

Heterogeneous photocatalytic degradation of Triton X-100 in aqueous TiO₂ suspensions

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Abstract: The increasing utilization of surfactants generates a great amount of wastes. Surfactants and their more toxic degradation by-products in the environment affect the biota greatly. In particular, the low biodegradation of nonionic surfactants requires efficient oxidation treatments. In addition, the extracted contaminants by high concentrations of non-ionic surfactants in soil remediation may be completely treated using advanced oxidation process and thus the degradation of non-ionic surfactants needs to be checked in this case. The photocatalytic degradation of Triton X-100, a non-ionic surfactant, in aqueous titania suspensions was investigated as a function of catalyst dosage, pH, addition of hydrogen peroxide, potassium persulfate, and Tert-butyl alcohol. For the treatment of 20 mg/L Triton X-100 solutions, the optimum catalyst dosage and pH were determined to be 1 g/L and 6, respectively. The degradation efficiency of Triton X-100 by potassium persulfate was higher than that by hydrogen peroxide when the same mol of oxidants were used. Tert-butyl alcohol can strongly inhibit the photocatalytic oxidation reactions of Triton X-100. The degradation rates as a function of initial surfactant concentrations were interpreted by using a Langmuir-Hinshelwood model. With 0.2 g/L titania or even an additional 0.1 g/L hydrogen peroxide to completely degrade 1 mg/L phenanthrene in a 2 g/L Triton X-100 solution within 30 min, in this case the degradation efficiency of Triton X-100 was less than 5%. This proved that the strategy that surfactants were used as solubilizing agents for the removal of contaminants from soils followed by heterogeneous photocatalytic degradation was feasible. Within 120 min, 2 g/L of Triton X-100 can be degraded up to 67% by the addition of both 1 g/L titania and 1 g/L hydrogen peroxide. Under the right conditions, Triton X-100 can be completely degraded.

Keywords: Triton X-100, Photocatalytic Degradation, Titania, Kinetics

1. Introduction

To date, non-ionic surfactants are the most widely used industrial-scale surfactants. They are used in the production of detergents, emulsifiers, wetting agents, solubilizers and dispersants. The volume of the global surfactant market is about 18 metric ton and an annual increase of 20% is estimated until 2012 [1].

However, the increasing utilization of surfactants generates a great amount of wastes during their production, use, and disposal. They have the potential to act as endocrine disrupters in aquatic organisms, wildlife, and even humans [2]. High concentrations of surfactants and their more toxic degradation by-products in the environment may affect the biota [3]. In particular, the low biodegradation of nonionic surfactants [4,5] require efficient oxidation treatments [6]. In this regard, various oxidation techniques have been

developed and applied for the elimination of low concentrations of surfactants from effluents because of recent stringent regulations concerning water quality [7-11]. Moreover, higher concentrations of non-ionic surfactants more than the critical micelle concentration (CMC) have been shown to be more effective [12] in the solubilization and extraction of organic contaminants from soil and underground water. The extracted contaminants may be treated using advanced oxidation process(AOPs). The heterogeneous photocatalytic degradation of contaminants using TiO₂ is a promising alternative technology that is an inexpensive, environment-friendly, and can be combined with solar energy/artificial light to enhance degradation [13-19].

Heterogeneous photocatalysis facilitates oxidation that is

capable of pollutant abatement under ambient condition via irradiation of some semiconductor solids [20]. These can in turn be used as photocatalysts suspended in water effluent to be treated or immobilised on various types of supports [21,22]. Photocatalytic degradation reactions are carried out in the presence of water, air, the target contaminant, and the photocatalyst. The process can achieve a complete mineralization of organic substrates to CO_2 , H_2O , and relevant inorganic ions.

To the best of our knowledge, no attempt has been made to investigate the photocatalytic degradation reactions of hydrophobic contaminants dissolved in a high concentration of surfactant above CMC. In the current study, the photocatalytic oxidation of Triton X-100, a famous non-ionic surfactant that possesses wide practical applications, in aqueous TiO_2 suspensions was investigated for both low and high concentrations. The effects of various operational parameters of TiO_2 dosage, initial Triton X-100 concentration, and pH on its degradation rate were determined. Kinetic relationships were also investigated.

2. Experimental

2.1. Materials

Triton X-100 (analytical grade) was purchased from Sigma Chemical Co., USA. 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. H_2O_2 (analytical grade, 30% content), Tert-butyl alcohol (analytical grade, TBA) were purchased from Tianjin Damao Chemical Reagent Co. Ltd, China. Potassium persulfate (analytical grade, $\text{K}_2\text{S}_2\text{O}_8$) was purchased from Tianjin Reagent Chemical Co. Ltd, China. Acetonitrile (HPLC grade) and formic acid were purchased from Kermer Chemical Co., China. All chemicals were used without any further purification. Deionized water was used to prepare solutions.

2.2. Photocatalytic Degradation Experiment

Fig.1 shows the photocatalytic reactor which is a cylindrical glass vessel with a 25 W UV lamp (253.7 nm, light intensity about $1.8 \times 10^{-6} \text{ Einstein L}^{-1}\text{s}^{-1}$). This lamp is protected by a quartz glass tube from direct contact with the aqueous solution and is located at the centre. Another big glass tube on its outside wall is used as a water cooler trough for prevention of the thermal catalytic effect. At the bottom of the quartz glass tube, there is a porous sieve through which air is pumped to mix the solution.

In a typical experiment, solutions of 20 mg/L and 2 g/L Triton X-100 containing 1 mg/L phenanthrene were added into a beaker containing a certain amount of titania, respectively. For 2g/L Triton X-100 containing 1 mg/L phenanthrene, 0.001 g phenanthrene 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 individual suspension was magnetically stirred in the dark for 60 min before

irradiation to ensure the establishment of an adsorption/desorption equilibrium on the surface of titania. Subsequently, the suspension containing titania was placed into the reactor vessel, followed by irradiation with the UV lamp. The slurry of the reaction sample was taken out at pre-determined intervals, filtered using a Millipore $0.22 \mu\text{m}$ membrane filter to separate the photocatalyst, and then analyzed using High Performance Liquid Chromatography (HPLC, LC10A, Shimadzu).

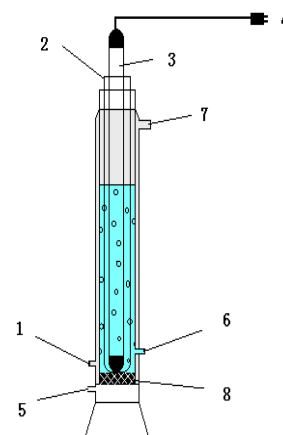


Fig 1. Sketch of the photocatalytic reactor (1. condensate inlet; 2. quartz glass vessel; 3. UV lamp; 4. power; 5. gas inlet; 6. sampling ports; 7. condensate outlet; 8. porous sieve)

2.3. Analysis of Triton X-100 and Phenanthrene

The concentration of Triton X-100 was analyzed using a Kromasil C18 reverse phase column (250 mm x 4.6 mm) in HPLC (LC10A, Shimadzu) with a mobile phase of 80% acetonitrile and 20% deionized water at a constant flow rate of 1.0 mL/min. The eluents were monitored at 224 nm using a diode array detector. A LC/MS system was employed to identify the degradation intermediates of Triton X-100. The HPLC system for the LC/MS analysis was an Agilent 1100 microbore system. The column was used the same Kromasil C18 reverse phase column. The mobile phase consisted of 20% deionized water (0.1% formic acid in it) and 80% acetonitrile (0.1% formic acid in it). The mass spectrum was obtained by using a Bruker Esquire HCT plus (Bruker Daltonics Inc., USA) fitted with standard electrospray source (ESI). Data acquisition was done in the positive ion mode. TOC was determined by a Shimadzu TOC 5000 analyzer.

The concentration of phenanthrene 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°C ; ramp rate at $15^\circ \text{C}/\text{min}$ to 230°C for 20 min. The injection volume was 1 μL via a splitless injection, and the detector temperature was 300°C . Under these conditions, the retention time for PHE was 10.32 min.

2.4. Calculation of Degradation Efficiency

Formula (1) was applied to calculate the degradation efficiency of Triton X-100.

$$\beta = \frac{C_0 - C_1}{C_0} \quad (1)$$

Where β is the degradation efficiency of Triton X-100; C_0 is the initial concentration of Triton X-100 before photocatalytic degradation, mg/L; C_1 is the residual concentration of Triton X-100 after photocatalytic degradation, mg/L.

3. Results and Discussion

3.1. Effect of Titania Dosage

To enhance the degradation efficiency of Triton X-100, titania was applied for the treatment of wastewater. Fig.2 illustrates the effect of titania dosage on degradation behaviour. Considering the natural light degradation of Triton X-100, degradation experiment in presence of TiO₂ was firstly performed in the dark to demonstrate the role of light. The degradation of Triton X-100 under this condition was negligible in 180 min as shown in Fig.2 (control curve). A significant improvement in degradation efficiencies from 75% to 99% at 180 min was observed when the catalyst dosages were increased from 0.5 to 1 g/L and then these slightly decreased because of the light scattering effect. Therefore, the catalyst dosage can be limited to 1 g/L, whereas the degradation efficiency was maintained at around the maximum level. Subsequent relevant experiments were performed using this dosage of TiO₂ particle. The degradation efficiency exhibited an increasing trend with an increase in TiO₂ dosage. The observations caused by TiO₂ addition may be interpreted with the effects on the overall photocatalysis reaction rate. The addition of TiO₂ particles in the solution caused two different effects: (1) an increase in the active catalyst surface which led to the generation of more active species in the media and more degradation efficiency and (2) an increase in media turbidity which led to a decrease in the amount of light, reaching the catalyst surface, hence diminishing the degradation efficiency. These two opposite effects result in an optimum amount for the catalyst dosage.

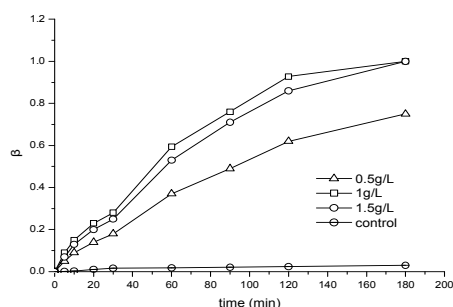


Fig. 2. Effect of TiO₂ dosage on the photodegradation of Triton X-100 over TiO₂

3.2. Effect of Hydrogen Peroxide, Potassium Persulfate, and TBA Dosages

The addition of H₂O₂ up to 0.5 g/L (15 mM) in the operation of the UV/TiO₂ process leads to a higher degradation efficiency, as shown in Fig.3. This can be attributed to the increase in the concentration of •OH radicals that are generated by the photocatalytic splitting of H₂O₂. At a low concentration of hydrogen peroxide, it inhibits electron-hole recombination and can act as an alternative electron acceptor (Eqs. 2-3).

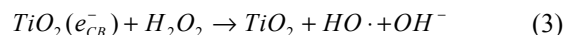
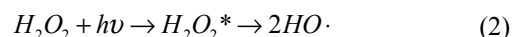


Fig.3 also showed the experimental result with 15 mM K₂S₂O₈ dosage in the presence of UV light and TiO₂ particles. The addition of 15 mM K₂S₂O₈ accelerated the degradation rate of Triton X-100. This degradation rate was enhanced by (1) the generation of SO₄^{-•} radicals as oxidizing species through interaction with UV light (Eq.4), (2) an increase in •OH radicals concentration (Eqs.5 and 6), and (3) the prevention of electron-hole recombination by accepting the conduction band electron (Eq. 7):

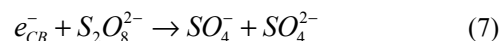
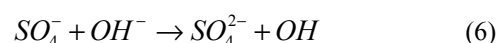
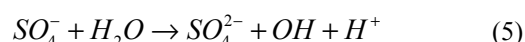
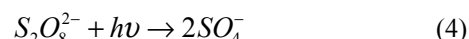


Fig. 3 indicates that when peroxide and persulfate oxidants were added to the UV/TiO₂ process with the same mols of 15 mM, the degradation efficiencies were enhanced from 28% to 84% for UV/TiO₂/H₂O₂ and to 90% for UV/TiO₂/K₂S₂O₈ at 30 min. At 60 min, degradation efficiencies reach to 100 for UV/TiO₂/K₂S₂O₈ and 96% for UV/TiO₂/H₂O₂, respectively. Meantime, the corresponding TOC removal shown in Fig.4 with the mentioned processes was 79 % and 73% at 60 min, respectively. The percentages for TOC removal were smaller than those for Triton X-100 removal. This may be due to different rates of adsorption of intermediate molecules on the TiO₂ and hence oxidize at different rates from the parent molecules.

From the above discussion, the use of UV/TiO₂/ K₂S₂O₈ proves to be a promising process for the degradation of Triton X-100 molecules in an aqueous solution. However, the treatment of drinking water by the addition of potassium persulfate is inappropriate because this can result in the high toxicity of harmful sulfur ions generated from the photocatalytic process under anaerobic conditions.

In the presence of TBA (3 mg/L), a hydroxyl radical scavenger, the photocatalytic oxidation reactions of Triton X-100 by UV/TiO₂, UV/TiO₂/H₂O₂, and UV/TiO₂/K₂S₂O₈ were strongly inhibited. The degradation efficiencies of Triton X-100 were about 38%, 79%, and 87% compared

with 59%, 96%, and 100% in the absence of TBA at 60 min, respectively. This experimental observation confirmed that hydroxyl radicals were the main active species for the photocatalytic degradation of Triton X-100 by titania.

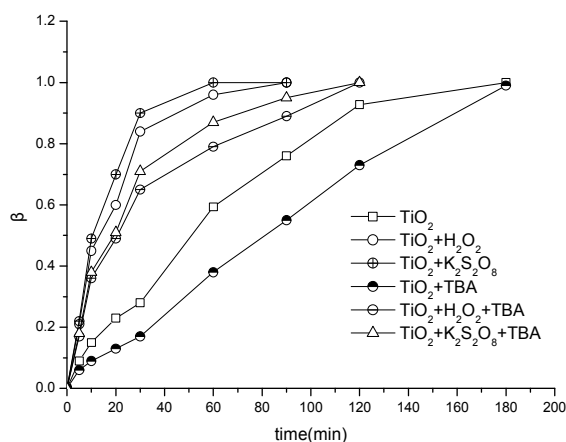


Fig. 3. Effect of H_2O_2 , $K_2S_2O_8$ and TBA on the photodegradation of Triton X-100 over TiO_2

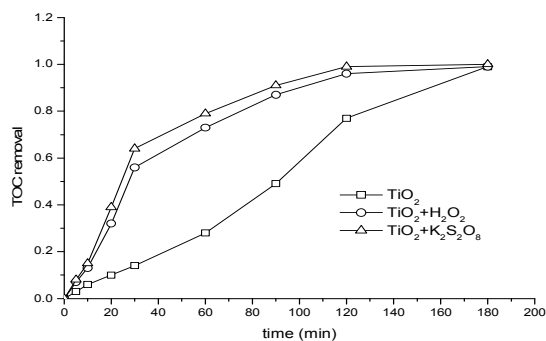
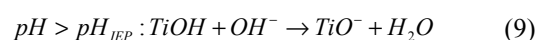
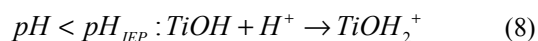


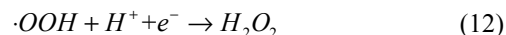
Fig. 4. Effect of H_2O_2 , $K_2S_2O_8$ on TOC removal of Triton X-100 over TiO_2

3.3. Effect of pH

pH is one of the factors that affect the degradation rate of contaminants in the UV/ TiO_2 process by changing the charge of the contaminant and catalyst surface, as well as the mechanism of hydroxyl radical generation [23]. Fig.5 demonstrates the pH from 3 to 9 on the degradation efficiency of Triton X-100 for cases of UV/ TiO_2 . The highest degradation efficiency in the UV/ TiO_2 process was attainable under pH 6.0. When the pH was decreased to 3, there was also a decrease in degradation efficiency. As the pH further increased to 9, the degradation efficiency decreased considerably. The decrease in degradation efficiency at acidic and alkaline media can be attributed to the repulsion between the contaminant and catalyst surface charges. The pH of the isoelectric point (IEP) of titania is 6.8 [24], so below and above this pH, the titania surface is positively and negatively charged, respectively, according to the following equations:



At a pH of 3, Triton X-100 was presumably partially positively charged. Therefore there was a repulsion between the positive titania surface and Triton X-100. This effect was related to the possibility of additional $\bullet OH$ radical formation in the acidic solution from Equations 10-13. However, the lifetime of superoxide anions was very short at an acidic pH, so the role of degradation in Triton X-100 was minor.



At a pH of 9, on the other hand, the titania surface and Triton X-100 were both partially negatively charged, and their repulsion also inhibited the degradation. The natural pH of 6 can be chosen as the optimum pH value, and the experiments used this pH.

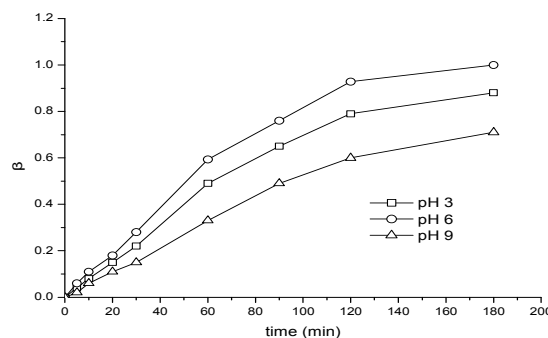


Fig. 5. Effect of pH on the photodegradation of Triton X-100 over TiO_2

3.4. Kinetic study of Degradation

The kinetic of degradation on the surface of the catalyst may also be described with the Langmuir-Hinshelwood (L-H) model according to [25]:

$$r = \frac{k_r K C}{1 + K C_0} = k_{app} C \quad (14)$$

where k_r (mg/L.min) corresponds to the limiting degradation rate at maximum coverage of the adsorbed Triton X-100, and K (L/mg) is the proportion of Triton X-100 molecules that adhere to the surface of TiO_2 particles. With reference to different initial rates, which correspond to different initial concentrations, it can be concluded:

$$k_{app} = \frac{k_r K}{1 + K C_0} \quad (15)$$

In fact, if the degradation rate by UV/ TiO_2 is in accordance with the L-H model, the variation in $1/k_{app}$ versus C_0 should be linear. The values of k_{app} can be obtained from the variation in $\ln C/C_0$ versus time for

different initial concentrations of Triton X-100. The results based on the obtained k_{app} values (Table 1) are depicted in Figs.6 and 7, which also revealed a good fit of the initial degradation kinetic with the L-H model. The L-H parameters of k_r and K were obtained accordingly as 0.92 (mg/L.min) and 0.287 (L/mg), respectively.

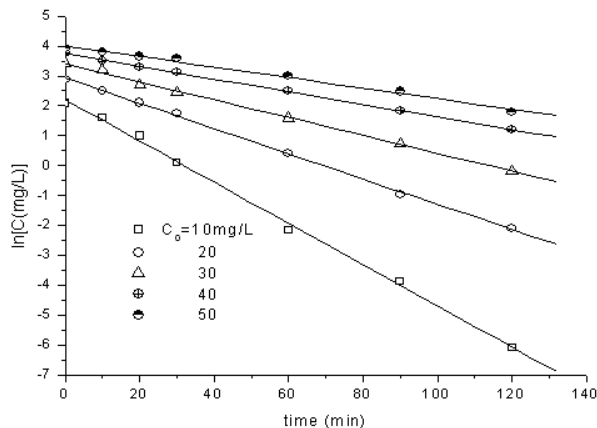


Fig 6. Effect of initial concentrations of Triton X-100 on the slope of the $\ln C$ versus time

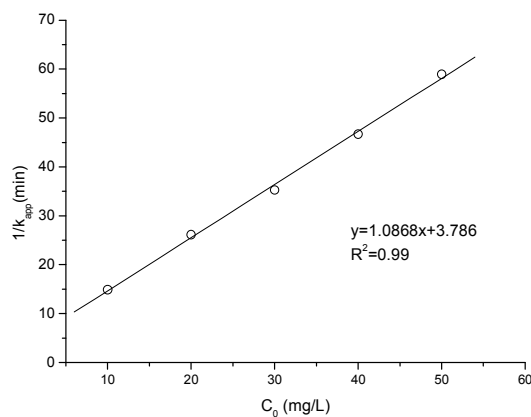


Fig 7. Plot of $1/k_{app}$ versus initial concentrations of Triton X-100

3.5. Degradation of 2 g/L Triton X-100

The use of surfactants as solubilizing agents in the removal of contaminants from soils followed by heterogeneous photocatalytic degradation may be a promising strategy for the recovery and/or reuse of surfactants [26]. The photocatalytic degradation of 1 mg/L phenanthrene in 2 g/L Triton X-100 micelle solution obtained from soil remediation in the UV/TiO₂ process was previously examined [27], and the experimental results are shown in Fig.8. Phenanthrene can be completely degraded using 0.2 g/L titania while simultaneously pumping oxygen or additionally adding 0.1 g/L H₂O₂ within 30 min. In this process of photocatalytic degradation of phenanthrene, the degradation of Triton X-100 also occurred. As a promising strategy of soil remediation whether surfactants may be recovered and/or reused after contaminants being completely degraded or not, it depends on the degradation of

Triton X-100 in the process of photocatalytic degradation. Therefore the degradation of Triton X-100 in the process of phenanthrene degradation with dosages of 0.2 g/L TiO₂ and 0.1 g/L H₂O₂, as well as an increase in the amounts of titania and hydrogen peroxide to both 1 g/L, was investigated. Fig.9 illustrated that the degradation efficiency of Triton X-100 was less than 5 % within 30 min using 0.2 g/L titania or even an additional 0.1 g/L H₂O₂ to degrade 1 mg/L phenanthrene in 2 g/L Triton X-100 micelle solution. According to the result of Fig.8, in this case phenanthrene can be completely degraded. This result proved the feasibility of applying the photocatalytic oxidation for the degradation of contaminants in surfactant micelle solution.

Table 1. Pseudo-first order apparent constants of different TritonX-100 initial concentrations

| C_0 (mg/L) | $k_{app} \times 10^2$ (1/min) | R^2 |
|--------------|-------------------------------|--------|
| 10 | 6.98 | 0.9880 |
| 20 | 4.11 | 0.9866 |
| 30 | 2.97 | 0.9936 |
| 40 | 2.14 | 0.9980 |
| 50 | 1.78 | 0.9864 |

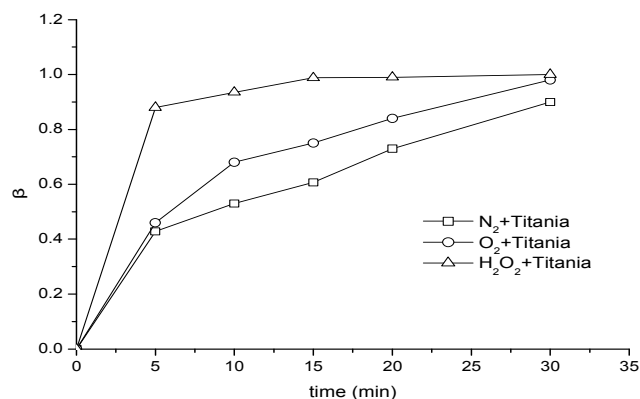


Fig 8. Photodegradation of 5mg/L phenanthrene over TiO₂(0.2g/L) and H₂O₂ (0.1g/L)

To degrade this high concentration surfactant completely, the dosages of the catalyst and oxidant must be increased. The degradation efficiency of Triton X-100 using 1 g/L titania can reach up to 26% at 120 min. However, TritonX-100 can be degraded up to 67% at 120 min with an additional 1 g/L H₂O₂.

Research on the photocatalytic degradation of non-ionic surfactants at low and high concentrations can correct some misconceptions on them. Non-ionic surfactants have been erroneously considered relatively stable under normal conditions because the primary alkoxy radical is stable enough at ambient temperature for the formation of alcohol by H abstraction from other molecules. In fact, polyether chains demonstrate behavior that is similar to that of simple ethers such as undergoing degradation readily by strong acids, certain oxidizing agents and certain metal ions.

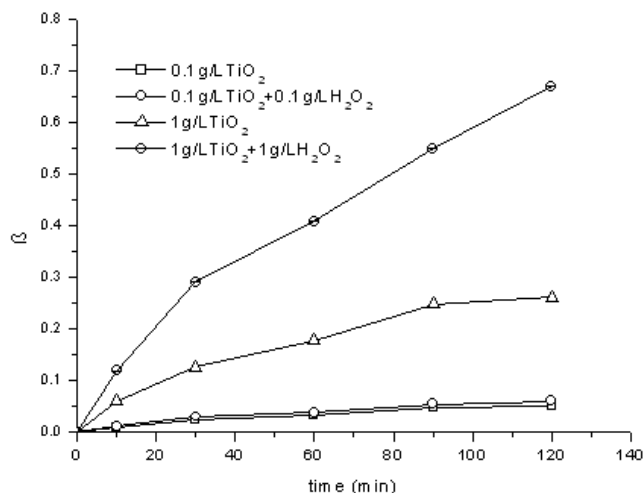


Fig 9. Photodegradation of TritonX-100(2g/L) at different dosage of TiO_2 and H_2O_2

We determined the photocatalytic degradation products of Triton X-100 irradiated by titania at 15 min by using LC-ESI-MS. As illustrated in Fig.10(a), one series of mass to charge ratios (m/z) of $195.2+44n$ (where n represents the EO number) was observed. The ratios differ from each other by 44 Da, which indicates the difference of a single oxyethylene unit (EO). The signal at m/z 195.2 can be assigned to the polyethylene glycols (PEG), indicating that PEGs with 4-13 EO subunits were produced during the degradation process. The series of $m/z=432.3+44n$ and $133.1+44n$ can be identified as the Na adducts of residual octylphenol ethoxylates (APEOs) and dicarboxylated polyethylene glycols (DCPEG), respectively. The first series ($m/z=432.3, 476.3, 520.4, 564.3, 608.4$) complex of APEOs with EO numbers of 4-8, which are lower than those of original Triton X-100 with an average EO number of 10, indicating the breakdown of the EO chain during the photodegradation process. The second series ($m/z=133.1, 177.1, 221.1$) can be identified as DCPEG containing EO subunits ranging from 0 to 2. In Fig.10(b-c), The second mass spectrum was used to identify the structure of two compounds which signals were at $m/z=432$ and 371. Based on the experimental results and literature reports, degradation pathway for Triton X-100 was proposed as shown in Fig.10(d). The oxidation of Triton X-100 involves the breakdown of the EO and oxidation of the methyl group to a hydroxyl group, and finally to a carboxyl group. Based on the degradation pathway, Triton X-100 could be fully deethoxylated to octylphenol. With the degradation prolonging, octylphenol can be further oxidated to produce carbon dioxide.

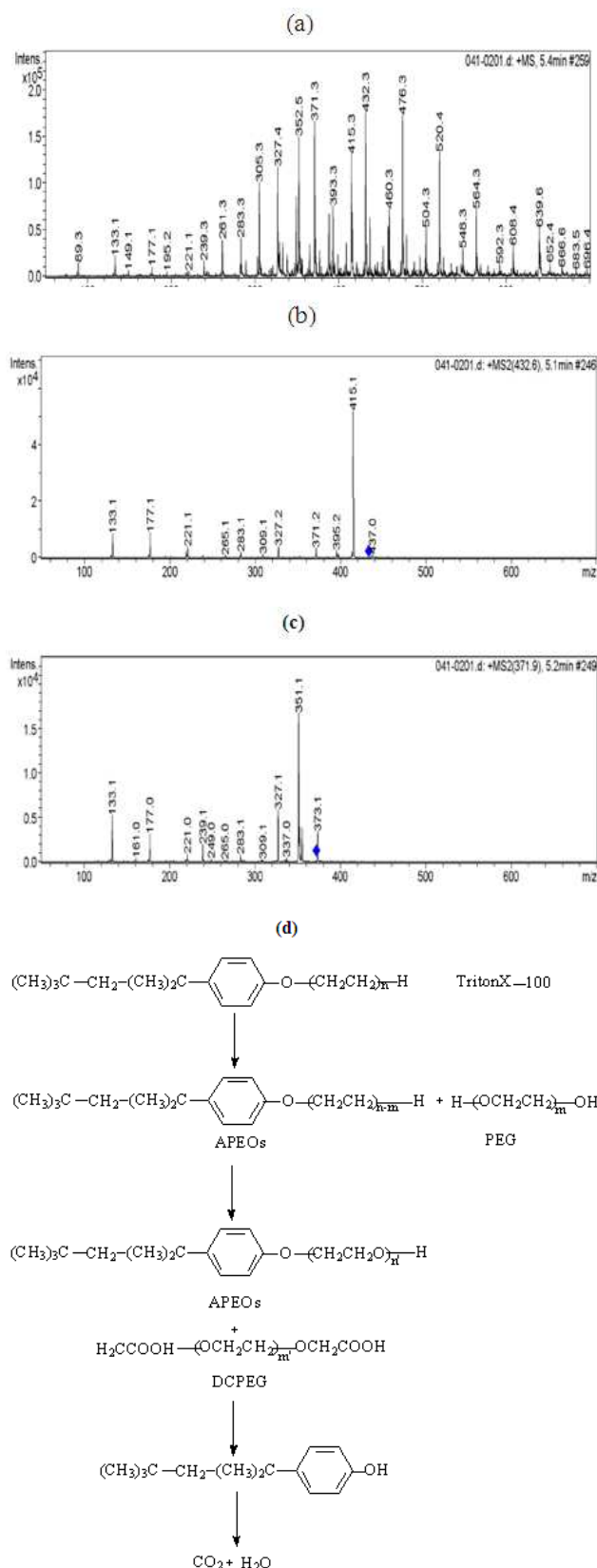


Fig 10. Possible pathway of Triton X-100 photodegradation over TiO_2 under UV irradiation

4. Conclusion

The optimum conditions obtained for the treatment of 20 mg/L Triton X-100 solution were 1 g/L of TiO₂ dosage and a pH of 6. The degradation efficiency of Triton X-100 by potassium persulfate was higher than that by hydrogen peroxide when the same mol of oxidants were used. The degradation rates of different initial TritonX-100 concentrations for the UV/TiO₂ process can be described well by the L-H kinetic model. The L-H parameters of k , and K were 0.92 (mg/L.min) and 0.287 (L/mg), respectively.

With 0.2 g/L titania or even an additional 0.1 g/L hydrogen peroxide to degrade 1 mg/L phenanthrene in 2 g/L Triton X-100 solution, the degradation efficiency of Triton X-100 was less than 5% within 30 min. The feasibility of applying the photocatalytic oxidation for the degradation of contaminants in surfactant micelle solution was proven.

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