



## Heterogeneous photocatalytic degradation of phenanthrene in surfactant solution containing TiO<sub>2</sub> particles

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### ABSTRACT

Photocatalytic degradation of phenanthrene (PHE) over TiO<sub>2</sub> in aqueous solution containing nonionic surfactant micelles was investigated. All photocatalytic experiments were conducted using a 253.7 nm mercury monochromatic ultraviolet lamp in a photocatalytic reactor. The surfactant micelles could provide a nonaqueous “cage” to result in a higher degradation rate of PHE than in an aqueous solution, but the higher Triton X-100 concentration (more than 2 g/L) lowered the degradation ratio of PHE because the additional surfactant micelles hindered the movement of micelles containing PHE so as to reduce their adsorption onto titania. Pseudo-second-order kinetics was observed for the photocatalytic degradation of PHE. Alkaline solution environment was beneficial to the photocatalytic degradation of PHE. PHE degradation could mainly be attributed to the formation of hydroxyl radicals as evident from the comparison of degradation efficiencies when O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and tert-butyl alcohol (TBA) were applied as oxidants or hydroxyl radical scavenger. Based on the GC/MS analysis of the intermediates, the possible pathways of the photocatalytic degradation of PHE were proposed.

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### 1. Introduction

Soil contaminated by toxic or hazardous organic pollutants is an environmental concern. Hydrophobic organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), are of special interest because they are strongly sorbed to soil and known as toxic, persistent, bioaccumulative and carcinogenic pollutants [1,2] in ecosystem. These compounds can reach the environment as a result of fossil fuels burning, coke oven, metal processing facilities, hydrocarbon production, and so on [3].

In China, the concentration of PAHs in soil has been found to be as high as 100–10<sup>4</sup> μg/kg in some contaminated areas [4], which is a great threat to the agricultural product quality, human health and ecological security. Thus great attention has been paid to the remediation of the soils contaminated with PAHs. Surfactants may be beneficial in soil-washing or soil-flushing pump-and-treat technologies by assisting desorption of the contaminant from the soil surface, and surfactant-enhanced remediation (SER) has continued to be one of the important remediation system [5]. The nonionic surfactant Triton X-100 could enhance the solubiliza-

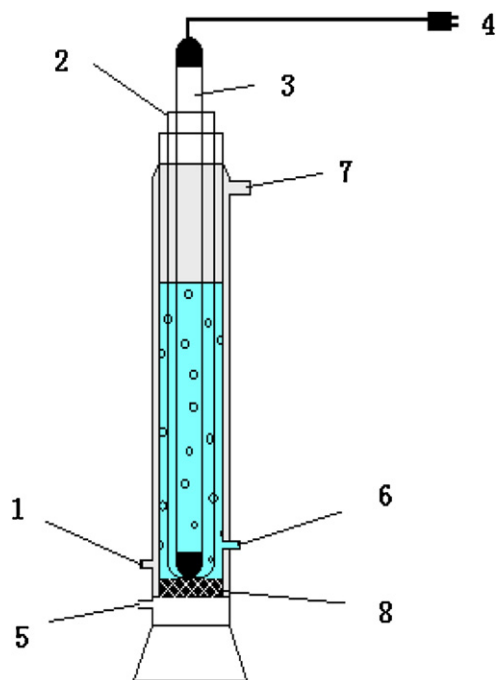
tion of hydrophobic contaminants through micellar solubilization in soil and was confirmed to be effective in removing PHE and benzo[a]pyrene from soils in our previous experiments.

Photolysis by UV/visible light and biological treatment are the important transformation ways for PAHs, but they are difficult to achieve complete mineralization [6,7]. Usually toxic PAHs are strongly adsorbed on soils because of their strong hydrophobicity. This feature makes them less bioavailable [8]. In addition, the drawbacks to be considered are the slow reaction rates, sometimes more toxic intermediates, control of proper pH and temperature.

In recent years, heterogeneous photocatalytic degradation of PAHs or pesticides is one of the most attractive methods, which can be combined with the solar energy/artificial light to increase the degradation [3,9–13]. Heterogeneous photocatalysis offers an oxidation capable of pollutant abatement under ambient condition via irradiation of some semiconductor solids [14], which can be used as photocatalysts suspended in the water effluent to be treated, or immobilised on various types of supports [15]. Photocatalytic degradation reactions are carried out in the presence of water, air, the target contaminant and the photocatalyst. The process could achieve a complete mineralization of organic substrates to CO<sub>2</sub>, H<sub>2</sub>O, and relevant inorganic ions. But up to date, most of the studies involved with the photocatalytic degradation were carried out in organic solvents [16–18], and there is very little information concerning the photochemical reactions of organic pollutants in micelle solutions. The use of surfactants as solubilizing agents to

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**Fig. 1.** Sketch of the photocatalytic reactor (1: condensate inlet, 2: quartz glass vessel, 3: UV lamp, 4: power, 5: gas inlet, 6: sampling ports, 7: condensate outlet and 8: porous sieve).

remove contaminants from soils followed by heterogeneous photocatalytic degradation may be a promising strategy through which the surfactants may be recovered and/or be reused [19].

In this study, factors that influence the photochemical degradation behavior of PHE in surfactant micelles were analyzed and the role of surfactant micelles in the photocatalytic degradation was also suggested. Simultaneously, the photodegradation intermediates and products were identified by gas chromatography/mass spectrometer (GC/MS) and the possible reaction pathways were proposed.

## 2. Experimental

### 2.1. Materials

Phenanthrene (PHE, 98% purity) and Triton X-100 were purchased from Sigma Chemical Co., USA. 1-Hexane (HPLC grade) was purchased from Tianjin Fuchen Chemical Reagent Co., China.  $\text{TiO}_2$  (P25) was obtained from Degussa, Germany, which is a non-porous mixture of 80% anatase and 20% rutile, with a BET surface area of  $50 \text{ m}^2/\text{g}$  and an average particle size of 30 nm.  $\text{H}_2\text{O}_2$  (AR, 30% content) and tert-butyl alcohol (TBA) were purchased from Tianjin Damao Chemical Reagent Co., China. The chemicals above were used without any further purification.

### 2.2. Photocatalytic degradation experiment

The photocatalytic reactor as shown in Fig. 1 is a cylindrical glass vessel in which a 8 W UV lamp (253.7 nm, light intensity about  $6 \times 10^{-7} \text{ Einstein L}^{-1} \text{ s}^{-1}$ ). The lamp protected by a quartz glass tube from direct contact with the aqueous solution is located at the centre. Another big glass tube on its outside wall is used as a water cooler trough to prevent thermal catalytic effect. At the bottom of the quartz glass tube, there is a porous sieve through which  $\text{N}_2$  or  $\text{O}_2$  is pumped to mix the solution or scavenge the electron generated from light irradiation.

Based on the result of PHE contaminated soil remediation, the concentration of PHE in a 2 g/L Triton X-100 solution was 1 mg/L. So in a typical experiment, 0.001 g PHE and 2 g Triton X-100 were first equilibrated to dissolve on a reciprocating shaker for more than 48 h at  $25 \pm 1^\circ \text{C}$ . The solution containing PHE was added into a beaker containing a certain amount of titania. The suspension was magnetically stirred in the dark for 30 min before irradiation to ensure the establishment of an adsorption/desorption equilibrium of PHE on the surface of titania. Then the PHE concentration was calibrated by GC analysis after adsorption as the initial concentration in Triton X-100 solution. Subsequently, the suspension containing titania was placed into the reactor vessel, followed by irradiating with the UV lamp. The slurry of reaction sample was taken out at predetermined intervals, filtered using Millipore  $0.22 \mu\text{m}$  membrane filter to separate the photocatalyst, extracted using 1-hexane, concentrated in nitrogen flow and analyzed using GC (Agilent 6890N, USA). To identify the degradation products, extracted samples were analyzed using GC/MS (ThermoElectron Finnigan TSQ, USA).

### 2.3. GC analysis for PHE

The concentration of PHE was determined using an Agilent 6890N GC system, equipped with a split-splitless automatic injector and connected to a FID detector. The capillary column employed was 5.5% phenyl methyl siloxane ( $30 \text{ m} \times 320 \mu\text{m} \times 0.25 \mu\text{m}$ ). The oven temperature was programmed as follows: hold time for 1 min at  $100^\circ \text{C}$ ; ramp rate at  $15^\circ \text{C}/\text{min}$  to  $230^\circ \text{C}$  for 20 min. The injection volume was  $1 \mu\text{L}$  via a splitless injection, and the detector temperature was  $300^\circ \text{C}$ . Under these conditions, the retention time for PHE was 10.32 min.

In order to identify the reaction products, a ThermoElectron GC/MS system was employed. About  $1 \mu\text{L}$  of each sample was injected into the GC/MS in the splitless mode. The injector temperature was held at  $280^\circ \text{C}$ . The MS detector was set at a temperature of  $300^\circ \text{C}$ .

## 3. Results and discussion

### 3.1. Effect of $\text{TiO}_2$ addition amount

The amount of  $\text{TiO}_2$  added to the surfactant solution containing PHE is a crucial parameter affecting the photocatalytic degradation. So the photocatalytic degradation of PHE was investigated employing different amounts of  $\text{TiO}_2$  varying from 0.1 g/L to 0.5 g/L. In order to ensure that the adsorption process had reached equilibrium, the mixture of  $\text{TiO}_2$ /PHE containing Triton X-100 ( $\text{TiO}_2 = 0.2 \text{ g/L}$ , PHE = 1 mg/L, and Triton X-100 = 2 g/L) was stirred in the dark and analyzed as a function of time as shown in Fig. 2. It indicated that the PHE adsorption could reach the adsorption/desorption equilibrium in 30 min. The saturated adsorption amount was about 0.76 mg PHE per gram titania.

Considering the natural light degradation of PHE, degradation experiment in the presence of  $\text{TiO}_2$  was firstly performed in the dark to demonstrate the role of light. The degradation of PHE under this condition was negligible in 30 min as shown in Fig. 3 (control curve). The degradation ratio of PHE increased with an increasing amount of  $\text{TiO}_2$ . The higher addition of  $\text{TiO}_2$  would cause the light obstruction and increase the cost of filtration, thus 0.2 g/L of  $\text{TiO}_2$  was the optimum amount in the subsequent experiments.

### 3.2. Effect of surfactant concentration

Amphiphilic structure of Triton X-100 can increase the solubility of PHE in the aqueous solution to significantly enhance the adsorption of PHE on the surface of titania and have an important role

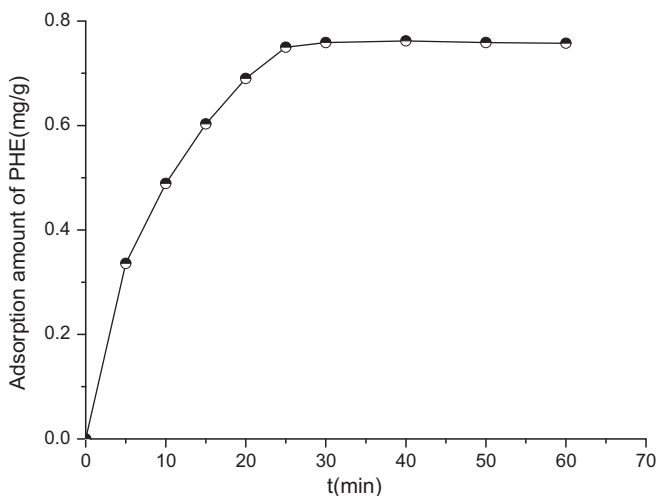


Fig. 2. The adsorption amount of PHE on the surface of TiO<sub>2</sub> with time.

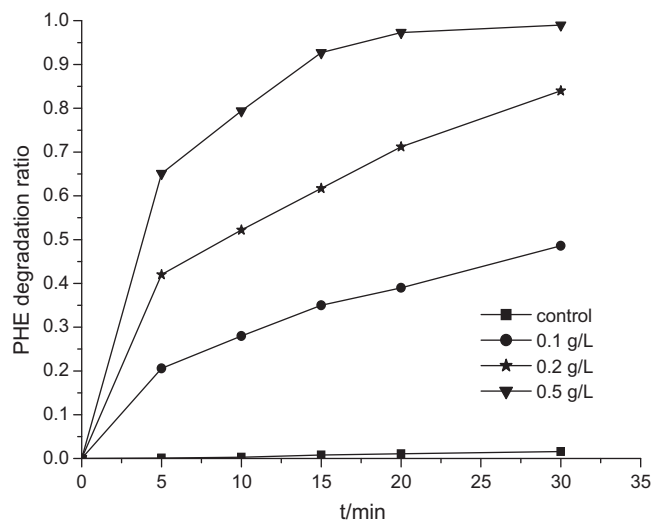


Fig. 3. Effect of TiO<sub>2</sub> amount on the photodegradation of PHE over TiO<sub>2</sub>.

on the degradation rate of contaminants. Chu [19] examined the photodecay rates of DDT with various nonionic surfactants under UV irradiation and found that the rates could be enhanced since the micelles could offer additional hydrogen sources for the photodechlorination reactions. Other researchers [20–22] also found that surfactant could promote the photocatalytic reaction of contaminants and reduce their toxicities.

When the surfactant concentration exceeds the critical micelle concentration (CMC), the “cage effect” of micelles, which provides a nonaqueous “cage” that allows for electron transfer photocatalytic degradation of PHE in a higher local concentration [22–24]. After the intermediates are generated, they do not diffuse out to the aqueous phase but mainly reside in the nonaqueous “cage” due to the similar hydrophobic properties of the intermediates. So the degradation ratio of PHE/intermediates in the nonaqueous “cage” was faster than that in aqueous solution, where the incident photons can be effectively absorbed by the concentrated PHE/intermediate molecules in the nonaqueous “cage” and then used for photoreaction. This resulted in higher reaction rates of PHE in the nonaqueous “cage”.

As shown in Fig. 4, low concentration of Triton X-100 (1 g/L) had no significant difference on the degradation ratio of PHE compared to that of 2 g/L Triton X-100. However, the concentration of Triton

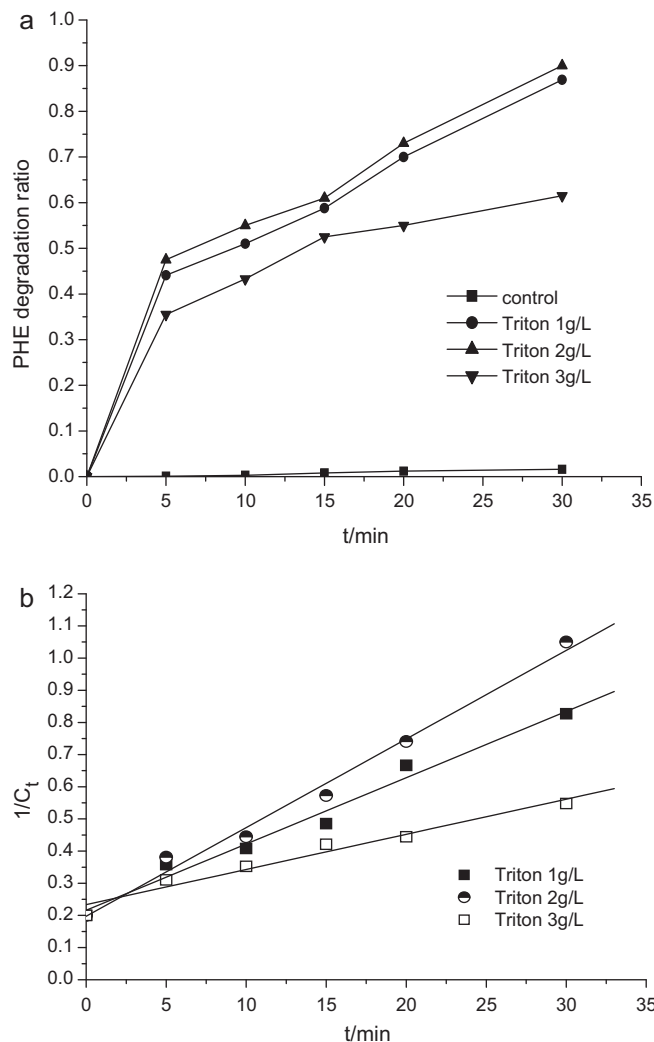


Fig. 4. (a) Effect of Triton X-100 concentration on the photodegradation of PHE over TiO<sub>2</sub>, (b) pseudo-second-order plot for the kinetic photodegradation of PHE over TiO<sub>2</sub> with different Triton X-100 concentrations.

Table 1

Kinetic parameters for the photocatalytic degradation of PHE at different surfactant concentrations.

Triton X-100 concentration (g/L)	$k$ (L mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
1	0.02061	0.9799
2	0.02755	0.9886
3	0.01092	0.9654

X-100 increasing from 2 g/L to 3 g/L lowered the degradation ratio of PHE.

Fig. 4(b) showed that the degradation rate with different surfactant concentrations were fitted pseudo-second-order kinetics well.

The pseudo-second-order kinetics form is [25]:

$$\frac{1}{C_t} = \frac{1}{C_0} + kt \quad (1)$$

where  $C_0$  and  $C_t$  are the PHE concentrations at time zero and  $t$ , respectively, and  $k$  is the rate constant.

The degradation rate constants were determined by regression analysis and listed in Table 1. It can be seen that  $k$  at 3 g/L of Triton X-100 was about one-third that of 2 g/L. So 2 g/L of Triton X-100 was chosen as the suitable concentration dissolved PHE for the subse-

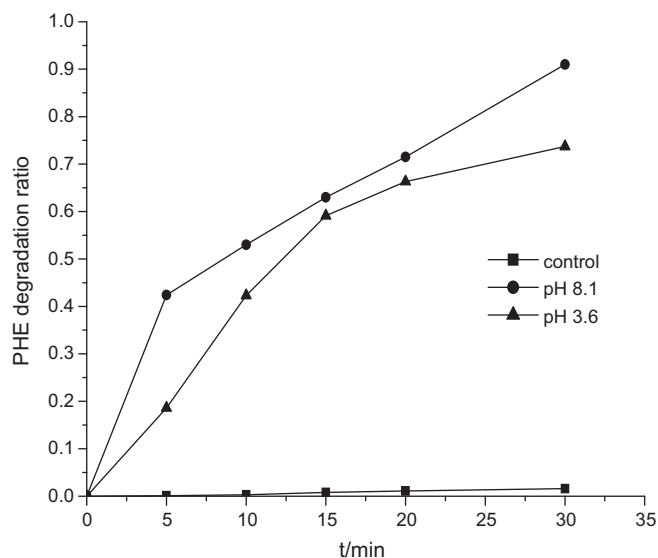


Fig. 5. Effect of pH on the photodegradation of PHE over TiO<sub>2</sub>.

quent experiments based on the considerations of degradation rate and solubility.

These results of degradation ratio and degradation rate contradicted with the results of dechlorination stated by Wei [19], who thought that the dechlorination reaction was promoted with the increasing concentration of the surfactant micelles. This might be due to two reasons: (1) entirely different mechanisms of PHE oxidation and DDT or PCBs dechlorination reduction. The additional hydrogen sources offered by surfactant micelles can substitute for the chlorine atoms of DDT in the dechlorination reduction reaction [19]. So more amount of surfactant micelles was beneficial to the dechlorination reaction. But there is no halogen atom in PHE molecular, the oxidation reaction does not depend on the hydrogen atom obtained from surfactant micelles; (2) the additional Triton X-100 micelles without wrapping PHE would partially occupy the sites of TiO<sub>2</sub> and thus hinder the movement of micelles containing PHE so as to reduce their adsorption onto TiO<sub>2</sub>.

### 3.3. Effect of pH

The pH of the surfactant solution containing PHE could greatly influence the surface charge of TiO<sub>2</sub>, thus changing its dispersion in solution owing to the amphoteric behavior of TiO<sub>2</sub>. When pH in the solution is close to the isoelectric point (IEP) of TiO<sub>2</sub>, particles easily agglomerate due to the role of the van der Waals attraction. Therefore, when the pH is far from the IEP of TiO<sub>2</sub>, well dispersion is achieved because of the repulsive force between particles in solution. In addition, pH also influences the adsorption and desorption of the main reactants and intermediates on the surface of TiO<sub>2</sub>, thereby affecting the photodegradation rate [26]. The effect of pH on the PHE degradation was depicted in Fig. 5. The degradation ratio of PHE was increased with increase of the pH, indicating that it had a comparative advantage in the alkaline solution compared to that in the acidic solution. The initial pH value of surfactant solution was 8.1 and was not adjusted externally during the experiment. In this experiment, the IEP of TiO<sub>2</sub> was about pH<sub>IEP</sub> = 6.8 [27]. The surface of TiO<sub>2</sub> was positively charged (pH < 6.8) in an acidic environment, while its surface was negatively charged (pH > 6.8) in an alkaline environment as given in Eqs. (2) and (3) [28].

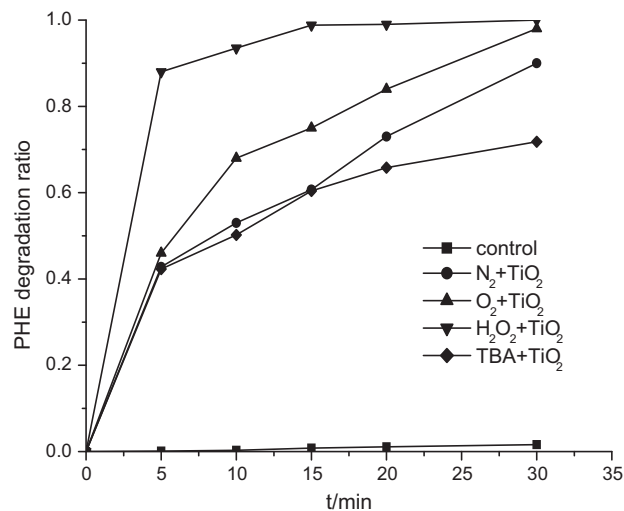
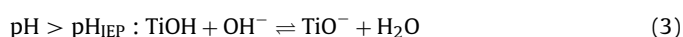
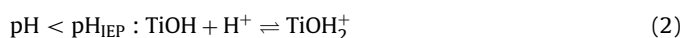
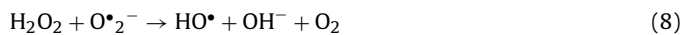


Fig. 6. Effect of N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and TBA on the photodegradation of PHE over TiO<sub>2</sub>.

Upon hydration, surface hydroxyl groups (TiOH) are formed on TiO<sub>2</sub>. These surface hydroxyl groups can undergo proton association or dissociation reactions. A low pH is associated with a positively charged surface which cannot provide hydroxyl groups to the hydroxyl radical formation. Consequently, the degradation ratio of PHE decreased. On the other hand, higher pH value can provide higher concentration of hydroxyl ions to react with the holes to form hydroxyl radicals, thereby enhancing the photodegradation of PHE.

### 3.4. Effect of O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and TBA

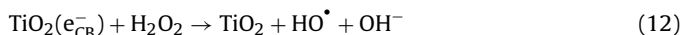
In order to verify whether the photocatalytic oxidation of PHE over TiO<sub>2</sub> involved hydroxyl radicals, some experiments were carried out in the presence of O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, TBA and the results were presented in Fig. 6. The two cases, pumping O<sub>2</sub> or N<sub>2</sub>, were compared in order to confirm the effect of O<sub>2</sub> on the degradation of PHE. Even for 30 min irradiation, the degradation ratio of PHE was less than 90% when O<sub>2</sub> was driven away from the surfactant solution by pumping N<sub>2</sub> continuously and lower than that by pumping O<sub>2</sub>, indicating that a synergistic effect happened when O<sub>2</sub> was added in the TiO<sub>2</sub> suspension increasing the reaction rate of photodegradation. It is well known that conduction band electrons (e<sup>-</sup>) and valence band holes (h<sup>+</sup>) are generated when TiO<sub>2</sub> is irradiated with photon energy greater than its band gap energy. The photogenerated electrons can react with electron acceptors such as O<sub>2</sub> to form superoxide radical anion(O<sub>2</sub><sup>-•</sup>), which can then generate highly active ·OOH and ·OH, as described through Eqs. (4)–(8):



The solution would also occur such a reaction as shown in Eqs. (9) and (10) to produce additional hydroxyl radicals under UV irradiation by titania without oxygen. But in this case, the photogenerated electrons and holes are easily recombined because there is no oxidant to trap the photogenerated electrons.



As seen in Fig. 6, 0.1 g/L of  $H_2O_2$  also accelerated the degradation of PHE. PHE could be completely degraded in 15 min, while at this moment the degradation ratio was 75% if oxygen was applied as the oxidant. It could be deduced that hydrogen peroxide increased the number of reactive hydroxyl radicals in two ways. Firstly, hydrogen peroxide to enhance the degradation ability is primarily through its photolysis decomposition into hydroxyl radicals, which gives priority to trap the photogenerated electrons as shown in Eq. (11). Secondly, the reduction of hydrogen peroxide at the conduction band would produce hydroxyl radicals according to Eq. (12):



In the presence of TBA (2 mg/L), a hydroxyl radical scavenger, the photocatalytic oxidation of PHE catalyzed by  $TiO_2$  was strongly inhibited. The degradation ratio of PHE was about 72% compared with that of 92% in the absence of TBA at 30 min. This experimental observation confirmed that hydroxyl radicals were the main active species for the photocatalytic degradation of PHE by titania.

### 3.5. Pathway of the PHE degradation

The photocatalytic degradation products of PHE irradiated by titania at 5 min were detected using the total ion chromatogram and the result was shown in Fig. 7. The intermediates detected and degradation pathways suggested were not complete since some intermediates had short lifetime and could not be detected in GC–MS analysis. According to the standard spectra in Wiley Registry 8 e library data, the peak at retention time (RT) of 15.19, 18.51, and 20.68 could be identified as the compounds tetradecane, hexadecane, and eicosane, respectively. Similarly, the peak

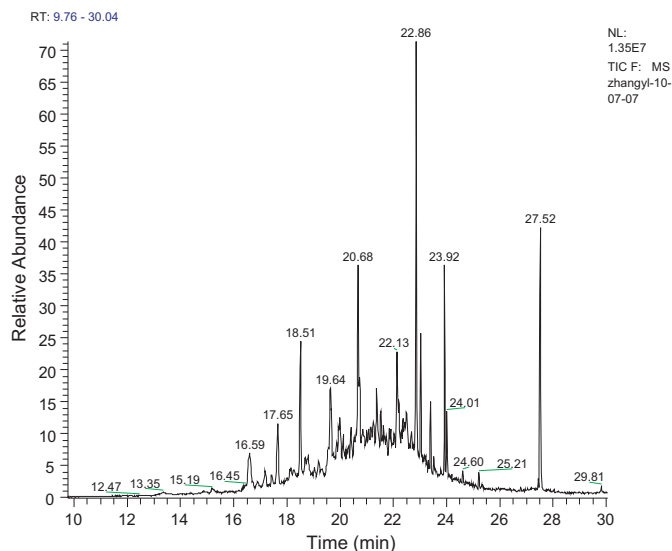


Fig. 7. Total ion chromatogram of photocatalytic degradation products of PHE over  $TiO_2$ .

at RT of 17.65, 22.86 could be assigned to the compounds 1,2-benzenedicarboxylic diethyl ester (Fig. 8a), phthalic acid diisobutyl ester (Fig. 8c) by analyzing the fragmentation pattern of mass spectra, respectively. In addition, there was small amount of other phthalate compounds, such as 1-butyl-2-decyl phthalate, and 1,2-benzenedicarboxylic acid butyl decyl ester. According to the quantitative analysis, a possible photooxidation mechanism of PHE over  $TiO_2$  under UV irradiation was proposed as Fig. 9 illustrated.

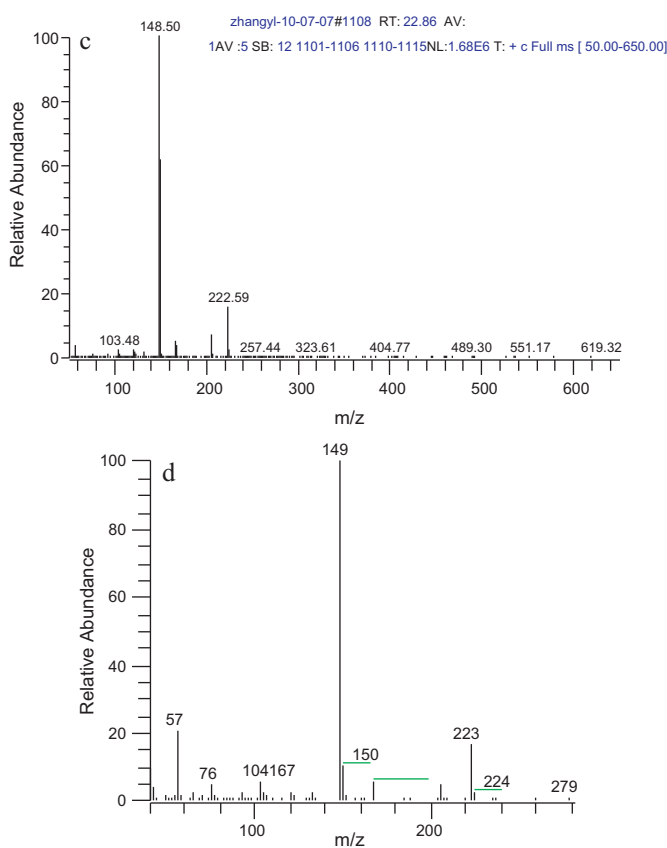
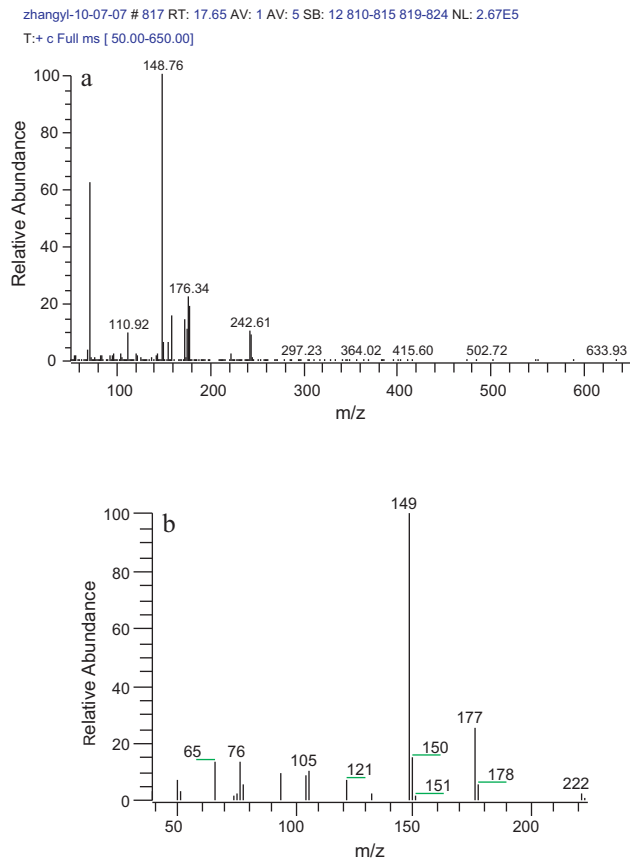


Fig. 8. Peaks of RT 17.65 and 22.86 from total ion chromatogram of photocatalytic degradation of PHE (a: 1,2-benzenedicarboxylic diethyl ester; b: standard spectra of RT 17.65; c: phthalic acid diisobutyl ester; d: standard spectra of RT 22.86).

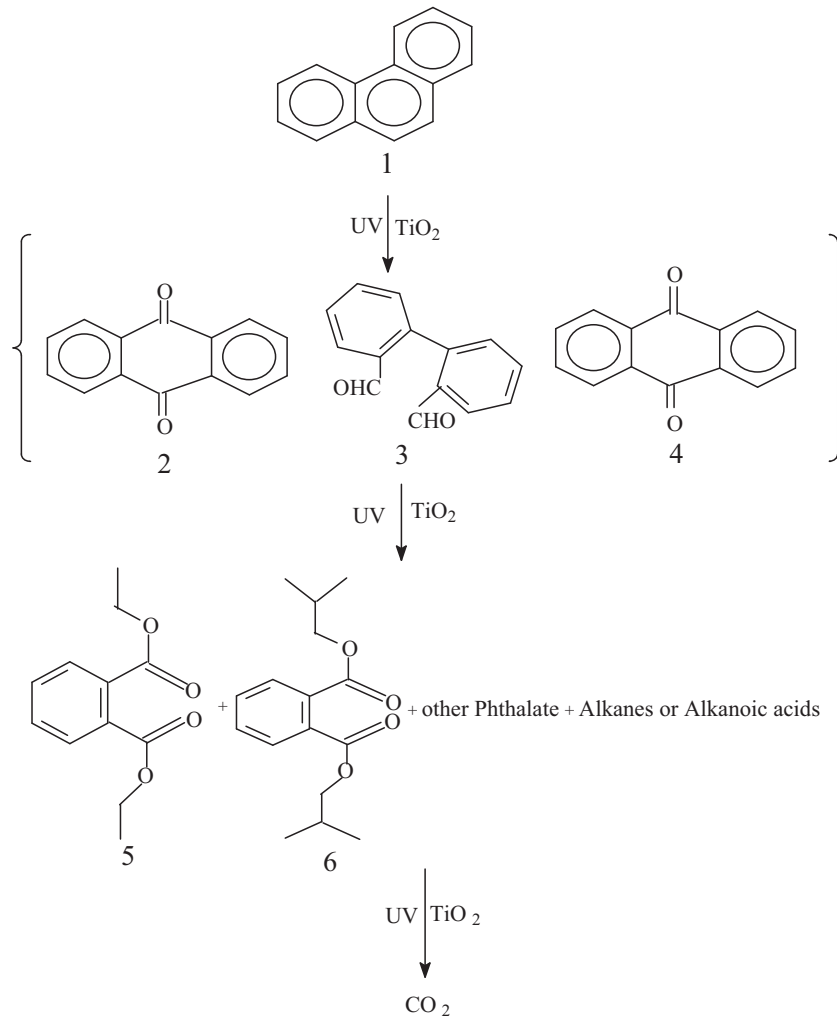


Fig. 9. Possible pathway of PHE photodegradation over  $\text{TiO}_2$  under UV irradiation.

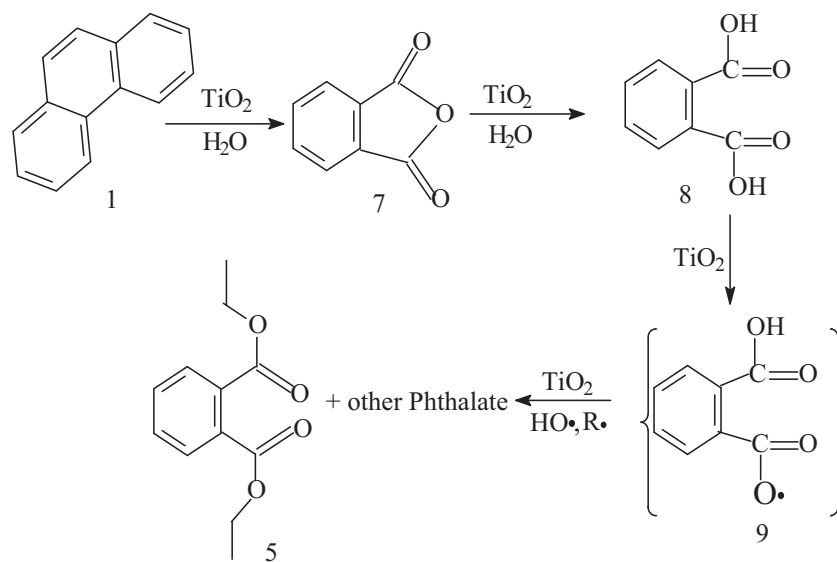


Fig. 10. Possible formation pathway of phthalate acid ester.



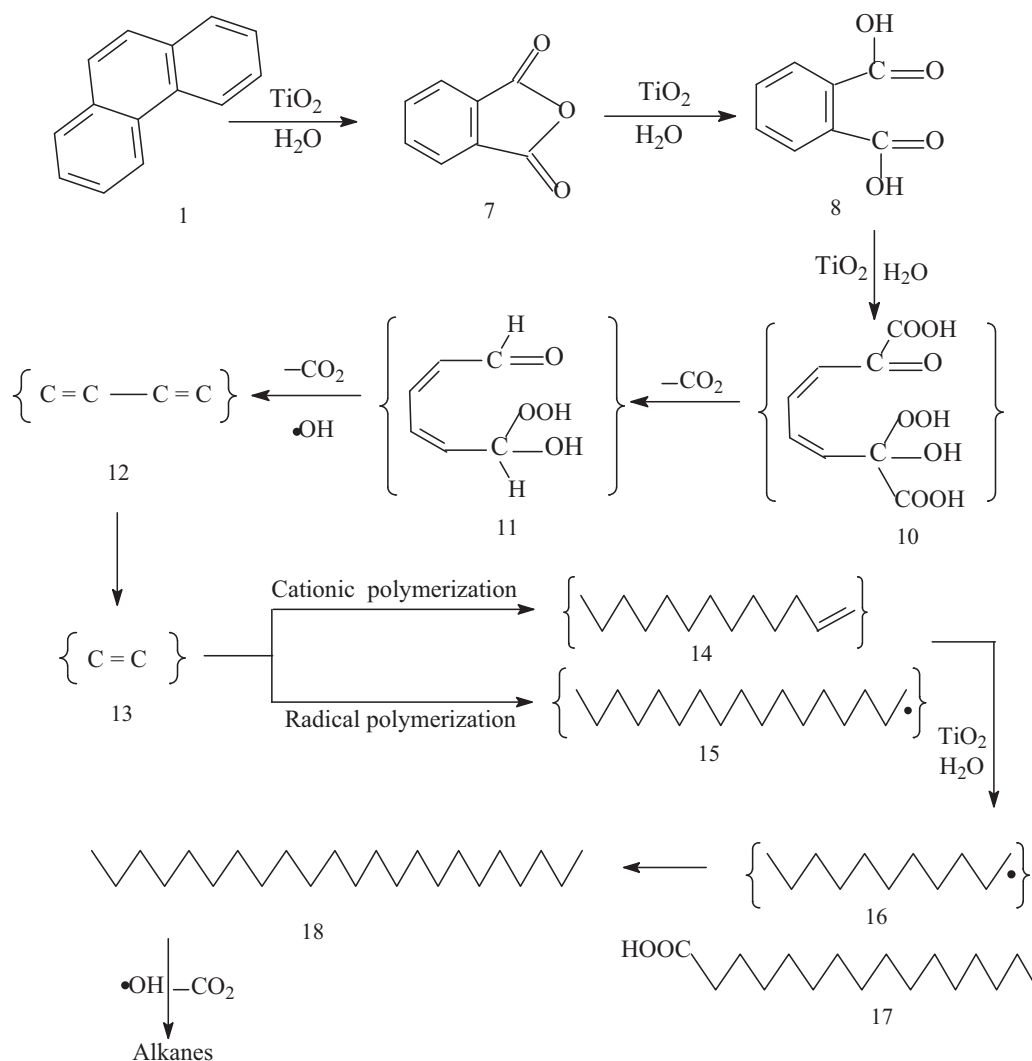


Fig. 11. Possible formation pathway of alkanes or alkanic acids.

The reaction products 2–4 in the bracket were theoretical products, which were not detected in this experiment. It is necessary to point out that three kinds of compounds: phthalates (products 5 and 6), alkanes and alkanic acids were detected as the main intermediates of PHE oxidation. Finally, the intermediates were further oxidated to produce carbon dioxide.

The open loop reaction occurred during the photodegradation of PHE. Referring to the formation pathway of phthalic acid esters Zeng [29] proposed, the intermediate phthalic acid ester formed in the process of photocatalytic degradation of PHE may be along the routes as shown in Fig. 10. In the oxidation process of compound 5, PHE was first oxidated to compound 7. Further oxidation of compound 7 led to the formation of product 8. The oxidation of hydroxyl position of product 8 could result in the formation of intermediates compound 5 and other phthalate.

The possible pathways of alkanes and alkanic acids were proposed and shown in Fig. 11. In the oxidation process of alkanes and alkanic acids, PHE was also first oxidated to compounds 7 and 8. Further oxidation of compound 8 led to the formation of a series of theoretical products 10–13. The theoretical product 13, ethylene, could occur two kinds of polymerization: cationic polymerization and radical polymerization. The cationic polymerization could result in the formation of alkane product 18. Further oxidation of product 18 led to the formation of all kinds of alka-

nes. Correspondingly, the radical polymerization could result in the formation of alkanic acid product 17.

To summarise, like hydroxyl radicals generated by ozonation reaction [29], the photocatalytic degradation by  $\text{TiO}_2$  not only generated the direct oxidation products such as compounds 5 and 6 but also generated some indirect oxidation products such as alkanes and alkanic acids. But as the reaction continued, all the intermediates were completely mineralized.

#### 4. Conclusions

The degradation ratio of PHE increased with the increase of  $\text{TiO}_2$  from 0.1 g/L to 0.5 g/L. The surfactant micelles could provide a non-aqueous "cage" to result in a higher degradation rate of PHE than in an aqueous solution, but more than 2 g/L of Triton X-100 lowered the degradation ratio of PHE. The photocatalytic degradation of PHE followed pseudo-second-order kinetics. The degradation ratio of PHE in the alkaline solution was higher than that in the acidic one because higher pH value could provide higher concentration of hydroxyl ions to react with the holes to form hydroxyl radicals. A synergistic effect happened when  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  were added in the  $\text{TiO}_2$  suspension increasing the reaction rate of photodegradation. It can be confirmed that PHE degradation was mainly attributed to the formation of hydroxyl radicals and the separation of photogen-

erated electrons and holes by the addition of TBA and pumping N<sub>2</sub>, respectively.

Based on the GC/MS analysis, the possible pathway of the photodegradation of PHE was proposed. The pathways of the intermediates phthalic acid ester, alkanes and alkanic acids formed in the process of photocatalytic degradation were also suggested.

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## References

- [1] Y.Z. Gao, L.Z. Zhu, Plant uptake, accumulation and translocation of phenanthrene and pyrene in soils, *Chemosphere* 55 (2004) 1169–1178.
- [2] Y. Yang, F. Hildebrand, Phenanthrene degradation in subcritical water, *Anal. Chim. Acta* 55 (2006) 364–369.
- [3] J. Kou, Z. Li, Y. Yuan, H. Zhang, Y. Wang, Z. Zou, Visible-light-induced photocatalytic oxidation of polycyclic aromatic hydrocarbons over tantalum oxynitride photocatalysts, *Environ. Sci. Technol.* 43 (2009) 2919–2924.
- [4] X.H. Li, L.L. Ma, X.F. Liu, S. Fu, H.X. Cheng, X.B. Xu, Polycyclic aromatic hydrocarbon in urban soil from Beijing, China, *Environ. Sci.* 18 (2006) 944–950.
- [5] J.W. Jawitz, D. Dai, P.S.C. Rao, M.D. Annable, R.D. Rhue, Rate-limited solubilization of multicomponent nonaqueous-phase liquids by flushing with cosolvents and surfactant: modeling data from laboratory and field experiment, *Environ. Sci. Technol.* 37 (2003) 1983–1991.
- [6] C.A. Reyes, M. Medina, C.C. Hernandez, M.Z. Cedeno, R. Arce, O. Rosario, D.M. Steffenson, I.N. Ivanov, M.E. Sigman, R. Dabestani, Photochemistry of pyrene on unactivated and activated silica surfaces, *Environ. Sci. Technol.* 34 (2000) 415–421.
- [7] M.E. Sigman, P.F. Schuler, M.M. Ghosh, R.T. Dabestani, Mechanism of pyrene photochemical oxidation in aqueous and surfactant solutions, *Environ. Sci. Technol.* 32 (1998) 3980–3985.
- [8] M. Teresa Alcántara, Jose Gómez, Marta Pazos, M. Angeles Sanromán, PAHs soil decontamination in two steps: desorption and electrochemical treatment, *J. Hazard. Mater.* 166 (2009) 462–468.
- [9] T. Garcia, B. Solsona, A.D. Cazorla, S.A. Linares, S.H. Taylor, Total oxidation of volatile organic compounds by vanadium promoted palladium-titanium catalysts: comparison of aromatic and polyaromatic compounds, *Appl. Catal. B: Environ.* 62 (2006) 66–76.
- [10] D. Dong, P. Li, X. Li, C. Xu, D. Gong, Y. Zhang, Q. Zhao, P. Li, Photocatalytic degradation of phenanthrene and pyrene on soil surfaces in the presence of nanometer rutile TiO<sub>2</sub> under UV-irradiation, *Chem. Eng. J.* 158 (2010) 378–383.
- [11] D. Dong, P. Li, X. Li, Q. Zhao, Y. Zhang, C. Jia, P. Li, Investigation on the photocatalytic degradation of pyrene on soil surfaces using nanometer anatase TiO<sub>2</sub> under UV irradiation, *J. Hazard. Mater.* 174 (2010) 859–863.
- [12] X. Quan, X. Zhao, H.M. Zhao, S. Chen, J.W. Chen, Y.Z. Zhao, Enhancement of p,p'-DDT photodegradation on soil surfaces using TiO<sub>2</sub> induced by UV-light, *Chemosphere* 60 (2005) 266–273.
- [13] M.M. Higarashi, W.F. Jardim, Remediation of pesticide contaminated soil using TiO<sub>2</sub> mediated by solar light, *Catal. Today* 76 (2002) 201–207.
- [14] H.-H. Huang, D.-H. Tseng, L.-C. Juang, Heterogeneous photocatalytic degradation of monochlorobenzene in water, *J. Hazard. Mater.* 156 (2008) 186–193.
- [15] R. Molinari, F. Pirillo, V. Loddo, L. Palmisano, Heterogeneous photocatalytic degradation of pharmaceuticals in water by using polycrystalline TiO<sub>2</sub> and a nanofiltration membrane reactor, *Catal. Today* 118 (2006) 205–213.
- [16] Z.H. Wang, Z. Shi, Kinetic and mechanistic study of photodechlorination of 2,2',4,4'-tetrachlorobiphenyl in surfactant solutions, *B. Environ. Contam. Tox.* 78 (2007) 162–165.
- [17] J. Hawari, A. Demeter, C. Greer, R. Samson, Acetone-induced photodechlorination of Aroclor 1254 in alkaline 2-propanol: probing the mechanism by thermolysis in the presence of di-t-butyl peroxide, *Chemosphere* 22 (1991) 1161–1174.
- [18] J. Hawari, A. Demeter, R. Samson, Sensitized photolysis of polychlorobiphenyls in alkaline 2-propanol: dechlorination of aroclor 1254 in soil samples by solar radiation, *Environ. Sci. Technol.* 26 (1992) 2022–2027.
- [19] W. Chu, Photodechlorination mechanism of DDT in a UV/surfactant system, *Environ. Sci. Technol.* 33 (1999) 421–425.
- [20] V. Ramamurthy, Organic photochemistry in organized media, *Tetrahedron* 42 (1986) 5753–5839.
- [21] G.A. Epling, E.M. Florio, A.J. Bourque, X.H. Qian, J.D. Stuart, Borohydride, micellar, and exciplex-enhanced dechlorination of chlorobiphenyls, *Environ. Sci. Technol.* 22 (1988) 952–956.
- [22] Ling Zang, Chun-Yan Liu, Xin-Min Ren, Photochemistry 5. Location of dyes in nanoparticles and effects of semiconductor particles reverse micelles containing TiO<sub>2</sub> on photoinduced interfacial electron transfer, *J. Photochem. Photobiol. A* 88 (1995) 47–51.
- [23] Z. Shi, M. Sigman, M. Ghosh, I. Rezadabestan, Photolysis of 2-chlorophenol dissolved in surfactant solutions, *Environ. Sci. Technol.* 31 (1997) 3581–3587.
- [24] W. Chu, Jun cai Jia, The photodegradation and modeling of a typical NAPL, trichloroethene, by monochromatic UV irradiations, *Environ. Sci. Technol.* 43 (2009) 1455–1459.
- [25] M.A. Rauf, M.A. Meetani, A. Khaleel, A. Ahmed, Photocatalytic degradation of Methylene Blue using a mixed catalyst and product analysis by LC/MS, *Chem. Eng. J.* 157 (2010) 373–378.
- [26] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, N. Serpone, TiO<sub>2</sub>-assisted photodegradation of dye pollutants II: adsorption and degradation kinetics of eosin in TiO<sub>2</sub> dispersions under visible light irradiation, *Appl. Catal. B: Environ.* 15 (1998) 147–156.
- [27] J. Zhao, K. Wu, H. Hidaka, N. Serpone, Photodegradation of dyes with poor solubility in an aqueous surfactant/TiO<sub>2</sub> dispersion under visible light irradiation, *J. Chem. Soc. Faraday Trans.* 94 (1998) 673–676.
- [28] J. Sun, L. Qiao, S. Sun, G. Wang, Photocatalytic degradation of Orange G on nitrogen-doped TiO<sub>2</sub> catalysts under visible light and sunlight irradiation, *J. Hazard. Mater.* 155 (2008) 312–319.
- [29] Y. Zeng, A.P.K. Hong, D.A. Wavrek, Integrated chemical-biological treatment of benzo[a]pyrene, *Environ. Sci. Technol.* 34 (2000) 854–862.