of phenolic wastewaters in single baffle reactor by solar/TiO_2/H_2O_2 process, Desalin. Water Treat., 24 (2010) 67–73.

[8] J. Chung and J.-O. Kim, Application of advanced oxidation processes to remove refractory compounds from dye wastewater, Desalin. Water Treat., 25 (2011) 233–240.

[9] S. Esplugas, J. Gimenez, S. Contreras, E. Pasual and M. Rodriguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res., 36 (2002) 1034–1042.

[10] A.S. Derbalah, N. Nakatani and H. Sakugawa, Photocatalytic removal of fenitrothion in pure and natural waters by photo-Fenton reaction, Chemosphere, 57 (2004) 635–644.

[11] B. Xu, N.-Y. Gao, X.-F. Sun, S.-J. Xia, M. Rui, M.O. Simonnot, C. Causserand and J.-F. Zhao, Photochemical degradation of diethyl phthalate with UV/H_2O_2, J. Hazard. Mater., B139 (2007) 132–139.

[12] S.H. Swan, Environmental phthalate exposure in relation to reproductive outcomes and other health endpoints in humans, Environ. Res., 108 (2008) 177–184.

[13] A.I. Balabanovich and W. Schnabel, On the photolysis of phthalic acid dimethyl and diethyl ester: a product analysis study, J. Photochem. Photobiol. A: Chem., 113 (1998) 145–153.

[14] M.R. Hoffmann, W. Martin, S.T. Choi and D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev., 95 (1995) 69–96.

[15] C.H. Ao, S.C. Lee, J.Z. Yu and J.H. Xu, Photodegradation of formaldehyde by photocatalyst TiO_2: effects on the presence of NO, SO_2 and VOCs, Appl. Catal. B 54 (2004) 41–50.

[16] V. Belessi, G. Romanos, N. Boukos, D. Lambropoulo and C. Trapalis, Removal of Reactive Red 195 from aqueous solutions by adsorption on the surface of TiO_2 nanoparticles, J. Hazard. Mater., 170 (2009) 836–844.

[17] B.V. Chang, C.S. Liao and S.Y. Yuan, Anaerobic degradation of diethyl phthalate, di-n-butyl phthalate and di-(2-ethylhexyl) phthalate from river sediment in Taiwan, Chemosphere, 58 (2005) 1601–1607.

[18] C.Y. Chen, C.C Chen and Y.C. Chung, Removal of phthalate esters by α cyclodextrin-linked chitosan bead, Bioresource Technol., 98 (2007) 2578–2583.

[19] M.R. Ghezzar, F. Abdelmalek, M. Belhadj, N. Benderdouche and A. Addou, Gliding arc plasma assisted photocatalytic degradation of anthraquinonic Acid green 25 in solution with TiO_2, Appl. Catal., B 72 (2007) 304–313.

[20] S. Kawat, G. Charles, J. Hill and A. Marc, Photocatalytic degradation of ethylene over thin films of titania supported on glass rings, Catal. Today. 54 (1999) 159–164.

[21] **S**.T. Martin, H. Herrmann, W. Choi W and M.R. Hoffmann, Time-resolved microwave conductivity. Part I:Quantum-sized TiO_2 and the effect of adsorbates and light intensity on charge-carrier dynamics, J. Chem Soc. Faraday. Trans., 90 **(**1994**)** 3315.

[22] C. Kormann, D. Bahnemann and M.R. Hoffmann, Photolysis of chloroform and other organic molecules in aqueous TiO_2 suspensions, Environ. Sci. Technol., 25 (1991) 494–500.

[23] M. Ismail and L. Bousselmi, Effect of adsorption on the photocatalysis performance of anthraquinone dye, Water Sci. Technol., 61(1) (2010) 2539–2548.

[24] M. Muruganandham and M. Swaminathan, Solar photocatalytic degradation of a reactive azo dye in TiO_2-suspension, Solar Energy Mater. Solar Cells., 81 (2004) 439–457.

[25] T.S. Kim, J.K. Kim, K. Choi, M.K. Stenstrom and K.D. Zoh, Degradation mechanism and the toxicity assessment in TiO_2 photocatalysis and photolysis of parathion, Chemosphere, 62 (2006) 926–933.

[26] T.F. de Oliveira, O. Chedeville, B. Cagnon and H. Fauduet, Degradation kinetics of DEP in water by ozone/activated carbon process: influence of pH, Desalination, 269 (2011) 271–275.

[27] L. Gomathi Devi, B. Narasimha Murthy and S. Girish Kumar, Heterogeneous photo catalytic degradation of anionic and cationic dyes over TiO_2 and TiO_2 doped with MO^{6+} ions under solar light: Correlation of dye structure and its adsorptive tendency on the degradation rate, Chemosphere, 76 (2009) 1163**–**1166.

[28] G. Mailhot, M. Sarakha, B. Lavedrine, J. Caaceres and S. Malato, Fe (III)-solar light induced degradation of diethyl phthalate (DEP) in aqueous solutions, Chemosphere 49 (2002) 525–532.

[29] C.C. Wong and W. Chu, The direct photolysis and photocatalytic degradation of alachlor at different TiO_2 and UV sources, Chemosphere, 50 (2003) 981–987.