Full Length Research Paper

Photocatalytic degradation of phenanthrene in nonionic-anionic surfactant using titania catalysts

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Photocatalytic degradation of phenanthrene by titania in nonionic-anionic surfactant micelles was investigated as a promising strategy for soil/sediment/groundwater remediation after using nonionic-anionic surfactant as solubilizing agents for removal of contaminants from soils/sediment/groundwater. All photocatalytic experiments were conducted using a 365 nm mercury monochromatic ultraviolet lamp in a photocatalytic reactor. Addition of 1 g/L titania is suitable to this photocatalytic degradation rate and efficiency of phenanthrene at the ratio of Triton X-100 (TX100) to sodium dodecyl sulfate (SDS) 1 : 2. Both the decrease in the critical micelle concentration (CMC) of mixed surfactant and the more negative free energy to easily sorb the contaminant on the surface of titania would lead to the gradual increase in the degradation efficiency of phenanthrene. Pseudo-second-order kinetics was observed for the photocatalytic degradation of phenanthrene. Acidic solution environment (pH< PZC_{TiO2}) was beneficial to the photocatalytic degradation of phenanthrene. Based on the GC/MS analysis of the intermediates, the possible pathways of the photocatalytic degradation of phenanthrene and TX100 were proposed.

Key words: Photocatalytic degradation, nonionic-anionic surfactant, phenanthrene, soil remediation.

INTRODUCTION

Hazardous hydrophobic organic compounds (HOCs) cause environmental concern by strongly sorbed into soils and sediments (Edwards et al., 1994; Woo et al., 2001) due to their toxic, low water solubility and carcinogenic properties (Cerniglia et al., 1992; Bamforth et al., 2005). Surfactant remediation technology has been suggested as the promising technology for the remediation of contaminated soils, sediments and groundwater (West et al., 1992; Jafvert 1996; Mulligan et al., 2001; Yang et al., 2006).

Mixtures of nonionic and anionic surfactants have always been chosen in surfactant remediation technology (Zhao et al., 2005) because of increased solubility of HOCs lower partitioning losses to non aqueous phase liquids due to precipitation or adsorption compared to individual surfactants (Yu et al., 2007; Zhou et al., 2007), and a wider range of temperature, salinity, and hardness conditions than the individual surfactant (Holland et al., 1992). The synergistic solubilization of nonionic -anionic mixed surfactant for HOCs was observed in some studies (Zhu et al., 2001, 2003) and thus nonionic-anionic surfactant mixtures have been studied extensively. But there is almost no report about the degradation of contaminants in nonionic-anionic surfactant solution.

Currently available water treatment technologies such as adsorption or coagulation merely concentrate the contaminants by transferring them to other phases, not being completely "eliminated" or "destroyed". Other conventional water treatment methods such as sedimentation, filtration, and membrane technologies need high operating costs and could generate toxic secondary contaminants into the ecosystem. These have lead to the research in the field of "Advanced Oxidation Processes (AOPs)" as the innovative water treatment technologies. Among these AOPs, heterogeneous

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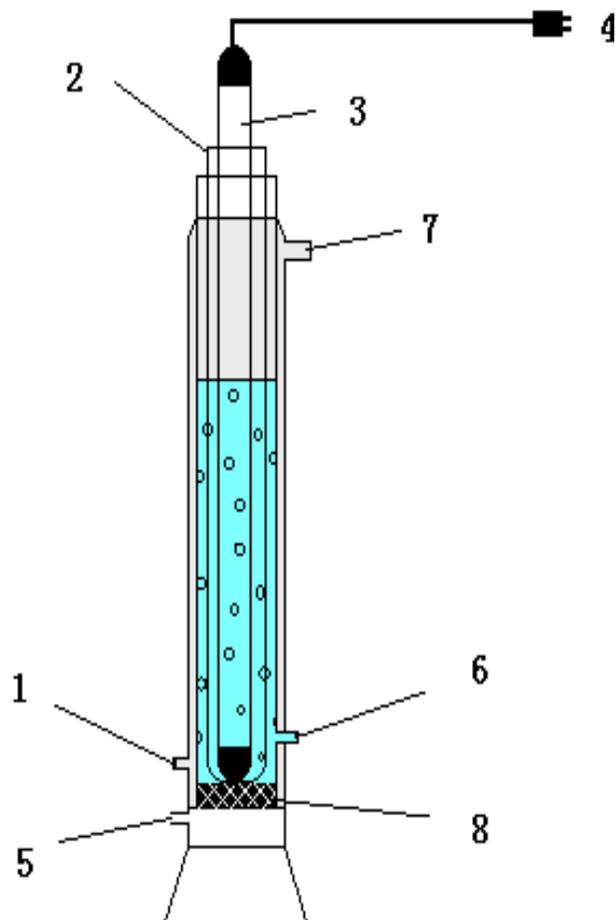
Figure 1. Sketch of the photocatalytic reactor (1. condensate inlet; 2. quartz glass vessel; 3. UV lamp; 4. power; 5. gas inlet; 6. sampling ports; 7. condensate outlet; 8. porous sieve).

photocatalysis, which offers an oxidation capable of pollutant abatement under ambient condition via irradiation of some suspended in the water effluent to be treated or immobilised on various types of supports of semiconductor solids, has demonstrated its efficiency in degrading a wide range of contaminants into readily biodegradable compounds, and eventually mineralized them to carbon dioxide and water as a low-cost, environmental friendly and sustainable treatment technology.

Photocatalytic remediation of wastewater using solar/UV irradiation is an active research field in modern environmental science. Although, biological treatment is broadly applied to the treatment of wastewater from urban areas, a large number of contaminants are not biodegradable due to their high toxicity.

According to previous studies (Zhou et al., 2007), TX100 and SDS were used as a nonionic surfactant and an anionic surfactant because they are widely used in industrial applications to soil washing, respectively.

Herein, we investigated the degradation of phenanthrene in different molar ratios of nonionic-anionic surfactant mixtures by photocatalytic technology and tried to establish a combined technology of applying nonionic-anionic surfactant remediation and photocatalytic degradation to remediate soils, sediments or groundwater.

MATERIALS AND METHODS

Materials

Triton X-100 (analytical grade, TX100), sodium dodecyl sulfate (SDS), and phenanthrene (98% purity) were all purchased from Sigma Chemical Co., USA. Titania (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 m^2/g and an average particle size of 30 nm. 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.

Phenanthrene solubilization

The solubilization of phenanthrene was performed in nonionic-anionic surfactant (TX100-SDS) mixtures having a total concentrations of 4 mmol/L. Surfactant mixtures used were molar ratios of 4:1, 2:1, 1:1 and 1:2. For each surfactant mixture, 0.008 g of phenanthrene in a 500 ml solution was placed in a 1 L vial equipped with a Teflon-lined septum to prevent loss of phenanthrene by volatilization. The vials of each mixture were shaken at 200 rpm for 72 h. 0.008 g of phenanthrene could be completely dissolved in the 500 mL solutions with different molar ratios of surfactant mixtures mentioned according to the literature (Zhou et al., 2007).

Degradation experiments

Figure 1 shows the photocatalytic reactor which is a cylindrical glass vessel with a 25 W UV lamp (365 nm, light intensity about 1.2×10^{-6} EinsteinL^{-1}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, a certain amount of titania was added into the mixture of TX100 and SDS. The suspension containing titania was magnetically stirred in the dark for 60 min before irradiation, to ensure the equilibrium of an adsorption/desorption on the surface of titania. Subsequently, the suspension 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 μm membrane filter to separate the photocatalyst, and then analyzed using High Performance Liquid Chromatography (HPLC, LC10A, Shimadzu).

Analytical methods

The concentration of TX100 was analyzed using a Kromasil C18 reverse phase column (250 × 4.6 mm) in HPLC (LC10A, Shimadzu) with a mobile phase of 80% acetonitrile and 20%
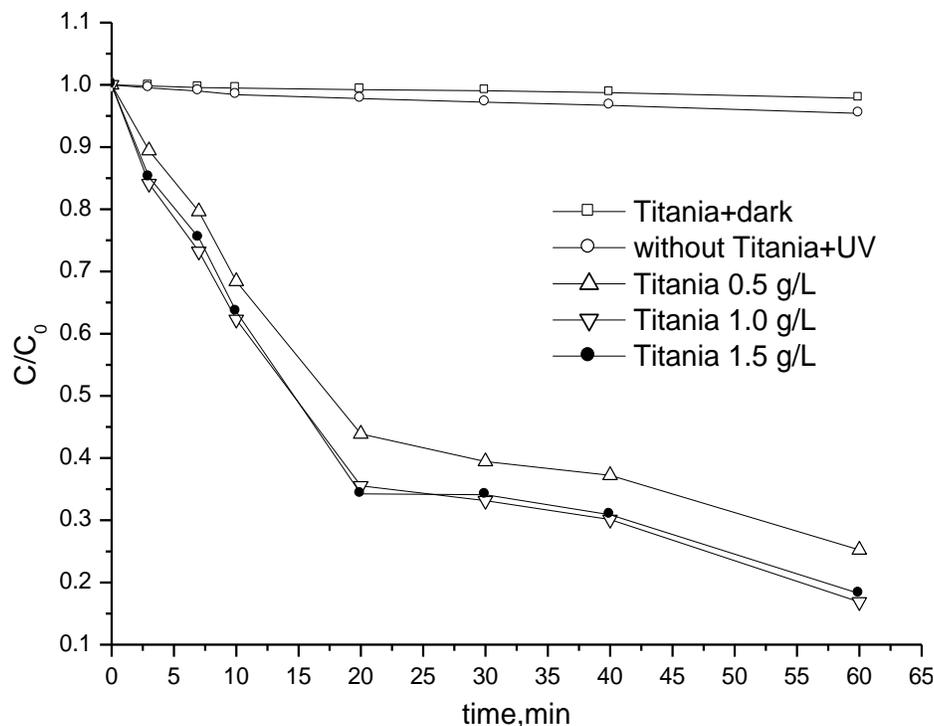
Figure 2. Effect of titania loading on the photodegradation of phenanthere (TX100/SDS=1 : 2).

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 TX100. The HPLC system for the LC/MS analysis was an Agilent 1100 microbore system. The column used the same Kromasil C18 reverse phase column. The mobile phase consisted of 20% deionized water (0.1% formic acid in water) and 80% acetonitrile (0.1% formic acid in acetonitrile). 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.

The concentration of phenanthrene was also analyzed using the HPLC system (LC10A, Shimadzu) with a mobile phase of 70% acetonitrile and 30% deionized water at a constant flow rate of 1.0 mL/min. A thermoelectron GC/MS system was employed to identify the reaction products. The capillary column employed was 5.5% Phenyl Methyl Siloxane (30 m x 3 20 μm x 0.25 μm). About 1 µl of each sample was injected into the GC/MS in the splitless mode. The injector temperature was held at 280°C. The MS detector was set at a temperature of 300°C.

The concentration of SDS in the surfactant mixture was quantified using modified methylene blue colorimetry. The assay mixture consisted of 4 ml of methylene blue solution (0.25 g/L), 6 ml of chloroform and 1 ml of the target sample. The mixture was vigorously mixed for 1 min and allowed to stabilize at room temperature for 2 h. The optical absorbance of the chloroform phase was measured at 650 nm using a spectrophotometer (DR-2010, HACH, USA).

RESULTS

In general, the oxidation rates and efficiencies of the photocatalytic system are highly dependent on the operational parameters that govern the kinetics of photocatalyzation, such as titania loading, pH and so on.

Effect of titania loading

When the solution of mixed surfactant contained more SDS, especially the ratio of TX100 to SDS 1 : 2, it would restrict the sorption of TX100 onto the natural soil. So the ratio of TX100 to SDS 1:2 was used as the proportion of mixed surfactant (Zhou et al., 2007). Firstly, degradation experiments in the presence of titania in the dark and in the absent of titania in the UV were performed. In these cases, both of the phenanthrene degradation were less than 5% in 60 min as shown in Figure 2 (Titania + dark and without Titania + UV).

Effect of the ratio of TX100 to SDS

The role of single surfactant on the degradation of contaminant has already been investigated. Bianco Prevot et al. (1999) observed an inhibitory effect of surfactants including single HTBA, SDS and Brij 35 on carbaryl degradation by photooxidation. A similar observation was made by Barrios et al. (2005) that the photocatalytic degradation of naphthalene was reduced in the presence of TX100. In order to explore the role of
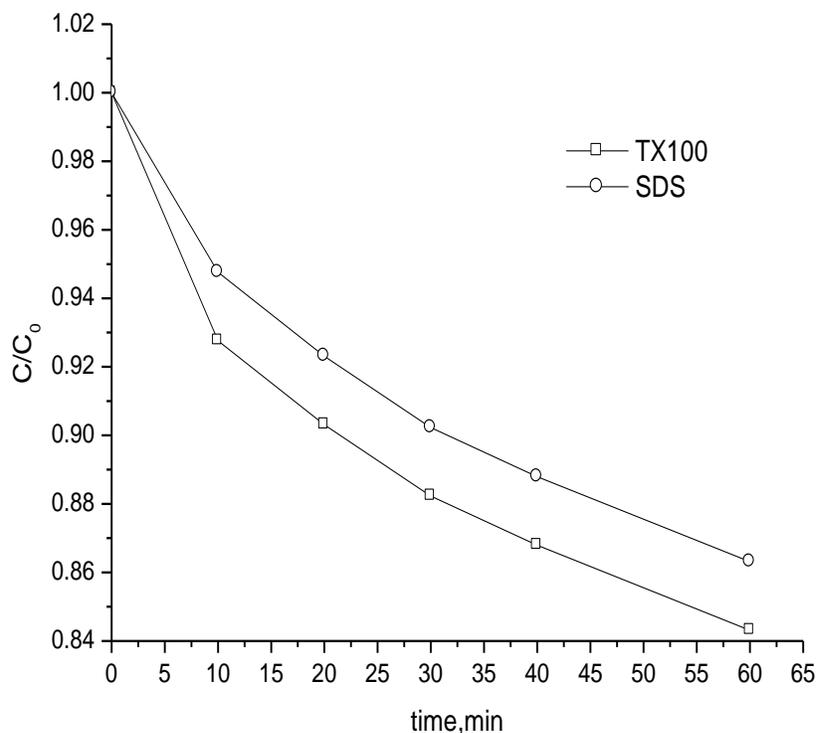
Figure 3. Comparison for the degradation of phenanthrene in TX100-SDS solution and in deionized water.

mixed surfactant on the degradation of phenanthrene, a comparative experiment was carried out in TX100-SDS mixed surfactant and deionized water, respectively. For the experiment performed in deionized water, the water solubility of phenanthrene was enhanced by dissolving phenanthrene in a small amount of methanol at first. Then, the methanol solution containing phenanthrene was diluted to the same concentration of phenanthrene as the TX100-SDS mixture. The result was illustrated in Figure 3.

In this process of photocatalytic degradation, the existence of TX100 and SDS could influence the degradation of phenanthrene. Simultaneously, as a part of promising strategy for the remediation of soil, sediment or groundwater, surfactants may be recovered and/or reused partly after the degradation of contaminants. Thus, the degradation degree of mixed surfactant should be considered corresponding to the degradation process of the major contaminant. Therefore, the degradation efficiencies of TX100 and SDS during the process of phenanthrene degradation using 1 g/L titania to degrade 16 mg/L phenanthrene at the ratio of TX100 to SDS 1 : 2 micelle solution were investigated, as shown in Figure 4.
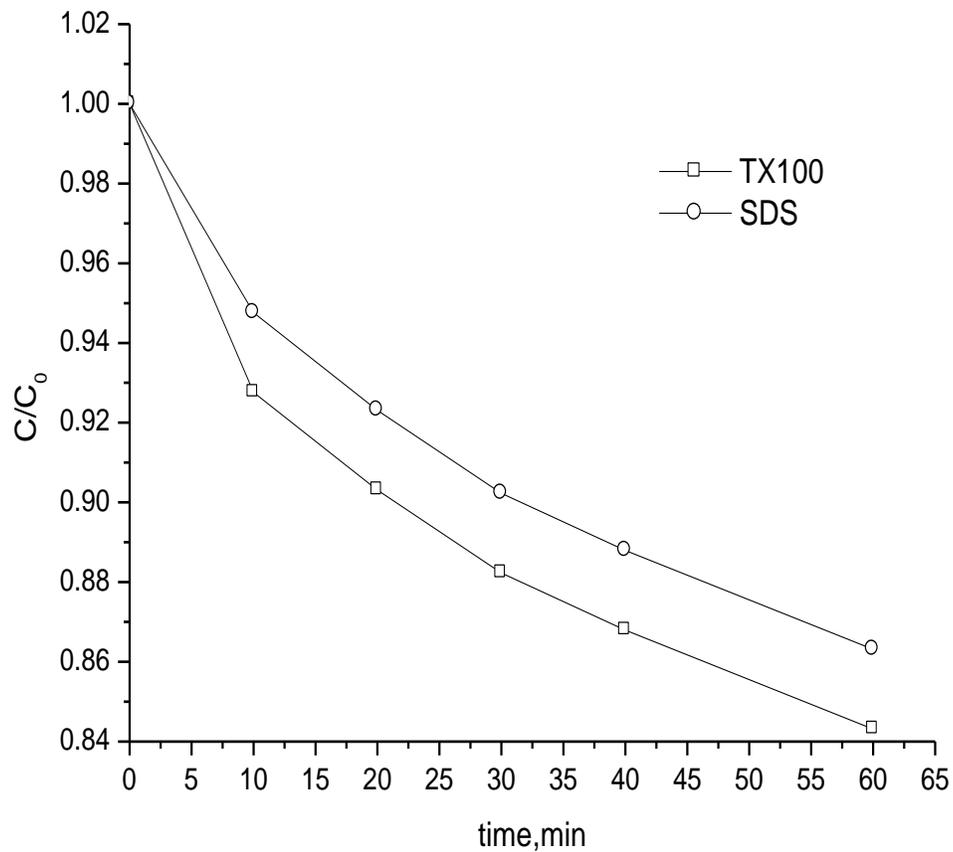
Effect of pH

In a heterogeneous photocatalytic treatment system, pH

is one of the most important operational parameters that affect the charge density of catalyst particles, size of catalyst aggregates and the position of conductance and valence bands. Due to the nature of titania used, any pH variation is known to affect the isoelectric point (PZC) or the surface charge of the photocatalyst used (Chong et al., 2010). At PZC of titania (pH = 6.2), the interaction between the photocatalyst particles and contaminants is minimal due to the absence of any electrostatic force. At pH > PZC_{TiO2}, the catalyst surface will be negatively charged and repulse the anionic compounds in water. The effect of pH on the phenanthrene degradation was depicted in Figure 5.

DISCUSSION

Degradation of phenanthrene in nonionic-anionic surfactant

Concentration of titania in the photocatalytic system affects the overall photocatalytic reaction rate. Figure 2 illustrated that the addition amount of titania from 0.5 g/L to 1 g/L is directly proportional to the increase in the overall photocatalytic degradation efficiency ($(C_0-C)/C_0$) of phenanthrene at the ratio of TX100 to SDS 1 : 2. The excess titania more than 1 g/L can create a light screening effect that reduces the surface area of titania

Figure 4. Photodegradation of TX100 and SDS at the ratio of TX100 to SDS 1:2.
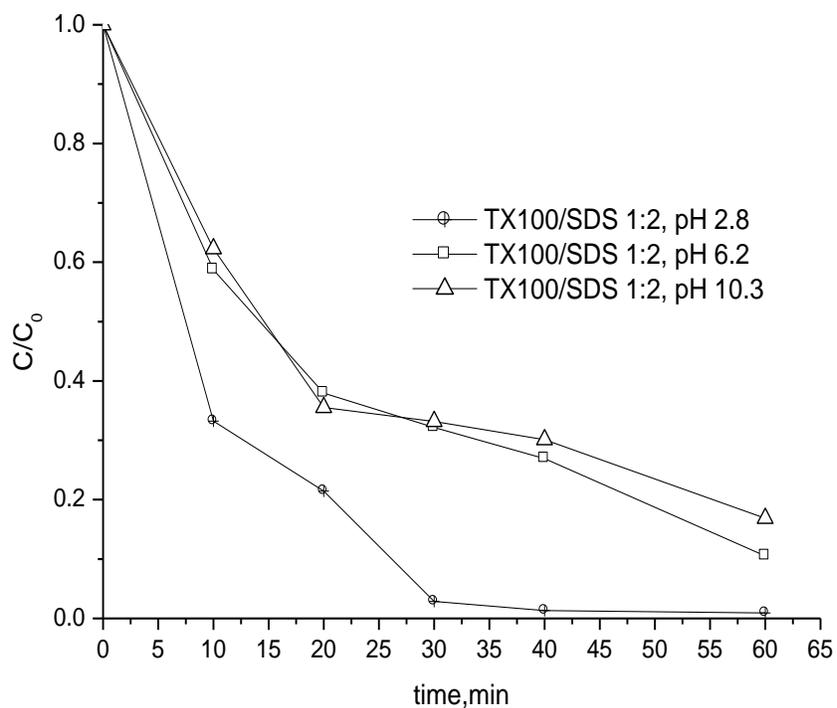
Figure 5. Effect of pH on the photodegradation of phenanthrene over TiO_2.
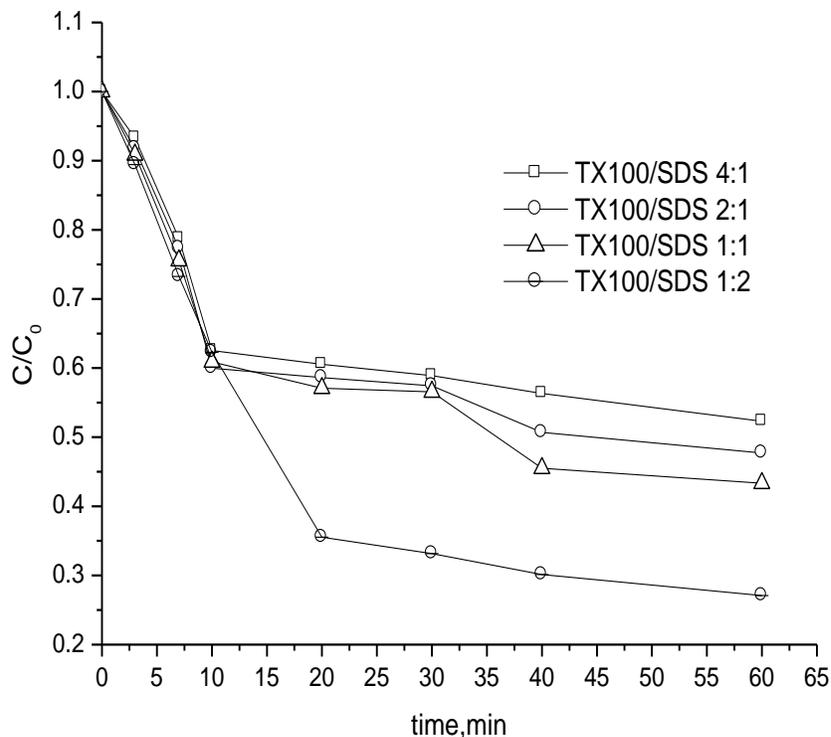
Figure 6. Effect of more ratios of TX100 to SDS on the photodegradation of phenanthrene.

being exposed to light illumination and the photocatalytic efficiency.

The CMC of the mixed surfactant decreased significantly when more SDS was added into the TX100 solution at the same total molar concentration of two surfactants. For example, the CMC of mixed surfactants with the ratios of TX100 to SDS 1 : 1 and 1 : 2 were 0.19 and 0.16 mmol/L, respectively. It was far lower than the single TX100 (0.29 mmol/L) and SDS (5.4 mmol/L) because of the formation of the mixed micelles. Nonionic surfactant molecules (TX100) were inserted into the anionic surfactant (SDS) micelles and the repulsion among the ionic heads of anionic surfactant might be reduced (Zhao et al., 2005). In this study, the concentrations of SDS in mixed surfactant were less than the CMC of SDS and thus the solubilization enhancement of SDS in mixed solution for phenanthrene was negligible.

The presence of TX100-SDS was found to slow down the degradation efficiency of phenanthrene. The decrease of phenanthrene degradation rate in the presence of TX100-SDS could be attributed to their competition and consumption with phenanthrene for hydroxyl radicals as active amphiphilic compounds, which reduces the opportunities for phenanthrene to be degraded and results in the unavailability of phenanthrene to hydroxyl radicals attack. In addition, this may be related that surfactant micelles could 'wrap' the phenanthrene molecule to result in the formation of relatively more

stable complex.

The degradation efficiency of TX100 was slightly higher than that of SDS and their degradation efficiencies were both less than 15% within 60 min. It can be deduced that the higher the TX100 concentration, the longer it took the time to achieve completed removal of phenanthrene. This inference can be confirmed from Figure 6, which depicted the effect of more ratios of TX100 to SDS on the photodegradation of phenanthrene. The degradation efficiency of phenanthrene increased with increasing SDS concentration because of the fact that TX100 could consume more hydroxyl radicals compared to SDS. This result also proved the feasibility of the application of photocatalytic oxidation for the degradation of contaminants in mixed surfactant micelle solution.

As a key factor in the photocatalytic reaction, the pH change during the degradation of phenanthrene in the absence and presence of TX100-SDS was monitored. No significant difference was found, indicating that the presence of surfactant did not affect the degradation efficiency due to pH changes and the effect of pH change can be neglected.

The addition of a nonionic-anionic surfactant mixture to titania in the single nonionic surfactant would cause the release of the preadsorbed nonionic surfactant and the free energy of mixed micellization was more negative than that of the single nonionic surfactant sorption, which indicated that the mixed micellization in   nonionic-anionic
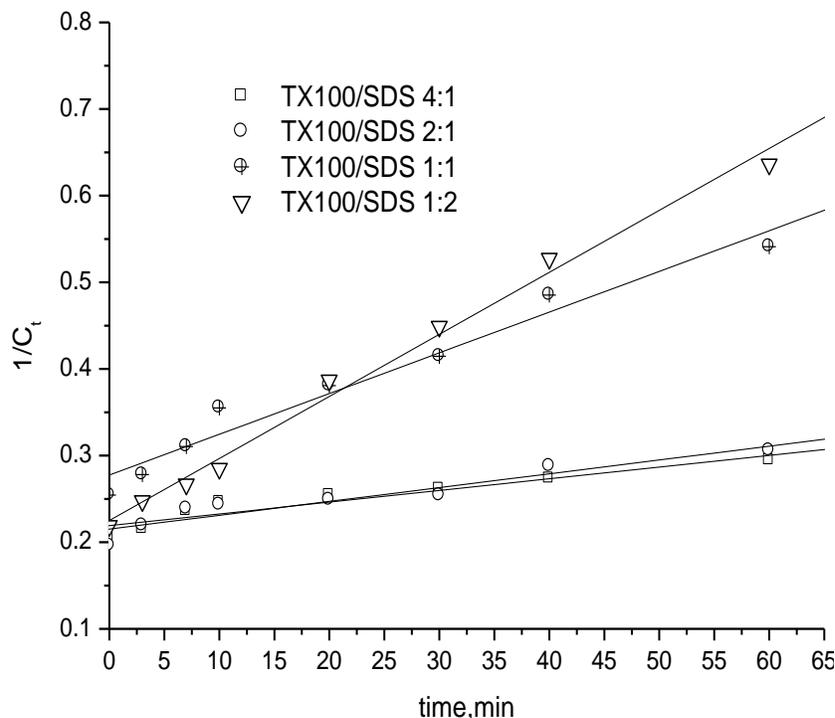
Figure 7. Pseudo-second-order plot for the kinetics of phenanthere photodegradation over TiO_2 with different ratios of TX100 to SDS.

Table 1. Kinetic parameters for the photocatalytic degradation of phenanthrene at different ratios of TX100 to SDS.

Ratio of TX100 to SDS	k (L.mg^{-1} min^{-1})	R^2
4:1	0.00135	0.9502
2:1	0.00159	0.9606
1:1	0.00470	0.9643
1:2	0.00716	0.9920

surfactant mixture was more favourable to sorb the contaminant onto titania than nonionic surfactant did (Zhou et al., 2005).

In a word, the more addition of SDS to the surfactant mixture not only decreases the consumption of hydroxyl radicals but also makes contaminants easier sorb onto the surface of titania because of the more negative free energy. In this case, the photodegradation of phenanthrene gradually increases from 45 to 75% in 60 min as the proportion of SDS in the surfactant mixtures increases. Figure 7 showed that the degradation data with different ratios of TX100 to SDS were fitted pseudo-second-order kinetics well. The pseudo-second-order kinetics form is (Rauf et al., 2010):

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

Where C_o and C_t are the phenanthrene 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 the ratio of TX100 to SDS 4:1 was about one-fifth that of the ratio of TX100 to SDS 1:2.

The degradation efficiency of phenanthrene increased at pH 2.8 compared with both 6.2 and pH 10.3. The surface charge density distribution for these titania catalyst clusters is highly dependent on the operating pH. It was reported that the distribution of TiOH is > 80% at 3 < pH < 10; TiO$^-$ > 20% at pH > 10 and TiOH$_2^+$ >20% at pH < 3 (Kormann et al., 1991). When operating pH < PZC$_{TiO2}$, the surface charge of titania becomes positively charged and gradually exerts an electrostatic attraction force towards phenanthrene, a negatively charged compound. Such polar attraction between titania and phenanthrene

A

B

C
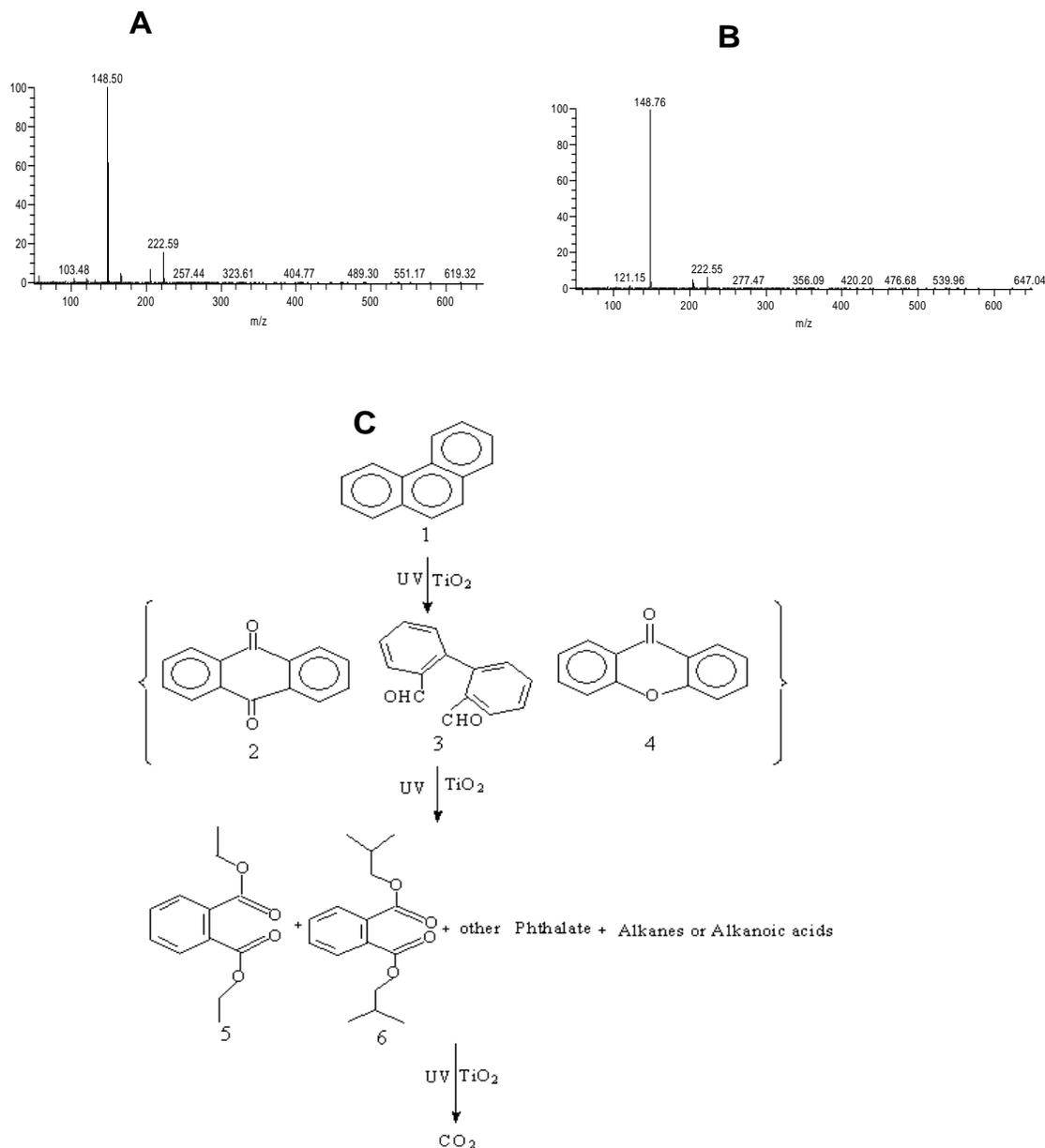
Figure 8. Possible pathway of phenanthrene photodegradation over TiO_2 under UV irradiation.

can enhance the adsorption onto the photon activated titania surface for photocatalytic reactions. This would cause more negative free energy with the mixed micellization (TX100-SDS) sorbed on the surface of titania increasing in solution. This is particularly significant when the anionic organic compounds (SDS) present in a low concentration level. Besides, the interaction between titania particles itself also exists and is dependent on the operating pH. At PZC of titania, the neutral surface charge of titania particles is unable to produce the interactive repulsion for solid-liquid separation. Thus, this causes the aggregation and sedimentation of titania as a result of decreasing the degradation efficiency of phenanthrene.

Pathways of degradation of phenanthrene and TX100

Photocatalytic degradation products of phenanthrene in the presence of mixed surfactant have been analyzed by GC/MS. According to the standard spectra in Wiley Registry 8 e library data, peaks at m/z 222.59 and 227.47, corresponding to compounds 1,2-benzenedicarboxylic diethyl ester (Figure 8a) and phthalic acid diisobutyl ester (Figure 8b), were detected. According to the quantitative analysis, a possible photooxidation mechanism of phenanthrene over titania under UV irradiation was proposed as Figure 8 (c) illustrated. The compounds 2 to 4 in the bracket were theoretical products, which were not

A

B

C

D

$(CH_3)_3C-CH_2-(CH_3)_2C-$⟨benzene⟩$-O-(CH_2CH_2)_n-H$ TritonX—100

↓

$(CH_3)_3C-CH_2-(CH_3)_2C-$⟨benzene⟩$-O-(CH_2CH_2)_{n-m}-H$ + $H-(OCH_2CH_2)_m-OH$

APEOs   PEG

↓

$(CH_3)_3C-CH_2-(CH_3)_2C-$⟨benzene⟩$-O-(CH_2CH_2O)_{n'}-H$

APEOs

+

$H_2CCOOH-(OCH_2CH_2)_{m'}-OCH_2COOH$

DCPEG

Figure 9. Possible pathway of TX100 photodegradation over TiO_2 under UV irradiation.

detected in this experiment. It is necessary to point out that three kinds of compounds: phthalates (products 5, 6), alkanes and alkanoic acids were detected as the main intermediates of phenanthrene oxidation. Finally, the intermediates were further oxidized to produce carbon dioxide. However, no further information could be obtained regarding the possible formation of complexes between phenanthrene and TX100-SDS or the formation

of TX100-SDS degradation products.

It has been well documented that nonionic surfactants have been and can be more easily analyzed by LC/MS due to their high nonvolatility. Thus, photocatalytic degradation products of TX100 irradiated by titania at 10 min were determined by using LC–ESI–MS shown in Figures 9a to c. As illustrated in Figure 9a, 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 to 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 to 8, which are lower than those of original TX100 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 Figures 9b to c), The second mass spectrum was used to identify the structure of two compounds which singals were at m/z = 432 and 371. Based on the experimental results and literature reports, degradation pathway for TX100 was proposed as shown in Figure 9d. The oxidation of TX100 involves the breakdown of the EO and oxidation of the methyl group to a hydroxyl group, and finally to a carboxyl group.

Conclusion

1 g/L of titania was selected for the photocatalytic degradation at the ratio of TX100 to SDS 1:2. Both the decrease in the CMC of mixed surfactant and more negative free energy to easily sorb the contaminant on the surface of titania would increase the degradation efficiency gradually with the increase of SDS in nonionic-anionic surfactant solutions. Pseudo-second-order kinetics was observed for the photocatalytic degradation of phenanthrene. Acidic solution environment was beneficial to the photocatalytic degradation of phenanthrene. Based on the GC/MS analysis of the intermediates, the possible pathways of the photocatalytic degradation of phenanthrene and TX100 were proposed.

ACKNOWLEDGEMENTS

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